BOOK OF ABSTRACTS

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XV-th INTERNATIONAL CONFERENCE ON PHOTOCHEMISTRY

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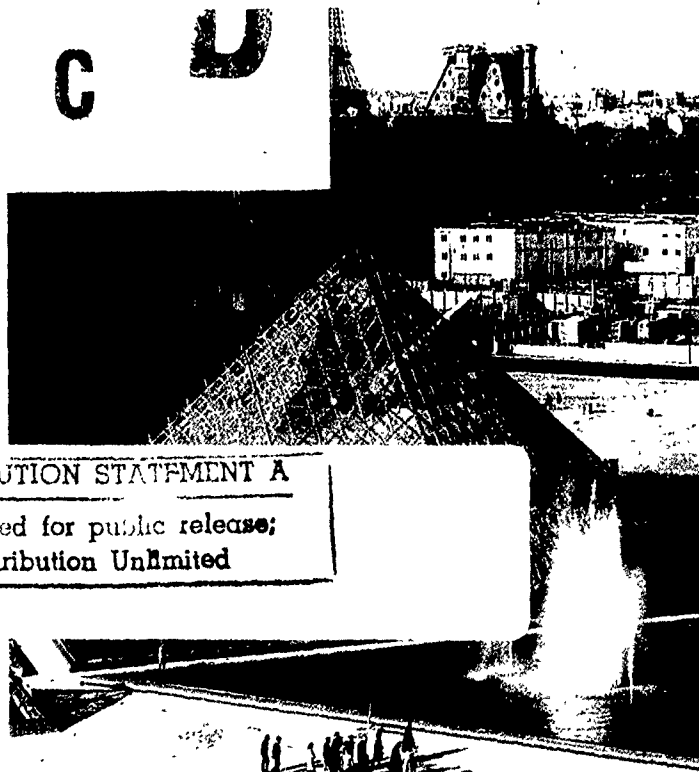
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RECUEIL DES COMMUNICATIONS
DE LA
XVème CONFÉRENCE INTERNATIONALE DE PHOTOCHIMIE

Paris, France (July 28 - August 2nd 1991)

XV-th INTERNATIONAL CONFERENCE
ON PHOTOCHEMISTRY

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ABSTRACTS

OF

INVITED LECTURES

AND

ORAL AND POSTER CONTRIBUTIONS

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RECUEIL DES CONFERENCES INVITEES

ET

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XVème CONFERENCE INTERNATIONALE
DE PHOTOCHIMIE

Paris, France (28 juillet - 2 août 1991)

Preface

This volume contains the abstracts of the scientific contributions which have been presented at the XV International Conference on Photochemistry (Paris, july 28 to august 2, 1991).

The 10 plenary lectures will be published separately as a special issue of the Journal of Photochemistry which will be sent by the end of this year to each active participant of the Conference.

The abstracts (received up to the first day of the Conference) contained in the present book - have been reproduced as submitted by the authors. The 4 pages abstracts of the invited lectures have been entered in alphabetic order according to the seven topics of the Conference : gas phase photophysics and photochemistry, photophysics and photochemical kinetics in condensed phase, modification of molecular assemblies, biological aspects of photochemistry, environmental photochemistry, instrumentation and new techniques in photochemistry, applications of photochemistry. The abstracts of the oral and poster contributions have been subdivided into the same seven topics and entered in order of arrival at the secretariat.

I would like to take this opportunity to thank my colleagues of the International and Local Scientific Committees for their precious help, my colleagues and coworkers of the Local Organizing Committee for their tremendous effort in the organization of the Conference, and the sponsors who helped the organization of the Conference by their financial support.

Paris, september 20   Jean Kossanyi

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TITLE OF ABSTRACTS

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I - GAS PHASE PHOTOPHYSICS AND PHOTOCHEMISTRY

II - PHOTOPHYSICS AND PHOTOCHEMICAL KINETICS IN CONDENSED PHASE

III - MODIFICATION OF MOLECULAR ASSEMBLIES

IV - BIOLOGICAL ASPECTS OF PHOTOCHEMISTRY

V - ENVIRONMENTAL PHOTOCHEMISTRY.

VI- INSTRUMENTATION AND NEW TECHNIQUES IN PHOTOCHEMISTRY

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O- INVITED LECTURES

MULTIPHOTON SPECTROSCOPY OF FREE RADICALS

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The current generation of pulsed, tunable dye lasers can provide narrow bandwidth radiation of sufficient intensity that multiphoton excitation processes become a real possibility. Multiphoton excitation methods provide spectroscopists with a means of reaching, and therefore probing, excited states the population of which may be forbidden, by the electric dipole selection rules, in conventional one photon spectroscopy. They can also offer the benefits of operational convenience: using multiphoton excitation methods it is possible to probe excited states lying at vacuum ultraviolet (VUV) equivalent energies without the attendant practical difficulties traditionally associated with working in the VUV spectral region.

In addition to being convenient and (as shown below) species selective, multiphoton excitation methods can offer very high sensitivity. This sensitivity arises because molecules that undergo multiphoton excitation to the resonant state of interest will, almost inevitably, absorb one (or more) further photons from the intense radiation field prevailing within the focal region of a focussed dye laser pulse and thereby be raised to an energy above the ionisation potential (I.P.). The resulting ions (and/or electrons), being charged particles, can be detected with high efficiency. Such multiphoton ionisation processes provide a means of preparing internal state and/or energy selected ions for studies of ion fragmentation pathways and ion-molecule reactions [1]. Here we concentrate attention on what information multiphoton ionisation (MPI) spectroscopy can provide about the resonant intermediate state of the neutral molecule reached by the initial multiphoton excitation process. One area of great current interest concerns the application of such methods to free radical species [2]. In this contribution we describe recent multiphoton ionisation studies of the imidogen, NH, radical which illustrate many of the virtues of multiphoton excitation methods.

Using near UV photolysis of $HN_3(DN_3)$ as a convenient source of NH(ND) radicals in their metastable $a^1\Delta$ state we have obtained numerous new, rotationally resolved, resonance enhance MPI spectra of these two species. Spectroscopic analysis shows the resonance enhancement in all cases to date to be provided by singlet excited states resonant at the two photon energy.

The longest wavelength features observed [3,4] in the spectra of both NH and ND ($\lambda_{a.x} \sim 285$nm) may be shown to involve the origin levels of the high lying $d^1\Sigma^+$ valence state previously identified via analysis of its emission to the lower lying $c^1\Pi$ and $b^1\Sigma^+$ states [5]. All levels with $v' \leq 2$ in both isotopic species have been characterised in the present work, and we have been able to provide the first accurate estimate of the well-depth of the d state potential function. Note that this $d^1\Sigma^+-a^1\Delta$ transition will not appear in the one photon absorption spectrum of $a^1\Delta$ imidogen radicals since it involves a $\Delta\Lambda = -2$ change. The most interesting aspect of these spectra, however, is the observation that the MPI process via these levels of the $d^1\Sigma^+$ state yields both parent $NH^+(ND^+)$ and atomic fragment N^+ and $H^+(D^+)$ ions, with relative yields that are strikingly dependent upon the precise excitation wavelength and/or the particular rovibronic level causing the two photon resonant enhancement [4,6]. Fig. 1, which shows excitation spectra for forming ions with m/z=16 (ND$^+$), 14(N$^+$) and 2(D$^+$) following excitation of ND($a^1\Delta$) radicals at wavelengths around 285nm, provides clear illustration of this dependence. Three possible mechanisms for fragment ion formation have been considered [4], of which four photon ionisation doubly resonance enhanced first (at the two photon energy) by levels of the $d^1\Sigma^+$ state and then (at the three photon energy) by autoionising members of Rydberg
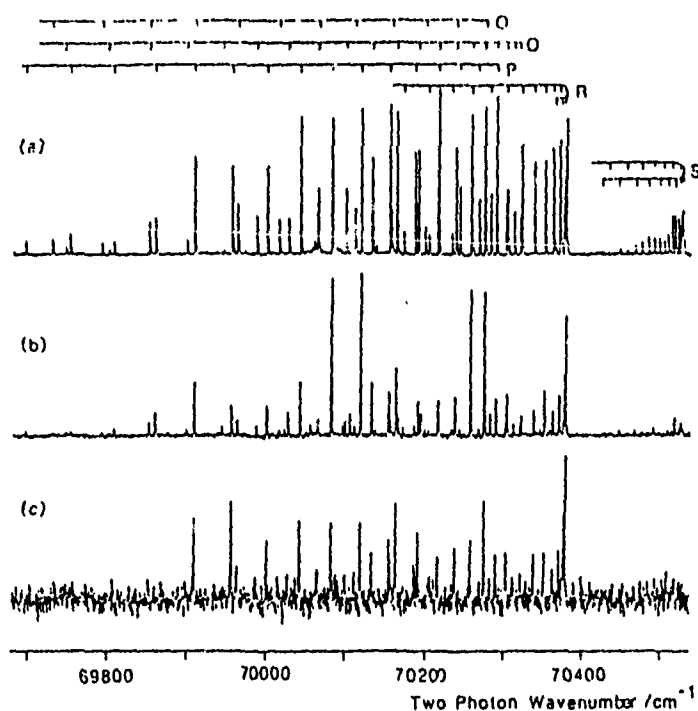
Figur 1. Two photon resonant MPI spectra of the ND($d^3\Sigma^-$-$a^1\Delta$) origin band
obtai ed using linearly polarised laser excitation and monitoring (a) the
m/z=1 , (b) the m/z=14 and (c) the m/z=2 ion mass channels. Each spectrum has
been arbitrarily scaled to the same maximum peak height. Individual line
assignements are indicated by the combs superimposed above the excitation
spectrum for forming parent ions.

series converging to one or more of the excited ionisation limits is considered
most likely to account for the substantially enhanced N* ion yields observed
when MPI occurs via a selected subset of the d-a resonances.

To date, we have recorded, and analysed, resonance enhanced MPI spectra of
$a^1\Delta$ state NH(ND) radicals down to excitation wavelengths around 236nm. The
spectra become increasingly complex and densely structured as the laser
excitation frequency is increased. In the case of NH we are able to assign
virtually all of the observed lines. The corresponding spectra in ND are
'enriched' by the presence of quite strong hot-band transitions originating from
$a^1\Delta$ state levels with v > 0 and, in addition, show evidence of quite strong
perturbations; as a result we have so far only succeeded in assigning about 80%
of the observed rovibronic features. Here we choose to summarise the results of
just one of these analyses, involving a $^1\Pi$ excited state, which illustrate
several features of interest. The origin band of this $^1\Pi$ - $a^1\Delta$ transition
appears strongly in both NH and ND at excitation wavelengths around 272nm. We
assign this excited state as a Rydberg state, with dominant configuration
....$3\sigma^2 1\pi^1 3p\sigma^1$. The NH spectrum is noteworthy in as much that it reveals the
excited state to be affected by a local, rotational level dependent,

predissociation - as evidenced by the anomolously weak showing of transitions
involving levels with J'= 7-9 (fig. 2). Our NH spectra reveal no evidence of
resonance enhancements involving levels of this $^1\Pi$ state with v') 0. In

Two Photon Transition Energy (cm^{-1})
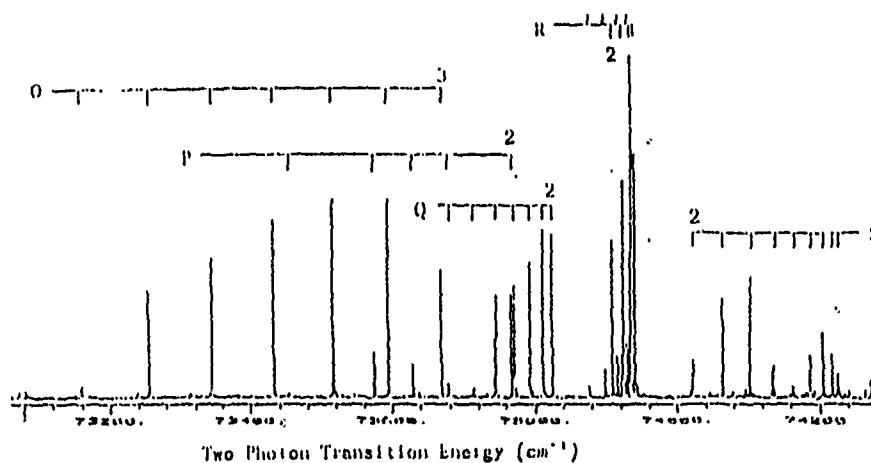
Figure 2. Two photon resonant MPI spectrum of the NH($^1\Pi$-a$^1\Delta$) origin band
obtained using linearly polarised laser excitation and monitoring the m/z=15 ion
mass channel. Individual line assignments are indicated by the superimposed
combs. Note the anomolous weak showing of transitions involving $^1\Pi$ state levels
with J'=7,8,9.

contrast we see features attributable to the v'= 1 and 2 levels of ND($^1\Pi$) but,
upon analysis, it is clear that these appear only because they interact with,
are perturbed by, and borrow transition intensity from, the near resonant v'= 0
and 1 levels of the higher lying $^1\Delta$ Rydberg state arising from the configuration
....3$\sigma^2$1$\pi^1$3pπ^1. Deperturbed spectroscopic constants for both sets of
interacting levels have been obtained.

These examples serve to highlight the following advantageous features of
resonance enhanced MPI spectroscopy as a means of probing free radical species:
(i) In the case of small free radicals which happen to possess one or more
excited states with a lifetime in excess of a few picoseconds, resonance
enhanced MPI can provide spectra, with high signal to noise, that are utterly
characteristic of the species under investigation. Thus, resonance enhanced MPI
spectroscopy can provide a highly sensitive, selective and specific detection
method.
(ii) Multiphoton excitation spectra generally satisfy different selection rules
from those governing traditional one photon transitions. As a result, the
technique has the potential to reveal many hitherto unknown excited electronic
states of molecules, some of which can be expected to feature in new and
improved detection schemes.
(iii) As fig. 2 illustrates, the competition between the final one photon
ionisation step and any other population loss processes from the resonant
intermediate state (e.g. predissociation) can show up particularly clearly -
most notably through a marked diminution in the intensity of spectral features
involving the more short lived levels. Thus careful analysis of the relative
rovibronic line intensities in such multiphoton ionisation spectra have the
capacity to reveal dynamical as well as spectroscopic information about the
resonance enhancing excited state [7].

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DYNAMICS OF PHOTOINDUCED REACTIONS IN CLUSTERS

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The effect of weak solvation bonds on molecular reactions is a fundamental topic in chemical dynamics in condensed phases. The study of photochemical reactions in clusters opens a novel approach to this subject, via systems that enable important theoretical and experimental advantages. There has been vigorous experimental activity in this field recently, e.g., [1]-[3]. The theoretical results described in this presentation deal with three questions in this field: (1) Is there a cage effect for photodissociation in clusters, and how does the effect depend upon cluster size. This is examined particularly for the photolysis of HI in $Xe_N(HI)$, for N in the range from N=1 to N=12. (2) What is the role of collisions between photofragments and "solvent atoms" in the cluster. This is described, e.g., for photolysis of HCl in the ArHCl cluster. (3) What are the mechanisms of reactions between photofragments and molecules in the cluster. This questions is explored for $(HCl)_2$. In part, the studies were carried out using classical trajectory calculations. The other method used extensively in this work is a hybrid quantum/classical approach treating light atoms (H) by time-dependent quantum wavepackets, and heavier atoms by classical dynamics, the coupling between the classical and quantum modes being treated by the Time-Dependent Self-Consistent Field (TDSCF) scheme.[4]

The main specific results obtained for photolysis of HI in $Xe_N(HI)$ are: (1) Even for the case of a simple solvent atom, XeHI, a weak cage effect is found. It leads to resonances in the photodissociation corresponding to bouncing of the H atom between the

heavy atoms. (2) For $N \geq 5$, the resonances dominate the photodissociation behavior, leading to a dramatic increase in the photodissociation lifetime, to a "statistical" distribution for the final energy of the H product, and to a behavior quite similar to that in condensed matter Xe. This sharp change in behavior with cluster size at $N=5$ is due to steric "trapping" of the H photofragment. The lifetime distribution vs. cluster size is shown in Fig. 1.

Fig.1. The "survival probability" as a function of time
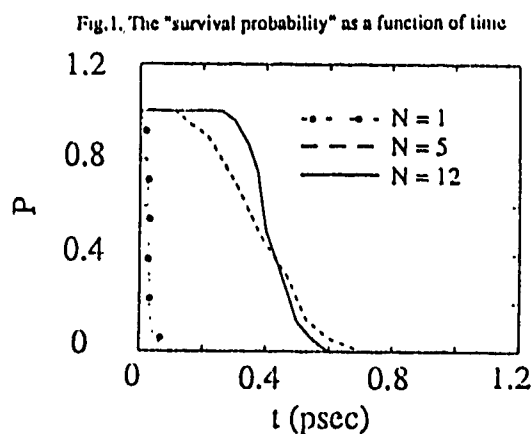
The studies on photolysis of HCl in ArHCl showed that collisions between the H fragment and the heavy atoms play an important role in the process, and multiple collisions (up to $n \leq 5$) are significant. The collisions lead to a broad energy distribution for the H fragment, in sharp contrast to isolated HCl photolysis. The energy distribution in the photolysis of ArHCl is shown in Fig. 2.

Fig. 2. Classical and quasiclassical kinetic energy distribution of H photofragment.
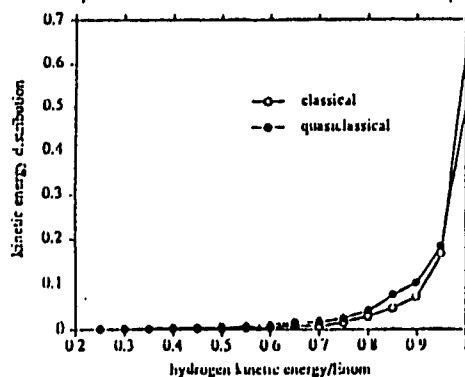
The studies on the photolysis of $(HCl)_2$ have shown that the "floppy" geometry results in a high probability for the intra-cluster substitution reaction in which a nascent H photofragment displaces the H of the other HCl. The geometry of this process implies very high v,J states for the final HCl. An important typical path for the intracluster reaction is shown in Fig. 3.

Fig. 3. The Sn2 mechanism.

H' + ClH(v=0,J=0) ------> H'Cl(v=6,J=30) + H
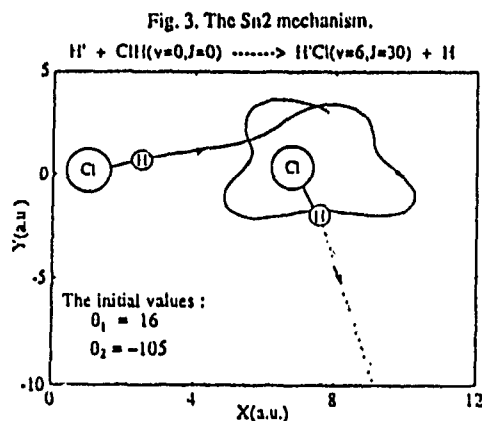
This work shows that photodissociation in clusters can be, and very often is, very different from the corresponding process in isolated monomers. Very often, the cluster effects manifest themselves as new interesting types of resonances. Some of the effects found suggest a strong link between photochemistry in clusters and the corresponding processes in condensed matter.

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THE HCO POTENTIAL ENERGY SURFACE:
PROBES USING MOLECULAR SCATTERING AND PHOTODISSOCIATION

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An *ab initio* HCO potential energy surface has been calculated by Bowman, Bittman, and Harding. Two types of experiments in our laboratory have been performed to probe the accuracy of this surface. First, hot hydrogen atoms with center-of-mass collision energies of 1.6 or 2.3 eV have been scattered from CO. The H atoms are created by photodissociation of H_2S at 222 and 193 nm, respectively. The resulting CO vibrational and rotational distribution has been measured using tunable VUV laser-induced fluorescence. Comparison between experiment and theory is shown in Fig. 1.
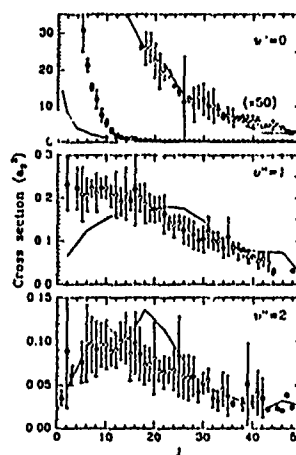
Figure 1   Relative populations for $v=0$, 1, and 2 scattered CO. The Circles give experimental measurements, while the solid line gives the result predicted by the classical trajectory calculations.

Second, HCO has been created from photolysis of acetaldehyde and then dissociated using visible light on the $\tilde{A}$ (A'') ← $\tilde{X}$ (A') transition. Following a crossing back to the $\tilde{X}$ (A') surface, the HCO dissociates to H + CO. These fragments are then probed by VUV laser-induced fluorescence. By fixing the probe wavelength and scanning the visible HCO photolysis wavelength, we learn about the HCO $\tilde{A}$ (A'') surface. A sample photofragment excitation spectrum obtained by monitoring the $CO(v=0, J\approx30)$ product is shown in Fig. 2.

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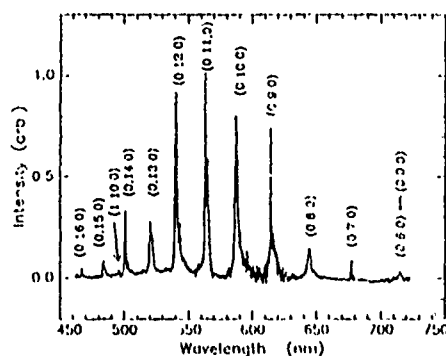
Figure 2 PHOFEX spectrum of HCO monitoring CO(v=0,$J\approx$30).

By fixing the photolysis wavelength and scanning the probe laser, we learn about the dynamics of dissociation on the A and X surfaces. For example, increased excitation of HCO bending results in rotational excitation of the CO product, as shown in Fig. 3. The talk will summarize the results and discuss the agreement between experiment and theory.
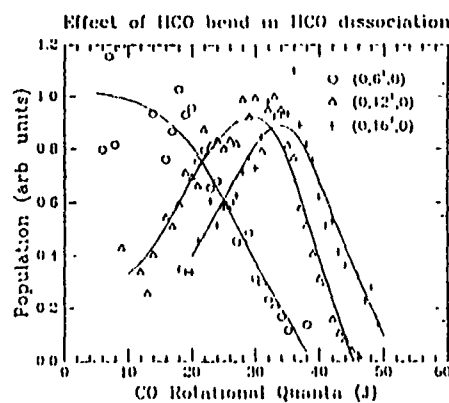
Figure 3 The rotational distribution of the CO (v=0) product shifts to larger J as the number of quanta of HCO bending vibration is increased.

SOLVATION EFFECTS ON SUBSTITUTED AROMATIC MOLECULES IN SUPERSONIC JETS

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Résumé :

   Les interactions soluté-solvant dans les complexes de van der Waals, constitués de molécules aromatiques substituées, associées à des solvants usuels, ont été étudiées par les techniques de fluorescence induite par laser. Deux systèmes sont examinés plus particulièrement : le 9-methoxyanthracene associé à des solvants protiques et le 1-cyanonaphtalene liés à des solvants polaires. Les déplacements spectraux, la modification des propriétés photophysiques, la formation d'isomères mettent en évidence l'influence des interations locales avec le substituant sur le comportement de la molécule monosolvatée.

-■-■-■-

   The generation of molecular complexes of weak bonding energy in supersonic expansions provides an unique way to study in isolated conditions the interaction between molecules. When combined with laser excitation, this method allows to investigate at the molecular level the modifications of excited states properties (energy and relaxation processes) induced by the presence of a perturbing ligand.

   Jet spectroscopies on molecular complexes involving large aromatic compounds have been widely developed since a few years with the aim to give a better understanding of the photochemistry and photophysics in solution[1].

   Although the understanding of solvatochromism when going from gas phase to solution requires investigations of the influence of the size of the cluster on molecular properties[2], it is also of interest to study solute-solvent site dependent interactions in the case of 1:1 complexes. Substitution of aromatic molecules by an electron accepting or donating group introduces a new site for the attachment for the ligand different from the aromatic ring where the interactions are mainly determined by dispersive forces.

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Such studies are expected to provide models to test the theory of solvent effects in relation with the modification of electron distribution density, the description of intra and inter-molecular charge transfer and acid-base properties in the excited state.

Several aspects of the behavior of the complexes formed between polar aromatic molecules and polar solvents in a supersonic expansion probed by laser induced fluorescence techniques will be illustrated here with particular focusing on the solvent induced spectral shift of the S_0-S_1 0-0 transition, fluorescence decay times and isomer formation.

COMPLEXES OF 9-METHOXYANTHRACENE WITH PROTIC SOLVENTS

The 9-methoxyanthracene chromophore (MeOA) has been selected as an aromatic ether since the O atom of the methoxy substituent provides a site for specific interactions with hydrogen bond donating solvent. Thus these complexes differ from the hydrogen bonded complexes investigated so far which involve an acidic chromophore such as phenol or 1-naphtol and proton accepting solvents[3].

Microscopic solvent shift

We have carried out a systematic study of the microscopic solvent shift induced by complexation with a large series of proton donating solvents extending from H_2O, CH_3OH, ethanol, 1-propanol, 2-propanol, 1-butanol, tert-butanol, CF_3CH_2OH, $(CF_3)_2CHOH$ and HCl. Addition of these protic ligands to jet cooled 9-methoxyanthracene gives rise to new bands in the fluorescence excitation spectrum readily assignable to the formation of 1-1 complexes.

In most cases, the strongest band is blue shifted with respect to the origin of the MeOA origin. For the MeOA-CH_3OH system, a red shifted spectrum similar to that appearing in the complexation of methylanthracene with CH_3OH has been observed and assigned to the complex involving the interaction of the solvent with the anthracene ring. Blue shifted bands have also been identified for the complexes of MeOA with 2 molecules of H_2O and Ch_3OH. Complexation of MeOA with higher alcohols gives rise to multiple origins in the excitation spectrum which have been attributed to the presence of different conformers in the supersonic jet. These attributions have been confirmed by the hole burning spectroscopic techniques.

The blue shift of S_0-S_1 transition of MeOA is characteristic of the presence of the methoxy group and constitutes the signature of an hydrogen bond between the aromatic ether and the acidic hydrogen of the alcohol. The magnitude of the blue shift has been related to the

acidity of the solvent. The acidity of the alcohols in the gas phase is known to increase from methanol to tert-butanol while the reverse order is observed in solution. The observed trend of microscopic solvent shift in jet follows the solution behavior rather than the gas phase order.

Relaxation processes

In many anthracene derivatives such as MeOA an efficient nonradiative ISC channel from the S_1 is opened due to the presence of a nearby higher triplet state T_n[4]. In solution this process is thermally activated indicating that T_n is located higher in energy than S_1. In jet cooled conditions, the S_1-T_n energy gap is reversed, S_1 lying at higher energy than T_n. However, due to the sparse set of T_n levels coupled with S_1 0^0 level this process is expected to be very sensitive to accidental degeneracies. These expectation is illustrated in the case of MeOA-1-propanol complex which exhibits at origin a much shorter decay time (10 ns) than the other complexes.

In the case of excitation of higher vibronic levels of the anthracene ring, the fluorescence of the excited complexes does not originate from the initial excited state as seen in the dispersed emission spectra but from the many levels populated by internal vibrational redistribution. This process results from the vibrational coupling with intermolecular as well as intramolecular low frequency modes. Thus the decays may differ according to the nature of the populated levels.

An example of this behavior is observed in the case of MeOA-$(CH_3OH)_{1,2}$ complexes excited in the 383 cm^{-1} vibronic level of anthracene. The 1:1 complex decays with a shorter lifetime (13 ns) than the bare molecule (19 ns) while the 1:2 complex decay is longer (28 ns). These result may be explained by considering that for 1:1 complex IVR is incomplete and leads to S_1 intramolecular modes which are located above and mixed with T_n. In the case of 1:2 complex, the excess energy is totally redistributed among the intermolecular and solvent modes from which the ISC process is prohibited. This result may be taken as an example where two molecules of solvent attached to the chromophore are sufficient to induce microscopic vibrational relaxation.

COMPLEXES OF 1- CYANONAPHTHALENE WITH POLAR SOLVENTS

1- cyanonaphthalene (1-CNN) provides an interesting example of a molecule with two closely lying and strongly coupled S_1 (L_b) and S_2 (L_a) singlet states whose spectroscopic properties are influenced by a polar environment. In polar solvents the modification of fluorescence spectra has been interpreted by the L_a-L_b levels inversion induced by solute

solvent relaxation. This effect has been related to the charge transfer character of the L_a state which exhibits a larger stabilization energy in polar media[5].

Addition to jet cooled 1-CNN of acetonitrile and diethylether leads to the apparition in the fluorescence excitation spectrum of two strong bands in the region of 1-CNN L_b origin. One of this new feature is red shifted while the other is blue shifted with respect with the bare molecule 0-0 transition. Both absorptions can be assigned to 1:1 complexes from the pressure dependance of their relative intensity. The fluorescence decay times of the acetonitrile complexes excited either at the red shifted (52ns) or the blue shifted (37ns) feature are both longer than that arising from the bare molecule O^0 level (22 ns).

The dispersed emission spectra of these complexes are with minor differences very similar to that of the free molecule when excited at origin.

The dispersed fluorescence from higher vibronic states are typical from vibrational redistribution. The red shifted and blue shifted species have different spectra at lower excess energy but they exhibit both components independently from the excited level at higher energy. Similarly the fluorescence decays are distinct below the energy threshold but become identical above the energy barrier. These results may be interpreted by the presence of two different conformers in the ground state involving different orientation of the solute and solvent molecules. Interconversion between the two forms take place in the excited states with an energy threshold above 450 cm^{-1}. These observations may be related to specific local interactions at different sites of the 1-cyanonaphthalene chromophore which modifies the mixing of the L_b and L_a excited states.

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JET SPECTROSCOPY AND EXCITED STATE DYNAMICS OF FREE RADICALS

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The spectroscopy and excited state dynamics of free radicals are studied in the supersonic free jet. Parent molecules are photolyzed to generate cold radicals just after an orifice. Special radicals studied are benzyl and p-substituted benzyls, and silylene radicals. Laser induced fluorescence spectra and fluorescence lifetimes are measured. Rotational analyses are carried out using high resolution LIF excitation spectra.

1. Benzyl radicals

Benzyl and its p-fluoro, p-chloro, p-cyano and p-methyl derivatives are produced from their chlorides. The vibronic bands are assigned from the LIF excitation and dispersed spectra.

p-Fluorobenzyl: Fig. 1a shows LIF excitation spectrum of p-fluoro-benzyl. The longest wavelength band at 464.602 nm was assigned to 0^0_0 from the dispersed spectrum excited at this band, which showed long progressions of the symmetric ring breathing mode ν_1, that is, 1^0_n and $6a^0_1 1^0_n$. They are typical progressions appearing in the dispersed spectra excited at the 0^0_0 band of monosubstituted benzenes. The LIF excitation spectrum of p-fluorobenzyl is very similar in vibronic structure up to about 1000 cm^{-1} from the 0^0_0 band to that of p-fluorotoluene (Fig. 1b) measured in the jet[1] except for the shift of spectral region from uv to visible. The assignment of the vibronic bands is, therefore, straightforward. It is noteworthy that the
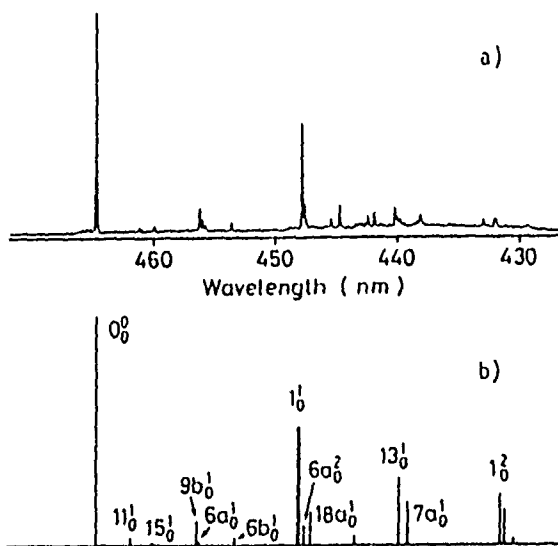
Fig. 1. Excitation spectra of (a) p-fluorobenzyl and (b) p-fluorotoluene.

0^0_0 band has strong intensity which shows sharp contrast with the weak intensity of the 0^0_0 band of benzyl itself due to the accidental forbidden D_1-D_0 transition. The similarity of the band structures suggests that the change in a substituent group of benzene ring from CH_3 to CH_2 exerts little influence on frequencies of ring vibrations, though the electronic energy is considerably changed. However, the vibronic structure above 1000 cm^{-1} from 0^0_0 is more complicated than that of p-fluorotoluene and many bands remain unassigned. The complication of the band structure is understood as a result of the vibronic coupling between D_1 and D_2. p-Chlorobenzyl shows similar feature to p-fluorobenzyl; the vibronic structures of the LIF excitation spectrum is similar to that of MPI spectrum of p-chlorotoluene.

p-Methylbenzyl: The LIF excitation spectrum of p-methylbenzyl does not show good agreement with that of p-xylene.[2] The longest wavelength band at 468.381 nm was attributed to 0^0_0 because its energy almost agreed with that measured in low temperature matrix[3] and film.[4] The dispersed spectrum excited at the 0+351 cm^{-1} band has common features with that of p-xylene obtained by the 0^0_0 excitation in the jet.[2]: progressions of 1_n, $6a_1 1_n$, and $6b_1 1_n$. These facts indicate that the 0+351 cm^{-1} band is 0^0_0 of the D_2-D_0 transition. The complicated structure of the 0+351 cm^{-1} band is understood as the vibronic coupling of the zero vibrational level of D_2 with the 9b level of D_1. The very complicated band group around 0+700 cm^{-1} was interpreted by the vibronic coupling among the $D_2,v_{9b}=1$ level and $D_1,v_1=1$ and $v_{12}=1$ levels from dispersed spectra and vibrational energies.

Benzyl: The LIF excitation spectrum of benzyl is compared with that of toluene measured in the jet[6] as shown in Fig. 2. These spectra does not show agreement with each other, indicating vibronic coupling between D_1 and D_2 similar to p-
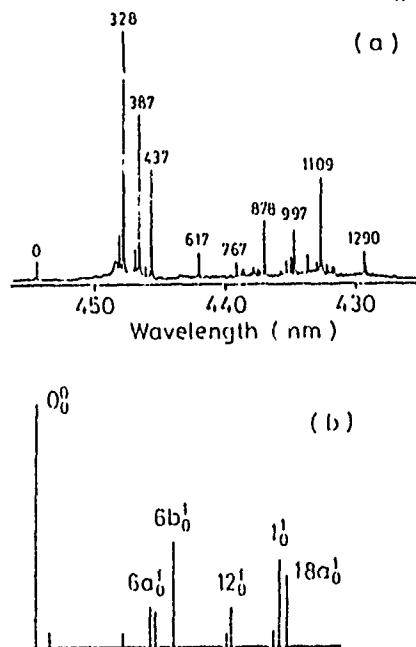
Fig. 2. Excitation spectra of (a) benzyl and (b) toluene.

methylbenzyl. The longest wavelength band at 454.545 nm was assigned as 0^0_0 from the dispersed spectrum. Band type was determined from rotationally resolved high resolution LIF excitation spectra. Fig. 3 shows an example of high resolution spectrum for the 0^0_0 band. The band type of this band was determined as b-type. This indicates that the lowest electronically excited state is 1^2A_2. It is though from the dispersed spectra that the 0+328 and +387 cm^{-1} levels have the 6b vibrational character and the 0+437 cm^{-1} level has the 6a character. These
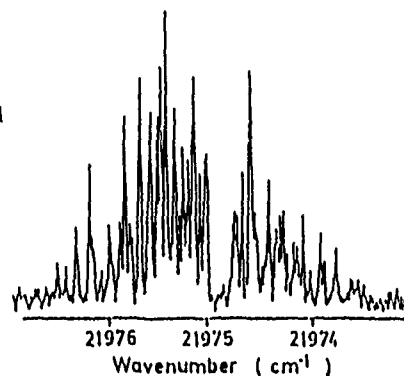
Fig. 3. High resolution excitation septrum of the 0^0_0 band of benzyl.

assignments are consistent with observed band types; symmetric vibrational band $6a^1_0$ is of b-type and bands having 6b vibrational character are of a-type. The weak intensity of the 0^0_0 band reflects the accidental forbidden character of the D_1-D_0 transition of benzyl. The strong intensity of the $6a^1_0$ and $6b^1_0$ bands is interpreted by the breakdown of the accidental forbiddenness due to state mixing.

2. Silylene

SiH$_2$ and SiD$_2$ were generated by the ArF laser photolysis of phenylsilane and phynylsilane-α-d$_3$, respectively. LIF excitation and dispersed spectra were measured for the bending vibronic bands of the A^1B_1-X^1A_1 transition. The rotational analysis was carried out from the high resolution LIF excitation spectra. The heterogeneous predissociation to $Si(^3P)$+H$_2$ is proposed from the anomalous rotational structure in the excitation spectra; the rotational lines of the r(1) sub-branch terminating on the K_a'=0 rotational level have stronger intensity than those of the r(0) sub-branch terminating on K_a'=1, though the latter is expected to be stronger due to the low temperature Boltzmann distribution in the jet. The time-resolved excitation spectra shown in Fig. 4 demonstrate shorter lifetime of K_a'=1 rovibronic levels in the A^1B_1 state. The heterogeneous predissociation is interpreted with the second order perturbation; A^1B_1-(a-type Coriolis)$\rightarrow X^1A_1$-(spin-orbit)$\rightarrow a^3B_1 \rightarrow Si(^3P)$+H$_2$. It is experimentally demonstrated that there is a potential barrier at the dissociation path of

the bottom of the A^1B_1 state. The onset of the second predissociation channel to $Si(^1D)+H_2$ at the (0,7,0) vibronic level of $SiH_2 A^1B_1$ is manifested as sharp decrease in the observed fluorescence lifetime. The electronic transition moment of the A^1B_1-X^1A_1 transition is estimated to be $|\mu_0|^2=0.26e^2a_0^2$ from the Einstein equation for spontaneous emission using measured fluorescence lifetimes for single rovibronic levels with $K_a'=0$ and calculated Franck-Condon factors.
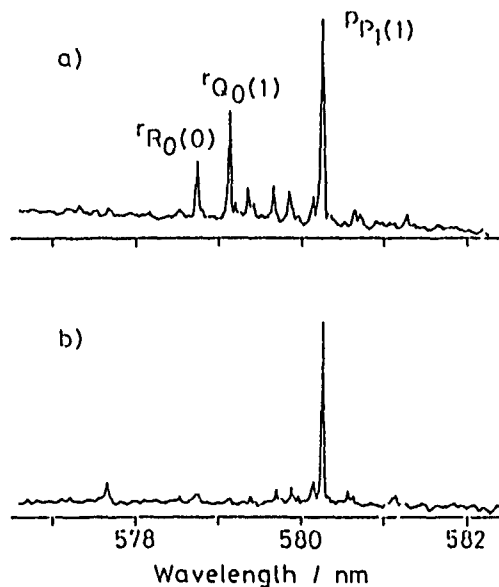
Fig. 4. Time-resolved excitation spectra of SiH_2. (a) 0-50 ns and (b) 50-100 ns

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ELECTRONIC EXCITATION AND DISSOCIATION OF MATRIX ISOLATED

MOLECULES RESULTING FROM ACCUMULATION OF VIBRATIONAL ENERGY

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Certaines espèces diatomiques telles que CO, NO, O_2 dispersées en matrice cryogénique ont une durée de vie vibrationnelle très longue. Elles possèdent l'étonnante propriété d'accumuler, lorsqu'on les excite vibrationnellement à l'aide d'un laser infrarouge, un grand nombre de quantas dans un petit nombre de sites favorables. Les molécules fortement excitées vibrationnellement peuvent alors échanger en une seule étape un nombre de quantas suffisant (6-10) pour atteindre un état électronique excité. Au cours d'un tel processus, plusieurs dizaines de quantas de faible énergie (~ 0,2 eV) donnent naissance à une excitation électronique d'énergie beaucoup plus grande (7 à 8 eV). Cette conversion d'énergie vibrationnelle en énergie électronique résulte en une luminescence UV-visible ou conduit à la dissociation moléculaire.

Diatomic molecules such as CO, NO, O_2 dispersed in low temperature matrices have a very long vibrational lifetime. When they are vibrationally excited by an IR laser, they amazingly tend to accumulate a large number of quanta in a small number of favourable sites. Strongly vibrationally excited molecules can then exchange a bunch of vibrational quanta (6-10) in a single step and thus reach an excited electronic state. The vibrational energy corresponding to several tens of small quanta (~ 0.2 eV) is converted into a much more energetic electronic excitation (6-8 eV) which results either in electronic luminescence or in molecular dissociation.

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Vibrational relaxation of diatomic molecules such as CO, NO, CN, N_2, O_2 dispersed in low temperature rare gas crystals is extremely slow. In these systems the rate of spatial transfer of vibrational excitation induced by long range forces exceeds the rate of loss due to radiative or radiationless relaxation by orders of magnitude. In particular the non resonant exchange of vibrational energy among a collection of molecules excited into the v = 1 level produces molecules in the v = 2 level according to

$$AB_{site\ 1}(v=1) + AB_{site\ 2}(v=1) \rightarrow AB_{site\ 1}(v=0) + AB_{site\ 2}(v=2) + \Delta E_{anh}$$
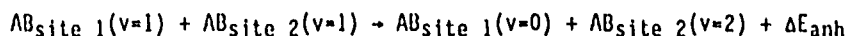
This reaction describes the fusion of two v = 1 excitations into a v = 2 one, a process which is quite analogous to triplet-triplet annihilation in organic crystals (1) or to up conversion among rare earth ions in crystals (2). The energy mismatch $\Delta E_{anh} = h\nu_{10} - h\nu_{21}$ should be made up by the thermal bath, i.e. the lattice phonons. In the same way the repetitive fusion of vibrational excitations, described by the general reaction

$$AB_{site\ 1}(v) + AB_{site\ 2}(v') \rightarrow AB_{site\ 1}(v-1) + AB_{site\ 2}(v'+1) + \Delta E_{vv'}$$
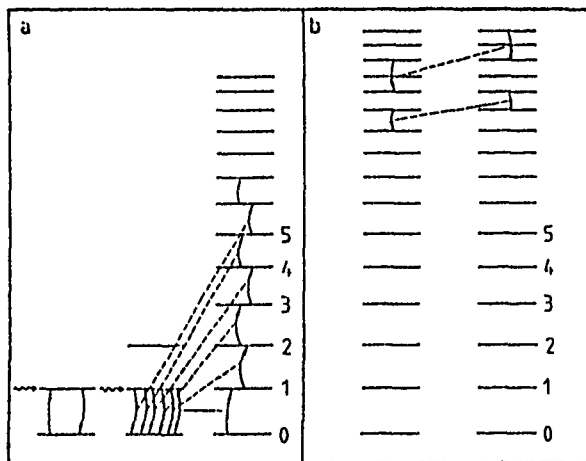
Figure 1

Accumulation of vibrational quanta in matrix isolated molecules

a) the v = 1 excitations are resonantly exchanged from site to site until they get trapped at a favourable site. However the number of $h\nu_{1\rightarrow 0}$ quanta which can be stacked is limited due to the increase in ΔE.

b) the accumulation of vibrational energy can continue owing to the exchange of one or two quanta $h\nu_{v\rightarrow v-1}$ among localized high-v excitations at a large distance from each other (~ 100 Å).

and illustrated in fig. 1, results in accumulation of energy into the upper vibrational levels. Several tens of quanta can be stacked on a single molecule. Such a strong excitation corresponding to several eV of vibrational energy has been observed in matrix isolated CO and NO (3).

Vibrational energy may also be converted into electronic excitation. When the vibrational excitation exceeds that of the first electronic excited states, internal conversion or intersystem crossing may bring the molecule from high vibrational levels of the ground electronic state to nearly resonant vibronic levels. The efficiency of this process is strongly dependent upon the magnitude of the Franck Condon factors associated with the intramolecular radiationless process. In molecules such as CO or NO such a process does not occur. However there is an other mecanism leading to electronic excitation. For high v levels, the transition dipole moment associated with vibrational overtone transition involving a large change in the vibrational quantum number, i.e. $\Delta v = 6$ to 10, takes an appreciable. value. This is due to the intrinsic anharmonicity of the intramolecular potential and also to the perturbation by the solid environnement. Though multipolar interactions are not strong enough to allow multiquantum V-V exchange with a large Δv, in return they give rise to intermolecular V-E transfer processes described by :

$$AB_{site\ 1}(v) + AB_{site\ 2}(v'') \rightarrow AB_{site\ 1}(v-n) + AB^*_{site\ 2}(v') + \Delta E$$
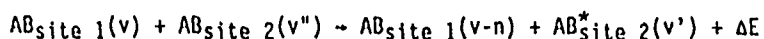
and illustrated in fig. 2. Here AB^* denotes an electronically excited molecule. In this case the weakness of the overtone transition in the donor is compensated by the strength of the electronic transition in the acceptor. The excitation of a bound state gives rise to electronic luminescence. In the most spectacular case the up -conversion process transforms the IR photons ($\lambda = 6\mu$) used for vibrational excitation into UV light ($\lambda = 250$ nm). The excited state may also be either repulsive or predissociated. The accumulation of vibrational quanta can then lead to the dissociation of the acceptor molecules provided the excess energy with respect to the gas phase dissociation limit is large enough to overcome the potential barrier resulting from the solid environnement.
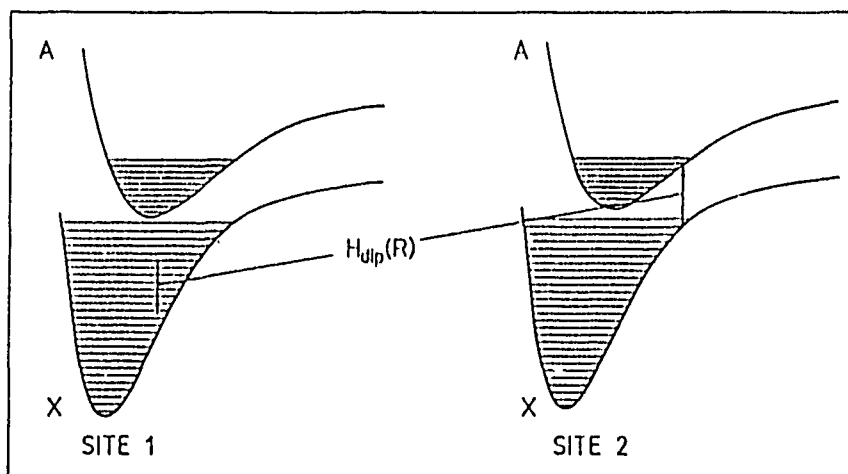
Electronic excitation resulting from the transfer of a bunch of vibrational quanta between molecules which are both strongly vibrationally excited. This process resulting from dipole-dipole interaction involves an high overtone vibrational transition in the donor at site 1 and a vibronic transition in the acceptor at site 2.

These processes will be discussed on the basis of selected experimental observations on CO, NO and O_2 molecules.

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Vibronically Induced Chemistry of Collisional Pairs in a Cryogenic Matrix
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An inert solid matrix is a natural environment to conduct controlled bimolecular photochemistry by exciting reactants to low energy surfaces. Reactant nearest neighbors enclosed in a matrix cage are held in contact indefinitely, hence absorption of a photon occurs while the partners are in a state of collision. This is crucial if product specificity is a main objective since irradiation *during* a collision is an ideal way to initiate chemistry of molecules that are excited to levels below the dissociation threshold (which requires that the excitation is sustained up to the moment of collision). Photochemistry induced by accessing pathways that lie below reactant dissociation limits favors product control because it ensures that no free atoms are generated that may lead to non-selective attack on substrate molecules.

We will discuss examples of controlled oxygen, halogen, and methylene group transfer reactions induced by selective vibronic excitation of reactant collisional pairs in rare gas matrices. Preparation of sustained collisional pairs in a rare gas solid at cryogenic temperature is a convenient approach to explore vibronically induced bimolecular chemistry in detail. Reaction paths can be mapped by trapping transients and determining their structure by FT-infrared spectroscopy. Continuously tunable CW dye lasers can be employed to monitor the photolysis photon energy dependence of reaction quantum efficiencies and thereby learn about the dynamics of the reaction.

Single photon excitation of NO_2·alkene pairs at wavelengths as long as 600 nm results in O atom transfer to the CC double bond [1-3]. Photons of this energy excite NO_2 to vibronic levels 25 kcal mol^{-1} below its 398 nm dissociation threshold. High product specificity is manifested by formation of epoxides as sole final oxidation products with high stereochemical integrity (e.g. cis-2-butene → cis-epoxide, trans-2-butene → trans-epoxide). Photooxidation of olefins with terminal C=C bonds (isobutylene, ethylene) give aldehyde as well. Red light induced O atom transfer to allene results in exclusive central atom attack (allene oxide, cyclopropanone), while ketenes are the only oxidation products of alkynes [4]. Product specificity is lost when tuning the photolysis photon energy above the $NO_2 \rightarrow O(^3P) + NO$ dissociation threshold.

In each reaction an intermediate was trapped concurrently with the final oxidation product, namely an alkyl nitrite radical in the case of olefins and allene, and an iminoxy radical upon O atom transfer to CC triple bonds. D isotope effects on branchings between trapped intermediate and final oxidation product revealed that the two species share a common transient precursor. Stereochemical correlation between alkyl nitrite radical and epoxide, and especially the fact that O

atom transfer to CC double and triple bonds gives different types of trapped radicals indicates that these are transient oxirane biradicals (in the case of alkenes) or ketocarbene biradicals (in the case of alkynes) that are chemically trapped by NO cage coproduct. Hence the primary reaction step of vibronically excited NO_2 is large amplitude O atom transfer to the multiple bond to produce a transient biradical . Competition between intramolecular stabilization of the the biradical and combination with NO dictates the branching between final oxidation product and trapped radical. For example, in the case of ethylene + NO_2 the observed threshold ɔ O atom transfer of 574 nm indicates that $\dot{C}H_2$-CH_2-$\dot{O}$ is produced directly in the $^1D(\sigma\sigma)$ ground electronic state according to comparison with literature ab initio results. Competition between combination with NO and

$$CH_2=CH_2\ NO_2 \xrightarrow{h\upsilon} \begin{bmatrix} +NO \\ \dot{C}H_2\text{-}CH_2\text{-}\dot{O} \\ ^1D \end{bmatrix}$$

overset: products

$$\overset{O}{\underset{CH_2\text{-}CH_2}{\diagup}} + NO \quad (EO)$$

$$CH_3\text{-}C\underset{H}{\overset{O}{\diagup}} + NO \quad (A)$$

$$\downarrow$$

$$\dot{C}H_2\text{-}CH_2\text{-}ONO$$

	h_4	d_4
$\dfrac{EO}{A}$	≤.03	167
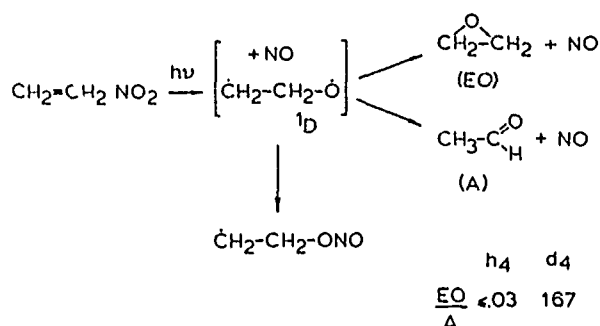
1,2-H shift (ring closure) must be very fast (psec) as the reaction is completely stereospecific in the case of cis and trans-CHD=CHD + NO_2 (no stereochemical scrambling by rotation about the biradical CC bond).

Since the transient oxirane biradical is trapped by NO in its nascent form (including conformation), determination of the structure of the trapped alkyl nitrite radical by vibrational analysis allowed us to elucidate for the first time detailed regio- and stereochemical paths of alkene oxidations. For example, we have trapped two diastereomeric cyclohexyl nitrite radicals upon photooxidation of cyclohexene (a chair form with an axial, and one with equatorial C-O group), indicating that reaction proceeds along both diastereomeric paths (arrows), leading to a specific cyclohexene oxirane biradical stereoisomer in each case. This result cannot be inferred from the

$$\text{cyclohexene} + NO_2 \xrightarrow[600\,nm]{h\upsilon} \overset{+\ NO}{\text{cyclohexyl oxirane}}$$
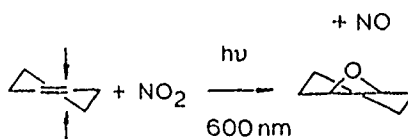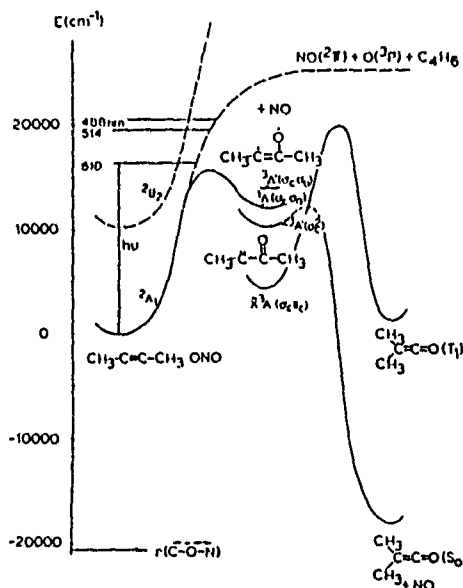
structure of the cyclohexene oxide product. Iminoxy radical formed upon O atom transfer to dimethyl acetylene indicates that the reaction proceeds through the singlet $A'(\sigma_c^2)$ ketocarbene biradical state (Figure). Branching between ketene and iminoxy radical is dictated by the competition between Wolff rearrangement of $CH_3\ddot{C}C(=O)CH_3$ and combination with NO. Using this method of chemical trapping of transient ketocarbene we have been able to uncover the regiochemical path of methylacetylene oxidation. Only iminoxy radical with an aldehydic C=O group is observed, which implies that O atom transfer occurs exclusively to the terminal carbon leading to the most stable CH_3-$\ddot{C}$-C(=O)-H biradical. This selectivity with respect to the reaction path is again not apparent from the structure

$$CH_3-C\equiv C-H \ + \ NO_2 \ \xrightarrow[615\,nm]{h\upsilon} \ \left[\begin{array}{c} +NO \\ \overset{O}{\underset{}{CH_3-\ddot{C}-\overset{\|}{C}-H}} \end{array} \right]$$
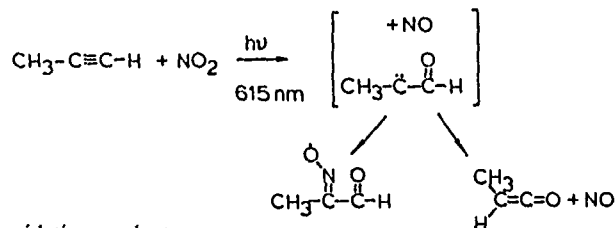
of the final oxidation product.

Loss of product specificity upon excitation of NO_2 at photon energies above the 398 nm dissociation threshold to $O(^3P)$ + NO was indicated by the appearance of additional reaction products, e.g. 2-cyclohexen-1-ol and cyclohexanone in the case of cyclohexene + NO_2, ketene in the case of the ethylene + NO_2 reaction. Some products (cyclohexenol and ketene) were shown to emerge from the dissociation - addition path (dissociation of NO_2 to $O(^3P)$ followed by thermal addition of O to alkene). Nevertheless, product growth kinetics shows that there remains substantial propensity for alkene·NO_2 collisional pairs to react along the large amplitude O atom transfer path even upon excitation above the NO_2 dissociation limit. This observation is closely related to recent reports on photochemical reaction of weak complexes in cryogenic matrices and in

molecular beams that demonstrate coupling into large amplitude atom transfer coordinates in cases of favorable precursor geometries (Soep [5], Wittig [6], Pimentel [7]).

Interestingly, thermal reaction of unsaturated hydrocarbons in gas phase or solution leads to nitroalkyl radicals, i.e. to C-N bonds formation rather than O atom transfer. This difference between matrix and fluid phase alkene + NO_2 chemistry is surprising in view of the fact that NO_2 excited by low energy visible photons has predominantly the character of a highly vibrationally excited, electronic ground state species, hence would be expected to have chemistry similar to that of thermally excited $NO_2(^2A_1)$. It indicates preferred access of the vibronically excited collisional pair to a large amplitude O atom transfer coordinate while ignoring a lower barrier translational (in the solid: van der Waals) coordinate that would lead to C-N bond formation through NO_2 addition.

We have expanded our work on vibronically induced O atom transfer reactions to CH_2 group transfer reactions. For example, excitation of $CH_2=C=O\cdot1,3$-butadiene pairs at 400 nm (10 kcal mol^{-1} below the $CH_2(^3B_1)$ + CO dissociation barrier) led to methylene group transfer to yield vinylcyclopropane + CO.

Controlled chemistry of collisional pairs in a matrix is not limited to large amplitude atom or group transfer reactions. Other examples are cycloaddition reactions of metastable electronically excited molecules like singlet SO^8 and singlet O_2^9, and reaction from non-predissociative levels of charge transfer states, e.g. O_2 + alkene [10].

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PHOTOTAUTOMERISM OF HETEROAROMATIC MOLECULES WITH INTERNAL HYDROGEN BONDS.
SINGLE AND DOUBLE PROTON TRANSFER IN ELECTRONICALLY EXCITED STATES

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Some heteroaromatic molecules possessing internal hydrogen bonds undergo an
extremely fast process that may be followed on the levels of three diffe-
rent electronic states: S_1, T_1 and S_c. This is the proton transfer (PT)
reaction.

A. SCHIFF BASES
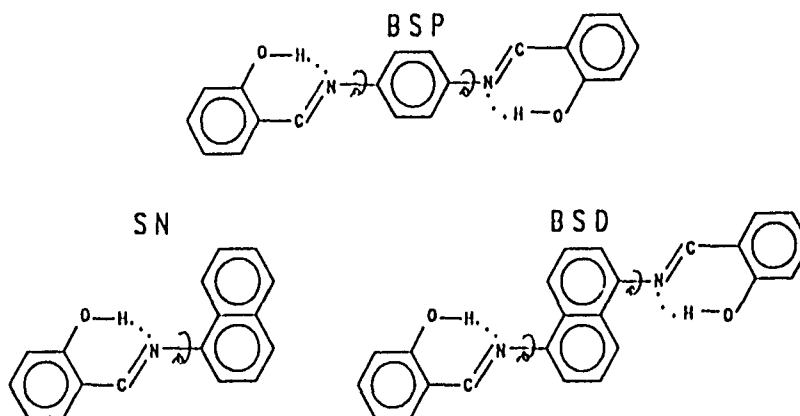
B: Bipyridyl-diols.
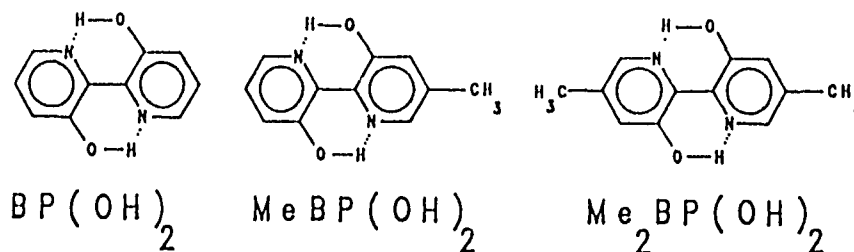
Scheme 1. BSP: N,N-bis(salicylidene)-p-phenylenediamine; SN: N-salicylide-
ne-α-naphthylamine; BSD: bis-salicylidene-1,5-diaminonaphthalene; BP(OH)$_2$:
2,2'-(bipyridyl)-3,3'-diol; MeBP(OH)$_2$: 5- methyl-2,2'-(bipyridyl)-3,3'-di-
ol; Me$_2$BP(OH)$_2$: 5,5'-dimethyl-2,2'-(bipyridyl)-3,3'-diol.

Two families of molecules will illustrate some problems connected with pho-totautomerization in S_1 state. These are Schiff bases and bipyridyl-diols shown in Scheme 1. The choice of compounds is not fortuitious: thus SN is "one half" of BSD molecule, and MeBP(OH)$_2$ represents a possibly delicate perturbation of the symmetry of the BP(OH)$_2$ structure. The typical spectral symptom of fast reaction occuring in excited state is shown in Fig.1 on the example of two structurally related Schiff bases: absorption and strongly Stokes shifted fluorescence spectra are here the manifestation of the PT reaction in S_1 state. Two groups of molecules, A and B, although sharing the common feature - phototautomerism - are very different: molecules B are firmly kept planar by two strong internal hydrogen bonds, while structures A contain freely rotating groups, shown by arrows in Scheme 1. Molecules B reveal a strong phototautomeric fluorescence (typical $\eta_F \approx 0.3$ at room temp.), and even lasing abilities[1]. In contrast, structures A are mostly controlled by the radiationless transitions ($\eta_F \approx 10^{-3} - 10^{-4}$). For both groups of molecules the phototautomeric fluorescence is red shifted by 10000 cm^{-1} and no normal emission is observed.
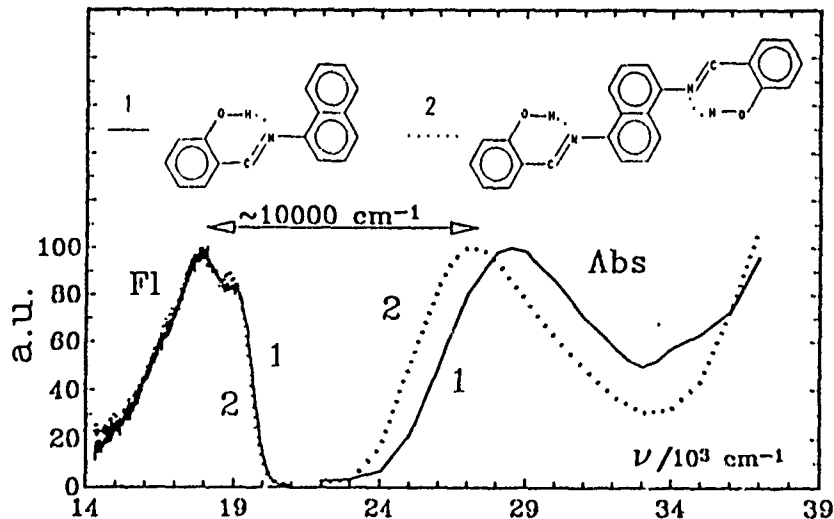
Fig.1 Room temp. absorption and fluorescence spectra of two Schiff bases; solvent: butyronitrile

The main question to be discussed is as follows: the driving force for PT reaction created in excited state may be used by a molecule just as shown in Scheme 2 on the example of $BP(OH)_2$: would a molecule undergo the single Scheme 2.
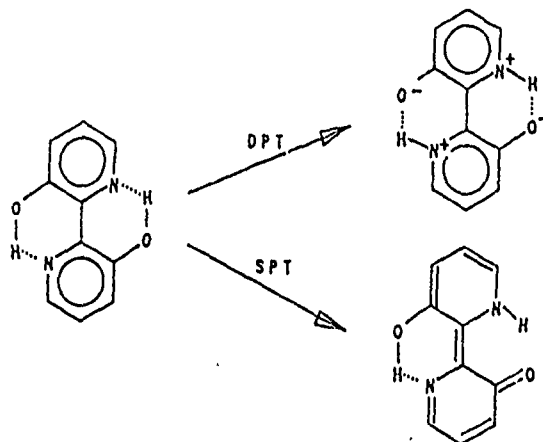
PT (SPT), forming a true keto-group, or would it preserve the symmetry undergoing the double PT (DPT), but adopting the structure represented in Scheme 2 by a doubly zwitterionic species? As a method of distinguishing between a monoketo (MK) and a diketo (DK) phototautomers, the dipole moment determination of excited molecule was applied, compared with the results of calculations. Calculations were performed with molecular mechanics method (ground state of BSP) and INDO/S method. For experimental determination of the excited state dipole moments, a solvatochromic method was applied. However, no shift, either of absorption or of fluorescence bands, was detected in all studied molecules. The expected zero or small dipole moments of fluorescent species were verified for molecules B by the electrooptical IEOEM method[2]. All data are collected in Table 1. It is easily seen that the direct determination of the dipole moment of the fluorescent species nicely confirms the DPT mechanism in excited bipyridyldiols. The values $\mu^*=0$ and 0.46 D for the excited symmetric parent molecule $(BP(OH)_2)$ and its monomethylated derivative leave no doubt that monoketotautomers are not responsible for fluorescence emission. Their dipole moments were predicted to exceed 4 D. This is one of very few well documented examples of intramolecular double PT in excited state. In contrast, for molecules A a dipole moment determination of the excited tautomer is not a

good way of decoding the reaction mechanism.

Even the symmetric (BSP) molecule has a quite large dipole moment, calculated with allowance of the free rotation around the single bond, and nicely reproduced by experimental determination in the G state. Moreover, the differences between mono- and diketotautomers are predicted to be rather small. So, for molecules A a comparison of symmetric structures with

Table 1. Calculated and experimental values of dipole moments of the molecules studied in the ground (G) and fluorescent (F) states; DE, MK and DK stand for a dienol, monoketo- and diketotautomer, resp.

molecule	el. state	tautomer	dipole moment [D] calc.	exp.
BSP	G	DE	3.0	2.8±0.5
	G	MK	4.7	-
	F	DE	5.1	-
	F	MK	7.3	-
	F	DK	6.2	-
BP(OII)$_2$	G	DE	0.01	-
	F	MK	4.3	-
	F	DK	0.02	0.0±0.2
MeBP(OII)$_2$	G	DE	0.45	0.54±0.01
	F	MK	4.90	-
	F	DK	0.41	0.46±0.03

model compounds will be discussed, as an alternative method of studying the PT reaction in excited state.

The singlet vs triplet state reactivity of proton transferring molecules B will also be discussed.

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FROM POLYENALS TO RETINAL:
AN ELECTRON-SPIN-ECHO STUDY OF THEIR TRIPLET STATE.

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Electron-spin-echo spectroscopy is found to be a powerful tool in the study of the electronic structure of the non-radiative, short-lived, lowest triplet state of polyenals. This state is of $\pi\pi^*$ character. We will focus on all-trans-retinal and relate the zero-field splittings, relative populating rates and decay rates of the spin sublevels for this molecule to the corresponding data for model compounds.

Molecules whose chromophore is based on a linear conjugated carbon chain continue to attract attention of spectroscopists because of their role in many photochemical and photobiological processes. In order to gain insight into photoisomerization, energy transfer and photoprotection in biological systems and photoconductivity in conjugated polymers, one should have a detailed knowledge of the change in the electronic structure of such molecules upon excitation. We have studied all-trans polyenals, molecules that consist of a chain of alternately single and double carbon-carbon bonds ending in an aldehyde group. From its composition one would judge this chromophore to be a relatively simple one but its characterization still presents a challenge to spectroscopists. This is particularly true for the triplet state, as its non-radiative character hampers the use of optical techniques.

It will be shown that a time-resolved electron-paramagnetic-resonance (EPR) study of the short-lived lowest triplet state T_0 of all-trans polyenals is feasible by the use of electron-spin-echo (ESE) spectroscopy in combination with pulsed laser excitation. We report results for all-trans-retinal and the model compounds all-trans-2,4,6,8,10-dodecapentaenal (DP), all-trans-2,4,6,8- decatetraenal (DT), and their methylsubstituted analogues MDP and MDT (fig. 1). We include not only DP and MDP but also DT and MDT because steric hindrance between the substituted cyclohexene ring and the polyenal chain may well lead to a non-planar skewed C_6-C_7 conformation of retinal in the triplet state.

The polyenals were dissolved in polyethylene films that were stretched by approximately 500%. All compounds were optically excited at 355 nm by the third harmonic of a Nd:YAG laser (5mJ/pulse). The ESE

experiments were performed at 1.2 K by applying a two-pulse echo sequence after the laser flash. For the experiments in a magnetic field microwaves of a fixed frequency of 9.35 GHz were used, for those in zero-field the microwave frequency could be varied between 1 and 4 GHz.
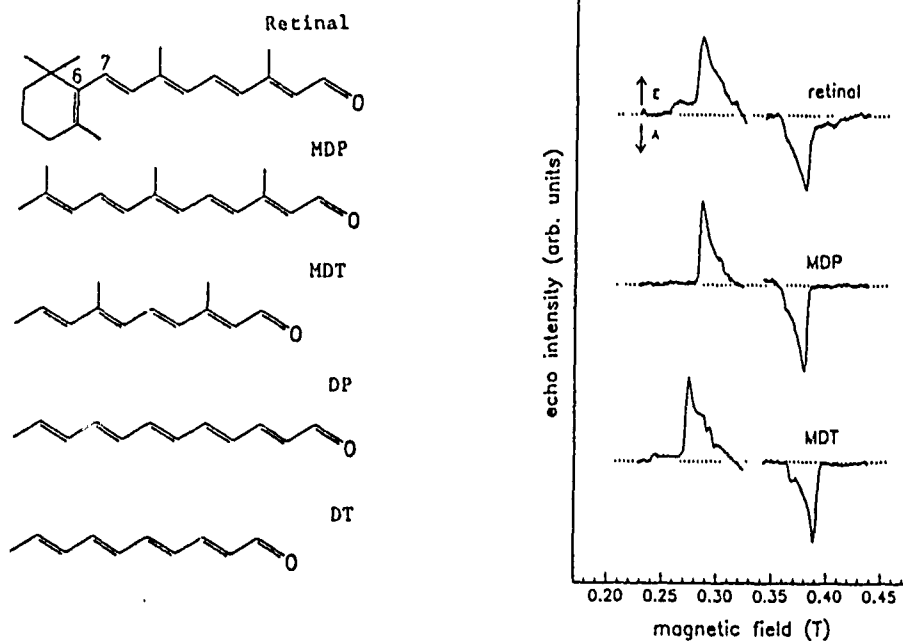
Fig 1. *Molecular structures of the polyenals.*
Fig 2 *ESE-detected EPR spectra of three polyenals in stretched polyethylene films for $\vec{B}_0 \perp \vec{s}$.*

Upon excitation into the singlet manifold ESE signals have been observed for all polyenals listed in fig. 1 and triplet EPR spectra have been detected by monitoring the echo intensity at a fixed time after the laser flash while sweeping the magnetic field $\vec{B}_0$. The spectra only depend on the orientation of $\vec{B}_0$ with respect to the stretch direction $\vec{s}$ of the film; the samples have cylindrical symmetry. In fig. 2 some ESE-detected EPR spectra are displayed as observed for $\angle(\vec{B}_0, \vec{s}) = 90°$. The spectra show emission and absorption of microwaves over a wide range of magnetic-field strengths and consist of sharp features and broad shoulders. For this orientation of $\vec{B}_0$ with respect to $\vec{s}$, the magnetic field is parallel to one of the principal axes of the fine-structure tensor of T_0 (the one indicated by x in fig. 3) for a perfectly aligned molecule. Two more of such canonical orientations of $\vec{B}_0$ have been found for each polyenal and

for all spectra the signals at low field are in emission while the signals at high field are in absorption. Qualitative considerations and numerical simulations based on a Gaussian orientation distribution of the molecules in the film around $\bar{s}$ prove that the ESE-detected EPR spectra indeed derive from the triplet state of the polyenals.

Table 1 *Frequencies of the observed zero-field transitions, the relative populating rates of the T_z sublevel and the decay rates of all three sublevels of T_0.*

	(Z–X)/h (MHz)	(Z–Y)/h (MHz)	p_z	k_x (ms^{-1})	k_y (ms^{-1})	k_z (ms^{-1})
retinal	2370 ± 15	1990 ± 40	0.88 ± 0.04	14.0 ± 2.5	59 ± 12	85 ± 4
MDP	2360 ± 10	1995 ± 10	0.85 ± 0.04	12.0 ± 1.5	53 ± 13	95 ± 7
DP	2496 ± 3	2125 ± 3	0.91 ± 0.02	4.6 ± 0.5	25 ± 4	73 ± 5
MDT	2370 ± 15	2460 ± 10	0.94 ± 0.02	6.5 ± 1.5	34 ± 7	55 ± 2
DT	3041 ± 4	2620 ± 3	0.93 ± 0.01	1.9 ± 0.2	8 ± 1	36 ± 3

From such experiments in a magnetic field estimates of the zero-field splittings have been obtained. Subsequently we have observed the T_z-T_x and T_z-T_y (cf. fig. 3) transitions in zero-field. The corresponding frequencies are summarized in table I. The sublevel ordering, given in fig. 3, is found to be the same for all polyenals. The triplet state is a $^3\pi\pi^*$ state. Previously we concluded that the zero-field splitting of unsubstituted polyenals, including DP and DT, is determined by the length of the conjugated chain [1]. The zero-field parameter X turned out to be inversely proportional to (n+1), n being the number of carbon-carbon double bonds. As table I shows, substitution only slightly changes the frequencies of the zero-field transitions. The values for retinal and MDP are even nearly identical. The double bond of retinal that is part of the cyclohexene ring apparently fully participates in the triplet excitation which suggests that the chromophoric part of retinal is more or less planar in the triplet state. If retinal in polyethylene has a skewed 6-s-cis conformation with a dihedral angle of 50° or 60° in the ground state, this would mean that the molecule undergoes a profound structural change upon triplet excitation.

The dynamics of T_0 has been investigated both in a magnetic field and in zero field by monitoring the echo intensity as a function of t_d, the time between the laser flash and the first microwave pulse. A typical

example of a decay curve for retinal is reproduced in fig. 4. From such experiments we have obtained the relative populating rates and the decay rates of the individual spin sublevels. Data for the various polyenals, summarized in table I, reveal that upon optical excitation into the singlet manifold invariably about 90% of the molecules end up in the T_z spin sublevel. This large selectivity of the populating process arises from the spin-orbit coupling between the lowest $^3\pi\pi^*$ and the $^1n\pi^*$ state that is governed by a dominant local contribution on the oxygen atom.
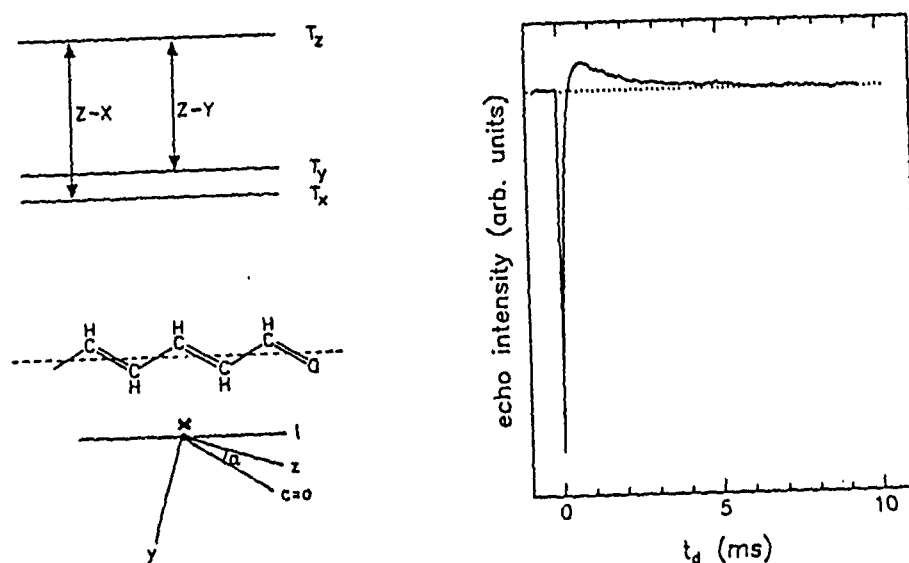
Fig 3. Sublevel ordering of the $^3\pi\pi^*$ state; position of the principal axes of the fine-structure tensor with respect to the polyenal chain.

Fig 4. Echo intensity for retinal as a function of the delay time t_d for the high-field transition with $\bar{B}_0 \perp \bar{s}$.

Unlike for the zero-field parameters and the relative populating rates, addition of substituents on the polyenal chain significantly influences the radiationless decay of T_0 (table I). The lifetimes of all spin states become shorter and the sublevel selectivity decreases. The change already occurs upon methyl substitution, while the presence of the cyclohexene ring does not noticeably affect the decay anymore. The average of the decay rates corresponds to a lifetime $\tau = k_{av}^{-1}$ varying from 65 μs (DT) to 19 μs (MDP and retinal).

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FEMTOSECOND SPECTROSCOPY OF SOLUTION PHASE

ISOMERIZATION REACTIONS

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Time-resolved spectroscopic studies of the photoisomerization of *cis*-stilbene have yielded a large amount of information on these simple reactions in solution.[1-7] The isomerization of electronically excited *cis*-stilbene (cis*) occurs in 0.5 to 2 ps even in relatively high friction solution-phase environments.[5,7] These results have been interpreted in terms of either unrestricted motion on a barrierless potential surface or motion over a very small barrier (1.2 kcal/mole).[5,6] The initially created cis* population is partitioned between two primary reaction pathways, one involving geometric rearrangement leading to *trans*-stilbene production and the second involving electronic rearrangement leading to dihydrophenanthrene (DHP) production. This is shown schematically in Fig. 1.
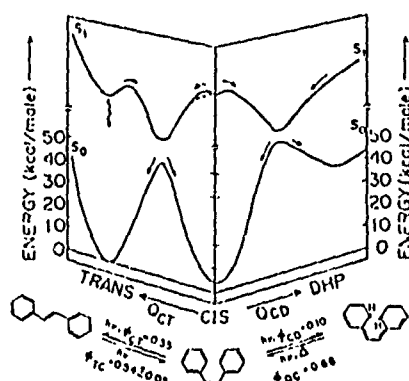
Figure 1. A schematic diagram of the electronic states surfaces responsible for the photoisomerization reactions of *cis*-stilbene. Approximate quantum yields for the various reactions are indicated on the figure.[8-11]

The fast photoisomerization reactions of *cis*-stilbene provide an excellent opportunity to perform detailed studies of the initially formed isomerization products. In room temperature alkane solvents the photoisomerization products of *cis*-stilbene are produced within 1 to 2 ps of excitation. As this time scale is much faster than rotational diffusion times in these solvents (typically 10 to 100 ps for *trans*-stilbene),[12] the intramolecular rearrangements will occur while the molecule is essentially fixed in space. In this situation the average relative alignments of the reactant and product molecules can be measured with

polarized light pulses. In addition, the time scale for photoisomerization is comparable to or faster than the time scales required for intramolecular vibrational redistribution and faster than the ca 10 's of ps time scales required for the transfer of internal vibrational energy from aromatic molecules to the surrounding solvent.[13-15] As a result it is compelling to assume that the product molecules are formed vibrationally hot and very likely possess a non-Boltzmann distribution of excess vibrational energy at early times. Thus, it is possible in this system to begin to pose and answer several questions which have not been addressable in previous studies of solution-phase photochemical reactions.

One of the more interesting questions is that of energy disposal during a photochemical reaction. The photoisomerization of *cis*-stilbene following excitation by a 312 nm pulse results in the formation of *trans*-stilbene and DHP with excess energies of 33650 cm^{-1} and 20000 cm^{-1} respectively. The excess energy available in these reactions will initially be partitioned between internal and external degrees of freedom. Some of the energy will be dumped directly into the solvent during the photoisomerization process as a result of the solvent rearrangements necessary to accommodate the change in the size and shape of the photoproduct. This represents the external friction on the reaction coordinate. The remainder of the energy is retained as vibrational excitation of the resulting product molecules. In a polyatomic molecule having a sufficiently large number of modes, the internal excitation resulting from relaxation might be expected to generate a distribution of vibrationally excited product molecules characterized by a single temperature. In this limit the energy dissipation to internal modes may be referred to as the internal friction on the reaction coordinate. The energy retained as vibrational excitation of the product molecule will be transferred to the surrounding solvent and thus dissipated on a time scale of 10's of ps.

Four types of experiments have been performed to investigate the initially formed isomerization products of *cis*-stilbene: (1) Pump/probe measurements in the regions of the DHP and trans product absorptions have been performed to accurately determine the rates of appearance and cooling of the isomerization products. (2) Anisotropy measurements in the
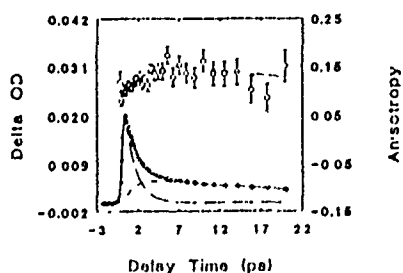
Figure 2. Transient absorption and anisotropy obtained using a 330 nm probe pulse following the excitation of cis-stilbene in hexadecane by a 312 nm pump pulse.

regions of the product absorptions have been performed to determine the relative alignments of the pumped (reactant) and probed (product) transition dipoles. Typical kinetics and anisotropy measurements are shown in Fig. 2. (3) Fluorescence-detected measurements of the appearance of the trans product have been performed to study the trans product independently of the presence of DHP. Typical results are shown in Fig. 3. In these experiments the initial (pump) pulse produced cis* which isomerized to form trans. The probe pulse excited the trans product molecules and the resulting trans* fluorescence was detected. As neither DHP or cis fluoresce near 350 nm the signals obtained are due entirely to trans product molecules. (4) The UV transient absorption spectra at 6 ps, 15 ps and 50
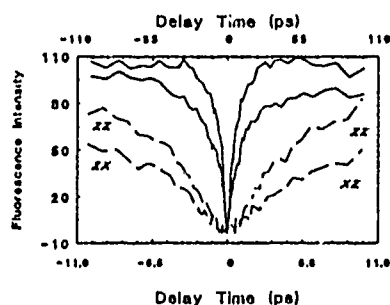
Figure 3. Trans fluorescence rise curves obtained from a sample of cis-stilbene pumped at 312 nm and probed at 312 nm. The fluorescence was detected by a photomultiplier tube through a 12 nm interference filter centered at 350 nm near the peak of the trans fluorescence. The designations ZZ, ZX and XZ indicate the relative polarizations of the pump and probe beams.

ps have been obtained between 315 nm and 375 nm on the red edge of the trans absorption band using multichannel detection. The 50 ps spectrum is identical to the pure trans spectrum indicating that trans-stilbene is indeed responsible for most of the product absorption observed in this region of the spectrum. The spectrum obtained at 6 ps indicates a great deal of vibrational excitation in the Franck-Condon active modes.

These ultrafast studies of the pathways of isomerization begin to expose the chemical dynamics of such processes. The solvent influences on motion confined to barrierless potentials and on nonadiabatic transitions become crucial intermediate steps in these chemical transformations. Thus an important part of understanding the primary process of photochemical reactions of this sort is the quantum statistical mechanical description of the solvent action and reaction to these intramolecular forces.
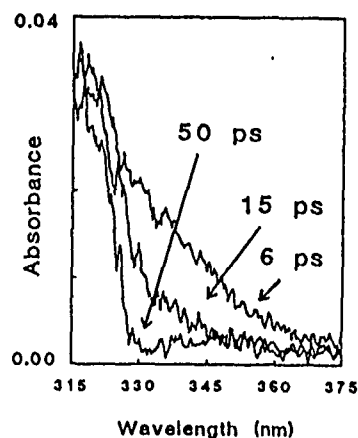
Figure 4. The transient absorption spectrum obtained following the excitation of cis-stilbene at 312 nm for delay times of 6 ± 1 ps, 15 ± 1 ps and 50 ± 1 ps.

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SOME SOLVENT EFFECTS IN EXCIPLEXES AND TICT MOLECULES

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Conformational changes within solute molecules and dielectric relaxation of the solvent both effect the rate of electron transfer processes. As an example of the former, the well-known anolous charge-transfer fluorescence from dimethylamino benzonitrile DMABN occurs via a twisting of the amino moiety which facilitates intramolecular charge-transfer, followed by stabilization by polar solvents.[1] The effects of conformational change and solvent relaxation are difficult to distinguish, but we present have three approaches which can provide evidence concerning the relative importance of these two effects

(i) Studies of exciplexes in non-polar solvents

(ii) Time-resolved Raman spectroscopy on exciplex systems

(iii) Study of specifically solvated complexes in supersonic jet expansions

(i) Exciplexes in non-polar solvents

We have reported a study of viscosity and temperature effects on the rate of back-electron transfer (BET) on an exciplex between 9,10 dicyanoanthracene and N,N'-dimethylaniline, which has strong charge-transfer character, in six non-polar solvents.[2] Since viscosity effects cannot in this case be attributed to dielectric relaxation, conformational changes must be involved. The extent of charge-transfer was estimated by solvatochromic and thermochromic shifts of the fluorescence. Data were fitted to the simple scheme I

$$(A^- D^+)_I^* \underset{k_{-cc}}{\overset{k_{cc}}{\rightleftharpoons}} (A^- D^+)_{II}^* \xrightarrow{k_{BET}} A + D$$
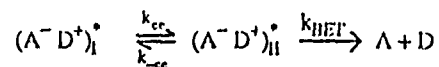
where $(A^- D^+)_I^*$ is the exciplex formed initially by forward electron transfer, and $(A^- D^+)_{II}^*$ that following conformational change.

This simple model reasonably fits the results in the two extreme cases of $k_{cc} \gg k_{BET}$, when $k_{obs} \approx k_{BET}$, typified by all results in hexane, and other solvents at high temperatures, and $k_{cc} \ll k_{BET}$, when $k_{obs} \approx k_{cc}$, typified by the more viscous solvents decalin and butylbenzene at low temperatures. However, a better fit is obtained if the Marcus-Hush

model[3], equation 2, is modified by inclusion of a time and solvent dependent electron coupling constant V, whose value varies as the conformation changes.

$$k_{ET} = \frac{4\pi^2 V^2}{h(4\pi\lambda_o k_B T)^{1/2}} e^{-s}$$

$$\times \sum_{\nu=0}^{\nu=\infty}\left[\frac{S^\nu}{\nu!}\exp\left(-\frac{(\Delta G_{ET}+\lambda_o+\nu h\nu)^2}{4\pi\lambda_o k_B T}\right)\right] \qquad \dots\dots\dots (2)$$

With this modification, the semiclassical equation of non-adiabatic ET can fit the observed data independently of the solvent viscosity. Indeed, the BET is in all cases studied a non-adiabatic process as its rate constant always depends on V^2, but in viscous solvents the value of V at the time of ET depends strongly on viscosity. For this reason, we can speak of a transition from a "solvent-independent" to a "solvent-controlled" non-adiabatic regime as viscosity is increased. These results show that conformational changes within the solute molecules can lead to very similar effects to those of dielectric relaxation.

(ii)   Time-resolved Raman spectroscopy on exciplex systems

Back electron transfer in the exciplex formed between anthraquinine AQ and TMB in acetonitrile, tetrachloroethylene and carbon tetrachloride has been studied using nanosecond time-resolved resonance Raman spectroscopy[4], in the hope that observation of changes in · vibrational frequences in transients might permit structures of intermediates to be assigned tentatively.

Very preliminary results, typified by Figure 1, show that in acetonitrile, there are three prominent transient peaks at 1519 cm^{-1}, 1607 cm^{-1} and 1618 cm^{-1}; that at 1618 cm^{-1} disappears at a faster rate than the others. In carbon tetrachloride, a peak at 1592 cm^{-1} is the only feature observed, while in tetrachloroethane, at times less than 10ns, a peak at 1608 cm^{-1} is observed, which decays to form a transient with signal at 1590 cm^{-1}, a feature at 1518 cm^{-1} remaining constant. At times longer than 50ns, the spectra in tetrachloroethane are identical to those in carbon tetrachloride.

The results suggest that AQ$^-$ and TMB^{+} produced upon excitation as shown in the equation 3, undergo geminate recombination either via the triplet state or directly via the singlet state of the ion pair. In carbon tetrachloride, the initially produced triplet ion pair proceeds exclusively to the singlet state; in acetonitrile the favoured pathway is in separation, followed
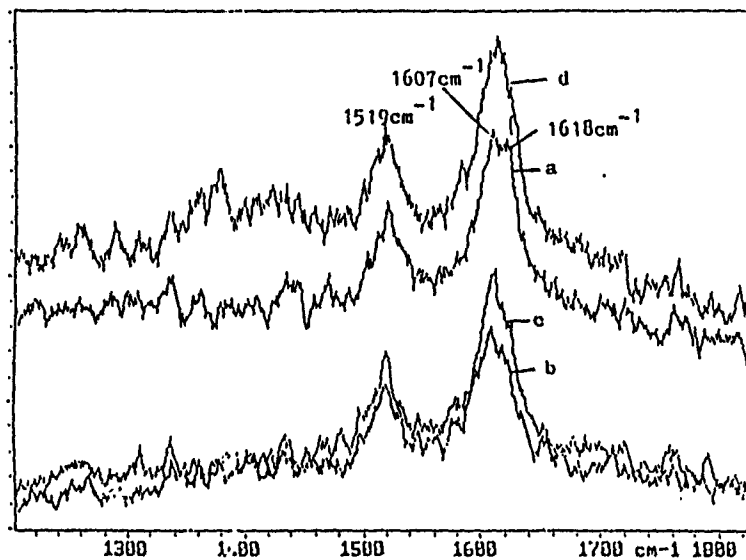
Figure 1 Time-resolved Raman spectra of anthraquinine-tetrâmethylbenzene in acetronitrile. Pump wavelength 351nm, probe 460nm. Delays a, Ons, b 7.7ns, c 35ns, d 100 ns. Spectra not standardised.

by geminate recombination. In tetrachloroethane, both pathways occur. These data will be presented in fuller form.

$$AQ + h\nu \longrightarrow {}^1AQ \longrightarrow {}^3AQ \xrightarrow{TMB} {}^3(A\bar{Q} \ .... \ TMB^{.+}) \xrightarrow{separation} A\bar{Q} + TMB^{.+}$$

back electror transfer

geminate recombination

$${}^2(A\bar{Q} + TMB^{.+})$$
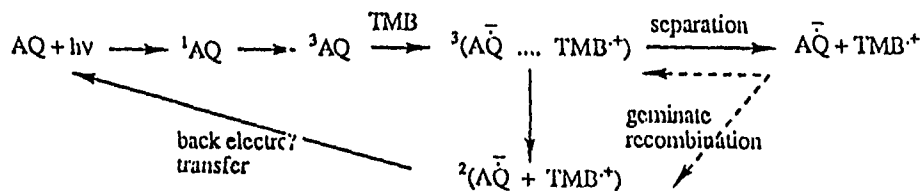
(iii) <u>Fluorescence from jet cooled complexes</u>

The solvent is known to play a very significant role in the stabilization of charge-transfer state arising from intramolecular motion, giving so-called TICT (twisted intramolecular charge-transfer) states, typified by dimethyl amino benzonitrile, DMABN, which in polar solvents is well-known to give rise to anomalous red-shifted fluorescence from the TICT state. Attempts have been made to observe TICT emission from <u>specifically</u> solvated complexes under supersonic expansion conditions, and Figure 2 shows that red-shifted emission can indeed be

seen.[5] However, the dependence of the intensities of the bands upon concentration of DMABN, and the fact that non-polar solvents also give rise to red-shifted emission, shows clearly that the 'anomalous' emission in these cases is due to dimers and possibly higher complexes of the DMABN. No emission uneqivocably assignable to TICT emission from DMABN has been observed under jet conditions, and hence care is needed in the interpretation of anomalous fluorescence from these molecules.
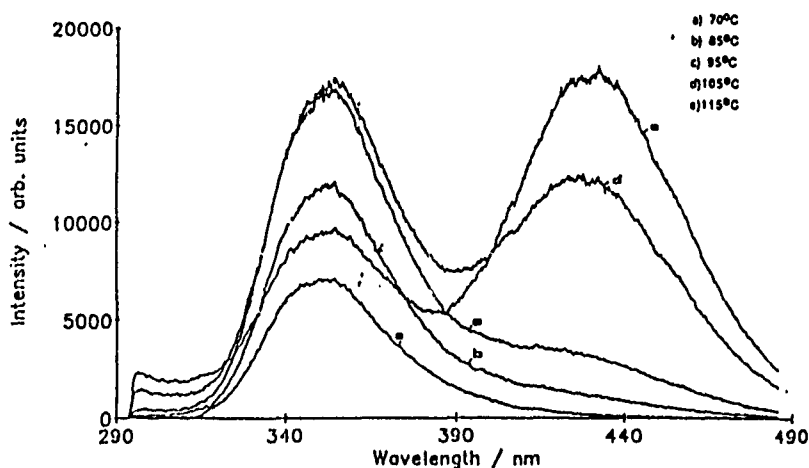
Figure 2 Fluorescence spectra from DMABN/methanol mixtures excited in supersonic expansion. Temperature refers to over temperature before expansion, thus higher temperatures means higher concentration of DMABN. Emission is due to solvated monomeric DMABN, solvated dimers of DMABN. No evidence for TICT emission is seen.

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THIONES AS MODELS FOR STUDIES OF THE PHOTOCHEMISTRY AND PHOTOPHYSICS OF POLYATOMIC MOLECULES IN SOLUTION

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Molecules containing the thiocarbonyl group possess excited electronic states which are substantially shifted to lower energies compared with their carbonyl counterparts. Thus, even in relatively small, unconjugated thiones transitions to the S_1, $^1(n,\pi^*)$ states appear in the visible, those to S_2, $^1(\pi,\pi^*)$ states appear in the near uv-blue, and the lowest Rydberg states are accessed in the quartz ultraviolet (Figure 1). In addition, strong spin-orbit coupling in the S-containing species enables the triplet states to acquire sufficient intensity to be readily observable by standard absorption methods. In weakly-interacting media T_1 is frequently of $^3(n,\pi^*)$ character and lies only a few hundred cm^{-1} below S_1, whereas T_2 of $^3(\pi,\pi^*)$ character lies only slightly higher in energy. T_1 and T_2 may invert in strongly-interacting solvents. This disposition of electronic energies in the thiones permits highly selective, direct excitation to T_1, S_1, S_2 and higher states not only in the gas phase and in low temperature matrices but also in fluid solutions at room temperature.

Equally important to an examination of their photochemistry and photophysics is the observation that thiones exhibit readily measurable emission from several states. Intense $S_2 \rightarrow S_0$ fluorescence is frequently observed from photostable aromatic thiones in perfluoroalkane solvents because this radiative transition is electric-dipole allowed, and the S_2 radiationless decay rate is slow

owing to the large S_2-S_1 energy gap. (Weakly-interacting perfluoroalkane solvents are used to suppress intermolecular physical and chemical interactions which could otherwise mask their "intramolecular" relaxation processes.) Very large quantum yields of phosphorescence are also measured in fluid solutions of thiones which are sufficiently dilute to suppress diffusion-limited self-quenching of T_1. In addition, thermally activated delayed S_1 fluorescence in some aromatic thiones and very weak prompt S_1 fluorescence in some smaller aliphatic thiones can also be observed. Both steady state emission quantum yield and dynamic emission lifetime measurements (ps for S_2 and S_1, μs for T_1) can therefore be employed to obtain information about the mechanisms and rates of excited state relaxation in these systems.

By determining in perfluoroalkane solvents the rate constants for radiative, non-radiative, intramolecular photochemical and intermolecular quenching processes of thiones having a variety of structures, we have been able to come to the following conclusions.

(i) For the photostable aromatic thiones the majority of S_2 states decay by radiationless relaxation to S_1 in accordance with the energy gap law (cf. Figure 2). In thiones possessing H atoms "β" to the thiocarbonyl group, a minority of molecules may also decay by a mechanism which bypasses S_1 and T_1 and which likely involves a reversible photochemical path.

(ii) Adamantanethione has been described as a model thione for photochemical studies of the S_2, $^1(\pi,\pi^*)$ state. However, we have shown that the S_2 states of this and similar alicyclic thiones are too short-lived ($\gtrsim 1$ ps) to account for the intermolecular photochemical processes which are initiated when the molecule is excited to S_2. Alternatives, including short-lived singlet biradicals or "dark", doubly-excited states must be considered. Evidence supporting the involvement of dark, doubly-excited states based upon the spectroscopy and dynamics of Cl_2CS and calculations on H_2CS will be presented.

(iii) The rates of vibrational relaxation, vibrational activation, $S_1 \rightsquigarrow> T_1$ intersystem crossing and $T_1 \rightsquigarrow> S_1$ back-intersystem crossing are all comparable in the thiones in fluid solutions near room temperature. Together with the small S_1-T_1 energy gaps in these thiones, this results in (a) the observation of thermally activated delayed fluorescence from S_1 following direct excitation to T_1, and (b) a remarkable increase in the quantum yield of phosphorescence when exciting on the far red edge of the $T_1 \leftarrow S_0$ absorption band (Figure 3).

(iv) Unhindered thione triplets are self-quenched at or near diffusion-controlled rates. Evidence in support of a mechanism which involves the formation of triplet excimers will be presented.

(v) The S_2 states of many thiones are deactivated efficiently in solution by almost all classes of compounds except the perfluoroalkanes (Figure 4). For saturated quenchers the quenching mechanism involves neither electron nor electronic energy transfer and often yields almost no observable photochemical products. The use of a wide variety of thione-quencher combinations to uncover the relaxation mechanism will be described.

The thiones also offer excellent opportunities to observe excited state-excited state interactions. We previously reported the observation of efficient singlet-singlet electronic energy pooling, $2S_1 \rightarrow S_2 + S_0$, in Cl_2CS in the gas phase. The opportunities for related studies, including triplet-triplet annihilation in solution and electronic energy partitioning in van der Waals dimers both in cold supersonic beams and in solution will be discussed.

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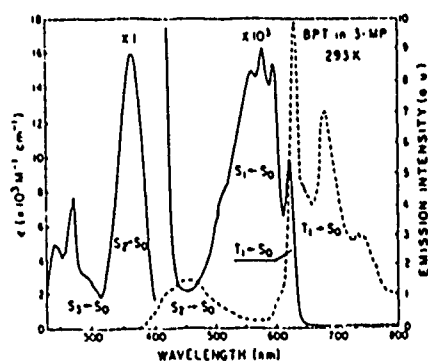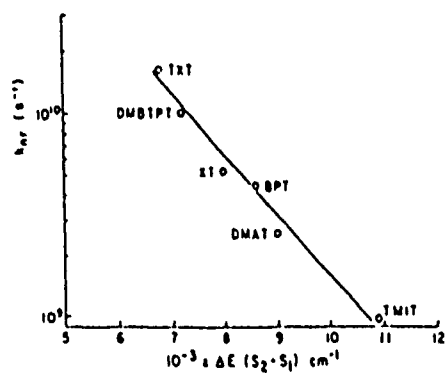
Figures

Figure 1

Figure 2
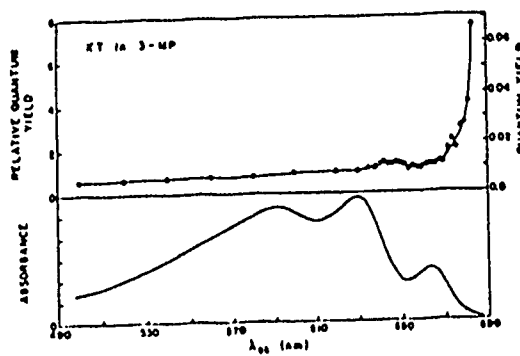
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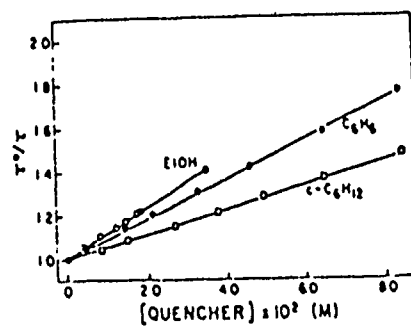
Figure 4

A CARBENE TO BIRADICAL REARRANGEMENT: REACTION PATHS FROM 1-(8-METHYLNAPHTHYL)CARBENE TO ACENAPHTHENE

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Introduction. 1,8-Naphthoquinodimethane (b) has been identified by ESR spectroscopy as a non-Kekulé conjugated hydrocarbon biradical with a ground state of triplet multiplicity (^{3}b). It was generated by low-temperature photolysis of the azo compound (1)[1] and of the diazo compound (2, X=N$_2$).[2] The high photochemical reactivity of ^{3}b has largely prevented its detection by spectroscopic techniques other than ESR.[1b] Several derivatives of ^{3}b have been extensively characterized by a variety of spectroscopic methods both as transient intermediates at room temperature and as persistent species at low temperature.[4] The hypothetical precursor of ^{3}b in the photolysis of the diazo compound (2, X=N$_2$), carbene intermediate a, has remained elusive.[2b, 3]
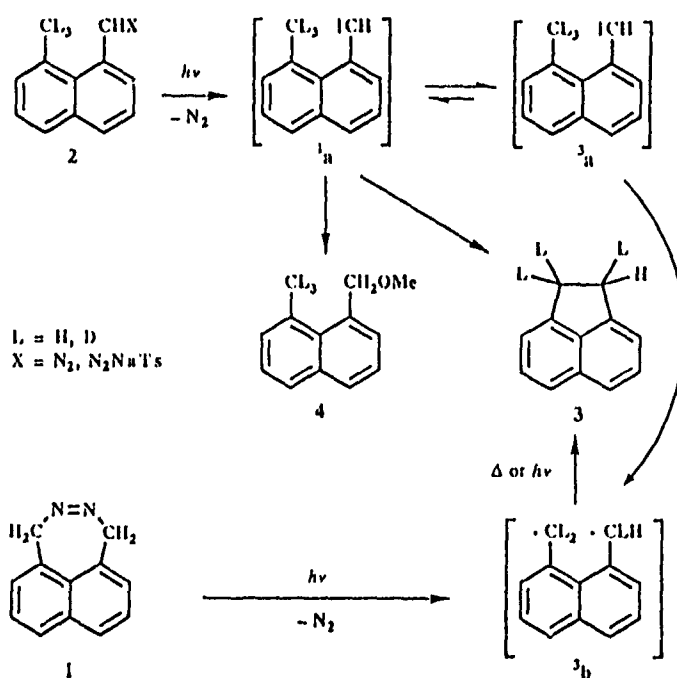
The electronic absorption of the biradical ^3b has now been observed both by low-temperature photolysis and by room-temperature flash photolysis of the diazo compound 2 ($X=N_2$). Moreover, the precursor carbene a was trapped with methanol in fluid solution (*Scheme*).

The Carbene Intermediate (a). The biradical ^3b was formed within the time resolution of our flash photolysis experiments which sets an upper limit of 100 ns to the lifetime of the carbene a at ambient temperature. The carbene was, however, sufficiently long-lived to undergo intermolecular trapping. The yield of ^3b was reduced when the carbene a was trapped by methanol, but the trapping reaction did not obey a linear Stern-Volmer relationship. The formation of 4 upon photolysis of 2 in the presence of methanol provides clear evidence for the existence of the carbene a as a true reaction intermediate.

The Biradical Intermediate (^3b). 1,8-Naphthoquinodimethane (^3b) was the major product obtained by photolysis of 2 ($X=N_2$) at 77 K and was persistent in the dark; its absorption spectrum is shown in the Figure. Further photolysis of ^3b at 77 K gave acenaphthene in the lowest triplet state which was detected by its characteristic phosphorescence emission. The yield of ^3b was only about 10 % at room temperature and it decayed to ground state acenaphthene with a lifetime of ca. 100 µs in degassed solutions. The deuterated compound 2 (L=D) gave a somewhat higher yield of ^3b (about 15%) in CH_3CN and of the trapping product 4 in methanol.

Discussion. At room temperature, the singlet state and the triplet ground state of the carbene a appear to be in rapid equilibrium, and intra- and inter-molecular reactions from both states, ^1a and ^3a, compete for product formation. We attribute the formation of ^3b to intramolecular hydrogen abstraction occurring from ^3a, the formation of acenaphthene (3) and the trapping by methanol to reactions occurring from ^1a. If the major pathway from ^1a to 3

proceeds via [1]b, we should expect a strong kinetic isotope effect upon deuteration of the 8-methyl group (L=D). The moderate effects observed indicate a concerted CH insertion from [1]a to 3 as the major pathway.

At low temperature, the formation of the biradical [3]b by 1,5-H shift originating from [3]a predominates. Combined evidence from studies of the effects of temperature, solvent heavy atoms, and isotopic substitution lead to the conclusion that the rate-determining step in the thermal ring closure of [3]b involves intersystem crossing to the singlet ground state surface. This is not obvious on thermochemical grounds. Thermal adiabatic cyclization of [3]b to the lowest triplet state of acenaphthene ([3]3) is estimated to be about thermoneutral. Nevertheless, [3]3 is not formed by photolysis of 2 at ambient temperature.

The ring closure of singlet perinaphthadiyl to naphthocyclopropane is not inhibited by a significant energy barrier.[4c] Why does cyclization of [3]b to [3]3 not occur on the triplet surface? The answer is that adiabatic cyclization is forbidden by *state symmetry* for both the disrotatory and conrotatory reaction paths, i. e., [3]b and [3]3 belong to different symmetry species. State-symmetry considerations are of no concern for thermal reactions in the electronic ground state, since closed-shell molecules generally have a totally symmetric ground state wavefunction. However, state-symmetry rules have been discussed for pericyclic reactions of organic radical cations.[5]

Two pathways for the reaction [3]b → 3 have been identified. At ambient temperature, the product 3 is formed in the singlet ground state following rate-determining intersystem crossing of [3]b to the singlet ground state surface. At 77 K, [3]b is persistent in the dark; photolysis of [3]b yields 3 in the lowest excited triplet state by an adiabatic pathway.

Figure: Absorption spectrum of [3]b in EPA glass at 77 K.
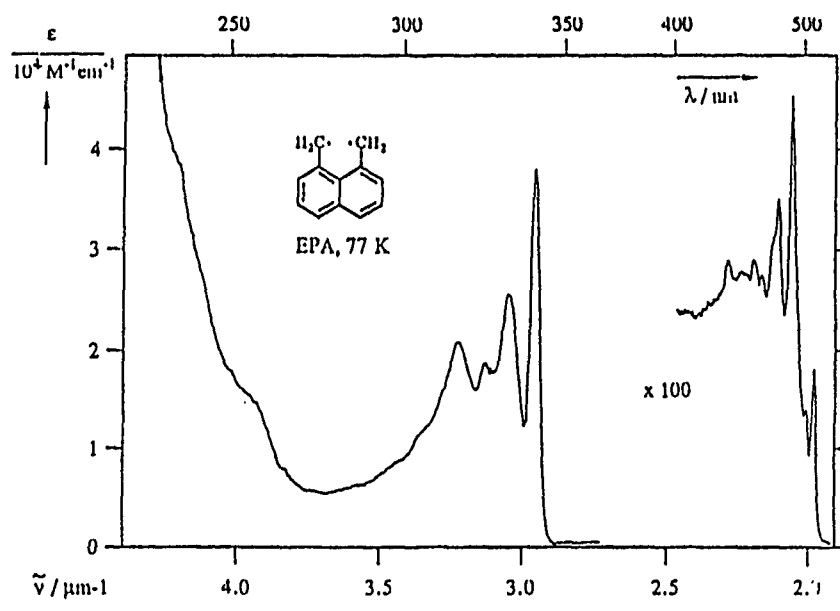
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THE ROLE OF α-AMINOALKYL RADICALS IN THE PHOTOREDUCTION OF DICARBOXIMIDES BY AMINES.

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It is now widely accepted that reactions between excited state ketones and amines proceed by rapid formation of charge transfer complexes[1-3]. In polar media, quenching occurs via a solvent separated ion pair to form free radical-ions[4,5]. Primary charge separation is often succeeded by proton transfer resulting in the formation of a ketyl and an amine-derived free radical which is often an α-aminoalkyl radical. Only few studies dealt with the fate of these radicals[6,7]. Here we present our recent results on the investigation of the photo-induced reactions of dicarboximides (first of all N-phenyl-1,8-naphthalimide) with tertiary-, secondary- and primary amines, respectively.

The $-NC_6H_5$ derivatives of naphthalimides have singlet lifetimes less than 50 ps, fluorescence yields around or smaller than 10^{-4} and triplet yields accounting to 0.1-0.2. An efficient internal conversion to the ground state occurs in case of the $-NC_6H_5$ compounds which is enhanced by the rotational (tortional) motion of the phenyl group[8].

All amines (A) used in this work react with the triplet states of the naphthalimides (N) as indicated by the decrease of the lifetime of the T-T absorption of N in the presence of A. Rate constants for triplet quenching by amines (k_q) were found to vary significantly with the amine structure. In acetonitrile, there is a change of almost five orders of magnitude in k_q for N-phenyl-1,8-naphthalimide (Ph-1,8-N) triplet quenching by amines varying from DABCO to n-pentylamine. Even more striking is the considerable effect of the solvent polarity. For the Ph-1,8-N + TEA system, the k_q rate constant increases by almost three orders of magnitude when n-hexane is replaced by the polar acetonitrile. The significant sensitivity of the triplet quenching rate on the ionization potential of the amine and specially on the solvent polarity indicates that the reaction of triplet N with A involves a large degree of charge separation or complete electron transfer.

Detailed transient absorption studies of photoinduced reactions of the N isomers with DABCO showed that, beside ^3N, another short-lived transient can be detected, too. This transient, which absorbs in the case of the Ph-1,8-N + TEA system in the 360-520 nm range (with maximum at

415 nm) is formed on the same time scale and with the same kinetic parameter as observed for the triplet state decay, thus indicating that ^3N is the precursor of the new transient. Moreover, the transient-absorption and transient conductivity time profiles observed seem to agree, thus suggesting that both belong to the same transient which is a charged species. Finally, the ESR spectrum - in accordance with all other observations - proves that the transient can be identified as the radical-anion $N^{\cdot -}$ formed by electron transfer between A and N.
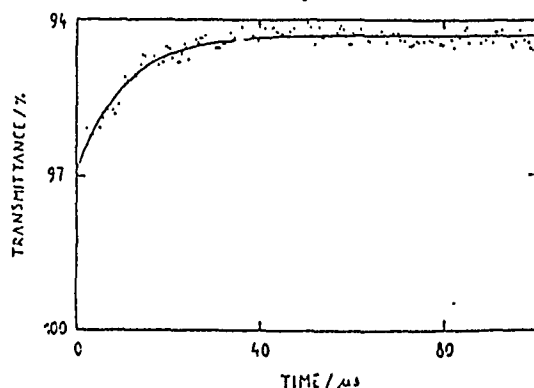
Fig. 1: $N^{\cdot -}$ absorption time profile

The strictly second order decay kinetics of $N^{\cdot -}$ observed with DABCO as the amine additive, suggests that the $N^{\cdot -}$ species is consumed by back electron transfer to the amine-derived radical-cation re-forming the ground state starting materials. In case of open chain aliphatic amines, strongly fluorescent products are formed and the transient kinetics is also more complicated. The $\left[N^{\cdot -}\right]$ time profile for Ph-1,8-N photoreduction by TEA is presented in Figure 1. It can be seen that there are two distinct stages in $N^{\cdot -}$ formation which are very well resolved in time : there is a fast primary build-up which occurs well within 1 µs and a much slower secondary formation of $N^{\cdot -}$ which lasts for several 10 µs. In the photoreduction of Ph-1,8-N by TEA in acetonitrile, the maximum value of the quantum yield of $N^{\cdot -}$ formation is twice the triplet yield, i.e. each primary production of an $N^{\cdot -}$ species is succeeded by a secondary $N^{\cdot -}$ formation.

However, $\Phi(N^{\cdot -})_{max}$ decreases to a value less than Φ_{isc}, the intersystem crossing quantum yield, if the polar (acetonitrile) solvent is replaced by an apolar one or if the electron donor is a primary amine like n-pentylamine.

Determination of $N^{\cdot -}$ yields significantly greater values than Φ_{isc} and the observation of the secondary formation of $N^{\cdot -}$ makes it clear that, beside reduction of ^3N by A, another efficient electron transfer process also occurs. We believe it to take place between an α-aminoalkyl free radical (known as a strong reducing agent[9]) and a ground state naphthalimide molecule. Thus, the suggested reaction scheme for the photoreduction of carboximides by amines possessing hydrogen atoms in the α-position would be the following :

$$N + A$$

$$\uparrow k_2$$

$$3N + A \xrightarrow{k_1} (N^{\cdot} + A^{+}) \xrightarrow{k_3} N^{\cdot} + A^{+} \xrightarrow{k_4} N + A$$

$$\downarrow +{}^3N \qquad\qquad\qquad k_5 \swarrow + A$$

$$\text{T-T annihilation} \qquad Et_2N\text{-}\overset{\cdot}{C}H\text{-}CH_3 + Et_3\overset{+}{N}H$$

$$k_6\downarrow + N \qquad\qquad +N^{\cdot}$$

$$Et_2\overset{+}{N}\text{=}CH\text{-}CH_3 + N^{\cdot} \qquad\searrow \longrightarrow \text{products}$$

$$\qquad\qquad\qquad\qquad\qquad k_8$$

$$k_7\downarrow + A \qquad\qquad\nearrow$$

$$Et_2N\text{-}CH\text{=}CH_2 + Et_3\overset{+}{N}H$$
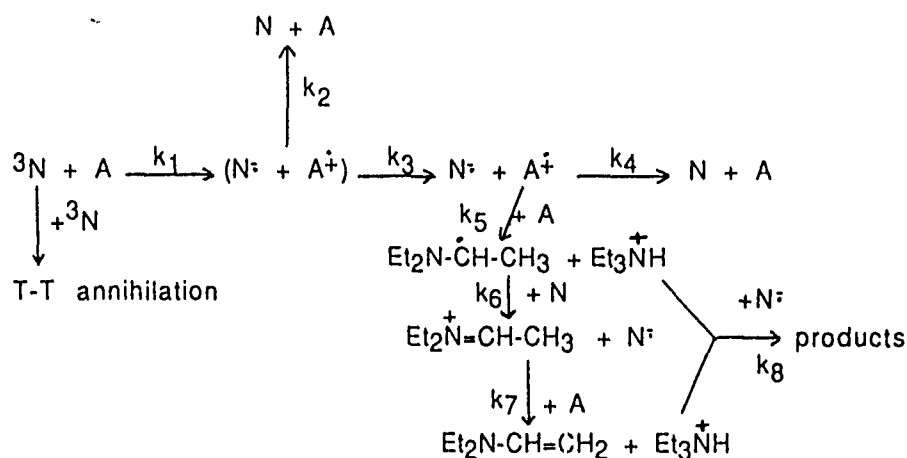
By computer modeling of the formation and decay of $N^{\cdot}$, it could be shown that the pseudo-first order rate constant k_6' (defined for the secondary $N^{\cdot}$ formation from the α-aminoalkyl radical) is indeed proportional to the naphthalimide concentration, i.e. $k_6' = k_6[N]$ (see Figure 2). Furthermore, $N^{\cdot}$ formation according to reaction (6) could be demonstrated by producing the α-aminoalkyl radical via hydrogen atom abstraction from the appropriate amine (by tertiobutoxy free radicals obtained photochemically) in the presence of naphthalimide. Our study indicates that $N^{\cdot}$ formation in reaction (6) is very fast, irrespectively of the type of amine.
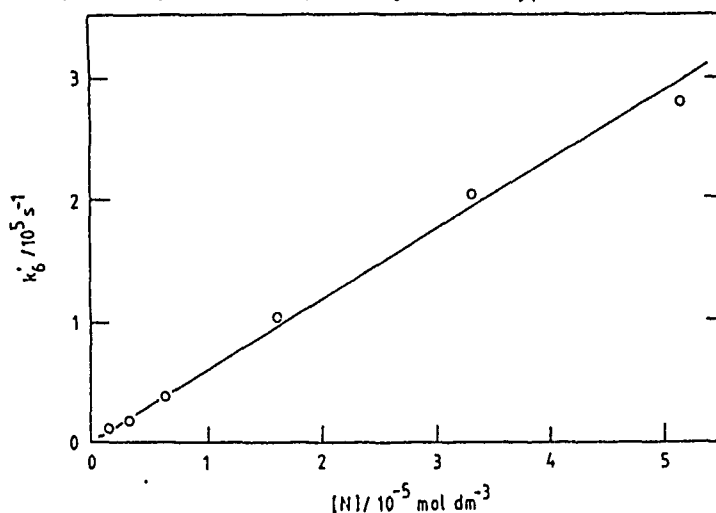
Fig. 2 : Plot of the rate constant k_6 versus $[N]$

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LIGHT INDUCED INTRAMOLECULAR ELECTRON TRANSFER REACTIONS

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Electron transfer and charge separation is one of the process upon which our existence depends and which is the basis for advanced developments including organic photoconductors, photoelectric conversion, nonlinear optical materials as well as the production and storage of electricity. Most important, nearly all of earth's life forms use directly or indirectly the transformation of sunlight into chemical energy, which occurs via an electron transfer and charge separation process. In this paper, various donor-acceptor substituted organic compounds with covalent bond and conjugated π-electric bond were synthesized and their photoinduced intramolecular electron transfer reactions were investigated.

1. Triad System

A new triad model compound porphyrin-viologen-carbazole (1) was synthesized to mimic photosynthesis. Photosynthesis in green plants and bacteria is carried out by highly ordered system. So it is very important that artificial photosynthesis system should be well organized at the level of molecules[1]. We report here the synthesis of molecule (1) and its diad molecule (2) which tend to form Langmuir-Blogett film so that we can conveniently assemble a practical molecular device for solar energy conversion.

The absorption spectra and fluorescence spectra of (1) and

(2) are the same as that of porphyrin in the region of 350-700nm and at 655nm respectively. Besides, there is another emission band in (1) ranged from 355 to 370nm, which is ascribed to the emission of carbazole moiety. Spectra studies indicate that there is no appreciable interaction between porphyrin, carbozole and viologen moieties in the ground state. The relative fluorescence intensities of (1) and (2) in THF are ca.80% of porphyrin. The fluorescence life-times of (1),(2) and porphyrin were measured by means of single photon counting technique and the calculated values of k_{et} of (1) and (2) are ca. $4.6 \times 10^6 s^{-1}$. All the above data support that photoinduced electron transfer takes place from the porphyrin moiety to the viologen unit.

(1): $R= C_{10}H_{22}-N$

(2): $R= C_{16}H_{33}$
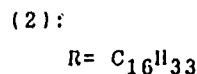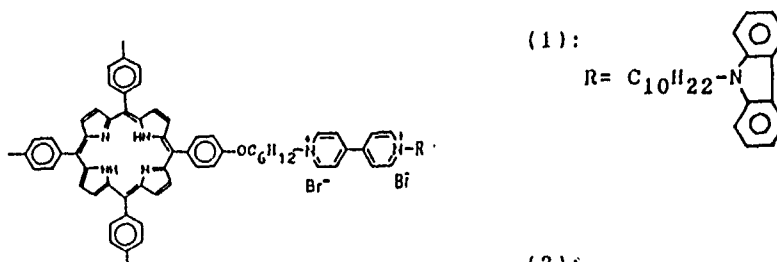
When only one layer of (1) is formed on the surface of SnO_2 electrode, the open-circuit voltage and photocurrent are 430mV, 0.2 uA/cm^2 respectively. However, those of (2) are only 274mV, 0.05 uA/cm^2. A mechanism including photoinduced electron transfer and two-step charge separation was suggested for compound (1).

2. Diad System

Two novel covalently bonded electron donor (carbazole)— electron acceptor (norbornadiene) diad systems with different chain length (3a) and (4a) were synthesized for the study of solar energy storage. The structures of these diad compounds were identified by ^{1}HNMR, IR and MS spectra and the relationship

between chain length and conformation of these diad compounds was discussed.

Acetonitrile solution of diad compound (3a or 4a) was irradiated and a new compound (3b or 4b) was produced with yield of ca. 70%. The characterization of the spectra showed this compound is corresponding the quadricyclane. The photoinduced intramolecular isomerization of norbornadiene diad to its isomer quadricyclane was achived. The results of photochemical and photophysical studies, especially the CIDNP experiment, are consistent with existence of intermediates of radical-ion pairs and a triplet recombination mechanism[2].

3a. n=6   3b. n=6
4a. n=2   4b. n=2
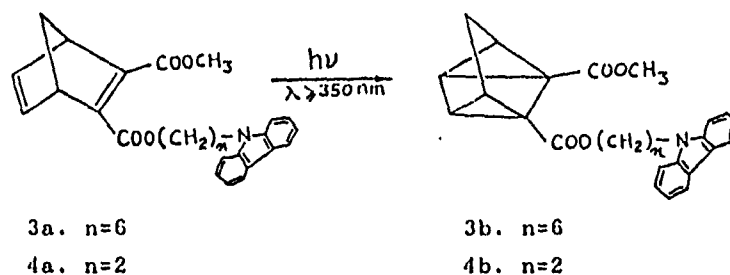
3. Conjugated π-Electric System

The following four types of electron donor-acceptor substituted conjugated π-electric compounds were synthesized and their intramolecular charge transfer behaviors and applications were investigated.
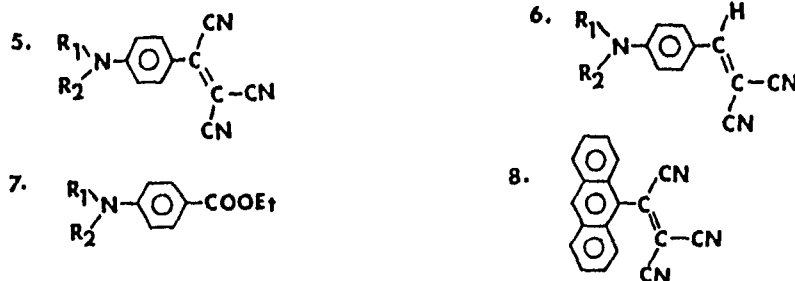
a) $R_1=R_2=CH_3$ b) $R_1=CH_3$, $R_2=C_{16}H_{33}$ c) $R_1=R_2=C_{16}H_{33}$

Type (5) compounds are positive solvatochromic molecules. The absorption maxima for 5a and 5b are 477nm, 485nm in heptane and 527nm, 534nm in dimethyl sulfoxide respectively. Type (7) compounds which are typical dual fluorescence molecules can emit fluorescence from TICT state (A band) and coplanar charge transfer ICT state (B band). In $DMSO-H_2O$ mixed solvent the absorption and fluorescence spectra of the compounds with long hydrocarbon chains (5b, 6b, 7b) show the aggregation behavior clearly. The fluorescence of compounds (7a, 7b, 7c) in acetonitrile is quenched by triethylamine. We attribute the quenching to the formation of three-electron bond between the amine lone-pair electrons and the cation radical of the compounds. These results demonstrate that the TICT state can be satisfactorily viewed as a charge-localized biradical state.

Spectroscopic studies reveal that: 1). The molecule of (8) has an angle ca. 90^0 between anthryl and trivinyl moiety in ground state. 2). It becomes more coplanar in excited LE state and an electron transfers to tricyanovinyl moiety from anthryl group in polar solvents. 3). Then compound (8) goes back to twisted conformation, TICT state[3].

Since efficient photoinduced intramolecular charge transfer and charge separation, these compounds (5, 6, 7, 8) reveal a series of very interesting photoelectric behaviors, e.g., these compounds show strong signal of surface photovoltage; compound (8) has a ca. 200 mV photovoltage in BLM; compound (5) has a large third order susceptibility, $x^3 \sim 10^{-8}$ esu with an optical bistability.

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SOME LIGHT ON PLASTIC MOLECULES

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Does it make any sense to think of making chemicals with sunlight? Table 1 shows calculations of the theoretical yield of a one hectare solar chemical plant, roughly the size of a football field (100 meters by 100 meters). With the normal average solar intensity of 300 watts/m² (Montreal or Toronto) you could make 32 tons a day of a chemical like Vitamin D. That is many times the entire annual consumption of Vitamin D in Canada. With radiation in the visible region, there is about 4000 kilowatts of solar energy which could theoretically produce about 200 tons of chemicals a day, comparable to the production of a full scale chemical plant [1].

Table 1. Theoretical Production of a 1-Hectare Solar Plant

Wavelength range (nm)	KW, noon	Production tons/day
Near UV -- 270-400	900	32
Visible -- 400-700	4,000	267
Near IR -- 700-1000	22,000	212

Since energy is a major component of the cost of many chemicals (e.g., fertilizers), the use of sunlight to make valuable chemicals could have important industrial applications.

The most important of all solar chemical systems is that of the green plant. However photosynthesis is complicated because the natural system contains what are called "antennas". In the leaf of a green plant the chlorophyll, which is green, is not distributed evenly throughout the leaf, but is localized in small units called chloroplasts. Furthermore, the arrangement is not even uniform within the chloroplasts. In a single photosynthetic unit, there is one active centre, plus about 200 extra chlorophyll units embedded in a lipid bilayer membrane. The purpose of these extra units is to act as antennas so that the light absorbed will be delocalized through the system and eventually will reach the active centre to drive the process of photosynthesis.

A number of years ago [2], polymer scientists discovered that aromatic polymers such as poly(vinylnaphthalene) and poly(naphthylmethacrylate) have similar properties. If these polymers are irradiated with near—UV light, an excitation on one of the naphthalene groups is localized for only a few picoseconds before it hops along the chain to some other adjacent group. In fact, it will move back and forth in a random walk until it is trapped or the energy is emitted as a photon of fluorescence. This is an example of what we call the "antenna effect", or "photon harvesting" in polymeric molecules. A polymer antenna is a polymer which, in solution, looks something like Fig. 1 where the N's are naphthalene, and A is anthracene. This random coil in solution is capable of absorbing near ultraviolet light, and transferring the excitation from the absorbing naphthalene groups — there may be a thousand of them — to a single anthracene trap in the middle. The fluorescent spectrum of the polymer shows that the emission intensity from the thousand naphthalene groups is less than that of the one anthracene on the chain. Clearly the energy absorbed by the naphthalene has been transferred to the anthracene. Over the last decade or so we have been looking at various ways in which one can use this energy—harvesting process to do useful chemistry.

It is now well established [2] that the energy is transferred by means of a singlet energy transfer (Förster) mechanism due to dipole—dipole interactions between the various groups in the chain.

The efficiency of this process approaches 95%, so we can build antennas which are just as good as Nature's antennas at collecting photons. The lifetime over which this excitation moves is very very short, of the order of 10-20 ns, or 10^{-8} s. After that there is a chance that the excitation will convert to a triplet which has a much longer lifetime, of the order of 0.1-2 s.

PHOTOZYMES

These new polymers are usually copolymers of a vinyl aromatic compound like vinylnaphthalene with styrenesulphonate or methacrylic or acrylic acid. These unusual polymers behave normally in an organic solvent to form something like a random coil, but if dissolved in water, they form pseudo-micellar structures in which the hydrophobic groups tend to go on the inside, and the hydrophyllic groups on the outside. There is nothing very surprising about this except that one might have expected that with polyelectrolytes the repulsions between the ionic groups would spread the chain out into a linear rod-like chain. Apparently the hydrophobic interactions are too strong and the polymer adopts a pseudo-micellar conformation, which has very interesting properties.

For example if the polymer is dissolved in water in the presence of a hydrophobic organic material, the organic compounds will seek out the centre of the "hydrophobic pocket". If the solution is then irradiated, light will be absorbed by the many naphthalene groups and their energy transferred either or directly or electronically, to the molecules in the centre, inducing extremely rapid photochemical reactions. Because of the analogy between these pseudo-micelles and an enzyme, which also has a hydrophobic pocket, and which is capable of doing rapid and rather specific chemical reactions in living systems — we have called them "photozymes".

The exact molecular conformation of these polymers in water has not yet been determined. They are random polymers. All of the naphthalene cannot be in the centre and all of the sulphonates on the outside. Clearly there must be some distribution where the larger sequences of vinylnaphthalene are in the centre and the individual sulphonic acids are towards the outside. Light scattering data indicate that the effective hydrodynamic radii are larger than one would predict from a random coil model, presumably because of the repulsion of the charged ionic groups within [3]. Studies by light scattering, quasi-elastic light scattering, and by ultracentrifuge, indicate that there is no coagulation of these polymers [4]. They are single molecules in solution with molecular weights from 50,000 to 200,000, and they appear to be spherical.

Most of our studies of photozymes to date have used a copolymer of nearly equal proportions of sodium styrene sulfonate and 2-vinylnaphthalene, denoted PSSS-VN, with a molecular weight of about 200,000 (by ultracentrifuge). The fluorescence of a very dilute solution of this polymer (of the order of 10 or 100 ppm) shows two emission bands, one from the naphthalene "monomer" and the second from what is called an excimer of naphthalene (Fig. 2). If a very small quantity of perylene is added to this solution, the naphthalene emission decreases and superimposed on it is a strong characteristic emission from the perylene, even though it represents only one part in a thousand of the total composition (Fig. 2). This is clear evidence for energy transfer from naphthalene to perylene via the antenna effect.

If the concentration of polymer is increased, the amount of perylene solubilized also increases. Increasing the perylene (at constant polymer concentration) the fluorescence emission reaches a constant value, indicating that the polymer is fully saturated. From these data the partition coefficient between water and the interior of the hydrophobic pocket can be calculated. Table 2 shows the number of aromatic probe molecules at saturation in PSSS-VN. Six molecules of anthracene can be dissolved in each polymer molecule, two of diphenyl anthracene and only one of perylene. The partition coefficients are greater than 10^8. Thus nearly all of the aromatic compounds present in an aqueous solution will be localized inside the hydrophobic pocket of the photozyme.

Table 2. Partition Coefficients K and Solubility of Various Aromatic Probes in PSSS-VN

Wavelength range (nm)	$K \times 10^{-7}$ ($\pm 5\%$)	Mol/mol of polymer
Anthracene	12.70	6
9,10-Dimethylanthracene	15.80	3
9,10-Diphenylanthracene	36.70	2
9-Methylanthracene	0.36	10
Perylene	1870.00	1

The dimensions of these polymer coils can be changed by adjusting either the pH or the ionic strength. At high pH or ionic strength, the coil is compressed. At low and high pH (and high ionic strength) the volume decreases by an order of magnitude. However the solubility does not change very much, indicating that even though the photozyme is not as non—polar when it is expanded, it still retains its affinity for hydrophobic molecules.

Irradiation of photozyme solutions of aromatic molecules in the presence of oxygen leads to very rapid conversion of the aromatic, such as dimethylanthracene, into an endoperoxide which eventually is converted to a quinone.
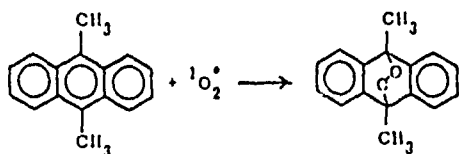
Since this compound does not fluoresce, there is an immediate decrease in the fluorescence intensity. The rate can thus be followed by fluorescence measurements. However, in this case the rate of photooxidation does depend on the expansion of the coil.

In the highly expanded form, the singlet oxygen may be generated too far away from the probe for reaction to occur. Thus, in this type of photozyme reaction, the rate can be adjusted by the simple addition of salt or acid. Since the photozyme is in equilibrium with the aqueous solvent, the photochemical reaction can be carried out sequentially. More substrate can be added after reaction and this process repeated many times. By analogy to an enzyme there is a cycling of the reagents through the catalyst, hundreds of cycles can be carried out in some of these systems to produce substantial yields of product. There are also indications that there is a certain selectivity to the chemical reactions within the photozyme [5,6].

Polychlorinated biphenyls (PCBs) have solubilities of the order of 1 ppb in ordinary water, but many people think that they are so toxic that their concentration must be reduced to parts per hundred trillion. That represents a technical problem because the law of mass action predicts that the rate of any reaction is proportional to concentration. With only 1 ppb of one reagent, the rate of reaction will be very slow unless a large excess of the other reagent is used. Fortunately, the enzyme—like nature of photozymes means that the PCB can be concentrated in the reactive centre. We have found that the photozyme PSSS—VN is very efficient to dechlorinate typical PCBs. For example, solar irradiation of hexachlorobiphenyl, a model PCB, results in substantial conversion to less toxic compounds, often after only a few days of solar radiation [7]. It seems that the photozyme itself plays a part in the mechanism by forming a complex with the PCB before the halogen is removed. Further studies with commercial Arochlor samples confirm the efficacy of the photozyme [8].

A typical Arochlor consists of hundreds of chlorinated biphenyls, and the higher components are eliminated over a period of time. Those which are the most dangerous toxicologically, are gradually transformed. In a possible application the photozyme could be added at parts per million levels to a tailings pond containing contaminated water. The rate of dechlorination is probably 100 times greater than if the water is irradiated directly.

As these experiments illustrate, these photocatalytic polyelectrolytes (photozymes) have a number of potentially important practical applicatons to industrial photochemistry.

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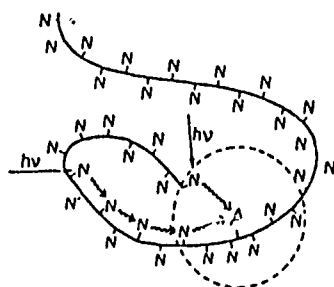
Figure 1. A conceptual illustration of energy transfer in an antenna polymer.
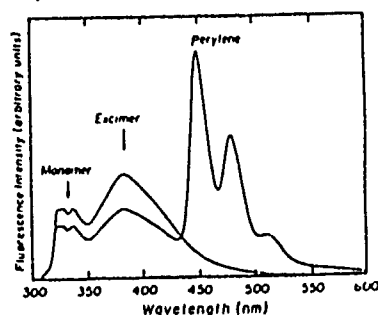
Figure 2. Steady-state fluorescence spectrum of PSSS-VN in aqueous solution.
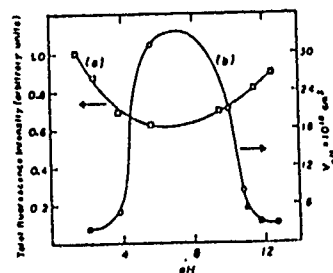
Figure 3. Perylene emission intensity and PSSS-VN hydrodynamic volume as a function of pH (ionic strength).

PHOTOCHEMISTRY IN ORGANIZED MONOLAYERS

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The organization of amphiphilic molecules in monolayers at the air-water interface is controlled by parameters like monolayer and subphase composition, surface pressure and temperature. The reactivity of molecules in monolayers at the air-water interface is different from that in monolayer systems due to different mobility. This may be particularly important in interactions with components in the adjacent aqueous phase, since a floating monolayer can incorporate appropriate molecules and relaxe whereas water soluble components may only be adsorbed to the surface of a monolayer system. Binding of small charged molecules to a monolayer depends strongly on the nature of the dipoles at the monolayer-air interface or on the underlying structure of monolayer systems on solid substrates.

1. Brewster angle microscopy. No p-polarized light is reflected from the air-water interface if the angle of incidence is the Brewster angle. Keeping the angle fixed, reflected light is detected after formation of a monolayer on the water surface, and reflectivity/area isotherms can be measured upon monolayer compression simultaneously with surface pressure/area isotherms[1]. This is quite different from measurement of reflectivity isotherms or reflection spectra[2] with normally incident light absorbed by the dye, since light absorption is intentionally avoided here in order to prevent photoreactions.

The reflected light may also be imaged on a CCD camera, and a microscopic image of the monolayer is recorded showing domains and phase transitions in the absence of fluorescent probes[1,3]. Brewster angle microscopy (BAM), therefore, provides information on the lateral structure of monolayers on the μm scale. The contrast between the areas covered with liquid state monolayer (dark) and those with liquid-condensed domains (bright) originates from different thickness and/or different refractive indices of the areas. Therefore, BAM may be useful in the investigation of photoreactions in organized monolayers.

2. Spiropyran/Merocyanine System at the Air-Water Interface. The use of the photoisomerization reaction of an amphiphilic spiropyran SP in mixed monolayers

with octadecanol for generation of a surface pressure jump has been described earlier[4]. We have now investigated the behaviour of mixed monolayers at the air-water interface of an amphiphilic spiropyran SP and phospholipids such as DMPC, DMPA and DPPS as matrix were investigated. The reflection spectrum shows the two chromene bands at about 370 nm and 280 nm which are slightly shifted to longer waves with respect to the solution spectrum. The reflection spectra are sensitive to the matrix molecule and monolayer relaxation indicating polarity effects and change of chromophore orientation at the air-water interface.

Irradiation of the mixed SP/phospholipid monolayer with 366 nm radiation leads to large changes in surface pressure and the appearance of a reflection band at 550 nm corresponding to the merocyanine form MC. This MC form reverts to the SP form both in the dark and photochemically with corresponding changes in surface pressure. The MC form emits a fluorescence at 650 nm which can be excirted either directly (545nm to 575 nm) or indirectly (370 nm). The kinetics of the isomerization from SP to MC was measured using the fluorescence signal of the MC form.

3. Reversible Isomerization of an Amphiphilic Azobenzene. In contrast to the spiropyran where the chromophore is the head group of the amphiphile, here the chromophore is part of the hydrophobic chain. The isomerization of the azobenzene AP812 (structure below) was investigated in monolayers at the air-water interface as well as in transferred monolayers. The reflection spectra of the trans and cis forms of an AP812 monclayer at a surface pressure of 30 mN/m are shown in Fig. 1. Trans-cis isomerization was obtained by illumination with 366 nm radiation. The cis form reacts b · ' to trans upon illumination at 436 nm. Both kinetics and degree of cis-trabns isomerization depend on surface pressure and light intensity. The reflection spectra of the trans form show a blue shift with increasing surface pressure. The isomerization can also be carried out reversibly in transferred monolayers.

4. Photoinduced Electron Tra..sfer in Monolayers at the Air-Water interface. In dense-packed monolayers of a pyrene-labelled palmitoyl-phosphatidylcholine (PyPPC) and DPPA the pyrene is located at the monolayer-air interface. The adsorption of the electron acceptor methyl viologen (MV) from the aqueous subphase to the negatively charged head groups of the mixed monolayer was characterized by measuring the reflection spectrum of MV with maximum at 265 nm.

Upon excitation of the pyrene photoinduced electron transfer across the mono-
layer to MV causes steady state quenching of the pyrene monomer emission.
The surface density of adsorbed MV and consequently the extent of quenching
depends on the bulk concentration of MV.

5 Effect of Dipole Layers on Photoinduced Electron Transfer. Investigations of
protonation equilibria at the interface monolayer system-water have revealed a
strong influence of the underlying system on the apparent pK of a fluorescent
probe located at the interface in an unchanged near environment[5,6]. We have
studied fluorescence quenching of an amphiphilic pyrene located at the system-
water interface of a bilayer on glass in contact with an aqueous phase by
methyl viologen (MV) adsorbed to the negatively charged head groups of the
monolayer matrix. Quenching depends strongly on the nature of the first layer in
contact with the glass surface, although the second layer in contact with water
has the same composition. No quenching in contact with 10^{-6} M MV is observed
when the first layer is eicosylamine, considerabel quenching was found under the
same conditions with cadmium arachidaie as first layer. The phenomenon is
ascribed to the effect of charges and dipoles at the glass surface on the MV
concentration near the system-water interface.

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C₈H₁₇—〈benzene ring〉—N=N—〈benzene ring〉—O—(CH₂)₁₂—N⁺〈pyridinium ring〉 Br⁻
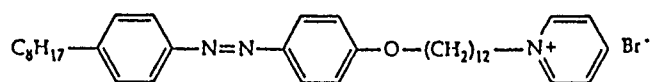
N-[p-(p-octaphenylazo) phenyloxy] dodecylpyridinium bromide
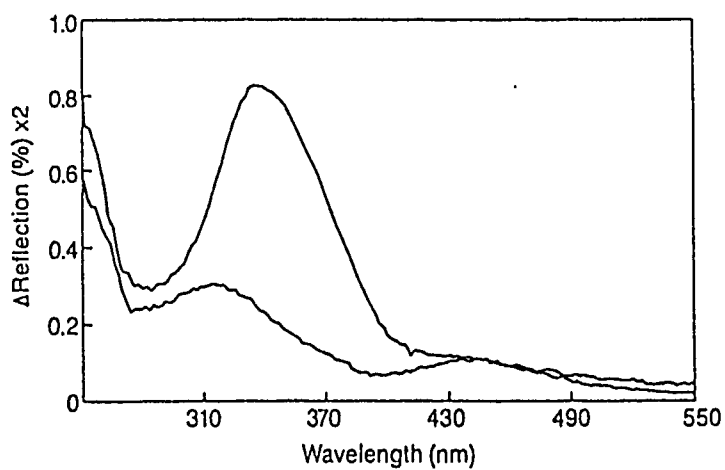
Fig. 1: Reflection spectra of monolayers of the amphiphilic azobenzene AP812, cis form with maxima at 315 nm and 445 nm, trans form with maximum at 335 nm.

PHOTOINDUCED ELECTRON AND ENERGY TRANSFER IN COVALENTLY LINKED SUPRAMOLECULAR SPECIES BASED ON METAL COMPLEXES

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Supramolecular photochemistry is a new and rapidly developing field of research,[1] in which aspects of fundamental and applied nature are deeply intertwined. In a supramolecular system made up of suitably linked molecular components, the study of photoinduced intercomponent processes offers substantial mechanistic advantages over that of analogous bimolecular processes. It is indeed from the study of covalently linked "dyads" that some major advances in the understanding of fundamental aspects of electron and energy transfer processes have recently been obtained.[2,3] On the other hand, the world of biology, with the supramolecular structure of its reaction centers and active sites, represents a continous source of inspiration to the field. Natural systems are able to achieve *light-induced functions at a molecular level*, an outstanding example being givren by the transmembrane charge separation occurring in photosynthetic reaction centers.[4,5] Extension to artificial systems leads to the concept of *photochemical molecular devices*, i.e., appropriate assemblies of molecular components (supramoiecular structures) capable of performing valuable light-induced functions (vectorial charge separation, directed migration of electronic energy, remote photosensitization, switch on/off of electrical or light signals, modulation of receptor ability, control of cavity size, etc.).[6] For most ligth-induced functions, likely mechanisms involve sequences of elementary acts (radiative or radiationless processes within single components as well as intercomponent energy and electron transfer processes).

Transition metal complexes are attractive building blocks for supramolecular systems, due to their flexibility with respect to excited-state and redox properties. Supramolecular systems made ̣ of metal complex covalently linked via bridging ligands are commonly termed *polynuclear complexes*, and their photochemistry is receiving an increasing amount of attention.[7] The subject of this presentation is the behavior of some polynuclear complexes containing Ru(II), Re(I), Rh(III), and Cr(III) subunits, designed to the purpose of studying photoinduced intercomponent energy and electron transfer processes between metal-containing components. The main results obtained can be summarized as follows.

Polychromophoric systems. These systems are made of a number (two to five) of metal-bipyridine chromophores linked by bridging cyanides. The excited-state energies of the various chromophores, while similar, are not exactly the same due to differences in metal (Re(I), Ru(II)), ancillary ligands (bpy, CN$^-$, CO), and bonding mode (N- or C- bonded) of the bridging ligand. In all cases, fast intercomponent energy transfer has been observed, leading to 100% efficient population of the lowest-energy excited chromophore. These systems behave as (supra)molecular *antennas*. This effect has been used as a means to increase the light absorption efficiency of sensitized semiconductors.

Chromophore-luminophore complexes. In these complexes, one or two Ru(II)-bipyridine units, characterized by intense visible absorption, have been coupled via bridging cyanides to Cr(III) complex units, which practically lack of visible light absorption but have a very typical narrow and long-lived red emission. Fast and efficient intercomponent energy transfer has been observed, leading to efficient emission from the Cr(III) luminophore following visible absorption by the Ru(II) chromophore. Two-component systems of this type are better suited than simple molecular species for *separate* optimization of the light absorption and emission properties, and could represent a useful strategy in the design of, e.g., luminescent labels.

Photoinduced electron transfer. "Bis-bipyridine" ligands, where two bpy-type ligands are covalently attached in the 4 position by a two-methylene chain, are used to build up systems in which intercomponent electron transfer can be studied. The absorbed light is used to trigger the electron transfer event either directly (A*-B --> A$^+$-B$^-$, *photoinduced electron transfer*) or indirectly (to produce a site-selectively reduced species that undergoes *charge shift*, B$^-$-C --> B-C$^-$). Attempts to couple the two types of system to obtain photoinduced *charge separation* over a three-center system (A*-B-C --> A$^+$-B-C$^-$) are in progress.

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Photoinduced Electron Transfer and Photo-conduction in Langmuir Blodgett Films

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Photo-induced electron transfer in monolayer assemblies has been observed by fluorescence quenching[1],[2] of dye molecules or aromatic moieties incorporated in Langmuir Blodgett films and by the generation of photo-currents perpendicular[3],[4],[5] and parallel[6],[7] to Langmuir Blodgett films.

When a monolayer of an ω-(2-anthryl)-fatty acid and a mixed monolayer of a cyanine or xanthene dye and arachidic acid are deposited successively on an anthracene single crystal (figure 1) a photo-sensitized hole current is observed upon excitation of the dye. The photo-current injected by this monolayer assembly saturates at considerably lower field strengths than photo-currents injected by adsorbed dye molecules. This could be attributed[8] to a decrease of the image potential that binds the injected hole to the first layer of the crystal, leading to a more efficient escape[9] of the injected hole. The decrease of the quantum yield of the sensitized photo-current observed upon increasing the length of the ω-(2-anthryl)-fatty confirms that the low overall quantum yield is due to competition between the monomolecular decay of the excited state of the dye and the primary electron transfer step. A quantitative interpretation of this effect suggests that the electron transfer is assisted[10] by the interaction between the highest occupied π-orbital of the dye and the highest occupied σ-orbital of the alkyl chain. Replacing arachidic acid by tripalmitine changes the electric field at the interface between the two monolayers and decreases the efficiency of the electron transfer by 90 %.

While some experiments suggest[11]-[12] that condensed Langmuir Blodgett multilayers of saturated fatty acids consist of a conglomerate of twodimensional microcrystals more homogeneous multilayers can be obtained

from low molecular polymers[13]. Polymers with mesogenic triphenylene[14],[15] side chains (figure 2a), forming discotic bulk phases, were able to form stable monolayers on a water surface. By transfer of those monolayers to a substratum is was possible to obtain multilayers where the triphenylene moieties were arranged in stacks oriented parallel to the surface of the substratum (figure 2b).

The absorption spectra of the Langmuir Blodgett films are characterized by a maximum at 278 nm and a shoulder at 310 and 350 nm. They correspond to the absorption spectrum of a dilute solution of the same hexa-alkoxy-triphenylene which is characterized by a main maximum at 278 nm and smaller maxima at 306 nm and 347 nm. The fluorescence spectra of both the LB-film and the solution consist of a band with a maximum at 385 nm. The 0-0 transition of the fluorescence spectrum is for both samples observed at 370 nm. Those data suggest that no strong interaction occurs between the triphenylene moieties in the Langmuir Blodgett film.

The dark and photo currents of the mono- and multilayers at applied electric fields between zero and 5.0×10^4 Vcm^{-1} were determined. In order to have no interference from pinholes the conductivity was determined parallel to the quartz substratum on which 15 interdigitized gold electrodes with a spacing of 0.1 mm and a length of 5 mm were deposited. When the applied voltage was increased from zero to 500 V the dark current increased to 1.2×10^{-11} A (8.3×10^{-6} Acm^{-2}) for samples covered by a single monolayer of the triphenylene derivative. For a slide covered by 15 monolayers dark currents between 1.2×10^{-10} and 2.9×10^{-10} A (5.3×10^{-6} and 1.3×10^{-5} Acm^{-2}) were obtained at 500 V. The dark currents could be compared to those obtained for mixed mono- and multilayers of a copper phtalocyanines and stearyl alcohol[16]. Upon illumination with a light flux of 1.0×10^{-3} W at 350 nm the photo-current amounts to 5.9×10^{-11} A (5.5×10^{-6} Acm^{-2}) at an applied field strength of 5.0×10^4 Vcm^{-1} for a single monolayer. For fifteen monolayers photo-currents between 4.6×10^{-9} A and 4.4×10^{-9} A were (2.1×10^{-3} and 2.0×10^{-3} Acm^{-2}) obtained under those experimental conditions. The photo current responds with a relaxation time of 40±15 s to a variation of the light intensity.

The dark current obtained for a slide covered by fifteen monolayers of 1/1 mixture of the hexa-alkoxytriphenylene oligomer and trinitrofluorenone was of the same magnitude as that obtained in the absence of trinitrofluorenone.
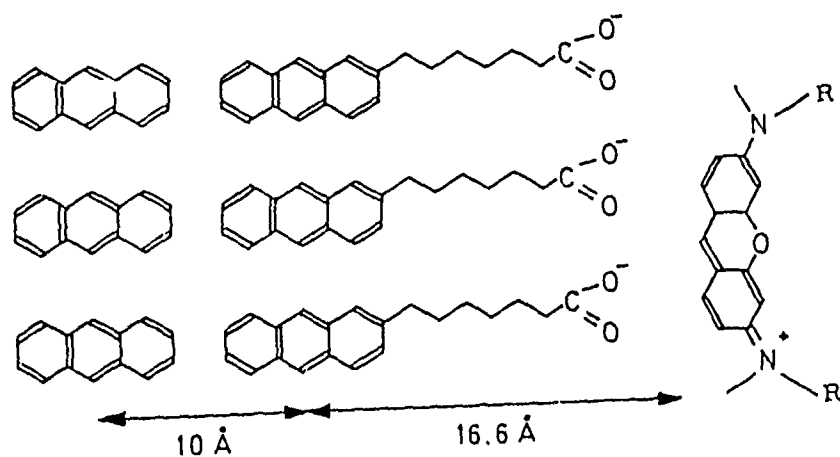
Figure 1: The monolayer assembly used for the photo-sensitized injection of holes in anthracene single crystals.
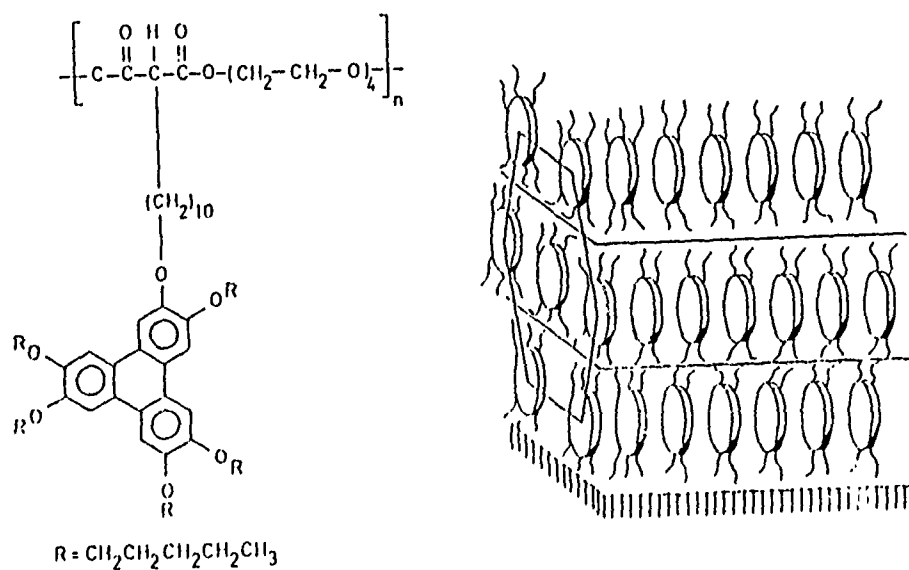
Figure 2: The building block of the discotic liquid crystalline polymer and a schematic representation of the Langmuir-Blodgett film.

For the mixed multilayer no photo-current could be obtained. Introduction of trinitrofluorenone quenched the fluorescence by 90 % without changing the features of he emission spectra. This could indicate that partial demixing occurs and that all residual fluorescence comes from parts of the multilayer containing no trinitrofluorenone.

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THE POTENTIAL ENERGY SURFACE OF THE LOWEST EXCITED TRIPLET STATE OF 1,3,5-HEXATRIENE.

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1. Introduction

In previous studies[1,2] we considered the time-resolved resonance Raman (TRRR) spectra of 1,3,5-hexatriene (HT) in its lowest excited triplet state in order to obtain information about the geometry of the T_1 intermediate and the mechanism of the cis-trans photoisomerization in T_1.

In the present paper some results of the most recent experimental and theoretical studies are presented, and the present picture of the potential energy surface in the lowest excited T_1 state of 1,3,5-hexatrienes evolving from these and our previous investigations is summarized. A more detailed account of this work is to be published[3-5].

In order to obtain information on the T_1 state of HT, several experimental and theoretical methods are used:

Time-resolved resonance Raman spectroscopy: The experimental method giving the most detailed structural information on equilibrium geometries in the excited T_1 state is TRRR spectroscopy. Vibrational *frequencies* in the T_1 state provide characteristic fingerprints of the equilibrium geometry or geometries in the T_1 state. Thereby, detailed structural information on the relative minima of the potential energy surface is obtained. *Intensities* of resonance Raman bands are dependent on the relative populations of scattering molecules and characteristic of the changes in molecular geometry occurring upon excitation from the T_1 to the T_n state of the resonance transition. Hence, information not only on the T_1, but also the T_n state is available from the spectra.

By variation of the *temperature* in TRRR experiments information on the relative populations among different minima and hence on the *relative energy of different minima* is obtained.

The *kinetics of equilibration* among different minima on the T_1 potential energy surface at various temperatures, as revealed by TRRR spectra, allows to draw conclusions about the *height of barriers* separating different minima from each other. If barriers are sufficiently small, equilibration occurs rapidly, i.e. within the lifetime of the T_1 state; if they are large, on the other hand, no equilibration will be observed. Equilibration along torsional coordinates around formal C=C double and C-C single bonds can be studied by *varying the ground state configurations and conformations* of the HT derivatives by studying different isomers and rotamers.

The study of *deuteriated molecules* provides a means to further support the assignment of vibrational spectra.

Time-resolved absorption spectroscopy: Time-resolved absorption spectroscopy allows to determine triplet-triplet absorption spectra and kinetics of triplet state formation and decay. In particular, $T_1 \rightarrow T_n$ *absorption spectra* are important for an assignment of the T_n state active in the resonance transition, which is necessary to calculate TRRR intensities. *Kinetics* of triplet decay as a function of temperature

yield activation energies and frequency factors of Arrhenius plots and are interpreted in terms of *torsional barriers* on the T_1 potential energy surface. The measurement of rate constants of *triplet energy transfer* using HT as either donor or acceptor yields information on energies of vertical and relaxed triplet states of HT.

Photostationary triplet state photochemistry: The measurement of *photostationary states* and *quantum yields of photoisomerization* by sensitized stationary photochemistry for a variety of donors and acceptors with different triplet energies is an additional, more indirect, method to determine triplet state energies and minima on the T_1 potential energy surface.

Theoretical quantum chemical calculations: The understanding of the results of the above mentioned experimental investigations are crucially dependent on a comparison with results from theoretical calculations. The experimental TRRR spectra were interpreted by quantum mechanical calculations (QCFF/PI and CNDO/S) of equilibrium geometries and vibrational frequencies at the trans (E), cis (Z) and centrally twisted (P) geometries in T_1 and in the T_n state responsible for the TRRR activity. On the basis of these calculations the T_1 normal modes showing the strongest Franck-Condon activity in the TRRR spectra can be identified for each geometric isomer of HT.

2. Results and Discussion

The observed TRRR spectra for unsubstituted HT are shown[1-3] to result from a superposition of the spectra of the Z and E forms with possible weak contributions from the P form. It was concluded that the transient T_1 intermediate in the photoisomerization of HT, monitored by TRRR spectra, exists as an equilibrium between several geometric structures, in which planar molecules represent a substantial fraction, and that a possible minimum of the potential energy curve at the centrally twisted geometry must be rather shallow. An example of experimental and calculated spectra is shown in Figure 1 for 3-d-HT.

In this paper we consider the combined results of TRRR spectra and decay kinetics of the T_1 intermediate of HT, some of its deuteriated derivatives, and of its 2,5-dimethyl- (DMHT), 2-methyl- (2-MHT), and 3-methyl- (3-MHT) derivatives. The T_1 TRRR spectra of the two isomers of non-deuteriated DMHT have been reported previously[6]. We now report the spectra of E- and Z-3,4-d_2-DMHT and of E-3-d-DMHT together with remeasured spectra of DMHT-d_0. Furthermore, resonance Raman spectra of E-2-MHT, E-4-d-2-methyl-1,3,5-hexatriene (E-4-d-2-MHT), Z-2-methyl-1,3,5-hexatriene (Z-2-MHT), E-3-methyl-1,3,5-hexatriene (E-3-MHT), and Z-3-methyl-1,3,5-hexatriene (Z-3-MHT) in the lowest triplet state T_1 are reported and discussed. QCFF/PI calculations are performed to determine energies and optimized geometries in the S_0, T_1, and T_n electronic states. For each T_1 species, $T_1 \rightarrow T_n$ transitions, vibrational frequencies, and RR intensities are calculated and compared with the observed frequencies and intensities (as exemplified in Fig.1). An example of determination of the activation energy of the decay of the T_1 state is shown in Fig. 3 for 2-MHT and 3-MHT.

Finally, in Fig. 4 the qualitative potential energy surfaces in the T_1 state of the methyl substituted HT's are shown, resulting from different pieces of information as discussed above. It can be seen that characteristic differences are found for the different molecules. The T_1 potential energy surface of 3-MHT is very similar to that of unsubstituted HT[1]. Steric interaction is responsible for the high energy of the Z isomers of DMHT. The barrier along the torsional coordinate of the central CC bond at the P geometry is seen to vary, being 0.7-0.8 Kcal/mol for HT, cPt-DMHT and 3-MHT, while 2-MHT shows a lower barrier of 0.4 kcal/mol and no barrier is found for the tPt form of DMHT.
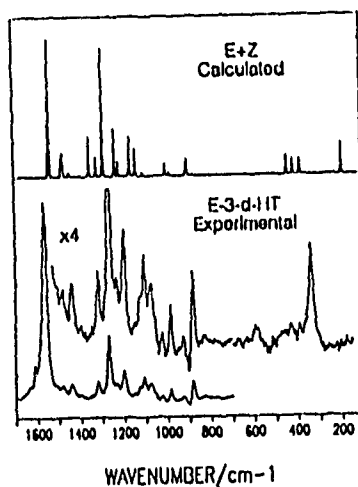
Figure 1: Calculated and experimental T_1 resonance Raman spectrum of 3-d-HT.
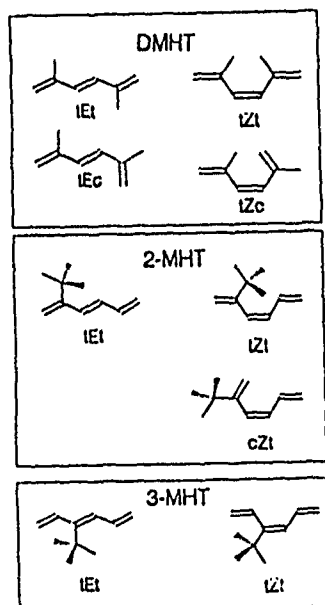
Figure 2: Planar geometries of DMHT, 2-MHT and 3-MHT.
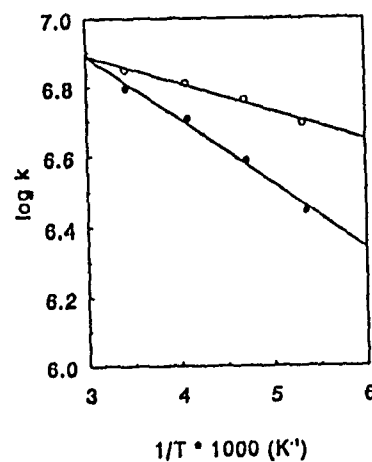
Figure 3: First order rate constant for T_1 decay for 2-MHT (open circles) and 3-MHT (filled circles).
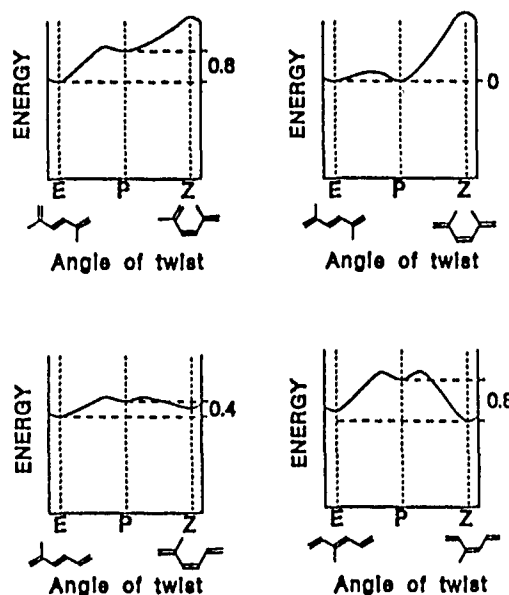
Figure 4: Potential energy curves in T_1 for DMHT, 2-MHT and 3-MHT.

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FEMTOSECOND ELECTRON TRANSFER IN THE ELECTRON DONATING
SOLVENT: A NEW TYPE OF ELECTRON TRANSFER

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Introduction
Studies on photo-induced intermolecular electron transfer
reaction are usually carried out in solutions of electron
donor and acceptor in non-reactive solvent, in which the rate
of electron transfer is limited by the   translational
diffusion rate.   To obtain direct information on the rate
constant of fast intermolecular electron transfer, it is more
favorable to perform the experiment in contact systems of
electron donor and acceptor, in order to eliminate the
limitation by translational diffusion.   Two kinds of contact
systems had been developed previously: i) dyes adsorbed on the
surface of organic single crystals [1] and ii)dyes dissolved
in molten aromatic hydrocarbons as electron donors or
acceptor [2].
Here we report the ultrafast fluorescence quenching of
excited dye molecule (nile blue A perchlorate; NB) due to
photo-induced intermolecular electron transfer in neat aniline
(AN) and N,N-dimethylaniline (DMA), acting as weakly polar
electron-donating solvents.   The present contact systems are
weakly interacting or non-interacting in the ground state, as
is manifest in unaltered absorption spectra, and are thus
distinct from the studies on the typical charge-transfer
complexes.
In the present work, rate constants of electron transfer,
which is up to 50 times faster than the longitudinal solvent
relaxation time, are discussed, and adiabatic and non-
adiabatic theories are applied to explain the phenomenon.
Strong contribution in weakly polar systems by ultrafast
nuclear reorientation can provide ultrafast pathways for
electron transfer.

Experimental
A homemade, hybridly mode-locked, synchronously pumped
dye laser, coupled with a cavity damper and a prism pair for
dispersion compensation, produces 595 nm pulses of 0.3 ps at
15 kW peak power and a repetition rate of 3.8 MHz.   The
fluorescence decay of NB is measured at the magic angle by a
conventional fluorescence up-conversion system, using a BBO
crystal. as shown in Fig. 1. Ground-state recovery time of
NB/AN (Fig.2) was measured by a subpicosecond pump-probe
apparatus.

Results

The fluorescence decay curve of NB/AN and NB/DMA are shown in Fig. 1a and b. Using the auto-correlation shape of the excitation laser pulse as an instrument response function, the decay lifetime can be obtained by an ordinary deconvolution procedure. The decay curve is clearly non-exponential and we tentatively adopt a two-exponential fitting procedure, yielding lifetimes of 0.4 (56%) and 2.5 (44%) ps for AN and 0.1 (95%) and 2.3 (5%) ps for DMA, with the lifetime of the slow component in case of DMA being approximate only. Both of the lifetimes are very much shorter than that obtained in inert solvent (5.6 ns). In order to get information about potential contribution by a dynamic Stokes shift, measurements of fluorescence decay are carried our at different wavelengths between 658 nm and 817 nm. At the shortest wavelength (658 nm) the contribution of the fast component is found to be only slightly larger (by about 10%), indicating that the effect of the dynamic Stokes shift on the fluorescence decay curve is small, as could be expected from the small Stokes shift observed in the steady-state spectra.

Fig. 2 shows a ground-state recovery of NB/AN, whose time constant is 2.8 ps. In the present cantact system, the back-electron transfer also occurs very rapidly (within 2.8 ps).
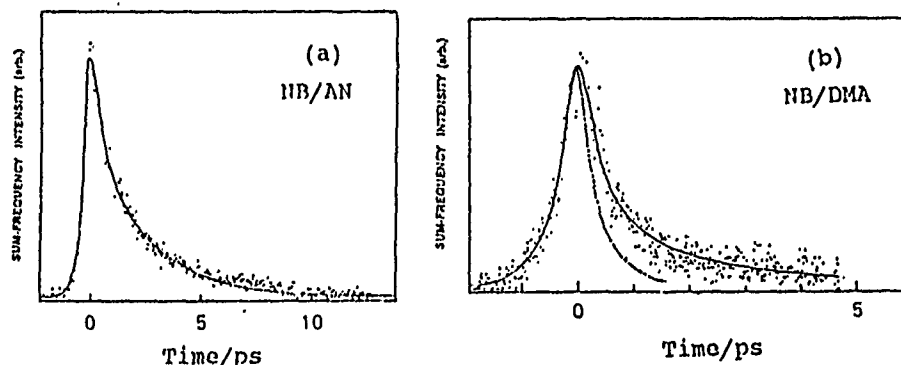
Fig. 1. Fluorescence decay curves of NB/AN (a) and NB/DMA with a convoluted decay curve. Observation wavelength is 690 nm. Broken line indicates the autocorrelation of laser.
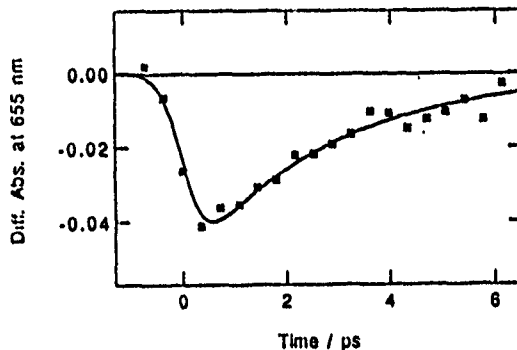
Fig. 2. Ground-state re-
covery of NB/AN observed
at 655 nm. Solid line
indicates the simulation
with a recovery time of
2.8 ps.

Discussion

For this ultrafast electron transfer reaction, we applied
both adiabatic and non-adiabatic models.

(1) Adiabatic Model. The solvent reorientation
energy, λ_s, in the present weakly polar systems had been
estimated to be 0.3 eV by Marcus theory with a crrection for
non-spherical molecules. The intramolecular reorientation
energy is obtained as λ_i = Shw = 1.8×1400 cm^{-1} = 0.31 eV.
Since $\lambda_i/\lambda_s \approx 1$, a strong contribution to the totally observed
polarization response in case of adiabatic electron transfer
by ultrafast vibrational nuclear relaxation can be expected,
in addition to solvent relaxation, limited by the longitudinal
relaxation time. Under these conditions, according to Sumi
and Marcus [3], two stages of the electron transfer reaction,
reflected in two "average survival times", r_a and r_b, can be
discriminated. In the first stage of the reaction, ultrafast
electron transfer, initiated by nuclear motion, occurs on a
time scale of r_a in the ensemble consisting of donor-acceptor
pairs, which happens to be surrounded by solvent molecules of
proper orientation at the moment of electronic excitation.
All the remaining donor-acceptor pairs will have to wait until
the solvent polarization assumes a suitable configuration for
electron transfer to occur, thus forming a second ensemble,
characterized by an average survival time, r_b, which will be
close the longitudinal relaxation time, r_L. For an
"intermediate reaction window", λ_i/λ_s = 1, at $\Delta G^*/kT$ = 1 and
r_L = 5 ps, we obtain r_a = 0.10 ps r_b = 1.0 ps with the
equilibrium electron transfer rate constant, k_e = 2×10^{14} s^{-1}.
This is in good agreement with the present tentative two-
exponential analysis with lifetimes r = 0.1 ps and r = 2.4 ps
for NB/DMA.

We estimated r_L = 5 ps for A and DMA, in analogy to other
monosubstituted benzenes: r_L = 4.2 ps for chlorobenzene, 5.7
ps for benzonitrile, and 7.4 ps for bromobenzene. A
comparison of the above longitudinal relaxation times with the
present fluorescence decay time indicates that the electron
transfer is faster than the solvent relaxation time in the
present case by approximately 50 times.
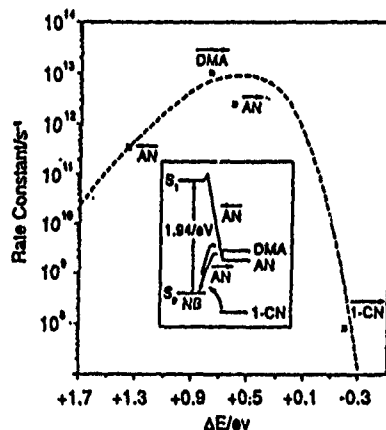
Fig. 3. Plot of rate constant of electron transfer vs. energy gap between donor and acceptor. The solid line is a fit according to a quantum mechanical theory of electron transfer (see text). AN and AN depict forward and backward electron transfer, respectively. The inset shows an energy level diagram.

(2) Non-adiabatic Model. Figure 3 shows a semilogarithmic plot of rate constant of electron transfer against free-energy, the solid line is a best fit according to Jortner's quantum mechanical formula [4] for the medium temperature range ($hw_s \ll kT \ll hw$) of non-adiabatic electron transfer, with coupling strength $S = 1.8$, quantum mode $hw = 1400\ cm^{-1}$, electron exchange matrix element $V = 0.035$ eV, and solvent reorientation energy $\lambda_s = 0.3$ eV. The inset in Fig. 3 shows the energy levels of present donor/acceptor systems, obtained from the application of non-adiabatic theory.

Conclusion

Ultrafast nonexponential fluorescence decays ascribed to intermolecular electron transfer is observed for nile blue in electron-donating solvent systems with a femtosecond laser/fluorescence up-conversion system. In N,N-dimethylaniline the decay is dominated by a lifetime as short as 100 fs, the process being up to 50 times faster than the solvent longitudinal relaxation. In this case electron transfer is limited only by ultrafast nuclear relaxation rather than by solvent reorientation and is thought to occur in a diffusionless, weakly polar, highly polarizable aromatic system. Nonadiabatic theory is also applied with physically reasonable values for both the coupling strength and electron exchange matrix element. The electron backward reaction was also studied with a subpicosecond laser flash photolysis system and the energy gap law was examined.

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TARGETING OF PHOTOCHEMICAL REACTIONS TO SPECIFIC SEQUENCES

IN NUCLEIC ACIDS

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Résumé : Des photosensibilisateurs variés ont été lié de façon covalente à des oligonucléotides. L'oligonucléotide se fixe sélectivement sur une séquence complémentaire dans un acide nucléique en simple hélice ou dans le grand sillon de la double hélice d'ADN en formant localement une triple hélice. Par irradiation des complexes formés, des réactions photosensibilisées (pontage covalent, coupure, photooxydation) sont induites dans l'acide nucléique cible au niveau de la séquence reconnue par l'oligonucléotide. Les propriétés des conjugés oligonucléotide-photosensibilisateur ouvrent de nouvelles perspectives en biologie moléculaire et cellulaire, notamment pour le contrôle selectif de l'expression des gènes.

Nucleic acids play a central role in all living cells : the double helix of DNA contains all genetic information ; transcription of DNA into messenger RNAS followed by translation of mRNAs into proteins are key steps in gene expression. Nucleic acids absorb radiations in the ultraviolet range (below 300 nm). Irradiation of nucleic acids induces different types of photochemical reactions leading to the formation of a large number of photoproducts [1]. Photosensitizers have been used either to selectively create one of these UV-induced photoproducts or to generate new photochemical reactions [1]. In all cases there is no sequence specificity except for the selectivity of the photochemical reaction itself : for example, UV-induced pyrimidine dimers involve cyclobutane ring formation between adjacent pyrimidine bases on the same strand of double-stranded DNA.

In order to target specific photochemical reactions to defined sequences we have designed bifunctional nucleic acid ligands which contain an oligonucleotide, which recognizes a specific sequence on either single-stranded or double-stranded nucleic acids, and a photosensitizer, which induces photochemical reactions at the site where the oligonucleotide is bound [2]. These oligonucleotide-photosensitizer conjugates can be used as tools to investigate

the selectivity of oligonucleotide binding, as artificial nucleases and as sequence-specific gene inhibitors.

Photo-induced cross-linking. Azido derivatives, such as azidophenacyl [3] and azidoproflavine [4], proflavine [5] and porphyrins [6] have been covalently attached to either end of short oligonucleotides. When the oligonucleotide binds to a complementary sequence irradiation in the UV or visible range induces covalent linkage between the photosensitizer and nucleic acid bases. Some of these photo-adducts weaken the glycosidic bond and alkaline treatment leads to cleavage of the phosphodiester backbone. These properties were used to demonstrate that oligo-α-deoxynucleotides synthetized with the unnatural α-anomers of nucleotide units bind in a parallel orientation with respect to their complementary sequence whereas oligo-β-deoxynucleotides synthetized with the natural β-anomers bind in an antiparallel orientation [3].

Homopyrimidine oligonucleotides can bind to the major groove of double-helical DNA where they form a local triple helix. Attachment of a photosensitizer at one end of such oligonucleotides allowed us to determine the orientation of the third strand in triple helices [4].

Psoralen derivatives can form two adducts with thymine bases in DNA. These two adducts involve cyclobutane ring formation between the 3,4 and 4',5' double bonds of psoralen and the 5,6 double bond of each thymine. At 5' TpA 3' sequences this two-photon reaction leads to a cross-link between the two strands of double-helical DNA. Using a psoralen covalently attached to an oligonucleotide we have been able to target this photochemical reaction to specific sequences of the DNA double helix, as a result of triple helix formation [7].

Photooxidation of nucleic acid bases. Some of the photosensitizers described above (proflavine, porphyrins...) generate singlet oxygen upon visible-light irradiation [5,6]. Singlet oxygen reacts with nucleic acid bases, especially guanine. Despite the long lifetime of singlet oxygen a high yield of oxidation is observed at the site where the photosensitizer is bound. Alkaline treatment induces a cleavage of the phosphodiester backbone at the level of the photooxidized nucleotides.

Photo-induced cleavage of nucleic acids. Ellipticine derivatives have been covalently attached to the 5'- or 3'-end of oligonucleotides. When bound to a complementary sequence UV-irradiation ($\lambda > 300$ nm) induces a cleavage of the phosphodiester backbone at the site where ellipticine is targeted by oligonucleotide binding [8,9]. When the target is a DNA double helix, triple helix

formation leads to a photo-induced cleavage of both strands of DNA [8]. This is the first description of a site-specific photo-induced artificial nuclease.

Conclusion. Covalent linkage of photosensitizers to synthetic oligonucleotides has allowed us to target photochemical reactions to specific sequences of nucleic acids. Both single-stranded and double-stranded DNA can be chosen as targets. Different photochemical reactions can be induced at specific sites on nucleic acids. These sequence-targeted photochemical reactions have various interests : i) they can be used as tools to investigate the nature of base-specific photochemical reactions or to obtain information on the local structure of nucleic acids ; ii) photo-induced cleavage at specific sites opens the possibility of developing sequence-specific artificial nucleases ; they can be used ,e.g., to map genes on long chromosomes by cleaving at a limited number of sites with appropriately chosen target sequences ; iii) photochemical modifications of DNA in living cells are recognized by repair enzymes which either correct the defect or introduce erroneous bases ; therefore site-directed mutations can be introduced within the DNA of living cells by oligonucleotide-photosensitizer conjugates : iv) sequence-specific modifications of nucleic acid bases can be used to block gene expression either at the transcriptional or translational level : cross-linking of an oligonucleotide to a single-stranded mRNA or to the DNA double helix is expected to arrest mRNA translation or DNA transcription and replication. The target can be a cellular gene ; alternatively a viral or a parasite genome can be selected as a target. The selectivity of oligonucleotide binding is such that it is possible to block the expression of a single gene within a living cell.

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LASER PHOTOCHEMISTRY OF WATER AND NUCLEIC ACID COMPONENTS

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This report is a brief review of main results on two-quantum photochemistry of nucleic acid components (NAC) in water solution obtained in the Institute of Spectroscopy, USSR Academy of Sciences during last twelve years.

The first experiments[1] on high-intensity laser UV irradiation ($I = 10^{13} W/m^2$, $\tau_p = 29ps$, $\lambda = 266nm$) of thymine in water solution ($c = 10^{-4} mol/dm^3$) have demonstrated that at least some of photoproducts at picosecond UV irradiation are formed by two-quantum (two-step) mechanism with the quantum yield being two orders of magnitude higher than the total quantum yield of single-quantum photoreactions of thymine dimerization and hydration. As the energy of two light quanta with $\lambda = 266nm$ is much higher than the ionization limit of all NAC molecules ($\sim 5{-}6eV$)[2], after sequential two-quantum absorption they should be effectively ionized. It is easy to show[2], that under picosecond UV irradiation of NAC molecules two-step excitation is realized via singlet channel ($S_0 \rightarrow S_1 \rightarrow S_N$) rather than via triplet channel ($S_0 \rightarrow S_1 \rightarrow T_1 \rightarrow T_N$).

When measuring the photoconductivity of neutral NAC aqueous solution at different concentrations under picosecond UV irradiation we discovered[3] that the photocurrent pulse oscillogram at sufficient dilution of the irradiated solution ($c < 10^{-5} mol/ /dm^3$) does not differ from the photocurrent pulse oscillogram attained at high-intensity picosecond UV irradiation of pure liquid water. From this it is follows that high-intensity picosecond UV irradiation of liquid water gives rise to charged particles. We showed[4] that the photocurrent pulse amplitude was a quadratic function of irradiation intensity. The amount of absorbed energy was squarely dependent on intensity, too. From this it is trnspires that the two-photon mechanism is res-

ponsible for the formation of photocurrent. The two-photon absorption coefficient of pure liquid water at λ = 266nm is 10^{-12}m/W[5].

Having absorbed two light quanta with λ = 266nm a water molecule acquires energy of 9.3eV. The ionization and dissociation limits of liquid water (E_{ion} = 6.5eV, E_{dis} = 5eV)[2] in this case are considerably exceeded which should lead to ionization and dissociation of water molecules. Using the method of picosecond flash photolysis we proved the effect of two-photon water ionization under high-intensity UV laser excitation (I = $5 \cdot 10^{13}$W/m^2, τ_p = 29ps, λ = 266nm)[5]. The passage of an exciting laser UV pulse through a 0.2cm layer of water was found to induce an absorption band with a maximum in the red region near λ = 720nm, which coincided well in shape with the literature spectrum of hydrated electron. The quantum yield of e_{aq}^{-} formation which corresponded to the quantum yield of two--photon ionization at λ = 266nm was 0.15 $\pm$ 0.02[5]. The quantum yield of two-photon water dissociation at λ = 266nm was 0.13 $\pm$ $\pm$ 0.07[5].

We proved the participation of two-photon water photolysis products in the decomposition of NAC molecules in aqueous solution under picosecond laser UV irradiation (λ = 266nm, I = = $6 \cdot 10^{13}$W/m^2, τ_p = 29ps)[3]. The experiment involved thymine solutions with different concentrations (from 10^{-3} to $4 \cdot 10^{-5}$ mol/dm^3) but with the same optical density (D = 1.6), i.e. the same number of thymine molecules was irradiated in each case, the number of water molecules varying. If water had not absorbed UV radiation energy, the photolysis quantum yield would have been independent of thymine solution concentration. On the other hand, if water had absorbed some incident energy of UV radiation with water photolysis products not participating in thymine decomposition, the quantum yield would have decreased with concentration. The increase in photolysis quantum yield observed as the concentration of solution was decreased, indicates unambiguously that the products of two-photon water photolysis take part in thymine photodecomposition under picosecond laser UV irradiation.

After that we investigated[6] primary photoprocesses from

highly-excited S_N levels of thymine molecule populated by means of two-quantum (two-step) absorption. Simple calculations show that when using sufficiently concentrated aqueous NAC solution ($c \approx 10^{-3}$mol/dm^3) the incident energy of picosecond UV laser pulse is absorbed principally by solute molecules and therefore the effect of two-photon water photolysis can be excluded. Nevertheless it was demonstrated that even in this case water radicals formed again, but by another mechanism namely by intermolecular energy transfer from highly-excited S_N levels of thymine molecule to water with its subsequent ionization and dissociation. The probability of such energy transfer for thymine molecule is about 6.5%, whereas the probability of thymine ionization from S_N levels measured after geminate recombination is about 0.7%. The geminate recombination time for Thy$^+$ - e$^-_{aq}$ pair is 4 ± 2ps.

It was shown[6] that in concentrated thymine aqueous solution most of products formed under picosecond UV irradiation are due to chemical reactions between water radicals and unexcited solute molecules. It is clear that in the case of picosecond UV photolysis of a diluted thymine aqueous solution when the laser radiation is absorbed directly by the water molecules via two-photon mechanism the photolysis quantum yield should increase. In the experiment[6] we observed 5-fold increase of photolysis quantum yield when changing concentration from $1.5 \cdot 10^{-3}$ to $3 \cdot 10^{-5}$mol/dm^3.

Using the method of thin-layer two-dimensional chromatography we managed to compare the products of γ-radiolysis and picosecond laser UV photolysis of thymine both in concentrated and diluted aqueous solution[7]. Despite a qualitative difference between the mechanisms of two-quantum laser UV photolysis and γ-radiolysis in all the cases the products formed were almost the same. This fact supports the dominant role of water radicals in the formation of the products of two-quantum laser UV photolysis of NAC molecules in aqueous solution.

Using HPLC method we isolated and identified[8] 6 main products of picosecond UV photolysis (λ = 266nm, τ_p = 23ps, I = 10^{13} - 10^{14}W/m^2) of uridine in water solution: four single-quantum products - two hydrates and two dimers, and two two-

-quantum products, including uracil formed as a result of N-
-glycosidic bond scission. The experiments showed that with
the increasing UV irradiation intensity the quantum yields of
two-quantum products grew while those of single-quantum drop-
ped.

Now we started experiments on two-quantum photochemistry
of amino acids[9].

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A NEW VIEW ON THE TROPOSPHERIC OZONE CHEMISTRY

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The photooxidant chemistry plays a key role in understanding all oxidation processes in the natural as well as the polluted atmosphere. During recent years great progress can be seen in the determination of kinetic parameters which form the data base for the model description of the oxidation processes. Typical oxidant components are H_2O_2, hydroperoxides, alcohols and organic acids in the regions of low NO_x concentrations and ozone, peroxynitrates, aldehydes, ketones and nitric acid in regions of high NO_x concentrations. The type and rate of oxidant formation depends critically on the $[ROG]/[NO_x]$ concentration ratio, ROG: Reactive Organic Gases. During nighttime the reactions of NO_3 initiate a significant production of alkoxy- and peroxy-type radicals eventually leading to organic nitrates. Further reactions of NO_3 with peroxy radicals produce OH radicals which initiate an oxidation chain similar to that during daytime. During daytime the radical chain,

$$OH \rightarrow RO_2 \overset{NO_2}{\underset{NO}{+}} RO \overset{O_2}{\rightarrow} aldehyde + HO_2 \overset{NO_2}{\underset{NO}{+}} OH$$
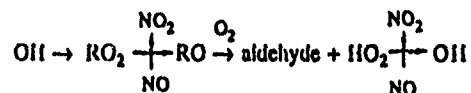
is characteristic for the ROG oxidation processes. Every NO which is oxidized to NO_2 by RO_2 and HO_2 will produce an ozone molecule in sunlight.

Today also biogenic hydrocarbons are considered as important precursors for O_3 formation in the presence of sufficient NO_x. At NO_x concentrations below a certain limit ROG does not lead to ozone production but to its destruction. It is a matter of speculation whether the global troposphere is changing more to the side of ozone destruction with lower OH concentrations or to production with higher background ozone, the situation is probably developing differently the two hemispheres.

NO$_3$ Radical Reactions

It is now evident that the NO_3 radical plays an important role in the nighttime chemistry of the troposphere. Volatile organic compounds are oxidized at night leading to alkoxy and peroxy radical formation together with a variety of oxidized products including carbonyl compounds, peroxyacyl and alkyl nitrates. Reaction of peroxy radicals with NO_3 provides a source of OH radicals thus accelerating the nighttime oxidation of organics. Nitrates formed in the oxidation of organics can act as temporary reservoirs of NO_x and are important

in long-range transport processes. Nitrate radicals provide the only source of nitric acid formation under nighttime conditions either directly by H atom abstraction from organic compounds or via hydrolysis of N_2O_5 formed in the reaction $NO_3 + NO_2$.

Reactions of OH Radicals

Due to their high reactivity and concentration levels OH radicals are the dominant oxidants of volatile organic compounds in the daytime troposphere. This applies to all saturated hydrocarbons, to aromatics and to most alkenes. For partially oxidized hydrocarbons such as ketones, as well as for nitrates and nitrites, which have appreciable absorptions in the actinic spectral region, photolytic degradation may dominate the rate of removal of these compounds in the troposphere.

The data base of OH reaction rate constants and hence for estimating lifetimes of ROG with primary degradation mechanisms by OH radical reactions is generally well established. However, significant gaps remain in the understanding of how the OH initiated ROG oxidation chain influences the net NO to NO_2 conversion, and hence the O_3 formation, as well as the storage and transport of NO_x via the formation of organic NO_y species. Whereas for alkanes and alkenes this information is slowly forthcoming by detailed mechanistic studies of the products of the OH initiated oxidation chains, substantial gaps still remain in the oxidation of aromatics. For these compounds essentially no studies have as yet been performed on the reactions of any of the expected oxidation intermediates.

Reactions of Peroxy Radicals

Organic peroxy radicals are well known key intermediates in the atmospheric oxidation of organic compounds. Their reactions with NO and NO_3 are propagating steps in the oxidation chains of hydrocarbons, while reactions with NO_2, HO_2 and, in hydrocarbon rich remote atmospheres, with other peroxy radicals, are generally terminating steps which greatly influence the ozone budget in the troposphere. Beside ozone, peroxy radical reactions also produce alcohols, aldehydes, organic acids, organic nitrates and reservoir species such as hydroperoxides or peroxynitrates.

Given the importance of peroxy radicals, a large body of research has been devoted to the studies of their kinetics and mechanisms in recent years; this has resulted in important advances in our understanding of the role of these reactions in tropospheric chemistry. The principal results concern: (i) the development of powerful techniques for the investigation of peroxy radicals, (ii) the determination of UV spectra and absolute absorption cross sections for several species and (iii) the investigation of the kinetics and mechanisms (reaction products and branching ratios) for self and cross reactions of peroxy radicals and for their

reactions with the nitrogen oxides NO, NO_2 and NO_3. Reliable data are now available for the simple radicals and the investigations are being extended to more complex species with the expectation of a general understanding of the reactivity of peroxy radicals.

Reactions of RO Radicals

Reactions of alkoxy radicals, RO, represent special cases in the oxidation chain of hydrocarbons in that they determine the nature of the stable products. Short chain RO radicals ($< C_4$) react exclusively with O_2 by abstraction of the α-H atom to form aldehydes. Larger RO radicals tend to be thermally instable and to react by C-C split or by isomerization. Although the direct interaction of RO with NO_x is apparently unimportant, the reaction behavior of RO has important consequences for the NO/NO_2 conversion and hence on the ozone formation. The reaction of short chain alkoxy radicals with O_2 leads to an aldehyde and HO_2, whereas isomerization and/or C-C bond cleavage of longer chain RO radicals creates further alkyl radicals and additional NO / NO_2 conversion.

Absorption Cross Sections and Quantum Yields

Photochemical processes play a critical role in the chemistry of the atmosphere, since they control the production of reactive radicals during daytime which initiate chemical transformation of many trace compounds. Photodissociation of atmospheric species occurs by absorption of solar ultraviolet and visible radiation. The photochemical processes are controlled by the strength and shape of the absorption spectrum and by the quantum yields of the various product channels. Accurate photolysis parameters are needed for model calculations of primary photochemical transformation processes occurring in the atmosphere.

Reactions of O_3

Recent work on the ozonolysis of alkenes has shown that an intermediate of the primary reaction step, probably the biradical, leads directly to the formation of hydrogen peroxide in the presence of water vapor. This new H_2O_2 source seems to contribute significantly to the H_2O_2 built-up in forest areas.

In a short overview new results on the photooxidant chemistry will be discussed and their implications in the atmospheric environment will be outlined.

KINETICS AND MECHANISM OF PEROXY RADICAL REACTIONS OF INTEREST IN ATMOSPHERIC CHEMISTRY.

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The tropospheric chemistry is dominated by the oxidation processes of hydrocarbons, in interaction with nitrogen oxides. The result of this chemistry is the production of ozone and other oxidant molecules in polluted areas while organic acids, alcohols and other oxidized molecules are produced in remote areas. The sources of hydrocarbons are organic fuels, widely used in urban and industrial zones and the vegetation, particularly forests, which produce various molecules such as isoprene, terpenes, etc ...

Generally, the first step of oxidation of any hydrocarbon is hydrogen abstraction by OH radicals, or addition to unsaturated compounds, producing an alkyl or an hydroxyalkyl radical which is rapidly converted into a peroxy radical by combination with oxygen :

$$RH \xrightarrow{OH} R \xrightarrow{O_2} RO_2 \qquad (1)$$

The type of products that result from the oxidation of hydrocarbons depends mostly on the way the RO_2 radicals react. In the presence of nitrogen oxides, the main process is the reaction with NO, resulting in a chain reaction producing ozone :

$$RO_2 + NO \rightarrow RO + NO_2 \qquad (2)$$

The photolysis of NO_2 produces O_3 and the alkoxy radical RO is a chain carrier. An important termination step is the reaction of RO_2 with NO_2, forming a peroxynitrate :

$$RO_2 + NO_2 + M \rightleftarrows RO_2NO_2 + M \qquad (3)$$
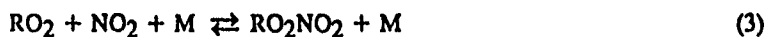
The kinetics of this reaction is very important for determining the yields of ozone, particularly in the case of acylperoxy radicals $RC(O)O_2$, which form peroxyacylnitrates (PAN's), the most stable of the peroxynitrates. These compounds are well known oxidant molecules in the atmosphere and contribute to the transport of nitrogen oxides over long distances.

In remote atmospheres, where the concentrations of nitrogen oxides are very low, it has been shown that peroxy radicals accumulate, since they have a general low reactivity and that they can react with themselves, including HO_2, forming various oxidized molecules :

$$RO_2 + HO_2 \rightarrow ROOH + O_2 \qquad (4)$$

$$RO_2 + RO_2 \rightarrow 2 RO + O_2 \qquad (5a)$$
$$\rightarrow ROH + R'CHO \text{ (or ketone)} \qquad (5b)$$

When R is an acyl radical, formed from an aldehyde, similar reactions produce organic acids and peracids. Large amounts of such compounds have been found over tropical forests.

This short review of peroxy radical reactions in the atmosphere shows that the knowledge of the kinetics and mechanisms of these reactions are essential for modelling the atmospheric oxidation of hydrocarbons and consequently the formation of ozone and other oxidized molecules. In this paper, we present an overview of some kinetic and mechanistic studies that we have performed in our laboratory, in collaboration with other laboratories in Europe, mainly the Max Planck Institute in Mainz - Germany (Moortgat), Harwell Laboratories - U.K (Cox, Hayman), Ford Motor Cie - USA (Wallington) and the University of Wuppertal - Germany (Zabel). The determination of reaction mechanisms generally needs an investigation of reactions over a wide range of temperature and therefore we have extended our studies from atmospheric temperatures up to 600-700 K.

Experimental

All reaction kinetics were studied by flash photolysis and UV absorption detection of peroxy radicals. The spectra of radicals and absolute cross sections were determined accurately between 200 and 300 nm for each radical, so that complex kinetics could be analysed by computer simulation of decay traces recorded at several wavelengths.

Radicals were normally generated by photolysis of molecular chlorine, which forms chlorine atoms, in the presence of an appropriate precursor :

$$Cl + CH_4 ----> HCl + CH_3 \xrightarrow{O_2} CH_3O_2$$

$$Cl + CH_3OH ----> HCl + CH_2OH \xrightarrow{O_2} CH_2O + HO_2$$
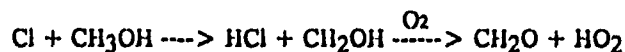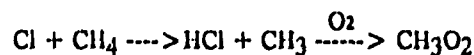
The direct photolysis of oxygen producing oxygen atoms, has also been used at high temperatures.

RO$_2$ + HO$_2$ reactions

Reactions of RO$_2$ radicals with HO$_2$ are important, due to the fairly high concentration of HO$_2$ in the atmosphere. In addition they are generally fast and are therefore important terminating reactions. After the self reaction of HO$_2$, now well understood, we have investigated the reactions of CH$_3$O$_2$ and CH$_3$C(O)O$_2$ in detail.

The rate constant of reaction (6)

$$CH_3O_2 + HO_2 \rightarrow CH_3OOH + O_2 \tag{6}$$
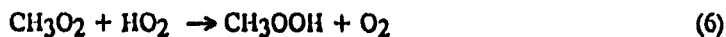
was measured from 248 to 718 K. The rate constant exhibits a fairly strong negative temperature coefficient which can be describe with an Arrhenius expression over the whole temperature range :

$k_6/cm^3molecule^{-1}s^{-1} = (2.9 \pm 0.3) \times 10^{-13} \exp(860K/T)$ (with $k_{298} = 5.2 \times 10^{-12}$)

This expression reflects a reaction mechanism involving an intermediate stable complex. No change in the mechanism was observed at high temperature, unlike for the self reaction of HO_2, for which a direct hydrogen atom transfer takes place above 700 K.

The reaction of the acetyl peroxy radical $CH_3C(O)O_2$ with HO_2 was shown to be an important process forming organic acids and peracids, particularly in the atmospheres of tropical forests.

$$CH_3C(O)O_2 + HO_2 \longrightarrow CH_3C(O)OOH + O_2 \qquad (7a)$$
$$\longrightarrow CH_3COOH + O_3 \qquad (7b)$$

The kinetics and branching ratios of this reaction have been investigated in detail. The reaction is fast : $k_{298}' = 1.4 \times 10^{-11}$ $cm^3molecule^{-1}s^{-1}$ and the branching ratio forming ozone equals 0.33 ± 0.05. This channel forming ozone seems to be a general process for acyl peroxy radicals, since it was shown that the equivalent reaction of the $CH_3CH_2C(O)O_2$ radical also forms ozone with a similar branching ratio.

A few other exemples show that all reactions between RO_2 radicals and HO_2 are fast, around 10^{-11} $cm^3molecule^{-1}s^{-1}$ and that the main product is the hydroperoxide, thus confirming the important terminating role of these reactions in atmospheric chemistry.

$RO_2 + RO_2$ reactions

Since RO_2 radical concentrations in the atmosphere are generally lower than those of HO_2, reactions of this type are normally less important than reactions of RO_2 with HO_2. They can play, however, a significant role in clean atmosphere containing high concentrations of natural hydrocarbons and they are important in the ignition of hydrocarbon combustion.

The reaction of methylperoxy radicals can be considered as the model for this type of reaction. It is now well described in the literature :

$$CH_3O_2 + CH_3O_2 \longrightarrow 2CH_3O + O_2 \qquad (8a)$$
$$\longrightarrow CH_3OH + CH_2O + O_2 \qquad (8b)$$
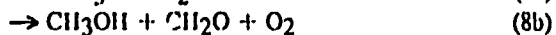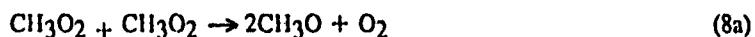
$k_8/cm^3molecule^{-1}s^{-1} = (1.0 \pm 0.1) \times 10^{-13} \exp(420 K/T)$ (with $k_{298} = 4.0 \times 10^{-13}$), from 248 to 700 K.

The important point is that the terminating molecular channel (8b) is the most important at atmospheric temperatures (75-80 %) while the propagating channel (8a) is preponderent at ignition temperatures (700-800 K). This behaviour seems general for other similar reactions of primary or secondary peroxy radicals.

Recent results will be presented for neopentyl peroxy and cyclohexyl peroxy radicals. In the last case, the reaction is very slow, confirming the presence of a positive activation energy for the self reactions of secondary alkyl peroxy radicals. It will also be shown from these new results, how our kinetic studies, complemented by end-product analysis, can

bring information on the way the corresponding alkoxy radicals react under atmospheric conditions. The neopentoxy radical readily dissociates into t-butyl radical and formaldehyde while ring-opening of the cyclohexoxy radical competes with reaction with oxygen.

If primary and secondary alkyl peroxy radicals seem to react in a similar fashion to the model self-reaction of CH_3O_2, only the propagating channel is seen to occur in the case of fully halogenated radicals. Kinetic studies have shown that this is the case for CCl_3O_2 and $CF_3CCl_2O_2$ radicals.

Reaction of RO_2 With NO_2

We have emphasized above that these reactions are important terminating reactions in the hydrocarbon oxidation chains forming ozone, particularly in the case of acyl peroxy radicals. A complete description of the reaction :

$$CH_3C(O)O_2 + NO_2 + M \; \rightleftarrows \; CH_3C(O)O_2NO_2 + M \tag{9}$$
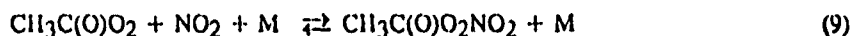
has been performed in our laboratory for the forward reaction, in collaboration with Zabel in Wuppertal - Germany, who investigated the reverse reaction. Rate constants, equilibrium constants and thermochemical data have been obtained over wide ranges of pressure and temperatures. The results confirm the stability of PAN (peroxyacetylnitrate) and show that its formation is faster than previously evaluated. This makes this reaction one of the key reactions to which modelling of the ozone formation in troposphere is very sensitive.

ELIMINATION OF ORGANIC MICROPOLLUTANTS

BY SEMICONDUCTOR-PHOTOSENSITIZED TREATMENT OF WATER

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Growing concern about our environment and a greater awareness of the risks have generated and will generate increasingly tighter regulations. Consequently, not only the improvement of existing technologies, but also the discovery and testing of new possibilities are expected from the scientists. In particular, concerning water treatment, alternatives to the existing processes, which all have disadvantages and cannot solve all problems, should be explored.

Semiconductor-photosensitized destruction of water microorganic pollutants has recently appeared as a promising prospect[1,2]. It is based on the production of strongly oxidising species at the surface of the appropriately illuminated semiconductor in the presence of dissolved dioxygen (air) and liquid water.

Principle. The basic phenomenon is the optical excitation of electrons from the valence band to the conduction band of the semiconductor. The nature of the resulting chemical species is still debated. It is generally admitted that the excited electrons are captured by O_2 yielding O_2^- species. However, the cations present in the medium can also intervene. The superoxide ions can then react with hydroxonium ions forming $HO_2^\bullet$ radicals. In principle the valence band holes can interact directly with the organic pollutant or they can readily generate $OH^\bullet$ radicals by being captured by surface/adsorbed OH^- groups or adsorbed water molecules. In fact, these latter interactions occur within a few picoseconds so that it seems difficult to discriminate between reactions involving trapped holes and $OH^\bullet$ radicals[3]. In addition, various oxidising species can be involved at different stages of the photocatalytic degradation process.

Photocatalysts. Various powdered semiconductor oxide samples have been examined for the elimination of different organic pollutants in several research groups. As expected, the effect depends not only on the chemical nature of the semiconductor, but also on the identity of the sample. Until now, no sample of a semiconductor oxide has been found more active than certain anatase specimens. Therefore, current laboratotry studies employ this oxide which, in addition, is non-toxic, stable and inexpensive. For laboratory studies the particulate form is generally preferred ; colloids are also used, especially for the spectroscopic techniques that cannot be employed with powders. Attempts are also made to anchor titanium dioxide on an immobile support or to prepare beads in order to avoid filtration[1,2]. Further work is needed to determine which parameters affect the efficiency of TiO_2 ; this is important to reduce the duration of the water treatment and therefore the consumption of electrical energy which is the dominant cost according to simulations[1].

Pollutants. The photocatalytic degradation of many classes of organic chemicals has been studied either in great detail or within the framework of systematic investigations based on one feature only, such as the initial rate of the pollutant disappearance or the initial rate of CO_2 formation or the time required for the total elimination of the pollutant. Both aliphatic and aromatic compounds with a variety of substituents have been considered. Complex molecules used as pesticides, dyes or surfactants have also been examined[1,2]. The results show that all the organic micropollutants are destroyed. Most of them can be totally mineralized. Atrazine (substituted triazine) constitutes the only reported exception ; this herbicide yields trihydroxytriazine which is innocuous and very stable irrespective of the oxidation method[4].

Some features of the TiO_2 - photosensitized method of destroying organic micropollutants in water will principally be illustrated in this lecture by studies carried out in the author's group[5] and dealing with aromatics, viz. chlorophenols, 2,4 - dichlorophenoxyacetic acid, benzamide, nitrobenzene and dimethoxybenzenes.

Comparison with direct photolysis. At $\lambda > 290$ nm, the disappearance of all these chemicals is much faster in aerated aqueous TiO_2 suspensions than under the same conditions without TiO_2. Furthermore, the comparison of the sums of the maximum concentrations in the main

organic intermediates also indicates that direct photolysis is much less efficient in degrading these intermediates. For all compounds the direct photolysis is insignificant at $\lambda > 340$ nm, which allows a clear discrimination between photocatalytic and photochemical processes to be made.

Effects of various factors. The initial rate of monochlorophenol disappearance as a function of the initial concentration has a Langmuirian shape and similar data have been collected for a number of other pollutants. However these variations can also be accounted by reaction steps that do not involve two kinds of adsorbed active species. From the practical viewpoint, these results clearly indicate that the photocatalytic degradation is not inhibited by high pollutant concentration provided the pollutants do not absorb too much the UV-radiations needed to activate the catalyst.

This also show that quantum yields cannot have the significance they have in photochemistry, since not only it is difficult to make allowance for the scattering by the solid particles, but also the values depend on the pollutant concentration. At $\lambda = 365$ nm, for pollutant concentrations close to 0.15 mM and TiO_2 Degussa P-25, quantum yields in the range 5×10^{-3} to 5×10^{-2} were derived from our calculations for the abovementioned molecules.

The nature and concentation of **ions** is of primary importance in water decontamination. For instance, the treatment of water with given bacteria can only be applied in a narrow pH range and HCO_3^- ions are detrimental for the purification by O_3 + UV as they quench the OH radicals. In the case of monochlorophenols and nitrobenzene, our results have shown that the initial rate of phorocatalytic elimination does not vary much from pH 3.5 to pH 10. An inhibiting effect of Cl^- and SO_4^{2-} ions has been observed only at acidic pH (positively charged TiO_2 surface) and for concentrations much higher than those found in natural waters.

Intermediates. Degradation pathways. Primary intermediates of the photocatalytic degradation of all the aromatics studied correspond to the hydroxylation of the aromatic ring with or without the removal of the substituent(s). Their maximum concentration were quite low and they generally disappear within about the same time as the initial pollutant ; the only exception is that of 2,4 - dichlorophenoxyacetic acid because of the ease of the cleavage between the aromatic ring and the

aliphatic chain. The successive degradations were substantiated by experiments dealing with the degradation of some of these intermediates under the same conditions. The identification and the temporal variations of the intermediates allow one to propose degradation pathways. However a complete scheme including the aliphatic intermediates en route to CO_2 remain to be determined ; very low concentrations make the analyses quite difficult.

Mineralization. For all types of chlorophenols (and for monochlorobenzenes as well)[6] complete dechlorination was achieved within a time not much longer than that needed for dearomatization. Nitrate ions are the final form of the nitrogen atoms of nitrobenzene and benzamide (or formamide as well) ; however, the oxidation of the amide function, in cases where it might be required, is much too slow to be accomplished entirely be photocatalysis

Total mineralization to CO_2 can be attained within a time that obviously depends on the pollutant for a given concentration, in particular on the presence of heteroatoms at a low oxidation state. However, to reach this stage may not be necessary or the technique may be combined with another treatment to bring the desired result.

The method is currently studied at the pilot plant stage in several companies (ENI, Italy ; NUTECH, Canada) or institutions (Sandia National Labs., USA).

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REACTION OF OH WITH α-PINENE AND β-PINENE IN AIR :

ESTIMATE OF GLOBAL CO PRODUCTION FROM

THE ATMOSPHERIC OXIDATION OF TERPENES

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Carbon monoxide (CO) plays a major role in controlling the concentration of OH radicals in the atmosphere. OH radicals are known to be the most important atmospheric trace species which determine the lifetime of most of the other atmospheric trace components. Recently, the concentration of methane is reported to increase rapidly, and the decrease of the concentration of OH is pointed out as one of the possible causes for this phenomenon[1].

The increase of CO should be the main cause of the decrease of OH radicals. Thus it is quite important to estimate the amount of global emission of CO into the atmosphere.

Recently, the emission rate of CO from the oxidation of natural hydrocarbons was reported to be 250 Tg C yr^{-1} (about 24 % of total CO emission, 1 Tg C of CO corresponds to 2.33 Tg CO), which is comparable to that from the oxidation of methane (260 Tg C yr^{-1} ~25 %) and larger than that from fossil fuel combustion (190 Tg C yr^{-1}, ~18 %)[2].

Monoterpene are among the most important natural hydrocarbons, and their atmospheric reactions play an essential part in the global carbon cycle. The global emission rates of terpenes were estimated to be 175-830 Tg yr^{-1}[3], which exceed the emission rates of anthropogenic hydrocarbons: 65-75 Tg yr^{-1}[4,5]. However, only very limited information is available so far on the formation of CO from the photooxidation of

terpenes. Hanst et al.[6] estimated the yield of CO from the oxidation of terpenes be use of Cl atoms in place of OH radicals. Recently, we reported[7] the estimate of the ultimate yield of CO from the oxidation of terpenes initiated by ozone, and the gross annual emission of CO with respect to the ozone-terpene reactions was estimated to be 74 Tg C yr^{-1}. In oreder to obtain a more complete estimate of CO emission the yield of CO from the oxidation of terpenes initiated by OH radicals is needed, since terpenes are consumed by both the ozone and the OH reactions in the atmosphere.

In the work reported here the reactions of pinenes with OH radicals were investigated to obtain the yield of gaseous and particulate products and to estimate the gross annual production of CO from the atmospheric oxidation of terpenes initiated by OH radicals.

A $6\text{-}m^3$ chamber was used for the analyses of gaseous products. The chamber is an evacuable and bakable one, and its inner surface is coated with PFA. The solar simulator and the end windows to introduce UV light were modified in order to utilize shorter wavelength light for the effective photolysis of H_2O_2 as a NO_x-free source of OH radicals.

Reactants and products were mainly analyzed by means of long-path Fourior transform infrared spectroscopy (FT-IR) (Block Engineering-JASCO International, FTS-496S; path length; 221.5m, resolution: 1 cm^{-1}, scan times: 64 or 128, ~2.5 or ~5 min, respectively) utilizing multireflection mirrors installed in the chamber.

Two types of experiments were done in this chamber. First experiments were made to elucidate the reaction mechanism in the presence of NO_x. In this study, photolysis of CD_3ONO with Pyrex filters was used as a source of OD radicals. Initial concentrations of pinenes were ~0.7ppm. CD_3ONO was varied from 0.5 to 2 ppm.

Second experiments were carried out to check the effect
of NO_x on the yield of the main products observed in the first
experiments. Photolysis of H_2O_2 was used as NO_x free OH
source. Initial concentrations were ~2.6 and ~1 ppm for pi-
nenes and ~8 and ~18 ppm for H_2O_2.

Major process of the reaction of OH+α-pinene is shown in
Scheme I. In the presence of NO the main product was pinon-
aldehyde and 6,6-dimethyl-bicyclo[3.1.1] heptan-2-one from α-
and β-pinene, respectively, and the yield was 56±4 and 79±8 %,
respectively. In the absence of NO the yield was remarkably
lower, and the yield of organic aerosols was enhanced. For α-
pinene 56±3 % was obtained as a yield of aerosols on the
carbon number basis. Gross annual emission of CO from the
reactions of OH with terpenes was estimated to be 22 Tg C yr^{-1}
(50 Tg CO yr^{-1}) by regarding α-pinene as the representative
of terpenes, on the basis of the annual emission rate of
terpenes, estimated lifetime of pinenes in the atmosphere, the
apparent rate constant for the intermediate to form CO, and
the estimated yield of CO from the secondary oxidation of
pinonaldehyde. The ultimate yield of CO from the tropospheric
oxidation of terpenes (including both ozone and OH reactions
) was estimated to be 20 % on the carbon number basis, and the
total annual emission of CO was evaluated to be 96 Tg C yr^{-1}
(222 Tg CO yr^{-1}).

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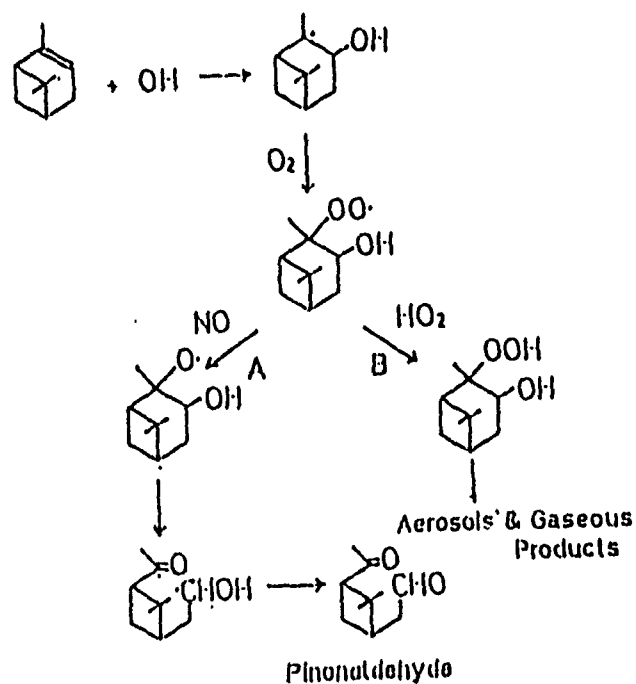
Scheme I

SYNCHROTRON RADIATION AT LURE - APPLICATIONS TO CHEMISTRY

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Résumé : Les applications développées à LURE, en photochimie en phase
gazeuse, grâce au rayonnement synchrotron dans l'ultra-violet lointain et
les rayons X mous, sont passées en revue. On montrera l'interêt d'une
source accordable dans l'UV sous-vide (E<25 eV) et pulsée pour l'étude de
la dynamique de fragmentation d'ions et des réactions ion-molécules, avec
des ions dans des états sélectionnés. On montrera aussi l'interêt
d'utiliser des photons de plus haute énergie (E de 30 à 500 eV et plus) en
y associant des méthodes de détection en multicoïncidences électron-ions,
pour l'étude de la multifragmentation d'ions positifs multichargés et
explorer les aspects sélectifs de la fragmentation attendus après
excitation de la molécule en couche interne. Enfin, le développement
d'expériences associant un laser visible et le rayonnement ultra-violet
lointain, à la spectroscopie photoélectronique sera évoqué dans le contexte
de l'étude d'"état à état" de la photodissociation moléculaire. Les autres
activités de photochimie en phase condensée et dans les agrégats libres
seront brièvement mentionnées ainsi que les perspectives de développement
d'autres thèmes, grâce au domaine infra-rouge lointain du rayonnement
synchrotron et au laser à électrons libres dans l'IR.

At the LURE laboratory, the French Synchrotron Radiation Facility,
two storage rings Super ACO and DCI operated respectively with 0.8 and 1.82
GeV positrons, are dedicated to the use of synchrotron radiation in a wide
wavelength range, continuously from the near ultra-violet to the X-ray
range. Photochemistry applications are essentially concentrated around
Super ACO, who has been especially built for synchrotron use (unlike DCI)

and is available for users since 1987.

The interest of synchrotron radiation is evidently the tunability in a range hardly accessible to lasers, i.e. far UV and soft X ray range. In molecular photochemistry, it is the domain of electronic excitation and ionization. Up to 30 eV typically, single ionization of valence electrons is energetically accessible and special aspects of ion chemistry and photodissociation can be studied ; At higher energy, double and multiple valence ionization channels are open as well as core ionization ones and it is the domain of high energy photochemistry which has developed only around SR centers. The following examples, chosen among recent works, will be reviewed.

Ion dissociation and ion-molecule reactions studied with state selected ions

The selection of a vibronic state of a singly charged ion is made by tuning the photon energy at a selected wavelength and by detecting (near) zero kinetic energy photoelectron, taking advantage of the pulsed character of synchrotron radiation. Fragmentation of such state-selected ions and ion-molecule reactions are performed in detecting the fragment products with threshold electron - ion coincidence techniques. Examples of statistical and non statistical processes are the dissociation of CH_4^+ and $CH_3OCD_3^+$ ions. Ion-molecule reactions realized with state selected N_2^+ and O_2^+ will show how the cross section depends upon the internal energy of the ion (electronic, vibrational and spin-orbit).

Fragmentation of core excited molecules : is site selective fragmentation tractable ?

The excitation of a core electron into a low lying unoccupied orbital allows to localise the effect of the photon on a specific bond, near a specific atomic site of the molecule, under certain conditions. Due to Auger-like processes, the molecule is left with one, two or more positive charges. We will show, on the basis of electron - ion - ion coincidence detection methods, which ideally complement conventional mass spectrometry, examples of site selective fragmentation processes in core

excited N_2O and the importance and the limits of the Coulomb explosion
model. We will show the limitations of site selective dissociation effects
in larger molecules, because of the efficiency of multifragmentation on a
microsecond scale.

*Dynamics of photodissociation by pump(laser)-probe(RS) and
electrons spectrosocopy methods.*

The high repetition rate of SR in the MHz range makes it a
quasi-continuous source and the combination with CW lasers is very
favorable. We show that pump-probe experiments can be used to study the
dynamics of unimolecular photodissociation. A CW argon ion laser is used to
photodissociate a molecule and SR is used to photoionise all fragments, the
detection of fragment photoelectrons allows to determine the internal
vibrational energy of the nascent fragments. In the s-tetrazine molecule,
$C_2N_4H_2$, which dissociates into three fragments ($2HCN + N_2$) when excited in
the visible, we show that the vibrational distribution of the fragments is
compatible with a direct three body process of the molecule in a transition
state with a particular geometry.

Current and future trends

Other photochemistry applications in the far UV range, will be
briefly mentionned. An example is offered by ion and neutral
photodesorption experiments from the surface of molecular solids. Another
is the study of free metallic clusters by photoionization.
We will outline other future developments, oriented by the use of
SR in the far infra-red range, and of the infra-red free electron laser.

3D MACHINING WITH LASERS : POSSIBILITIES AND LIMITS

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Possibilités et limites des procédés de réalisation d'objets 3D par laser

Nous présentons un procédé de stéréophotolithographie laser qui tire son origine d'une phototransformation induite par laser, résolue dans l'espace, liquide-solide en particulier qui permet de réaliser des pièces prototypes. Différentes améliorations au procédé actuellement commercialisé seront présentées.

A prototype is usually required before mass production. Furthermore, scale models are of wide use by architects and engineers. Until now, these models were made by traditional techniques. Recently, computer aided machine tooling has become possible and numerical data which define the shape of the object to be made is available. However, the tool that makes the object has to follow a path tangent to the surface and interference with adjacent surfaces has to be avoided. Furthermore, the tool wear has to be known in order to construct an object of fine quality. In order to surmount these difficulties, we have developped, along with others, a process which makes three dimensional objects by polymerizing a liquid monomer using a laser energy source. The laser beam can be focused precisely on a liquid so that a liquid / solid photochemical transformation can be achieved. The advantages over the traditional techniques mentioned earlier are that a mould is no longer necessary, the shape of the object can be totally arbitrary and the wear of the tool is not needed.

Here, we show how three dimensional objects can be created using computer aided design. In the current stage, this new technique which has led to very promising results, is limited by the choice of materials and the traditional CAD has to be thus adapted. After discussing briefly the manufacture of objects by computer aided laser polymerization, the coupling between the adapted CAD and the choice of materials is shown. The applications of this new technique are not all known ; however, future progress will depend on the ability of specialists in the fields of materials engineering, photochemistry and Computer Aided Design to work together.

I. Brief review of photopolymerization methods

If a sufficient amount of photons is absorbed per unit volume, unstable species are created and the liquid monomer polymerizes into a solid which is not soluble on the liquid monomer.

$$A + h\nu \rightarrow \text{unstable species}$$

$$\text{unstable species} + M \rightarrow \text{non soluble polymers}$$

The above simplified mechanism shows that two main difficulties have to be surmounted : the local light absorption and the choice of materials. If these two main difficulties are only partially mastered, a modification of the Computer Aided Design becomes necessary.

1.1. Light absorption

Two excitation techniques have been proposed up to date : multiphotonic absorption and monophotonic absorption. For now, the second seems more efficient for industrial applications.

The theoretical basis is the Beer-Lambert law. A light beam is incident on z, the concentration C_a is such that the light absorption during dt produces a polymeriztion of the monomer between z and $z + \Delta z$. If the beam thickness is Δr, the polymerized voxel volume is $\pi \Delta r^2 \Delta z$.

Successive layers of thickness Δz are made. This is shown qualitatively on figure 1. Starting from the base which contains a layer of thickness Δz, the laser beam is displaced in the xy plane in order to solidify the $z = 0$ plane. Afterwards, a new layer of monomer is added and the process is repeated. An object can be made with just one laser.

The laser beam is guided into the reactor containing the monomer. The guide must be very loosely attached to the created voxel otherwise deformation or rupture is possible. Several techniques enabling this exist.

In all monophotonic processes, the object coordinates stored in the computer are given in the form $z = f(x,y)$.

1.2. Materials

Unless a special mechanical property of the object is wanted, the liquid monomers should have the following characteristics : rapid reaction rate and lowest possible viscosity in order to reduce the time needed per layer and to limit hydrodynamic side effects caused by the guide displacement. Monomers M having such properties are mainly in the epoxy or acrylate groups. Photochemists know well how to start and control the reaction using these species. When a monomer is polymerized, a volume variation is observed due to the photoreaction. This has various consequences. A polymerized voxel which is not sustained and whose density is higher than that of the liquid, will tend to sink to the bottom unless held by surface tension forces. The manufactured object can thus have dimensions other than the ones specified. Furthermore, the object can deform.

In order to remedy these difficulties, materials which do not shrink and with the properties mentioned earlier have to be sought. These materials exist but their viscosity is often too big. Another solution is to adapt the computer aided design in order to limit memory effects induced by the polymerization.
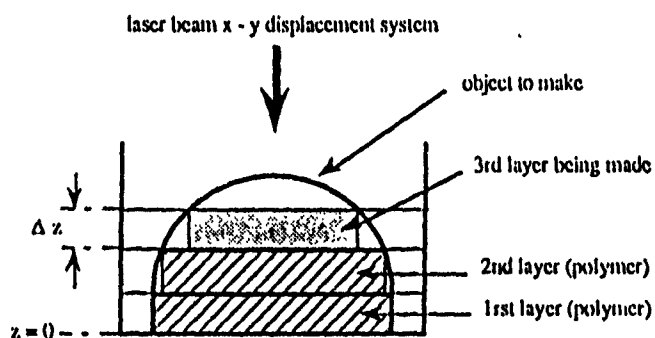
Figure 1': principe of the layer by layer space resolved polymerization

The principle consists in polymerizing voxels that are each separated. The volume variation of each element occurs independently and then the interstices separating the voxels is polymerized. Since the laser has to be continuously displaced, a galvanometric mirror controlled by a computer should be used.

II. Basis of a Laser CAD machine

II.1. The machine

The monophotonic process described earlier is split into several sub-systems which are : the computer system which includes the computer which receives the CAD data from another system. The computer system adaptes the data to define the optimum laser beam displacement.

- the photochemical reactor
- the laser
- a motor driven optical mechanical unit with several degrees of freedom which shapes the light beam and then reflects it into the monomer to be polymerized.
- a motor driven system which moves the object on the z axis.

II.2. CAD software

In our case, the objects to be made are solids either full or hollow. Furthermore, great care must be taken in their manufacture since they are intended to be duplicated. A model is more realistic if it accounts for a greater number of constraints of the object.

The system configuration must be able to use CAD software which is commercially available. The interface must be conceived and should :

- verify that the object can be made
- choose the best manufacturing order
- decompose the object into voxels

- predict and impede object deformation

- command the whole process.

We have previously shown that it is not acceptable to create voxels that are independent of the partially created object.

As indicated before, the object can be manufactured at z by laser induced polymerization on the whole or part of the surface. The polymerization time is proportional to h^3 for an object of size h and proportional to h^2 if only the surface is polymerized. It can be advantageous to polymerize the object only at the surface and in elements which contribute to the rigidity.

After taking the object out of the reactor, it contains liquid monomer. It can be used as such or a more total polymerization can be obtained in an annex system. One must take into account that in this latter case, the object can deform due to shrinkage. The definition of the points where the object must be re-enforced could be interesting. All these technical difficulties can be solved by adapting existing CAD software or by choosing carefully the used materials.

II.3. Optical mechanics

Carboxylic components are most well known and the most efficient photochemical reaction initiators, the absorption spectra is centered on 350 nm. A laser which emits in this spectral zone is usable (*HelCd, Ar⁺, etc...*). Other compounds for starting the reaction are available in the visible and the infra-red regions.

When using a z axis displacement to guide the light beam, it is preferable to use platinum moulted by a computer commanded step by step motor. For a system using the superposition of layers on the partially realized object, and in order to reduce manufacture time, it is advised to use displacement systems with very small inertia, for example computer commanded galvanometric mirrors.

Conclusions

It has been shown above that prototypes can be realized with an adequate CAD using a liquid monomer ; no mould or machine tooling is necessary. The CAD is complex and even more so if the object contracts during the solidification process. New materials which contract less or not at all are being investigated currently.

The CAD codes should, in the future, take into account the clamping of the object being made. In agreement with others we think that photochemical systems which have different properties after the beam exposure should allow us to use the CAD codes available today. In order to improve the process, CAD and photopolymer specialists working together would inevitably reach that goal rapidly. Even today, a huge demand exists and renders the subject very attractive.

Photochemical α-Cleavage of Ketones as Studied by the Enhancement
Factor of CIDNP

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In this paper we try to determine the spin state of the
precursor of the photochemical α-cleavage of ketones such as
dibenzyl ketone (DBK) and t-butylketone(TBK),

$$R-CO-R \quad \rightarrow \quad RCO\cdot \quad + \quad \cdot R$$

from the quantitative analysis of the CIDNP enhancement factor.
We wish to point out that qualitative analysis of the sign of the
CIDNP polarization alone may sometimes lead to erroneous
conclusion. Let us illustrate the problem for DBK as an example.
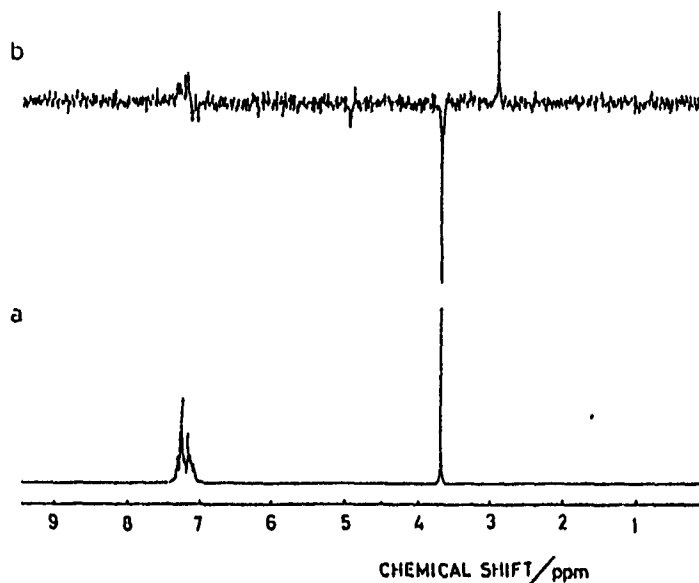
Figure 1. NMR spectra of DBK at room temperature
(a)before light irradiation and (b)during the irradiation
under the conditions of $P_{sat} = P_{obs} = 12.0 \mu s$, $\tau = 0.50$ s,
and $\tau_{obs} = 1.50$ s.

Figure 1 shows the NMR spectra measured (a)before the light irradiation and (B)after the light irradiation. The CIDNP signal for the benzyl protons of DBK (the recombination product) at 3.7 ppm is emissive, and the CIDNP signal for the methylene proton of dibenzyl (escaped product) at 2.9 ppm is absorptive. By application of the Kaptein rule, the precursor is predicted to be the triplet state, and this prediction agrees with the results of numerous studies reported so far. Complication arises, however, if reaction occurs from both triplet and singlet states. We should note that the enhancement factor of CIDNP greatly differs between the singlet precursor and the triplet precursor. Sometimes the absolute magnitude of the enhancement factor for the triplet precursor can be several orders of magnitude larger than that for singlet precursor. In order to avoid such misdetermination of the reaction precursor, not only the sign but also the magnitude of the enhancement factor of CIDNP should be analyzed with the aid of theoretical values.

Experimental determination of the enhancement factor is, however, very difficult. First of all, the observed CIDNP intensity is affected by relaxation and thus this effect should be properly taken into account. Second, in the present DBK photophysics case, the recombination product is chemically identical species with the reactant, and thus the amount of DBK produced by the reaction is hard to determine.

In this paper, the first difficulty was overcome by utilizing the saturation recovery pulse sequence, $(P_{sat}- \tau - P_{obs}- t_{obs})_N$, proposed by Lawler and Barbara. The second difficulty was overcome by the temperature dependence method to be outlined below. The observable physical quantities are a)CIDNP intensity I of DBK, (b)decrease of the NMR intensity $-\delta I_e$ of DBK by the light irradiation, and (c)the consumption rate constant K of DBK. From kinetic consideration we expect that the plot of 1/K verses the $I/(-\delta I_e)$ ratio obtained at various temperatures should become a straight line and the slope/intercept ratio of this straight line can yield the enhancement factor E or the Boltzmann population corrected enhancement factor $\varepsilon = (g_N \mu_N B/2kT)E$. The experimentally obtained plots are shown in Figure 2.
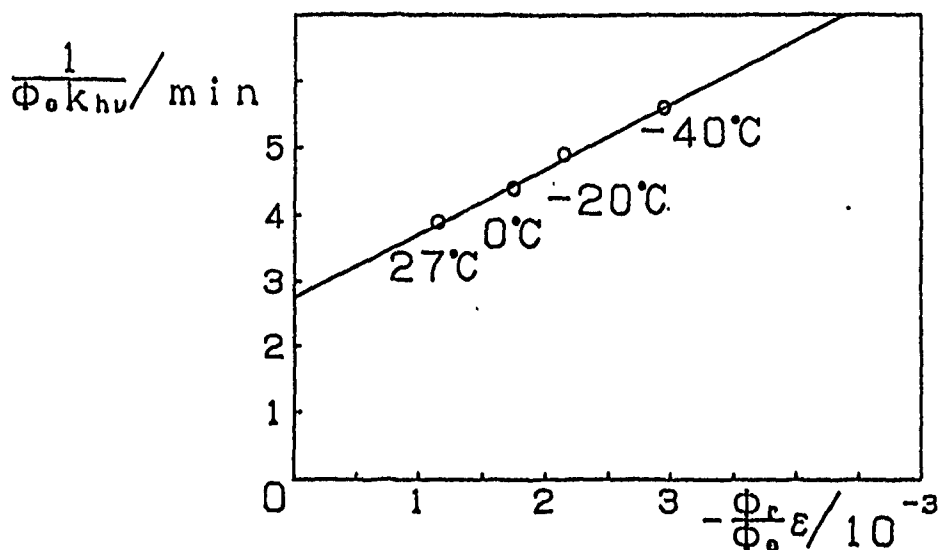
Figure 2. Plot of 1/K verses the 1/($-\delta I_e$) ratio obtained in chloroform-d at various temperatures.

We indeed obtained a rather good straight line, and this observation supports several underlining assumptions made in developing the above kinetics.

The ϵ value determined from Figure 2 is -2.88×10^{-3}. This value does not depend on the concentration of DBK in the 0.01 - 0.06 M range.

In order to analyze the experimentally obtained enhancement factor, ϵ values were calculated theoretically based on the theory of Pedersen and Freed. The theoretical value for the triplet precursor ϵ_T is -0.2237. On the other hand, the theoretical value for the singlet precursor ϵ_S is a very small positive value. ($\epsilon_S=5.5\times10^{-4}$ at 27°C, ($\epsilon_S=3.75\times10^{-4}$ at -40°C.)

In the course of the above kinetics, we are also able to obtain the quantum yield of the recombination (Φ_c) of DBK after the photocleavage reaction. The results are shown in Table 1.

Table 1. Temperature dependence of the quantum yield of the
recombination (Φ_c) of DBK after the photocleavage reaction.

Temp.	Φ_c
- 40 ^oC.	0.505
- 20 ^oC.	0.422
0 ^oC.	0.381
27 ^oC.	0.283

Although the qualitative features (the emissive polarization
and temperature independence of ε) suggests that the precursor of
the photocleavage of DBK is the triplet state, the quantitative
analyses of the experimental results encounters difficulties in
two points. First difficulty is a great discrepancy between the
observed and the calculated enhancement factor. The calculated ε
value for the triplet precursor is two orders magnitude as large
as the experimental value (-2.88×10^{-3}). The second difficulty
is that the yield of cage product (Φ_c) exceeds 1/3 below 0 ^oC.
(Table 1). Since the photoreaction occurs in the high magnetic
field (2.349T), only the T_0 state of the radical pair can mix
with the S state. In such a case, Φ_c for the triplet precursor
should be less than 1/3. We might be able to conceive of the
following five possibilities for the origin of the discrepancies
between the experimental results and theoretical expectation in ε
and Φ_e. a) Participation of the spin-lattice relaxation of
individual radical which composes the radical pair, b)
participation of the spin-orbit coupling (SOC) in the radical
pair state, c) regeneration of DBK from free radicals, d)
Overhauser effect, and e) participation of the singlet precursor.

Having examined these five possibilities very carefully, we
have finally reached the conclusion that the possibility e) is
most likely. From the examination of the data, we conclude that
nearly 80 % of the reaction takes place from singlet excited
state. This conclusion was also supported by the triplet
sensitizer experiments.

Chemical and Enzymatic Triggering of Chemiluminescent 1,2-Dioxetanes: Application to Ultrasensitive Biological Assays

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Enzymatically triggerable 1,2-dioxetanes which can serve as chemiluminescent substrates for alkaline phosphatase, ß-galactosidase, and aryl esterase have been developed.[1-4] These compounds are highly stable, crystalline materials which have half-lives for decomposition in the solid state of several years at room temperature. They also show excellent stability in aqueous solutions. Enzymatic removal of a protecting group X from the stable dioxetane produces the hydroxy-substituted dioxetane (X=H). Subsequent deprotonation of this species in the buffer produces an unstable aryloxide intermediate which spontaneously decomposes to generate the luminescence. The meta-phenyl phosphate dioxetane 1a (X=PO$_3$Na$_2$) (Lumigen® PPD) is now widely used for chemiluminescent detection with enzyme-linked immunoassays and DNA probes employing alkaline phosphatase conjugates.

a   X = PO$_3$Na$_2$

b   X = ß-D-galactose

c   X = acetyl
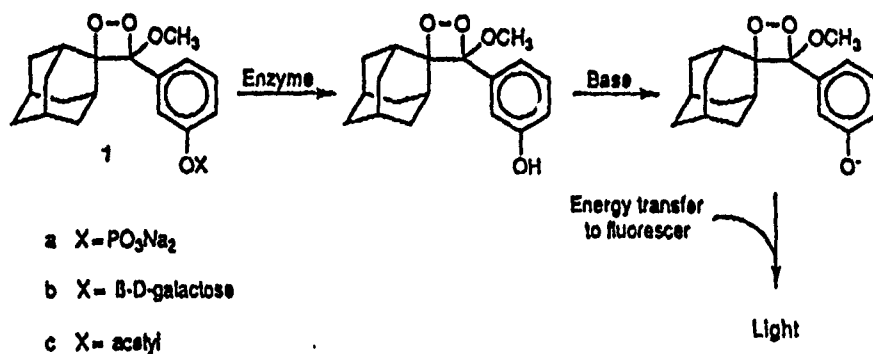
Lumigen® PPD is available commercially as Lumi-Phos® 530, a complete liquid formulation which contains the dioxetane in a basic buffer solution incorporating a fluorescent comicellar enhancer system. Alkaline phosphatase is readily detected in solution by adding an

aliquot of Lumi-Phos® 530 to a tube or microtiter well containing the enzyme at 37 °C and recording the emission using a luminometer, instant photographic, or green-sensitive X-ray film. At low levels of enzyme, chemiluminescence intensity rises to a plateau within approximately 30 minutes and remains constant for several hours permitting repeated measurements to be made if required. Chemiluminescent detection with Lumi-Phos® 530 affords ultrasensitive detection of alkaline phosphatase. A detection limit of 10^{-21} mol of alkaline phosphatase has been achieved using this detection system at 37 °C (Figure 1).[5] Further, the chemiluminescence intensity is proportional to the amount of alkaline phosphatase present over six orders of magnitude (Figure 2). Alkaline phosphatase conjugates are also rapidly detected on nylon and PVDF membranes using Lumi-Phos® 530 and X-ray film detection. Numerous applications in life science research and medical diagnostics have been developed using techniques including ELISA assays for haptens, Western blotting for protein detection, Southern blot analysis for detection of microbial and human DNA, and DNA sequencing applications.[6]
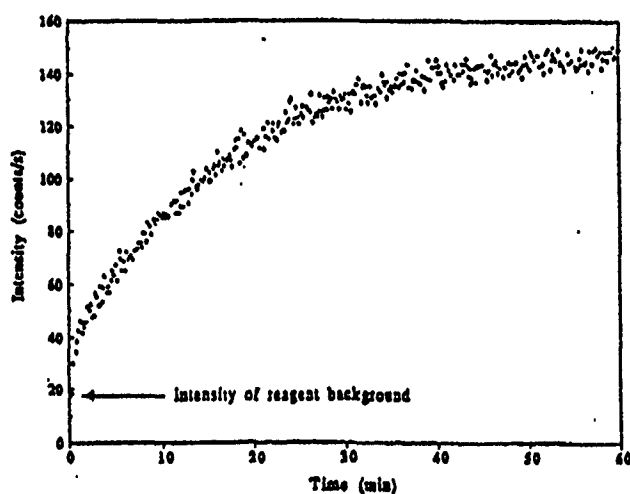
Fig. 1. Chemiluminescent intensity in counts/s (arbitrary units) vs. time for reaction of dioxetane 1a with 0.0016 amol of alkaline phosphatase in 100 μL of the Lumi-Phos® 530
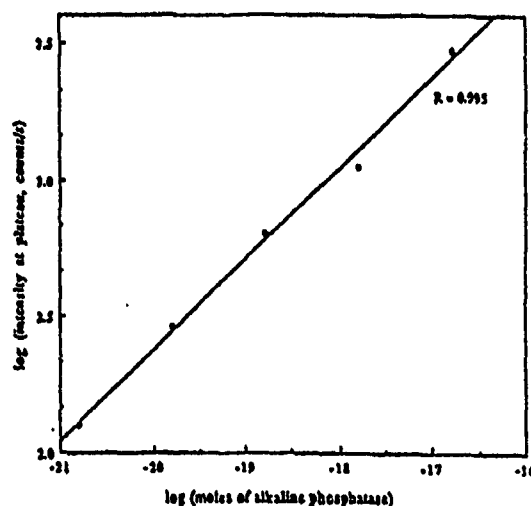
Fig. 2. Correlation of log (intensity at the plateau, counts/s) vs. log (moles of alkaline phosphatase)

Dioxetane 1b (Lumigen® GPD) bearing a galactose moiety as the protecting group is a highly sensitive reporter molecule for the chemiluminescent detection of free ß-galactosidase and conjugates in solution. Lumi-Gal™ 530 is a ready-to-use formulation which allows the rapid detection of ß-galactosidase from $E.$ $coll$ with ten-fold better sensitivity than colorimetric methods.[7] A set of assays can be performed in one hour compared to the incubation times of up to one day required in colorimetric analysis of low levels of ß-galactosidase. A noteworthy feature of the Lumi-Gal™ formulation is that it permits the efficient operation of $E.$ $coll$ ß-galactosidase at pH 9.6, which is significantly above the optimum pH. This property makes Lumi-Gal™ 530 especially useful for analysis in gene expression studies since the $E.$ $coll$ ß-galactosidase gene is commonly used as a reporter gene in molecular biology research.

While enzyme labels provide a powerful detection system, problems associated with non-specific absorption of enzyme-conjugates and background contamination with ubiquitous enzymes such as alkaline phosphatase can limit the sensitivity of actual assays. An alternative technique which may avoid these limitations involves the direct labeling of biological molecules with a chemiluminescent molecule. We now report the development of novel, chemically triggerable dioxetanes which can be used as chemiluminescent labels for a wide variety of

biological molecules. The highly efficient meta-phenyl type dioxetane has been functionalized with tethered reactive groups. For example, dioxetane 2 contains an N-hydroxysuccinimide group attached through a methylene linker arm. Antibodies and DNA probes bearing reactive amino groups are labeled with this dioxetane. Dioxetane 3 contains a biotin group for indirect labeling through the biotin-streptavidin binding interaction. Various OX groups can be used in combination with the appropriate activating agent to chemically trigger the chemiluminescence and provide an assay for the labeled biological molecule. We will describe possible applications of these novel labels to life science research and medical diagnostics.
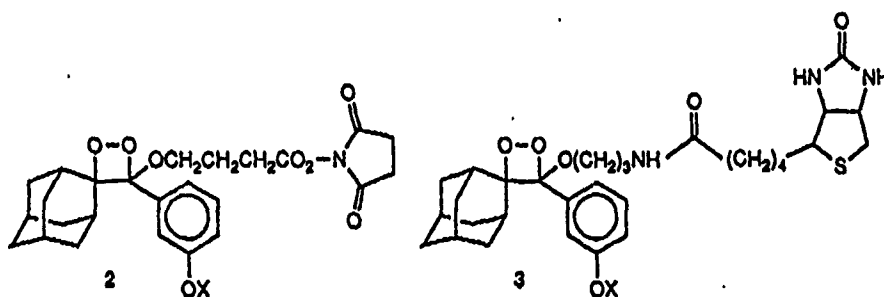
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I- GAS PHASE PHOTOPHYSICS
AND
PHOTOCHEMISTRY

MECHANISM OF CF(X²Π) GENERATION BY 248 NM MULTI-PHOTON DISSOCIATION OF CF₂Br₂ AND CFBr₃. DETERMINATION OF THE C-F BOND DISSOCIATION ENERGY

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Ground state CF(X) radicals were observed as a minor product of the 248 nm excimer laser photolysis of both CF_2Br_2 and $CFBr_3$. The resulting $[CF(X,v''=0)]$ was measured by L.I.F. (excitation : 1–0 band of the $^2\Sigma^+ \leftarrow {}^2\Pi_{1/2}$ transition at $\lambda \simeq 224$ nm) as a function of the excimer laser fluence over a range $\mathbf{f} \simeq 10^{16}$ to 10^{18} photons cm⁻² pulse⁻¹. In both cases $[CF(X)]$ obeys a $\mathbf{f}^2$ law in the $\mathbf{f} \to 0$ limit. Photodissociation cross sections were obtained from the detailed analysis of $[CF(X)](\mathbf{f})$ over the full fluence range :

$$CF_2Br_2 + h\nu \to CF_2Br + Br \qquad \Delta H_r = 66 \text{ Kc/m} \qquad \sigma_1 = 7\ 10^{-19}\text{cm}^2 \quad (1)$$

$$CF_2Br + h\nu \to CF_2\ +\ Br\ (\text{major}) \qquad \Delta H_r = 35$$
$$\to CF +\ FBr\ (\text{minor}) \qquad \Delta H_r = 100 \qquad \Bigg\} \ \sigma_2 = 4\ 10^{-18}\text{cm}^2$$

$$CFBr_3 + h\nu \to CFBr_2 + Br \qquad \Delta H_r = 61 \qquad \sigma_1 = 4\ 10^{-18}\text{cm}^2$$

$$CFBr_2 + h\nu \to CFBr\ +\ Br\ (\text{major}) \qquad \Delta H_r = 43$$
$$\to CF\ +\ Br_2\ (\text{minor}) \qquad \Delta H_r = 69 \qquad \Bigg\} \ \sigma_2 = 2\ 10^{-16}\text{cm}^2$$
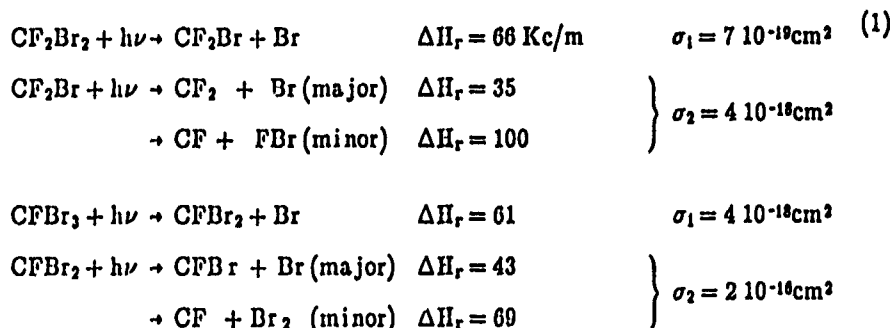
As evidenced by relaxation effects, CF from CF_2Br_2 arises for a large part in the $v'' = 0$ state, whereas CF from $CFBr_3$ is generated dominantly in higher v'' states, in agreement with the energetics of the processes involved.

The C–F(X) bond dissociation energy was determined from a $\Delta G(v'')$ vs.v'' Birge-Sponer relation, with $G(v'')$ values for $v'' = 0$ to 14 obtained from $CF(^2\Sigma^+, v' = 1)$ fluorescence (224–352 nm) induced by 224 nm probe laser excitation of the $^2\Sigma^+, v' = 1 \leftarrow {}^2\Pi_{1/2}, v'' = 0$ transition. Given the nearly perfect Morse behaviour of the $CF(X)$ potential energy function – as follows from recent highly refined ab–initio $V(r)$ data [2], a first-order Birge-Sponer analysis was carried out. Thus, we obtain $D(C–F) = 128 \pm 2$ Kc/mol.

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Perturbation facilitated optical-optical double resonance spectroscopy of Cl_2

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The 0_g^- ($^3P_1$) and $1_g(^3P_1)$ ion-pair states were studied by the perturbation facilitated optical-optical double resonance spectroscopy. It is known that the $\Delta\Omega=0$ selection rule holds for the ion-pair to valence state transitions, since their primary transition moments are parallel to the internuclear axis. For example, in order to detect the 0_g^- ion-pair state by optical-optical double resonance, this selection rule requires the $\Omega=0^-$ components of the $^3\Pi_u$ valence state as an intermediate, to which the optical transition from the $X^1\Sigma_g^+$ ground state is forbidden. In a previous publication,[1] we found the local perturbation by the $B'^3\Pi(0_u^-)$ state in the v=9 level of the $A^3\Pi(1_u)$ state. On this basis we adopted the excitation sequence shown in Fig. 1 to probe the $0_g^-(^3P_1)$ state, where the first step of excitation to the intermediate state was executed through its $A^3\Pi(1_u)$ - $X^1\Sigma_g^+$ property.

In the second step, the molecules were excited to either the $0_g^-(^3P_1)$ or $1_g(^3P_2)$ state lying in the 58000 cm^{-1} region, according to the $\Delta\Omega=0$ selection rule depending on the probe laser wavelength by its $B'^3\Pi(0_u^-)$ and $A^3\Pi(1_u)$ double-faced character. On the other hand, we analyzed the $2_u(^3P_2)$ ion-pair state through the $A'^3\Pi(2_u) \sim A^3\Pi(1_u)$ interacting state, whose results will be discussed in the poster session.
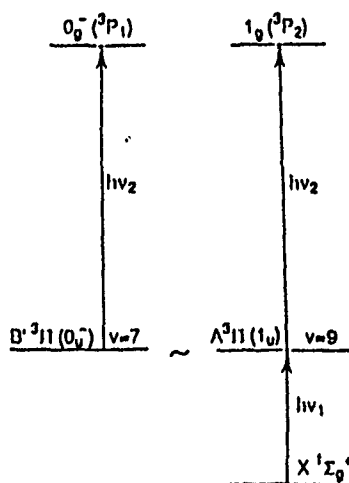
Fig. 1

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KINETICS OF C_2O RADICALS FORMED IN THE PHOTOLYSIS OF CARBON SUBOXIDE AT 308 NM AND 248 NM

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The photolysis of carbon suboxide at 248 and 308 nm was investigated at 4 Torr total pressure and 295 K. It was observed that when C_3O_2 is photolyzed at 248 nm the photolysis product C_2O, whose time behaviour was monitored by means of laser induced fluorescence, is initially formed in one of the low lying singlet states whereas at 308 nm the $^3\Sigma^-$ ground state is the dominant photolysis product. At 248 nm the addition of CO caused an efficient conversion of the singlet C_2O to its triplet electronic ground state, which is probably caused by intersystem crossing in a C_3O_2 collision complex.

In addition, rate coefficients for the reactions of $C_2O(X^3\Sigma^-)$ with CO, CO_2 and O_2 as well as quenching rate constants for the deactivation of $C_2O(A^3\Pi_i)$ by N_2, SF_6, CO and CO_2 were determined.

Infrared Diode Laser Study of the Reaction of
O(^{1}D$_2$) Atom with CH$_4$

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The reaction dynamics of polyatomic molecule involving internal (vibrational) coordinate(s) has not been well understood. In the present study we investigate hydrogen abstraction by O(^{1}D$_2$) atom from methane, O(^{1}D$_2$) + CH$_4$ → OH + CH$_3$ (ΔH$_{298}$ = -179 kJ mol^{-1}), which involves the large out-of-plane bending deformation of CH$_3$ moiety of CH$_4$ from a pyramidal to a planar structure. The bending deformation dynamics of CH$_3$ in the reaction are expected to be reflected by the product state distribution over the v_2 (out-of-plane bending) mode of the CH$_3$ radical. The reaction was initiated by the generation of O(^{1}D$_2$) atoms by excimer laser photolysis of N$_2$O, O$_3$, or NO$_2$ at a total pressure of 100 - 200 mTorr, and the v_2 bands of CH$_3$, v_2 = 1 ← 0 up to 4 ← 3, were measured as functions of time by infrared diode laser kinetic spectroscopy. The result shows that the vibrational distribution of v_2 ($v ≤ 3$) is non-inverted and much less excited than a prior distribution. The nascent vibrational distribution determined for the gas mixture N$_2$O/CH$_4$ (100/100 mTorr) was 1 : 0.58 : 0.35 : 0.15 for v_2 = 0, 1, 2, 3 and the fraction of the available energy released to v_2 vibration, <f_v(CH$_3$ v_2)>, was estimated to be about 0.02. These results contrast with the strongly-excited inverted vibrational distribution of the OH counterpart radical, which has a maximum at v = 2 and <f_v(OH)> ≈ 0.3.[1] For the O(^{1}D$_2$) reaction with CH$_4$, there has been a controversy whether the reaction proceeds via insertion or abstraction mechanism. For comparison, we also measured the vibrational distribution of CH$_3$ produced by the direct hydrogen abstraction reaction of the ground state O(^{3}P) atom with CH$_4$ (ΔH$_0$ = 8 kJ mol^{-1}) using the precursor of SO$_2$ and obtained a similar non-inverted distribution. Therefore, the O(^{1}D$_2$) and O(^{3}P) reactions have similar CH$_3$ deformation dynamics. The feature of energy partitioning is also similar to that of the F atom reaction with CH$_4$. The results may suggest that in these reactions the CH$_3$ moiety deforms fast enough to follow the motion of the abstracted atom, as reported for the A state photodissociation of CH$_3$I.[2]

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[1] (a) P.M.Aker et al., J.Chem.Phys., 73, 1143 (1986); (b)S.G.Cheskis et al., Chem.Phys.Lett., 155, 37 (1989)
[2] (a)T.Suzuki et al., J.Chem.Phys. in press; (b) S.Amatatsu et al., J.Chem.Phys.,in press; (c)H.Guo and G.C.Shatz, J.Chem.Phys, 93, 393 (1990)

CHANGING INTRAMOLECULAR VIBRATIONAL REDISTRIBUTION RATES
BY CHEMICAL MODIFICATIONS

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Some simple chemical modifications of the aromatic p-difluoro-
benzene (pDFB) can change or introduce IVR processes whose rates span
approximately four orders of magnitude. IVR rates among the ring modes
of pDFB at 300K lie in the range 15-300 psec. If we replace a fluorine
with a CH_3 group, IVR rates increase as much as 100X, becoming in some
cases, sub-picosecond. Moving the CH_3 group to the ortho or meta position
increases the rate further. Alternatively, if we return to pDFB and add
an Ar atom to form the pDFB-Ar van der Waals complex, we introduce slower
IVR processes, about 5000 psec. A change in the pDFB-Ar complex by again
replacing a fluorine with a methyl group accelerates the slow IVR by at
least an order of magnitude.

The underlying causes of these changes can be understood in general
terms, and details of the IVR mechanisms are emerging. Theoretical
modelling provides some insight into the van der Waals IVR. The methyl
effect is due to the interaction of its internal rotation with overall
rotation and ring vibrations. Cold jet fluorescence spectroscopy has
provided a detailed picture of these state-to-state couplings.

PHOTOISOMERIZATION RATES OF STILBENE AND DIPHENYLBUTADIENE: AN RRKM ANALYSIS BASED ON COMPUTED VIBRATIONAL FREQUENCIES

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The trans-cis photoisomerization of stilbene (St) and diphenylbutadiene (DPB) has been studied extensively in a variety of different environments, both in the dense phase[1,2] and under collision-free conditions in supersonic beams[3,4]. The energy dependence of k(E), the microcanonical rate coefficient of the photoisomerization process, shows a very well defined threshold for this process at an excess vibrational energy of ca. 1200 cm^{-1}. The rate constant k(T) measured in the dense phases matches the thermally averaged k(E) for DPB, but is larger by a factor of 30 for St.

We have analyzed these observations by performing RRKM calculations of the rate coefficients k(E) based on computed vibrational frequencies of reactant and of transition state. From the computed k(E), the rate coefficients k(T) are obtained. In DPB where the lowest excited state is 2A along the entire reaction path, the theoretical and the experimental k(T) and k(E) are in good agreement. In St a correct k(E) is found introducing non-adiabatic effects associated to the nature of the barrier which is originated by the avoided crossing of the states 1B and 2A: the neglect of these effects leads to an overestimate of k(E). On the contrary the computed k(T) is significantly lower than the observed rate: this difference is explained in terms of a lowering of the barrier by the solvent[5]. The observed deuterium effects[6] are reproduced correctly.

These results indicate that a) the RRKM method can describe successfully the rate parameters of photoisomerization in isolated diphenylpolyenes and b) the anomalous effects observed in St are related to the nature of the barrier in these molecules.

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4) J.Troe, A.Amirav, J.Jortner, Chem.Phys.Lett. 115, 245 (1985).

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Optical-optical double resonance spectroscopy of Cl_2

using (1 + 2) photo-excitation sequence

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We have carried out a series of experiments on the Cl_2 molecule to examine the excited states of ion-pair character by optical-optical double resonance. The previous publication showed an approach to those excited states using (1 + 2) photo-excitation sequence through the $B^3\Pi(0_u^+)$ state.[1] However, this experiment only allows to probe the 0_u^+ ion-pair states, since the $\Delta\Omega = 0$ selection rule holds for the valence to ion-pair state transitions of the charge transfer type along the internuclear axis. To solve this problem, we have recently developed this technique using the $A^3\Pi(1_u)$ state as an intermediate and new spectra covering the same region (58500 - 61000 cm^{-1}) were observed. This experiment extended our observation to the 1_u state, and the perturbation facilitated double resonance transitions through the $A^3\Pi(1_u)- B'^3\Pi(0_u^-)$ and $A^3\Pi(1_u)-A'^3\Pi(2_u)$ perturbing states allow us to gain access to the 0_u^- and 2_u ion-pair states, respectively. Finally we were able to characterized all of the 6 ungerade ion-pair states (2 x 0_u^+, 0_u^-, 2 x 1_u, and 2_u) correlating to the lowest ionic state $Cl^-(^1S) + Cl^+(^3P)$, whose results are summarized as follows: (1) These ion-pair states of Cl_2 show case (c) tendencies and their relative positions can be rationalized by spin-orbit coupling between the $^3\Sigma_u^-$ and $^3\Pi_u$ states arising from $Cl^-(^1S) + Cl^+(^3P)$. (2) The $^3\Sigma_u^-$ state lying at ~58800 cm^{-1} is characterized by $\omega_e \sim 235$ cm^{-1} and $r_e \sim$ 2.8 Å. The $^3\Pi_u$ state is slightly long-bonded ($r_e \sim 3.1$ Å) and located at ~ 59400 cm^{-1} with $\omega_e \sim 250$ cm^{-1}. (3) Due to the crucial difference of molecular constants between the $^3\Pi_u$ and $^3\Sigma_u^-$ states, the interstate couplings between the ion-pair states are indispensable analyzing the spectra.

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INTERSYSTEM CROSSING AND CHEMICAL REACTIONS

IN NH(a¹Δ) COLLISIONS

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NH(a¹Δ), which is isoelectronic with O(¹D) and the carbene CH$_2$($\tilde{a}$), is a model system to study the kinetics and dynamics of electronically excited species. The two channels, chemical reaction and intersystem crossing (to different vibrational states in the electronic ground state (X³Σ⁻)), can be followed directly by laser-induced fluorescence (LIF).

NH(a¹Δ, v" = 0 - 4) is formed in the laser photolysis of HN$_3$ at λ = 248 nm and NH (a¹Δ, v" = 0) at λ = 308 nm. The time delay between the photolysis laser puls and the LIF laser pulse brings about the time resolution.

The intersystem crossing of NH(a¹Δ, v" = 0 and 1) collision induced by N$_2$ takes place with an activation energy of 5 kJ/mol for both vibrational states; a result, which is in agreement with informations on the HN -- N$_2$ surface obtained from the HN$_3$ photolysis. In the quenching of NH(a¹Δ, v") by N$_2$, NH(X) is found exclusively in the vibrational ground state, whereas for Xe as the colliding partner NH(X) in v = 0 and v>0 is observed. The differences of these two isc-dynamics will be discussed.

For the reaction of NH(a¹Δ) with CH$_4$, C$_2$H$_6$, C$_3$H$_8$ and C$_4$H$_{10}$, which proceed with rate constants in the range 0.18 ≤ k · 10¹³ cm³ mol⁻¹ s⁻¹ ≤ 3.2 the chemical reaction was found to be the dominant channel; the intersystem crossing contributes less than 1%. The chemical reaction follows the insertion pathway on the lowest singlett surface with NH$_2$ as a decomposition product. The same dynamics is observed for the interaction of NH(a¹Δ) with NH$_3$, which reacts with a rate constant k = 8.9 · 10¹³ cm³/mol·s.

For the unsaturated hydrocarbons like C$_2$H$_4$, C$_3$H$_6$ and C$_4$H$_8$, which react with rates in the range 5.1 ≤ k·10¹³ cm³/mol·s ≤ 8.9, the chemical reaction is also the dominant pathway, but competition between the insertion of NH(a¹Δ) into the CH-bond and addition to the double bond occurs. The measured product distributions are discussed.

GENERATION OF Xe* ATOMS AND XeHal* EXCIMERS IN ACTIVE NITROGEN

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Excitation of Xe atoms as third body in the process of $N(^4S)$ atoms recombination was studied in our recent work[1], where Xe{6p} states were monitored via the Xe{6p} —> Xe{6s} emission. Xe{6p} levels lying close to the N_2 dissociation limit are directly excited in the process of three body recombination, while excitation of lower Xe levels involves energy transfer from the excited nitrogen molecules, stabilized by vibrational relaxation.

$$N(^4S) + N(^4S) \xrightarrow{(M)} N_2^* \qquad (1)$$

$$N_2^* + Xe \longrightarrow N_2(X,v) + Xe^*(\{6p\},\{6s\},\{6s'\}) \qquad (2)$$
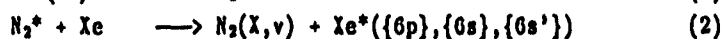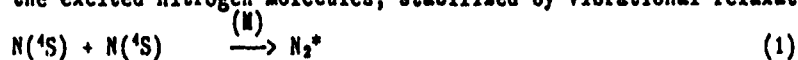
In the present work kinetics and yield of Xe atoms excitation was studied using emission of $XeCl^*$ (XeF^*) excimers formed in reaction:

$$Xe^* + Cl_2(CCl_4, NF_3) \longrightarrow XeCl^*(XeF^*) + Cl(CCl_3,NF_2) \qquad (3)$$
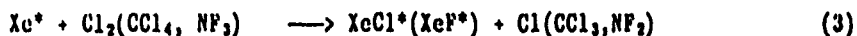
as a marker for Xe^* metastable states. This method permits to obtaine the total yield of Xe excitation in reactions (1,2), which is basically associated with Xe{6s} states formation. Termolecular rate constants for Xe excitation in reactions (1,2) were found to be : $k_{1,2}$ = 0.41, 0.86 and 1.1 (units, 10^{-33} cm^6s^{-1}) for M = He, Ar and Xe carriers respectively. Thus studied system manifests itself as having high yield for convertion of chemical energy, released in the process of recombination into energy of excited Xe atoms or excimers, which can be of interest for applications.

XeF^* production was also found when XeF_2 was added to active nitrogen. XeF^* formation in this case involves dissociative electronic energy transfer from N_2^* formed in reaction (1) to XeF_2.

$$N_2^* + XeF_2 \longrightarrow N_2(X,v) + XeF^* + F \qquad (4)$$

XeF^* excimers formation were monitored via their emission in the UV range. Termolecular rate constant for XeF^* excitation in reactions (1,4) was estimated to be $k_{1,4}$ = 10^{-34} cm^6s^{-1} for M = He.

(1) U.V.Ivanov, A.M.Pravilov, L.G.Smirnova and A.F.Vilesov, J.Photochem. Photobiol.A:Chem., 54 (1990) 139.

STATE-RESOLVED PHOTOFRAGMENT EXCITATION SPECTROSCOPY OF NO_2 NEAR PHOTODISSOCIATION THRESHOLD

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Photofragment excitation(PHOFEX) spectra of $NO_2 + h\nu \rightarrow NO(^2\Pi_{1/2}, v=0, j) + O(^3P_j)$ were observed by detecting O or NO in respective quantum levels. The initial rotational state of parent NO_2 was limited to the ground level by cooling it in a supersonic jet. PHOFEX spectra are composed of a line structure whose line-width is broadened homogeneously due to the dissociation reaction. This implies that NO_2 predissociates through a quasi-bound state of vibronically excited levels. The branching ratios to produce $O(^3P_j)$ in three spin-orbit sublevels are consistent with those predicted by a restricted statistical distribution model.[1]

An example of PHOFEX spectra observed by detecting $NO(^2\Pi_{1/2}, v=0, j)$ is shown in Fig. 1. Near the dissociation threshold where NO is produced only in the lowest rotational level, the predissociation rate is estimated to be 9×10^9 s^{-1} from the line-width. In the photon energies which allows production of NO in both $j=0.5$ and 1.5, the line-width is broader to be around 0.15 cm^{-1} which corresponds to the rate of 3×10^{10} s^{-1}. These values are close to those expected by the statistical theory. However, the rotational population ratio is far from the statistical expectation. The photodissociation dynamics will be discussed on the basis of these results.
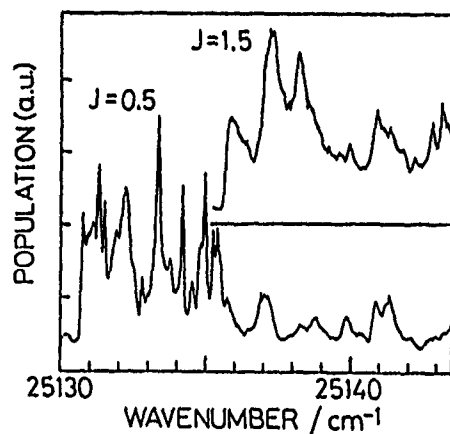
Fig. 1 PHOFEX spectra observed through detection of $NO(^2\Pi_{1/2}, v=0, j=0.5$ and $1.5)$. Dissociation threshold $= 25130.6$ cm^{-1}.

(1) J. Miyawaki, K. Yamanouchi and S. Tsuchiya: Chem. Phys. Lett. in press.

Réaction chimique photoinduite dans le complexe
de van der waals $NO_2-C_2H_4$

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La photodissociation de NO_2 dans le complexe $NO_2-C_2H_4$ excité à 355 nm et 266 nm conduit à la formation du radical vinoxy ($CH_2CHO^\cdot$). Cette réaction photochimique dans un complexe de van der Waals peut être considérée comme l'analogue de la réaction collisionnelle $O(^3P) + C_2H_4$, mais avec une géometrie fixe dans la voie d'entrée.

Quand NO_2 dans le complexe est photodissocié à 355 nm, la réaction est exoénergetique (6000 cm^{-1}), mais on observe une distribution d'énergie interne, rotationnelle ($E_{rot} \approx$ 150 cm^{-1}) et vibrationnelle ($E_{vib} \approx$ 300 cm^{-1}), froide et non statistique.

Quand la longueur d'onde de photolyse est 266 nm, la distribution d'énergie dans $CH_2CHO^\cdot$ est toujours froide rotationnellement, mais on trouve plus d'énergie vibrationnelle. La distribution d'énergie interne est interprètée avec un modèle impulsif à l'état de transition.

La distribution d'énergie internre du vinoxy produit par collisions en phase gazeuse de $O(^3P)$, issu de la photodissociation de NO_2, avec C_2H_4, est rotationnellement et vibrationnellement plus chaude que celle obtenue dans le complexe. Cette difference entre réaction dans le complexe et réaction collisionnelle peut être dûe à:

-la sélection de la géométrie dans la voie d'entrée qui peut donner lieu, dans le complexe, à une selectivité dans le produit

-l'agrégation peut être responsable du refroidissement du produit final (bien qu'aucune expérience n'ait mis en évidence ces agrégats)

-deux mécanismes différents peuvent être actifs en collision comme le suggère la dépendance en pression de la vitesse de réaction.

PHOTO INDUCED CHEMICAL REACTION IN THE $NO_2-C_2H_4$ VAN DER WAALS COMPLEX

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The photodissociation of NO_2 in the $NO_2-C_2H_4$ complex excited at 355 nm and 266 nm leads to the formation of the vinoxy radical $CH_2CHO\cdot$. This photoreaction in a van der Waals complex can be considered as the analogous of the collisional reaction $O(^3P) + C_2H_4$, but with a restricted geometry in the entrance channel. The product energy distribution is monitored by laser induced fluorescence. When the NO_2 in the complex is photodissociated with 355 nm, the reaction is exoenergetic by 6000 cm^{-1}, but a cold nonstatistical rotational ($E_{rot} \approx 150$ cm^{-1}) and vibrational ($E_{vib} \approx 300$ cm^{-1}) state distribution is observed. When the photolysis wavelength is set at 266 nm, the vinoxy product energy distribution is still rotationally cold, but more energy is found in vibration. The internal energy distribution is analyzed through an impulsive model in a late transition state.

The energy distribution in the vinoxy product obtained in gas phase collisions using $O(^3P)$ issued from the photodissociation of NO_2 colliding with C_2H_4, is rotationally and vibrationally hoter than that obtained in the complex. This difference between the reaction in the complex and the collisional reaction can be due to several reasons:
-the entrance channel geometry selection in the complex may give rise to the selectivity in the product
-clusterisation may be responsible for the cooling in the final product (although no experimental evidence for large clusterisation is observed)
-two different mechanisms may be active in collisions as suggested by the pressure dependence of the reaction rate.

FORMATION OF ELECTRONICALLY EXCITED NH(A) IN THE VUV PHOTOLYSIS OF N_xH_y SYSTEMS INCLUDING NH_2-RADICALS

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Ab initio calculations by Saxon et al.[1] have predicted an NH_2 transition to the (2^2A_1) state leading to the formation of electronically excited NH(A) and H. The corresponding absorption is given to occur at around 160 nm.[1] It has been previously shown in our laboratory, that NH_3 is photodissociated by ArF-excimer-laser light to yield rotationally excited NH_2 radicals in the ground state.[2] These highly rotating radicals thereafter absorb a second photon from the same unfocussed laser pulse to generate indeed $NH(A^3\Pi, v=0$ and 1) radicals. Practically all the excess energy from the first photolysis step is carried over to the NH_2 fragment making its photolysis just possible at the relatively long wavelength of 193 nm (ArF).

For the photolysis study of ground state $NH_2(\tilde{X}^2B_1)$ without internal excitation we have generated the radicals in flow systems by the reactions (I) $H + N_2H_4 \rightarrow N_2H_3 + H_2$ followed by $H + N_2H_3 \rightarrow 2\ NH_2$ and by (II) $F + NH_3 \rightarrow NH_2 + HF$. As a tunable vuv light source (105 - 200 nm), we have used the Berlin electron storage ring (BESSY) using a beam line equipped with a 1m Seya Namioka monochromator. In addition, fixed vuv rare gas resonance lines were used. NH(A) radicals were detected by their (A → X) transition to the ground state. Unfortunately such flow systems contain a number of N_xH_y species capable of producing NH(A). In order to discriminate the observed fluorescence against that from NH_2, we have first studied absorption and excitation spectra of N_2H_4 and N_2H_2, because these two molecules are possibly common to both flow systems due to NH_2 reactions. The remaining NH(A) emission is then attributed to the photolysis of NH_2.

In this work, we report excitation spectra for the formation of NH(A) from NH_2, N_2H_2, and N_2H_4. Furthermore the absorption spectrum of N_2H_4 has been reinvestigated in the light of recent *ab initio* calculations.[3]

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PHOTOCHEMISTRY OF METHYLACETYLENE AT 193NM

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Methylacetylene (MA) was found in interstellar clouds and the Titan (a Saturn's satellite) atmosphere. We have investigated the photochemistry of MA at 193 nm using FTIR spectrometer for product analysis. The quantum yields of acetylene and the disappearance of MA were measured at MA pressures in the range 0.1-10 Torr. The photolysis of mixtures of MA and other gases (Cl_2, Ar) was performed.

Acetylene was a main product of the photolysis. The quantum yield was 0.1 above 2 Torr of MA pressure. Below 2 Torr the value gradually rose up to 0.24 at 0.3 Torr. This result support the following mechanism

$$CH_3C_2H + hv \quad ----> \quad CH_2 + C_2H_2 \quad (A)$$
$$CH_3C_2H + hv \quad ----> \quad C_3H_3 + H \quad (B)$$

followed by

$$CH_3C_2H + H \quad ----> \quad C_4H_6{}^* \quad (C)$$
$$C_4H_6{}^* + M \quad ----> \quad C_4H_6 \quad (D)$$
$$C_4H_6{}^* \quad ----> \quad CH_3 + C_2H_2 \quad (E).$$
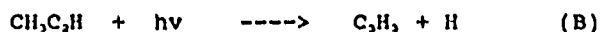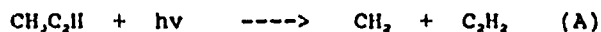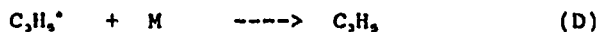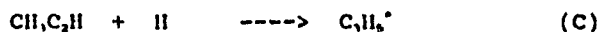
Reaction (C) is affected by MA pressure but (A) is not. Therefore The quantum yield of 0.1 is ascribed on Channel (A). An increase of the quantum yield of acetylene is based on Channel (B),(C) and (E). In the presence of 90 Torr Ar at a MA pressure 0.3 Torr the quantum yield of acetylene was 0.12. The presence of Ar reduces the quantum yield of acetylene, that is $C_4H_6{}^*$ is stabilized by the collision of Ar. Reaction (B) was suggested by L.J. Stief et. al.[1] at 147nm photolysis. They showed that the main reaction of methylacetylene photolysis was (B). The C_3H_3 was, however, not clearly assigned to CH_3CC or $CH2CCH$. We could show that The C_3H_3 was CH_3CC, because $CH2ClCCH$ was not found at the photolysis of MA including Cl_2.

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INVESTIGATIONS OF THE ONE AND TWO PHOTON DISSOCIATION OF KETENE

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1). Laser flash kinetic absorption spectroscopy has been used to monitor the temperature variation in the collisional removal of the CH_2 ($\tilde{a}$ $^1A_1$) radical produced via the one–photon pulsed photolysis of ketene (CH_2CO) at 308 nm. For the reaction of $^1CH_2$ with NO and H_2 there was no significant deviation in removal rate constant from the measured room temperature values of 1.6 and 1.0×10^{-10} cm^3 molecule^{-1} s^{-1} respectively. Quenching by Ar can proceed only via the spin-forbidden collision induced intersystem crossing (ISC) to the ground electronic state ($\tilde{X}$ $^3B_1$) and for this process the rate constant was observed to rise by about 50 % from its room temperature value to 7.6×10^{-12} cm^3 molecule^{-1} s^{-1} at 431 K. The mixed state model for ISC was used to explain the increase in quenching rate for Ar by calculating the variation in the fractional Boltzmann population of certain perturbed levels in the singlet manifold that act as "doorway" states for energy transfer into corresponding triplet manifold perturbed levels[1].

2). In a second experiment the ground state CH radical (X $^2\Pi$) was produced by the two–photon photodissociation of ketene at 279 nm and detected by laser induced fluorescence in the R–branch region of the A $^2\Delta \leftarrow$ X $^2\Pi$ transition. The presence of a large excess pressure of inert bath gas Ar was observed to always produce a propensity in population of the Λ–doublet pairs for higher rotational levels (N" > 11) with the Ar appearing to preferentially quench to states of A" symmetry. The nascent $\Pi(A")/\Pi(A')$ propensity ratio in photodissociation was found to be 1.0 and rises to a constant value of between 1.8 and 2.0 as the Ar pressure or probe delay was increased. Altering the relative polarisation vectors of the photolysis and probe lasers produced no change in observed Λ–doublet behaviour and indicates that there is little preferential alignment of the CH rotating plane on photolysis. Recent theory describes collisions with closed shell atoms using average and difference potential surfaces. Wavefunction mixing between the spin-orbit manifolds leads to interference between the scattering amplitudes of these potentials and the symmetry bias in the final state depends on their relative signs.

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MODE-SELECTIVE BOND FISSION IN FUNDAMENTAL STRETCHINGS OF HOD

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Stimulated Raman excitation and coherent anti-Stokes Raman scattering prepare and detect, respectively, HOD molecules with *one* quantum of vibrational excitation in the O-H or O-D stretch vibrations. This selective vibrational excitation prepares densities of the excited molecules in particular rotational levels that are sufficient for molecular reaction dynamics studies. An ArF excimer laser at 193 nm promotes vibrationally excited molecules to the first electronic surface $A(^1B_1)$ where they dissociate to produce OH + D or OD + H fragments. The photodissociation products OD and OH are detected via laser induced fluorescence. The photodissociation of the O-H stretching, HOD (0,0,1), produces the fragments more efficiently than the photodissociation of vibrationless molecules, but it produces OD 2.5 ± 0.5 times more than OH. In the photodissociation of the O-D stretching, HOD (1,0,0), no enhancement of the yield of the fragments is obtained.

The initially selected low energy vibrational state enhances the photodissociation cross section relative to vibrationless molecules, and this effect is vibrational mode specific. Also, these results demonstrate that bond cleavage does not necessarily occur on the weakened bond, and they agree with theoretical calculations[1,2] indicating that the yield of OD and OH fragments depends on the Franck-Condon overlap of the vibrational wavefunction with the repulsive surface of the upper state. Our results show that even the very lowest possible level of vibrational excitation can be "!~veraged" to effect selective bond breaking.

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REACTION MECHANISMS IN INFRARED MULTIPHOTON
DISSOCIATION OF UF_6 AND ZIRCONIUM ALKOXIDE COMPOUND

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The isotopically selective multiphoton dissociation of UF_6 with 16 μm Raman lasers is used for the isotope separation of uranium[1]. In the infrared multiphoton dissociation (IRMPD) of UF_6, primary dissociation of UF_6 occurs *via* the following reactions:

$$^{235}UF_6 \xrightarrow{nh\nu} {}^{235}UF_5 + F , \qquad (1)$$

$$^{238}UF_6 \xrightarrow{mh\nu} {}^{238}UF_5 + F . \qquad (2)$$
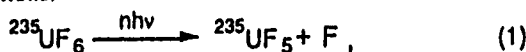
We investigated the radical reaction mechanisms in the 16 μm p-H_2 Raman laser-induced IRMPD of UF_6 cooled to -35 °C in the presence of F-atom scavenger gases. When CH_4 was added as a scavenger of F-atom, the dissociation rate of UF_6 became tens of times larger than when no scavenger gas was added. The reverse reactions of Eqs. (1) and (2), i. e. the recombination of UF_5 and F-atom, were inhibited by the addition of CH_4. Gas-chromatographic measurements of the irradiation products revealed that as low as 7% of the nascent CH_3 radicals were involved in the radical reaction with UF_6. When H_2 or C_2H_6 was added as a scavenger gas, both the dissociation rate of UF_6 and the contribution of the isotopically non-selective reaction with UF_6 increased.

The isotopically selective IRMPD of zirconium alkoxide compounds with CO_2 laser is used for the isotope separation of zirconium[2][3]. The reaction mechanisms in the TEA CO_2 laser-induced IRMPD of zirconium alkoxides, however, is not known. To investigate the reaction mechanism in the CO_2 laser-induced IRMPD of zirconium tetra-*tert*-butoxide ($Zr(t\text{-}OC_4H_9)_4$), we analyzed the chemical structure of the dissociation product by fast atom bombardment mass spectrometry, infrared absorption spectroscopy, Raman spectroscopy and nuclear magnetic resonance measurements. From the results, we could surmise a reaction mechanism in IRMPD of $Zr(t\text{-}OC_4H_9)_4$.

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REMPI MASS SPECTRUM OF THE OH RADICAL IN THE GAS PHASE

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The resonance enhanced multiphoton ionization (REMPI) of the OH radical in the gas phase was studied using an isothermal discharge flow reactor for the production of OH radicals ($H + NO_2 \longrightarrow OH + NO$), tunable laser light from an excimer pumped dye laser and a time-of-flight (TOF) mass spectrometer. A mass resolved REMPI spectrum was found in the wavelength region of 290 – 310 nm, which is assigned to a (3 + 1) ionization process. An ab initio quantum chemical calculation predicts the Rydberg state, verified by the experiment.

UV MULTIPHOTON EXCITATION STUDY OF THE DYNAMICS
OF VIBRATIONALLY EXCITED BENZYL RADICALS

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Vibrationally highly excited benzyl radicals in the electronic
ground state are prepared by UV absorption followed by fast
internal conversion. The UV photodissociation of precursors
like ethylbenzene yields vibrationally excited benzyl radicals
which are deactivated by collisions with inert bath gas mole-
cules before reexcitation with another photon. Variing the
number of deactivating collisions between the preparation of
benzyl and the photoexcitation the internal energy of the
benzyl radicals can be varied over large ranges. The colli-
sional deactivation of the benzyl radicals is monitored by
time-resolved UV absorption spectroscopy. It is found that the
rate of collisional deactivation of benzyl radicals agrees
with that of hydrocarbons of similar size[1]. For the highest
excitation energies applied there occurs a competition between
fragmentation and collisional deactivation. From the fragmen-
tation yields specific rate constants are derived which are
compared with results from a deconvolution of thermal high
pressure rate constants as obtained from shock wave measure-
ments[2].

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RYDBERG STATES OF NO IN A MAGNETIC FIELD
PROBED BY DOUBLE RESONANCE MULTIPHOTON IONIZATION

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The perturbation of molecular Rydberg states introduced by a constant external magnetic field yields a variety of different field regimes depending on the principal quantum number, the Rydberg orbital symmetry and the rotational excitation of the ionic core.

The (2+1) ionisation spectrum of NO via the resonant C $^2\Pi$ and and the (2+2) ionisation spectrum via the resonant $A^2\Sigma^+$(v=0) state have been recorded in a 1T external field. The Zeeman effect in the resonant state as well as the alignement by the two-photon excitation have been calculated in order to understand double resonance spectra on high Rydberg states via the A state[1].

Non penetrating nf (v=1) states have further been probed by one photon excitation from the two-photon pumped A state in the same magnetic field. Up to n=15, only the linear Zeeman perturbation has to be taken into account. This n-independent magnetic perturbation competes with the intramolecular long range interactions which scale as $1/n^3$. For the 7f level, the intramolecular field still overcomes the external field giving rise to a complex electronic-Zeemann substructure. For the 15f level, the anisotropy of the magnetic field overcomes the intramolecular anisotropy, and ℓ is already strongly coupled to the field axis, leading to the first observation of the Paschen-Back effect in a molecule[2].

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ETATS DE RYDBERG DE NO EN CHAMP MAGNETIQUE EXTERNE SONDES
PAR IONSATION MULTIPHOTONIQUE RESONANTE ; ANALYSE MQDT

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La perturbation des états de Rydberg moléculaires par un champ magnétique externe constant présente des régimes différents qui dépendent du nombre quantique principal, de la symétrie de l'orbitale de Rydberg et de l'excitation rotationnelle du coeur ionique.

Les spectres d'ionisation à une ou deux couleurs de NO via les états résonants $A^2\Sigma^+$ ou $C^2\Pi$ ont été enregistrés dans un champ magnétique externe de 1 T. L'effet Zeeman dans l'état résonant ainsi que l'alignement par excitation à deux photons ont été calculés afin d'interpréter les spectres de double résonance des états de Rydberg élevés via l'état A [1].

Dans le même champ magnétique, les états non pénétrants nf (v=1) ont été aussi sondés par une excitation à un photon à partir de l'état A lui-même pompé par deux photons. Jusqu'à n=15, seule la perturbation Zeeman linéaire doit être prise en compte. Cette perturbation magnétique, indépendante de n, est en compétition avec les interactions intramoléculaires à longue portée qui varient en $1/n^3$. Pour le niveau 7f, le champ intramoléculaire domine encore le champ externe donnant lieu à une sous-structure Zeeman-électronique complexe. Pour le niveau 15f, l'anisotropie du champ magnétique domine l'anisotropie intramoléculaire, et ℓ est alors fortement couplé à l'axe du champ, conduisant à la première observation de l'effet Paschen-Back dans une molécule [2].

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IR LASER-INDUCED DISSOCOIATION OF HALOMETHANES

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Concentration and kinetics of CF_2 radicals generated
in the IR-laser-induced dissociation of halomethanes at
pressures between 10^2 and $2*10^3$ Pa were measured using a
special laser-induced fluorescence (LIF)-technique.

The technique yielded 3D profiles of the concentration
of the CF_2 radicals in various vibrational states with a
spatial resolution of 50 μm at any point in time in the
range between 0 and 500 μs. These measurements show the
complex interaction between photolytic primary reactions
and thermally induced secondary reactions of differently
excited dissociation products in dependence on laser flu-
ence, gas type (CF_2Cl_2, CF_2HCl, buffer gas), and gas pres-
sure.

HIGH RYDBERG STATES OF CO STUDIED BY TRIPLE
RESONANT MULTIPHOTON IONIZATION

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We will report the measurement of the high Rydberg states ($n \geq 8$) of jet-cooled CO molecule by the triple resonant multiphoton ionization spectroscopy.   Though CO is one of the simplest diatomic molecules, its highly excited states have not yet been fully investigated.   In one-photon vuv absorption spectrum, Ogawa and Ogawa identified the $np\sigma$ series converging to the ground state of CO^+ ion and several other Rydberg states of low principal quantum number, but the analysis of the rotational structure is attempted only up 4p state.   Other groups have also performed the observation of Rydberg states but of only low principal quantum number ($n \leq 5$).

For the detailed study of the congested high Rydberg states, it is necessary to simplify the spectrum as possible as we can.   Figure 1 shows the excitation scheme in the present experiment.   The first laser light(ν_1) excites the jet-cooled CO to the $A^1\Pi(v=4)$ state by two-photon absorption. Second laser light(ν_2) pumps the A state molecules to a single rotational level of the second intermediate state, $3s\sigma$ $B^1\Sigma^+$ ($v=1$) or $3p\sigma C^1\Sigma^+$ ($v=1$). Third laser light(ν_3) further excites from the B(or C) state to high Rydberg states converging to the ionic state $X^2\Sigma^+$ with vibrational level of $v=1$. Four Rydberg series(ns, np, nd and nf) of $v=1$ level were clearly identified and their rotational structures will be presented. We also observed anomalous feature of the rotational structure in the spectra of the np-states and this feature can be explained as due to the admixture of several orbital characters in the B and C states.
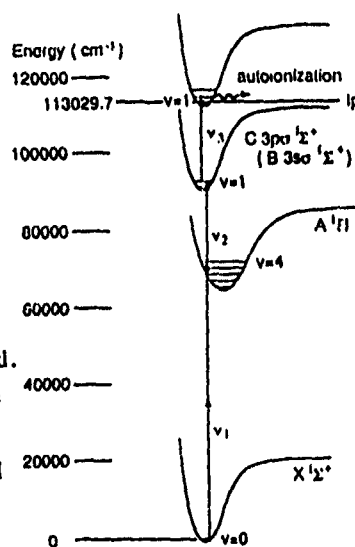
Figure 1

REACTIONS OF ORGANIC AND INORGANIC CLUSTERS WITH METAL IONS AS STUDIED BY

LASER ABLATION-MOLECULAR BEAM METHOD

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In the laser ablation-molecular beam method developed by the authors, metal ions laser-ablated from metal surfaces are allowed to react with inorganic, organic or organometallic molecules (and/or clusters) in a molecular beam injected nearby. A variety of novel product ions are formed, as probed by a quadrupole spectrophotometer. The present lecture addresses the reactions of metal ions with either of inorganic (ammonia) or organic (benzene)[1] clusters in the molecular beam. In the former case, either of clustered complex ions $M^+(NH_3)_n$ or fragment complex ions $M^+(NH)_m(NH_3)_n$ are formed depending on the identity of metal ions. Elimination of H_2 (or 2H) occurs in the ions of the latter type. For benzene clusters, either of clustered complex ions $M^+(C_6H_6)_n$ or fragment complex ions $M^+(C_6H_6)(C_xH_y)$ are obtained depending on the identity of metals. Elimination of H_2 (or 2H) or small hydrocarbon molecules occurs in this case in the formation of fragment complex ions. Mechanisms of formation of these ions are discussed.

Table 1. Clustered complex ions observed for $M^+ + (NH_3)_n$ reactions

$M^+(NH_3)_n$-type		$M^+(NH)_m(NH_3)_n$-type		$M_m^+(NH_3)_n$-type
Mg^+	$n<20$	Ti^+	$Ti^+(NH_3)_n$, $n=2-18$	$Sb^+(NH_3)_n$, $n=1-6$
Al^+	20		$TiNH(NH_3)_n$, $n=0-3$	$Sb_2^+NH_3$
Cr^+	19	V^+	$V^+(NH_3)_n$, $n=1-19$	
Mn^+	18		V^+NH	
Fe^+	18	Nb^+	$Nb^+(NH_3)_n$, $n=2-14$	
Co^+	14		$Nb^+NH(NH_3)_n$, $n=0-2$	
Ni^+	18		$Nb^+(NH)_2(NH_3)_n$, $n=0,1$	
Cu^+	15	Ta^+	$Ta^+(NH_3)_n$, $n=2-6$	
Ag^+	13		$Ta^+NH(NH_3)_n$, $n=0-6$	
In^+	15		$Ta^+(NH)_2(NH_3)_n$, $n=0,1$	
			$Ta^+(NH)_3$	

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CREUSAGE DE TROUS SPECTRAUX DANS LA FLUORESCENCE
DE DERIVES ANTHRACENIQUES EN JET SUPERSONIQUE

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Une technique pompe-sonde de creusage de trous spectraux (hole burning) dans les molécules et les complexes refroidis en jet supersonique, développée récemment[1,2] a été appliquée avec succès à quelques dérivés de l'anthracène. Cette technique exploite le fait que seulement une partie des espèces présentes dans le jet et qui sont excitées électroniquement par une impulsion laser pompe, retourne rapidement à l'état fondamental initial. La diminution de la population de l'état fondamental de l'espèce sélectionnée par le laser pompe apparait comme un trou dans le signal de fluorescence résultant de l'excitation de la même espèce par le laser sonde retardé dans le temps.

Le 9-methoxyanthracène ($A-O-CH_2$), ses complexes avec des alcools et le bis 9-anthryl ($A-O-CH_2-O-A$) ont été étudiés. L'existence de différents isomères a été démontrée pour les complexes de $A-O-CH_3$ avec les alcools. Dans le cas du bi-anthryl $A-O-CH_2-O-A$, il a été montré que la structure vibronique compliquée apparaissant à l'origine du spectre d'excitation de la fluorescence appartenait à un seul conformère. De plus, alors que le spectre d'excitation de la fluorescence ne présente plus de structure à 150 cm^{-1} au-dessus de l'origine, la transition vibronique caractéristique du noyau anthracénique à 385 cm^{-1} a été détectée par cette technique. Cette observation montre qu'un processus photochimique rapide a eu lieu pour cette faible énergie en excès. Ces résultats montrent que cette technique peut être appliquée à la spectroscopie sélective d'isomères et à l'étude d'états supérieurs non fluorescents.

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SPECTRAL HOLE BURNING OF ANTHRACENE DERIVATIVES IN A SUPERSONIC JET

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The pump-probe technique of spectral hole burning in jet cooled molecules and complexes developed recently[1,2] has been applied successfully to some anthracene derivatives. The technique exploits the fact that, only a part of electronically excited molecules (by pumping pulse) in a jet relax fast back to the initial ground state. A depletion of the ground state population is seen as a dip in the fluorescence signal resulting from the excitation of the selected species by the delayed probe pulse.

The 9-methoxyanthracene ($A-O-CH_3$), its complexes with alcohols and the bis-9-anthryl ($A-O-CH_2-O-A$) were investigated. The existence of different isomers for complexes between $A-O-CH_3$ and alcohols has been proved. For $A-O-CH_2-O-A$ it was shown that the complicated vibronic pattern of the fluorescence excitation spectrum near origin, belongs only to the one conformeric species. While the vibrational pattern of the fluorescence excitation spectrum disappears at about 150 cm^{-1} above the origin, the characteristic vibrational transition of anthracene ring at about 385 cm^{-1} was detected by spectral hole burning. This observation shows that a fast photochemical process occurs already for this small excess of energy. These results show that this technique, besides being isomer selective, allows to investigate higher non fluorescing electronic states.

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EXCIPLEX FORMATION IN VAN DER WAALS COMPLEXES

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An excited molecular complex of definite stoichiometry, which is dissociated in the ground state, is described as an exciplex. The excited-state wavefunction of a 1:1 exciplex formed between two molecules M_1 and M_2 can be expressed by

$$\psi = a\Phi(M_1{}^*M_2) + b\Phi(M_1M_2{}^*) + c\Phi(M_1{}^-M_2{}^+) + d\Phi(M_1{}^+M_2{}^-).$$

In this paper, we present the observation of the following three types of exciplexes formed in supersonic jets. In all cases, the exciplex formation takes place upon excitation of a van der Waals (vdW) complex formed by M_1 and M_2 into its locally excited state.

(1) *Excimer formed by two identical molecules:* $|a|=|b|$ and $|c|=|d|$.

The excimer formation has been observed through excitation of the vdW dimer of fluorene $(C_{13}H_{10})$.[1] The initially excited vdW-dimer state exhibits congested spectral features arising from exciton-phonon coupling.

(2) *Exciplex formed by two similar molecules:* $|a|\approx|b|$ and $|c|\approx|d|$.

The exciplexes formed between $C_{13}H_{10}$ and $C_{13}D_{10}$[2] and between $C_{13}H_{10}$ and 1,2,4,5-tetrachlorobenzene[3] are of this type. It has been found that the efficiency of the exciplex formation is dependent on the energy gap in the S_1 state between M_1 and M_2, suggesting the importance of exciton resonance interaction in the stabilization of the exciplex state (i.e. $|a|, |b| \gg |c|, |d|$).

(3) *Exciplex formed between a molecule with a large electron affinity and a molecule with a low ionization potential:* $|a|, |b| \ll |c|, |d|$.

The charge-transfer complexes can be formed by exciting the vdW systems of 1-cyanonaphthalene M_1 with aliphatic amines M_2 (i.e. $|c| \gg |d|$).[4] The efficiency is markedly dependent both on the ionization potentials of the amines and on the excess vibrational energy in the initially excited vdW state $(M_1{}^*-M_2)$.

1. J. Phys. Chem., 95, 2364 (1991). 2. J. Phys. Chem., 95, 1195, (1991).
3. J. Phys. Chem., 94, 2636 (1990). 4. J. Phys. Chem., in press.

PROTON TUNNELING IN THE S_1 STATES OF TROPOLONE DERIVATIVES

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The fluorescence excitation (FE) spectra have been measured for jet-cooled 3-chlorotropolone (3CTR), 3-bromotropolone (3BTR), and 3-isopropyltropolone in the S_1-S_0 region to invesitigate the intramolecular hydrogen bonds. The 0_+^+ and 0_-^- transitions have been detected in the FE spectrum of 3CTR, suggesting that the double-minimum potential functions are almost symmetric in the S_0 and S_1 states of 3CTR as it is the case for tropolone (TRN). The tunneling doublet separations for 3CTR-h and 3CTR-d have been determined to be 23 and 3 cm^{-1}, respectively. In contrast, only one electronic origin band has been detected in the FE spectrum of 3BTR. This implies that the proton is localized in one well. On the other hand, the 0^+ and 0^- functions have been found to be partially localized in one well in 3IPT. These findings suggest that the steric repulsion between the O atom and the substituent deforms the molecular structure, and tends to localize the proton in 3BTR and 3IPT.
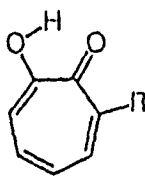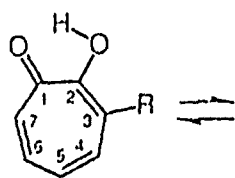
3CTR: R=Cl
3BTR: =Br
3IPT: =CH(CH$_3$)$_2$
TRN :   =H

Observation des Agregats Homogenes Doublement Charges de Para—Difluorobenzene

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Dans la plupart des observations d'agrégats van der Waals doublement chargés $(M_n^{++})^{1-3}$, la stabilité de ces espèces est expliquée par un modèle, proposé par Echt et al[4], basé sur l'approximation de la goutte liquide: ces agrégats sont stables si leur taille atteint une taille critique où la cohésion assurée par les forces de van der Waals est plus grande que la répulsion Coulombienne. Un exemple clair d'un tel système est le cas des agrégats doublement chargés de benzène[2] qui sont stables pour n>19

Après irradiation à 260nm, la double ionisation des agrégats de para difluorobenzene (PDFB) formés en jet supersonique $(PDFB_n^{++})$ est observée pour n≥3:

La comparaison de la stabilité des agrégats de benzène et de PDFB, calculée en utilisant des méthodes semi-empiriques[5], montre que:

-Dans $(PDFB^{++})_3$ il y a une barrière de 1.8 Kcal à la dissociation en $PDFB^+ + PDFB-PDFB^+$, donc l'espèce est métastable.

-Dans le benzène$_n^{++}$ cette barrière existe pour n≥5.

-Les différences observées dans la stabilité (n=19 pour benzène$_n^{++}$ et n=3 for $PDFB_n^{++}$) sont expliquées par les processus de formation.

1 T.D. Märk, Int. J. Mass Spectrom. Ion Proc. 79, 1 (1987) and references therein
2 M.Y. Hahn, K.E. Schriver, R.L. Whetten, J. Chem. Phys., 88, 4242 (1988)
3 W.R. Peifer, J. F. Garvey, J. Chem. Phys., 91, 1940 (1989)
4 O. Echt, D. Kreisle, E. Recknagel, Phys. Rev. A, 38, 3236 (1988)
5 P. Claverie, in Intermolecular Interactions (B. Pullman ed.) Wiley, New York (1978)

OBSERVATION OF VERY SMALL DOUBLY CHARGED HOMOGENEOUS
PARA-DIFLUOROBENZENE CLUSTERS

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In most experimental observations of doubly charged van der Waals clusters $(M_n^{++})^{1-3}$, the stability of these species was explained by a model, proposed by Echt et al[4], based on the liquid-drop approximation: the doubly charged cluster ions are stable if their size reaches a critical value where the cohesive forces of solvation overcome the coulombic repulsion: a clear example[2] of such a case is the benzene where the doubly charged cluster are stable for $n \geq 19$.

Double ionization of para difluorobenzene (PDFB) has been observed following irradiation of a supersonic cluster beam at 260 nm. $PDFB_n^{++}$ are observed for $n \geq 3$: the anomalously small critical size for stability cannot be explained by a simple liquid-drop model.

The comparison of the stability of these benzene and PDFB doubly charged, using semi empirical methods[5], shows that:

-In $PDFB^{++}$ there is a barrier of 1.8 Kcal to the dissociation in $PDFB^+ + PDFB - PDFB^+$, therefore this species is metastable.

-In $benzene^{++}$ such a barrier exists for $n \geq 5$.

The differences observed in stability (n=19 for $benzene^{++}$ and n=3 for $PDFB^{++}$) are explained by the formation process in the optical excitation.

1 T.D. Märk, Int. J. Mass Spectrom. Ion Proc. 79, 1 (1987) and references therein
2 M.Y. Hahn, K.E. Schriver, R.L. Whetten, J. Chem. Phys., 88, 4242 (1988)
3 W.R. Peifer, J. F. Garvey, J. Chem. Phys., 91, 1940 (1989)
4 O. Echt, D. Kreisle, E. Recknagel, Phys. Rev. A, 38, 3236 (1988)
5 P. Claverie, in Intermolecular Interactions (B. Pullman ed.) Wiley, New York (1978)

INTRACLUSTER ION-MOLECULE REACTIONS WITHIN THE PHOTOIONIZED VAN DER WAALS COMPLEXES

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Intracluster ion-molecule reactions of the photoionized van der Waals complexes of C_6H_5F with NH_3 and with H_2O have been investigated by means of two-color multiphoton ionization spectroscopy in combination with mass spectrometry. Two different intracluster reactions of C_6H_5F-NH_3, the substitution reaction yielding $C_6H_5NH_2^+$ and the dissociation yielding $C_6H_5F^+$, were induced by the selective photoionization of different isomers of the complexes. Ionization threshold spectra of the complexes and appearance energies of the reaction products were observed. Energetics of the reactions was discussed on the basis of the experimental results and of the calculated geometries of the isomers. It was concluded that the nucleophilic substitution reaction is responsible for the $C_6H_5NH_2^+$ production. Isomer dependent reactions occurring within the H_2O complexes were also presented and their energetics was discussed in relation to a barrier height to the substitution reaction.

References
(1) T. Maeyama and N. Mikami, *J. Phys. Chem.* 1991, in press.
(2) T. Maeyama and N. Mikami, *J, Phys. Chem.* 1990, *94*, 6973.
(3) T. Maeyama and N. Mikami, *J. Am. Chem. Soc.* 1988, *110*, 7238.

Structure et réactivité des agrégats paradifluorobenzene-eau dans une expansion supersonique

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Les agrégats para difluorobenzene-eau ($PDFB(H_2O)_n$) produits en jet supersonique ont été étudiés par ionisation à deux couleurs et deux photons et détectés par spectrométrie de masse à temps de vol.

Les spectres d'excitation de $PDFB(H_2O)_{n=1,4}$ ont été obtenus. Le spectre de $PDFB.H_2O$ présente des bandes attribuées à la fragmentation de $PDFB(H_2O)_2$. Cette fragmentation a lieu dans les agrégats ionisés. L'énergie d'ionisation de ces agrégats a été déterminée. La fragmentation de $PDFB.H_2O^+$ a été également étudiée. L'énergétique de ces dissociations en fonction de l'excès d'énergie a été déterminée. De ces résultats, il apparait que l'énergie de liaison de $PDFB...(H_2O)_n$ est environ de 1200 cm^{-1} à l'état fondamental.

L'étude des spectres de masse de ces agrégats révèle un autre fait important: les ions correspondant à du fluorophenol hydraté ont été détectés et sont dûs à une substitution nucléophile intra-agrégats d'un fluor de PDFB par un groupement -OH. Nos résultats montrent que cette reaction a lieu dans $PDFB(H_2O)_n^+$ ionisé et seulement quand $n \geq 3$

$$PDFB(H_2O)_{n \geq 3}^+ ---> Fphenol(H_2O)_{n \geq 1}^+ + H_2O + HF$$
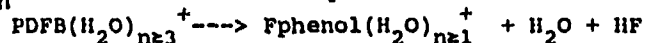
Comme proposé par B. Brutschy un mécanisme possible de réaction serait le suivant: après transfert d'un électron libre de l'oxygène de l'eau au système π de PDFB$^+$, une des premières étapes de la réaction de substitution dans l'agrégat consisterait en un transfert de proton aux agrégats d'eau avec formation d'un complexe σ intermédiaire suivi d'un réarrangement conduisant au fluorophenol avec perte d'eau et HF. Cette réaction intra-agrégat semble dépendre de l'affinité protonique de l'agrégat d'eau associé à PDFB.

STRUCTURE AND REACTIVITY OF PARADIFLUOROBENZENE--WATER CLUSTERS IN A SUPERSONIC EXPANSION

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para difluorobenzene-water clusters ($PDFB(H_2O)_n$) produced in a supersonic expansion have been studied via two-color two-photon ionization and detected by time of flight mass spectrometry.

Excitation spectra of $PDFB(H_2O)_n$ have been recorded for n=1-4. The $PDFB.H_2O$ spectrum shows bands which can be clearly attributed to a fragmentation of $PDFB(H_2O)_2$. This fragmentation has been shown to occur in the ionic cluster. The ionization energies of these clusters have been measured by two color experiments. In the same way we have studied the fragmentation of $PDFB.H_2O^+$. The energetic of these dissociations as a function of the excess of energy has been determined. From these data it appears that the binding energy of $PDFB...(H_2O)_n$ lies around 1200 cm^{-1} in the ground state.

The study of the mass spectra of these clusters reveals another very important feature: the ions corresponding to hydrated fluorophenol have been detected and are due to an intracluster nucleophilic substitution of one fluorine atom of PDFB by an -OH group. Our results show that this reaction occurs in the ionized $PDFB(H_2O)_n^+$ only when $n \geq 3$:

$$PDFB(H_2O)_{n \geq 3}^+ \dashrightarrow Fphenol(H_2O)_{n \geq 1}^+ + H_2O + HF$$
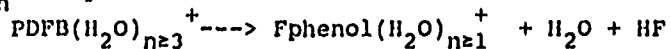
As proposed by B. Brutschy a possible mechanism of reaction would be the following: after an electron transfer from the lone pair orbital of oxygen of water to the π system of $PDFB^+$; one of the first steps of the substitution reaction in the cluster would consist in a proton transfer to the water clusters with formation of a σ intermediate complex followed by a rearrangement of this species leading to the fluorophenol with loss of water and HF. This intracluster reaction seems to depend on the proton affinity of the cluster of water associated to PDFB.

van der Waals Cluster and Excimer Formations in Jet-Cooled
1-Cyanonaphthalene and Methyl-Substituted 1-Cyanonaphthalenes

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and Yoshihisa Fujiwara

The fluorescence excitation and MPI TOF mass spectra of
1-cyanonaphthalene and methyl-substituted 1-cyanonaphthalenes
in supersonic expansion indicate the van der Waals dimer,
trimer and cluster (n > 3) formation. The excitation of the
main cluster bands shows the large Stokes shifted excimer
fluorescence (λmax 410-430 nm, $\tau \approx$ 140 ns), while only uv
resonance fluorescence was observed in the excitations of the
dimer and trimer bands, whose structures of dimer and trimer
were suggested to be coplanar with CN groups facing each other.
From vapor pressure dependence of the fluorescence intensity,
the size of cluster exhibiting the excimer fluorescence was
suggested to be n = 4 or 5 as the most plausible candidate.
Similar excimer fluorescence was observed in the excitation of
the ground-state dimer generated in the rigid glassy 3-methyl-
pentane solution at 77K and also of polycrystals of these
compounds. The x-ray crystallography of 1-cyano-2-methyl-
naphthalene indicates of partially overlapped π-electron
systems with a head-to-tail configuration in a single crystal.
Therefore, the fourth/fifth molecule may be overlaid on the
coplanar structure of the dimer/trimer so that the full or
partially overlap of the π-electron systems leads to the exci-
mer fluorescence.

PHOTOPHYSICS AND PHOTOCHEMICAL DYNAMICS OF
BENZENE AND ITS CHLORINATED DERIVATIVES

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Benzene molecules in a supersonic jet were photoionized using a
tunable(233-262 nm) pulsed dye laser, and the resonance-enhanced two-
photon ionization(RE2PI) processes of the S_1 state were investigated by
time-of-flight(TOF) mass-spectrometric technique. Without further
fragmentation of $C_6H_6^+$ ions under low power (<20 µJ/pulse) laser
irradiation high-resolution excitation spectra of the parent ion have
been measured for the $6^1 1^n$ progression(n=0,1,2,3). The relative
photoionization intensity determined from the excitation spectra and the
corresponding S_1 absorption spectra suddenly dropped at the onset of the
third channel band, $6^1 1^3$. For the wavelength region 241.5 – 243.1 nm,
covering the two specific vibronic bands, $6^1 1^3$ and 7^1, similar
experiments have been carried out under cold beam conditions. The
relative ion intensity for the 7^1 band was found to be much higher than
that of the $6^1 1^3$ band and to be even more than twice as large as that
of the $6^1 1^2$ band. Excitation of the rotationally resolved $6^1 1^3$ or
$6^1 1^2$ band under carefully controlled low laser powers has revealed the
fact that the relative intensity of the $6^1 1^3$ band(above 3rd channel) to
that of the $6^1 1^2$ band(below 3rd channel) decreases with decreasing the
excitation laser power, confirming the idea that the ionizing process is
competing with the nonradiative relaxation processes at the resonant
state. Two-color RE2PI excitation with the pumping(λ_1) and
electrically delayed probing(λ_2=272.0 nm) lasers has given population
decay rates of vibronic states longer than 20 ns. Excitation spectra of
the parent ion with scanning λ_1(241-248 nm) and the optically
delayed(2.8 ns and 8.0 ns) fixed wavelength of λ_2 have been observed.
Relative population yield at the delay time of 8.0 ns for the $6^1 1^3$
vibronic state agreed with the relative fluorescence yield for the same
excitation. The observed population decay rates of short life
components are also in good agreement with previously reported
fluorescence lifetimes.

We have applied the similar method to investigate photochemical
dynamics of chlorotoluene, which will be presented too.

Jet Spectroscopy of Benzyl and Benzyl-α-d$_2$

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Benzyl and benzyl-α-d$_2$ radicals are produced by the ArF laser (193 nm) photolysis of benzylchloride and benzylchloride-α-d$_2$, respectively, in a supersonic free jet. The spectroscopy of these radicals is studied by means of the LIF method. Measured LIF excitation spectra show vibrationally well resolved structure, but with unusual feature. The vibronic bands have been assigned from the SVL dispersed spectrum for each vibronic band excitation. The symmetries of pure electronic and vibronic levels in the D$_1$ state have been determined by transition band types derived from rotational analysis of high resolution LIF excitation spectra. The intensity anormaly of the vibronic bands in the excitation spectra is interpreted as the breakdown of the accidental forbiddeness, which characterized the D$_1$ - D$_0$ and D$_2$ - D$_0$ electronic transitions of benzyl.

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ELECTRONIC SPECTRA OF FLUOROBENZENE CATIONS
AS STUDIED BY MASS-SELECTED ION DIP SPECTROSCOPY

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The electronic spectra of benzene cation and its fluorine substituted cations were observed by mass-selected ion dip spectroscopy in a supersonic jet. Briefly, the cations were prepared by two-color resonant-enhanced multiphoton ionization (REMPI) of the jet-cooled neutral molecule via a particular vibronic level in the S_1 state (Fig.1). By selecting the vibronic level and the laser frequencies, the electronic ground state cation in a selected vibrational level can be produced. The state-selected cations are excited by another tunable laser light (ν_3) to an electronic excited state, where the parent cation dissociates directly or indirectly to fragmented species. The electronic transition was detected as a dip of the mass-selected ion signal of the parent cation. A similar spectrum can be obtained when the ion signal of the fragment is monitored.

We applied this spectroscopy (called mass-selected ion dip spectroscopy) to benzene cation, monofluorobenzene cation, o-, m-, and p-difluorobenzene cations and 1,3,5-trifluorobenzene cation in supersonic jets. All the observed spectra were assigned to the electronic transition from the ground state D_0 to the $\pi\pi$ excited state. The spectra of benzene cation and monofluorobenzene cation were broad and structureless, while difluorobenzene cations and trifluorobenzene cation showed well-resolved structures. The vibrational structures observed for difluorobenzenes and trifluorobenzene cations indicated an extensive vibronic coupling between the low-lying electronic excited states, suggesting an important role of the vibronic coupling in determining the emissive property of the cation. Based on the observed results, we discuss the emissive property in terms of the vibronic coupling among the low-lying electronic states.
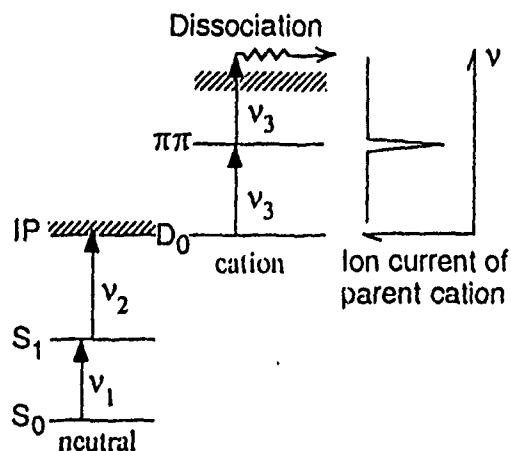
Fig.1 Schematic diagram showing the principal of the mass-selected ion dip spectroscopy.

Solvatation de $Hg_{1,2}$ par des agrégats de NH_3, $O(CH_3)_2$, et H_2O

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Le potentiel d'ionisation de nombreux agrégats métalliques diminue lorsque leur taille augmente. Cependant, dans certains cas, comme les agrégats d'argent, en solution dans l'eau, un comportement inverse est observé

Les potentiels d'ionisation de Hg and Hg_2 solvatés par NH_3 ou le dimethylether (DME), obtenus en jet supersonique ont été mesurés par ionisation à deux photons:

- pour les agrégats $Hg(NH_3)_n$, le potentiel d'ionisation décroit avec n; de plus, le potentiel d'ionisation de $Hg_2(NH_3)_n$ est supérieur à celui de $Hg(NH_3)_n$.

- A l'inverse, le dimère Hg_2 est plus stabilisé par le DME que par NH_3 et les énergies d'ionisation de $Hg(DME)_n$ sont plus grandes que celles de $Hg_2(DME)_n$.
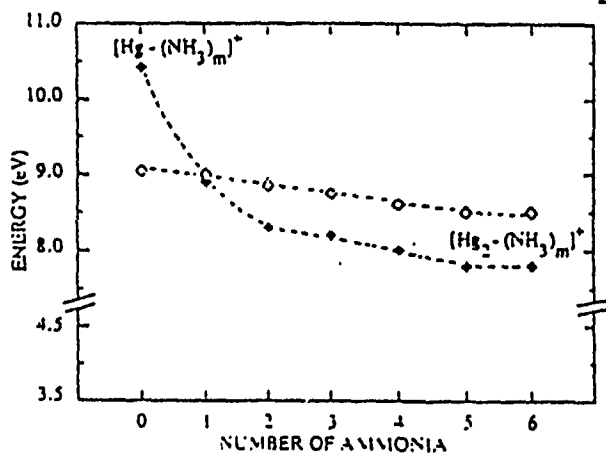
Variation du seuil d'ionisation en fonction du nombre de molécules de solvant: $Hg(NH_3)_n$ ◆ $Hg_2(NH_3)_n$ ◇

A partir de la spectroscopie des états intermédiaires et des mécanismes de fragmentation, on peut obtenir des informations sur la structure de ces agrégats.

Solvation of $Hg_{1,2}$ by clusters of NH_3, $O(CH_3)_2$, and H_2O

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The ionisation potentials of many metallic clusters decrease as the size increases. However, in some cases, solvated clusters, for example Ag_n, show an opposite behaviour.

Ionisation energies of Hg and Hg_2 solvated by NH_3, dimethylether (DME), obtained in a supersonic expansion have been measured through resonance enhanced two photon ionisation:

- for ammonia clusters of Hg, this energy decreases and is allways smaller than for $Hg_2(NH_3)_n$.

- at the opposite, the Hg_2 dimer has been shown to be more stabilized by DME than by NH_3 and the ionisation energies of $Hg(DME)_n$ are greater than those of $Hg_2(DME)_n$.
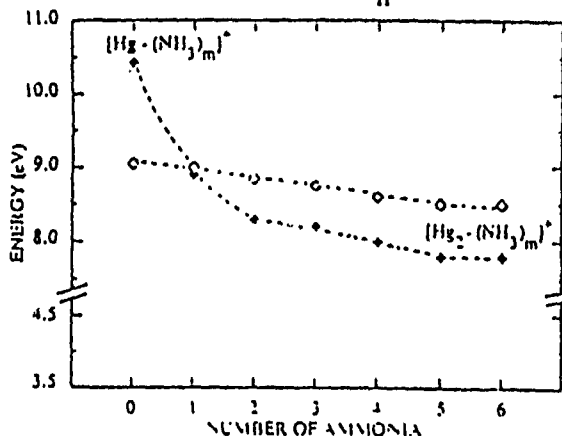
Variation of the ionisation energy threshold as a fonction of the number of solvent molecules: ◆ $Hg(NH_3)_n$ ◇ $Hg_2(NH_3)_n$

Structural informations on these clusters (with ammonia, DME or water) can be drawn from the spectroscopy of the excited states and the fragmentation patterns in the ionic status.

NO $A^2\Sigma^+$ CHEMILUMINESCENCE PRODUCED FROM THE REACTION OF

NO_2^* WITH TRIPLET STATE ORGANIC MOLECULES

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An NO_2/R mixture, where R is acetylene (Ac), methylacetylene
(MeAc), ethylacetylene (EtAc), phenylacetylene (PhAc), or benzene
(Ph), was excited via visible multiphoton absorption resulting in
$NO(A^2\Sigma^+)$ chemiluminescence. The relative efficiency of $NO(A^2\Sigma^+)$
production from the NO_2/R mixture was determined. The trend of
$NO(A^2\Sigma^+)$ production in order of decreasing efficiency is Ac >
MeAc > EtAc > PhAc > Ph. Based on the laser power dependence of
$NO(A^2\Sigma^+)$ chemiluminescence, the pressure-dependent variation, and
energetic considerations, a triplet mechanism for chemilumines-
cence is suggested.

$$NO_2 + h\nu \rightarrow NO_2^*$$
$$NO_2 \cdots R + nh\nu \rightarrow R^*(triplet) + NO_2$$
$$NO_2^* + R^*(triplet) \rightarrow NO(A^2\Sigma^+) + RO$$
$$NO(A^2\Sigma^+) \rightarrow NO + h\nu_f \ (\gamma\text{-band})$$
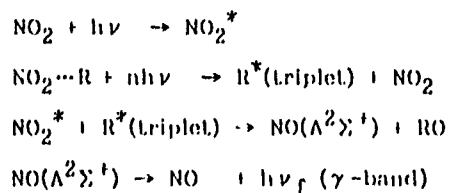
In order to reconcile the present investigation with the triplet
mechanism we concluded that a significant fraction of the excited
state NO_2 molecules (NO_2^k) must remain in a nonradiative colli-
sion-resistant excited state for a significant period of time.

Two-Photon Chemistry of Azoalkanes in the Laser Jet: Photochemical Transformations of 1,3-Cyclopentadiyl Triplet Diradicals by Triplet Benzophenone

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The triplet-sensitized nitrogen extrusion of azoalkane **1** was examined in the laser jet. Under lamp irradiation only bicyclopentane (**2**) was formed, whereas in the laser jet cyclopentene (**3**) and considerable amounts of dimers were found. The formation of the dimers is due to the high stationary concentration (micromolar) of the triplet diradical **T-4**.

The amount of cyclopentene (**3**) depended on the ratio of concentrations of benzophenone to azoalkane **1**, i.e. more rearrangement was observed at higher ratios. This suggested the existence of a second photochemical step in the pathway to cyclopentene (**3**).

The dependence of the lifetime of the triplet diyl **T-4** on the cylopentene yield could be demonstrated by using differently substituted azoalkanes. The longer the lifetime of the triplet diyl **T-4**, the higher the yield of cyclopentene.

Since the formation of cyclopentene (1,2-H-shift) in the photoinduced electron transfer reaction of azoalkanes **1** derives from the radical cation **5**, this species is presumably also involved in the benzophenone-sensitized photolysis of the laser jet experiment (Scheme 1). The first

Scheme 1

photolysis mode	rel. yields (%) of products		
	2	3	Dimers
Laser Jet	45	10	45
Lamp	>99	<1	0
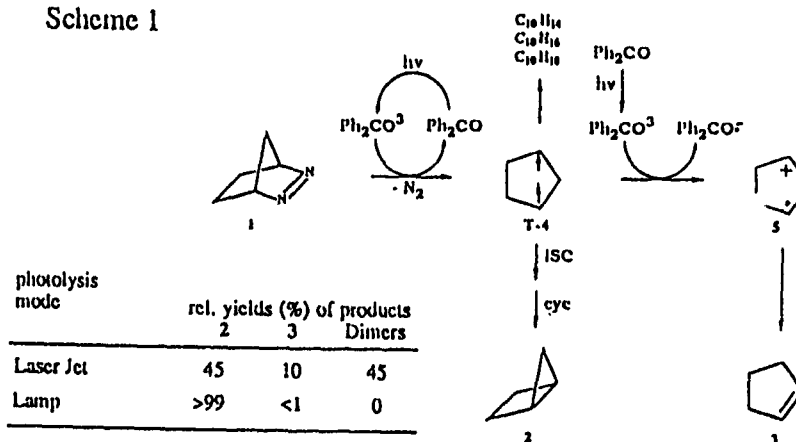
benzophenone triplet acts as sensitizer by energy transfer and the second as an electron acceptor by electron transfer; the overall photo-transformation thereby constitutes a two-photon process.

Acknowledgements

RELAXATION RADIATIVE ET REACTIVITE D'IONS MOLECULAIRES
DE LONGUE DUREE DE VIE

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Les durées de vie radiatives d'ions vibrationnellement excités ou dans des états électroniques métastables ont été déterminées dans un domaine de temps allant de la milliseconde à la seconde, en utilisant la technique de l'ion moniteur dans un spectromètre de FTICR à trois étages (1, 2). Les constantes de vitesse et les distributions en produit ont également été mesurées pour quelques réactions monitrices.

De nouveaux résultats sur $H_2O^+(X,v)$ avec CO_2, N_2O et CO comme gaz moniteurs seront présentés et comparés aux calculs théoriques.

Les mesures des déclins des ions diatomiques métastables $O_2^+(a^4\Pi_u,v')$ et $NO^+(a^3\Sigma^+,v')$ (2) seront réexaminées à la lumière de récents calculs ab initio.
La possibilité d'utiliser la dissociation induite par collision aussi bien que la réactivité, pour étudier les états électroniques métastables d'ions polyatomiques sera aussi discutée (3).

1   "Radiative relaxation of $NO^+(X, v=1-4)$"
    S. Fenistein, M. Heninger, R. Marx, G. Mauclaire and Y.N. Yang
    Chem. Phys. Letters, 172 (1990), 89

2   "Radiative Lifetimes and Reactivity of Metastable $NO^+(a^3\Sigma^+,v)$ and $O_2^+(a^4\Pi_u,v)$"
    R. Marx, Y.M. Yang, G. Mauclaire, M. Heninger and S. Fenistein
    accepté par J. Chem. Phys.

3   "On the Lifetime of Electronically Excited Acetone Molecular Ions"
    S. Fenistein, J. Futrell, R. Marx, G. Mauclaire and Y.M. Yang
    Chem. Phys. Letters, 179 (1991), 125

RADIATIVE RELAXATION AND REACTIVITY OF LONG LIVED EXCITED STATES OF MOLECULAR IONS

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Radiative lifetimes of vibrationally excited and metastable electronic states of ions, in the millisecond to second range, have been determined using the monitor ion technique in a specially deviced triple cell FTICR spectrometer [1,2]. Rate constants and product distributions for several monitor reactions have also been measured.

New results on $H_2O^+(X,v)$ with CO_2, N_2O and CO as monitors will be presented and compared to theoretical calculations.

The measured decay rates of diatomic metastable ions $O_2^+(a^4\Pi_u,v')$ and $NO^+(a^3\Sigma^+,v')$ [2] will be reexaminated in the light of recent ab initio calculations.

The possibility to use CID as well as reactivity to study metastable electronic states of polyatomic ions will also be discussed [3].

1   "Radiative relaxation of $NO^+(X, v=1-4)$"
    S. Fenistein, M. Heninger, R. Marx, G. Mauclaire and Y.M. Yang
    Chem. Phys. Letters, 172 (1990), 89

2   "Radiative Lifetimes and Reactivity of Metastable $NO^+(a^3\Sigma^+,v)$ and $O_2^+(a^4\Pi_u,v)$"
    R. Marx, Y.M. Yang, G. Mauclaire, M. Heninger and S. Fenistein
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3   "On the Lifetime of Electronically Excited Acetone Molecular Ions"
    S. Fenistein, J. Futrell, M. Heninger, R. Marx , G. Mauclaire and Y.M. Yang
    Chem. Phys. Letters, 179 (1991), 125

Comment arriver à la photo-sélectivité des états finaux dans la réaction Ca*+HX->CaX*(A,B)+H, ou l'utilisation des complexes de van der Waals en photochimie

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Le système Ca+HCl est l'un des rares exemples de réaction simple en phase gazeuse où une sélectivité orbitale a pu être mise en évidence. Nous avons étudié les réactions d'atomes de calcium excités avec des molécules HX (X=Cl,Br,F) par l'excitation électonique des complexes Ca-HX afférents. Les spectres d'action qui explorent la surface réactive font apparaître plusieurs configurations électroniques attribuées aux symétries Σ et Π, à l'intérieur desquelles une importante structure vibrationnelle a été analysée en termes de modes locaux de ce complexe. Ceci permet de caractériser la surface de potentiel dans sa vallée d'entrée.

Cette approche à la réactivité permet aussi d'accéder directement à la vallée de sortie par l'analyse de la distribution de l'énergie dans les produits, via la dispersion de la chimiluminescence et l'utilisation d'un laser sonde. La molécule CaX électroniquement excitée se retrouve portée sur un ensemble de niveaux vibrationnels qui vont jusqu'au seuil énergétique de réaction. Les deux états electroniques $A^2\Pi$ et $B^2\Sigma'$ du produit CaX sont accessibles. l'excitation des différentes configurations électroniques du complexe Ca-HBr présentent de grandes variations quant au branchement vers les états A et B du produit selon la nature de la configuration excitée. Celles que nous avons attribuées à la symétrie Π amènent davantage de population à l'état A tandis que la symétrie Σ conduit plutôt vers B. Ceci est un exemple frappant de la sélectivité réalisable dans une réaction photochimique induite dans un complexe de van der Waals.

Final state selectivity as produced in the Ca*+HX->CaX*(A,B)+H reactions through the van der Waals complex excitation

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The Ca+HCl system has been shown in the past as a model for orbital selectivity in simple gas phase chemical reactions. We have studied the chemical reactions of excited state calcium with HX molecules (X=Cl,Br,F) as produced within the electronically excited states of the Ca-HX complexes. The action spectra scanning the reaction potential energy surface reveal several electronic configurations assigned to Σ and Π symmetries and, within these configurations, extensive vibrational structure, analysed in terms of the local modes of the complex. This allows for the characterisation of the entrance valley of the reaction, through the bending and stretching motions of HX with respect to the Ca atom. If is also observed that the Ca-HX bending has a strong influence upon the reactivity.

This approach to reactivity also yields a direct access to the exit valley of the surface through the analysis of the products internal energy distribution which has been probed by dispersion of the chemiluminescence and also by a second laser. The vibrational energy content of the electronically excited CaX product is high and goes up to the energetical threshold. Two electronic states $A^2\Pi$ and $B^2\Sigma^*$ are accessible by the reaction. The excitation of the various electronic configurations of the Ca-HBr complex shows large variations in the branching ratio to the A or B state of the product depending upon the nature of the configuration. Configurations that we have assigned to the Π symmetry, preferentially populate the A state, and conversely for the Σ symmetry, the B state is preferred. This is a striking example of state selectivity as produced in a photochemical reaction

O_2 SCHUMANN-RUNGE ABSORPTION BANDS AND CONTINUUM AT 200-320 NM, AND O_3 PHOTODISSOCIATION STUDIES

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It has been proposed that photodissociation of highly vibrationally-excited O_2 in the $B^3\Sigma_u^- - X^3\Sigma_g^-$ Schumann-Runge bands is a source of ozone in the upper stratosphere. Simultaneously, this O_2(vib) population could be excited into the continua of the O_2(B) and $1^3\Pi_u$ states, providing additional ozone. Laboratory measurements indicate that both discrete and continuous processes are operative. Calculations of the Schumann-Runge continuum cross sections have now been carried out for $v'' = 12$-20, spanning the 200-320 nm wavelength range. The maximum cross sections are in the 1-2×10^{-18} cm^2 range, with the O_2(B) state contributing 2-3 orders of magnitude greater absorption than the $1^3\Pi_u$ state. For $v'' = 12$, it is shown that the Schumann-Runge band and continuum cross sections merge smoothly at 250 nm.

In laboratory experiments on ozone photodissociation at 248 nm, the principal absorption in product O_2(vib) involves the Schumann-Runge 2-7 band and Schumann-Runge continuum absorption from vibrational levels at $v'' = 12$ or higher. Although the cross section for line absorption is much higher than that for the continuum, it is shown that as a result of a variety of processes and mechanisms, photodissociation yields in the bands and the continuum are comparable in magnitude, thereby providing consistency with the laboratory observations. For linear absorption systems, such as the terrestrial atmosphere, high v'' absorption in the Schumann-Runge bands should be substantially more important than continuum absorption.

INTENSITY CURVES OF THE PH($b^1\Sigma^+ v'=0 \to X^3\Sigma^- v''=0$) EMISSION BAND

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Line strengths in emission spectra of electronically
excited diatomic radicals have been the subject of many
theoretical studies and experimental measurements based on
lifetime determinations. On the other hand intensity
measurements are lacking due to the experimental difficulties
in obtaining reliable data to be compared with the behaviors
predicted by the existing models. Spin forbidden transitions
such as PH($b^1\Sigma^+ \to X^3\Sigma^-$)[1] have an intensity dependence on
mixed transitions moments leading to longer lifetimes in
pulsed experiments and lower emission signals in equilibrium
conditions. Observations of the relative intensity of the
resolved rotational branches in the above transitions as
obtained in an Ar afterglow apparatus is reported as a
function of the rotational numbers N and J. Experimental
conditions, such as microwave intensity and observation
geometry, are very critical in order to obtain workable data
at high rotational numbers after temperature compensation.
Line strengths are an increasing function of the rotational
excitation as expected[2], but the detailed behavior of the
curves reveals peculiarities that deserve major refinements
of the existing literature expressions. Crossing of F_1 and F_3
terms, due to increasing rotation, leads to an exchange of
the mixing coefficients values and the active transition
moments are predominantly characterized by the parallel
component.

(1) G. Di Stefano, M. Lenzi, A. Margani and C. Nguyen Xuan,
      J. Chem Phys. 68 3832 (1977).
(2) J. G. Watson, Can. J. of Physics 46 1637 (1968).

OVERTONE SPECTROSCOPY AND OVERTONE INTENSITIES

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The gas phase overtone spectra of propane, acetone, and dimethyl ether have been measured by near infrared spectroscopy and intracavity dye laser photoacoustic spectroscopy in the region $\Delta v_{CH} = 2 - 7$. Overtone intensities are calculated with a harmonically coupled, anharmonic oscillator local mode model to obtain the vibrational wavefunctions, and *ab initio* calculations at the SCF level to obtain the dipole moment functions. The calculations, which have no adjustable parameters, can account for the spectral intensities with regard to their magnitude, their fall-off with increasing v, and their relative magnitudes within a given vibrational manifold and between molecules. The calculations are extended to include electron correlation for overtone intensities in hydrogen peroxide. The results are used to explain the rotationally resolved overtone spectra of hydrogen peroxide in the region $\Delta v_{OH} = 2 - 4$.

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EFFETS ISOTOPIQUES DANS LA DISSOCIATION DES IONS DE DIMETHYL-ETHER PARTIELLEMENT DEUTERIE CH3OCD3^{+}

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On a étudié la dissociation des ions de diméthyl-éther
partiellement deutérié $CH_3OCD_3^+$ dans un domaine d'énergie de
photons variant de 10,03 eV (potentiel d'ionisation) à 16 eV.
Les ions sont produits par photoionisation avec le rayonnement
synchrotron et sélectionnés en énergie interne par une méthode
de coïncidences entre photoélectrons de seuil et photoions.
Jusqu'à 13 eV, les fragments principaux correspondent à
une perte de H ou de D par simple rupture de liaison.
Néanmoins, le décalage des seuils de perte de H et de D
indique qu'il existe une faible énergie d'activation pour la
réaction inverse, qui vient des énergies de point zéro des
modes de déformation C-X. On en déduit une nouvelle valeur de
161,1 kcal/mole pour $DH_f°(CH_3OCH_2^+)$. Les produits CH_2OH^+ et
CD_2OD^+ apparaissent à 11,75 eV, 0,95 eV au-dessus du seuil
thermodynamique, et leur abondance reste faible dans tout le
domaine d'énergie étudié. On n'observe pas de mélange des
atomes H et D. Le calcul du diagramme de fragmentation par la
théorie RRKM montre que les fragments CX_2OX^+ (X= H ou D) sont
produits avec une barrière de 1,35 eV. On observe un effet
isotopique dans ces deux canaux de dissociation, qui est bien
expliqué par les différences d'énergie de point zéro et de
densités d'états calculées par la théorie RRKM. L'analyse
montre que, dans le domaine d'énergie étudié, l'effet tunnel
n'est pas un processus important dans la formation de CH_2OH^+.
Aux énergies de photon de 15 et 16 eV, les fragments
principaux sont XCO^+ et CX_3^+ (X= H ou D). On observe un
mélange non statistique des atomes H et D dans CX_3^+.
Les effets isotopiques observés permettent ainsi
d'obtenir des informations sur les mécanismes de dissociation
en fonction de l'énergie interne des ions parents.

ISOTOPE EFFECTS IN THE DISSOCIATION OF PARTIALLY DEUTERATED DIMETHYL ETHER, $CH_3OCD_3^+$ IONS

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The dissociation of partially deuterated dimethyl ether ions ($CH_3OCD_3^+$) is studied from the ionization potential of 10.03 eV to 16 eV photon energy. Ions are produced by photoionization with synchrotron radiation and selected in internal energy by threshold photoelectron-photoion coincidences.

Up to 13 eV the major fragments correspond to an H or D atom loss by a simple bond cleavage. However, the shift in the H and D loss onsets indicates that there is a small reverse activation energy as a result of the zero point energies in the C-X deformation modes. A new value for the $DH_f°(CH_3OCH_2^+)$ of 161.1 kcal/mol is derived. The CH_2OH^+ and CD_2OD^+ products appear at 11.75 eV, 0.95 eV above their thermochemical onset, and remain minor fragments in the whole energy range studied. No scrambling of the H and D atoms is observed. Modeling of the breakdown graph by RRKM theory indicates that the CX_2OX^+ (X= H or D) fragments are produced via a 1.35 eV barrier. We observe an isotope effect in both these dissociation channels which is well explained by zero point energy, and density of states differences in the framework of the RRKM calculations. The analysis shows that in the energy range investigated, tunneling is not an important process in the CH_2OH^+ formation. At 15 and 16 eV photon energy, the main fragments are XCO^+ and CX_3^+ (X =H or D). Non statistical scrambling of the hydrogen atoms in CX_3^+ is observed.

In view of all these isotope effects, the dissociation mechanisms are discussed as a function of the internal energy of parent ions.

Dynamiques de dissociation du Fer Carbonyle-Nitrosyle excité en couche interne.

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Depuis peu, l'excitation en couche interne de molécules polyatomiques est un sujet passionnant en ce qui concerne la chimie sélectivité [1-3]. En effet, l'idée de rompre sélectivement une liaison chimique repose sur les localisations du trou interne et des orbitales moléculaires antiliantes de certaines liaisons chimiques. L'utilisation du rayonnement synchrotron monochromatisé pour exciter sélectivement un atome en couche interne s'impose car c'est la seule source de photon accordable susceptible de fournir des photons dans cette gamme d'énergie.

(I) Dynamique de relaxation

Nous avons étudié $Fe(CO)_2(NO)_2$ en excitant sélectivement le ligand carbonyle ou le ligand nitrosyle en couche K du carbone ou de l'azote. Malgré la très forte localisation des trous formés, les processus de fragmentation semblent identiques : Les différentes voies d'ionisation multiple sont les mêmes après excitation en couche K du carbone ou K de l'azote. Nous interprétons ces résultats surprenant comme étant dû à une très rapide reconversion de l'énergie comparée à la dynamique de fragmentation.

(II) Dynamique de fragmentation

L'analyse détaillée de la corrélation des ions formés en coïncidence lors de la double ionisation dissociative permet de tirer des informations sur la séquentialité des phénomènes de fragmentation[4]. Nous avons pû en particulier montrer que le modèle de l'évaporation successive des ligands s'adapte particulièrement bien au Fer Carbonyle-Nitrosyle doublement ionisé.

1: J. Murakani, M. C. Nelson, S. Anderson, D.M. Hanson J. Chem. Phys. 85,5755,(1986)

2: R. Murphy, W. Eberhardt J. Chem. Phys. 89,4054,(1988)

3: W. Habernichl, H. Baiter, K. Muller-Delsihel, E. Schlag, Physica scripta 41,814 (1990)

4: J. II. Eland, Mol. Phys. 61,725 (1987)

Dissociation dynamics of Core Excited Iron Carbonyl-Nitrosyl

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Special attention has been paid recently to core excitation of polyatomic molecule in the quest for selective photochemistry[1-3]. Indeed taking advantage of core hole localization as well as localization of antibonding orbitals along a specific chemical bond, the simple idea merged up to expect a selective fragmentation following inner-shell excitation using monochromatized synchrotron radiation.

(I) Dynamics of relaxation

We have studied $Fe(CO)_2(NO)_2$ by exciting selectively the carbonyl ligand or the nitrosyl ligand from K shell of N and C. Despite the very localized character of the created holes, fragmentation pattern doesn't exibit any site selectivity : multiple ionization channels do not depend at all on wether the carbon or nitrogen has been excited. We interpret this surprising result as due to a very fast internal energy conversion as compared to fragmentation dynamics.

(II) Dynamics of fragmentation

Ions issued from dissociative double ionization are detected in coincidence. A detailed correlation analysis of their kinetic momemtum reveals information about fragmentation sequentiality[4]. We were able to show that the ligand succesiv evaporation model is particularly well adapted to the double ionized Iron carbonyl nitrosyl dissociation.

1: J. Murakani, M. C. Nelson, S. Anderson, D.M. Hanson J. Chem. Phys. 85,5755,(1986)

2: R. Murphy, W. Eberhardt J. Chem. Phys. 89,4054,(1988)

3: W. Habernicht, H. Baiter, K. Muller-Delslhel, E. Schlag, Physica scripta 41,814 (1990)

4: J. H. Eland, Mol. Phys. 61,725 (1987)

PHOTODISSOCIATION DE LA S-TETRAZINE DANS L'ETAT (S₁) : UN PROCESSUS REGI PAR LA GEOMETRIE DE L'ETAT DE TRANSITION

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La photodissociation d'une molécule polyatomique est un processus photochimique de base, à l'origine de nombreux travaux. Nous voulons ici nous pencher sur le cas de la s-tétrazine ($C_2N_4H_2$) qui est connue depuis le début du siècle pour se décomposer en trois fragments : $2HCN + N_2$. Plusieurs études ont eu pour objet le mécanisme lui-même[1-3], ainsi que la détermination de certaines distributions d'énergie vibrationnelle[4] (N_2, v_1 et v_3 de HCN).

Nous nous proposons ici de reconsidérer ce problème grâce à une technique déjà utilisée pour l'étude de la photoionisation de l'iode atomique produit par dissociation laser de I_2,[5] et qui consiste à utiliser un laser continu Ar+ pour exciter l'état (S_1), et à sonder les fragments par Spectroscopy de PhotoElectrons (SPE) à l'aide du rayonnement synchrotron. En enregistrant des SPE à une énergie de photons de 23 eV, nous avons observé une dissociation quasi-complète avec une puissance laser de 3 W, et, à l'échelle de temps de notre expérience (~100 ns), nous n'avons détecté aucun autre fragment que N_2 et HCN, ce qui penche en faveur du mécanisme de triple dissociation concertée proposé par Zhao *et al.*[2]. De plus, nous trouvons que 5.4 % des fragments N_2 sont dans l'état v=1, et qu'au moins 26 % de chaque fragment HCN est vibrationnellement excité, surtout dans le mode de pliage (n=1 à 6), et probablement très peu dans le mode d'élongation C-N (n=1). Ces résultats ne s'expliquent pas dans un modèle statistique de redistribution de l'énergie disponible (109.2 kcal/mol), mais sont, en revanche, parfaitement consistants avec le modèle de la géométrie de l'état de transition calculée par Scheiner *et al.*[3]. De plus, ces faibles distributions d'énergie vibrationnelle laissent à penser qu'une forte excitation rotationnelle est présente dans les fragments, en particulier pour HCN.

1. J.H. Glownia and S.J. Riley, Chem. Phys. Lett. 71, 429 (1980).

2. X. Zhao, W.B. Miller, E.J. Hintsa and Y.T. Lee, J. AM. Chem. Soc. 108, 8160 (1989).

3. A.C. Scheiner, G.E. Scuseria and H.F. Schaefer III, J. Am. Chem. Soc, 108, 8160 (1986).

4. D. Coulter, D. Dows, H. Reisler and G. Wittig, Chem. Phys. 32, 429 (1978).

5. L. Nahon, J. Tremblay, M. Larzillière, L. Duffy and P. Morin, Nucl. Instr. Meth. B 47, 72 (1990).

PHOTODISSOCIATION OF S-TETRAZINE IN THE (S$_1$) STATE : A PROCESS GOVERNED BY THE GEOMETRY OF THE TRANSITION STATE

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Photodissociation of a polyatomic molecule is a basic photochemical process, which study has motivated numerous works. We wish to focus here on the case of s-tetrazine ($C_2N_4H_2$) which is known since the begining of the century to decompose into three fragments : $2HCN + N_2$. Several studies have dealt with the mechanism of the dissociation itself[1-3], as well as the determination of some vibrational distributions of the fragments[4] (N_2, v_1 and v_3 of HCN).

We propose here to reconsider this problem, by means of a technique already used to investigate the photoionization of atomic iodine produced by the laser dissociation of I_2,[5] which consists to use a cw Ar+ laser to excite s-terazine in the (S$_1$) state, and to probe the fragments by PhotoElectron Spectroscopy (PES) with the synchrotron radiation. By recording PES at 23 eV photon energy, we have oberserved a nearly-complete photodissociation with a laser power of 3 W, and on the time scale of our experiment (~100 ns), we do not have detected any other fragments than N_2 and HCN, which is in favor of the triple concerted dissociation mechanism proposed by Zhao et al.[2]. Moreover, we find that 5.4 % of the nascent N_2 fragments depart with v=1, and at least 26 % of each HCN fragments are vibrationally excited, mainly in the bending mode (n=1 to 6), and probably to a very small extent in the C-N streching mode (n=1). These data cannot be explained by a statistical model of redistribution of the available energy (109.2 kcal/mol), but are fully consistent with the equilibrium geometry model of the transition state calculated by Scheiner et al.[3]. Moreover, these low vibrational energy distributions lead to the fact that a high rotational energy should be carried by the fragments, espocially for HCN.

1. J.H. Glownia and S.J. Riley, Chem. Phys. Lett. 71, 429 (1980)

2. X. Zhao, W.B. Miller , E.J. Hintsa and Y.T. Lee, J. AM. Chem. Soc. 108, 8160 (1989).

3. A.C. Scheiner, G.E. Scuseria and H.F. Schaefer III, J. Am. Chem. Soc, 108, 8160 (1986).

4. D. Coulter, D. Dows, H. Reisler and G. Wittig, Chem. Phys. 32, 429 (1978).

5. L. Nahon, J. Tremblay, M. Larzillière, L. Dully and P. Morin, Nucl. Instr. Meth. B 47, 72 (1990).

MICROSOLVATATION DE LA MOLECULE DE BENZENE PAR DES ATOMES DE GAZ RARE
STRUCTURE DES COMPLEXES BENZENE-Ar$_n$.

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De nouveaux résultats sur la microsolvatation de la molécule de benzène (Bz) par de atomes de gaz rare (Ar, Kr) ont été obtenus par la technique de l'ionisation résonnante à deux photons deux couleurs (IR2P-2C) couplée à une expansion supersonique et à un spectromètre de masse à temps de vol /1/.

La mesure des déplacements spectraux par complexation (transition $S_1 \leftarrow S_0$ 6_0^1 du Bz) et des spectres d'efficacité d'ionisation ont permis de montrer qu'il existe dans les complexes Bz-Ar$_n$ (1<n<7) deux classes distinctes d'isomères, responsables des deux séries de bandes (notées A et B) dans le spectre IR2P des complexes. Dans les isomères A les atomes d'argon sont distribués des deux côtés de la molécule de benzène alors que dans les isomères B tous les atomes sont situés du même côté /1/.

Une caractérisation des agrégats portant sur l'existence d'isomères, leur structure géométrique, et leurs propriétés thermodynamiques est présentée, notamment pour le complexe Bz-Ar$_2$. L'attribution des bandes A et B est réalisée d'après l'analyse de leur contour rotationnel (résolution $\simeq 0.09$) et avec l'aide d'un calcul de structure (potentiels atome-atome) et de simulations Monte Carlo /2/. Les contours rotationnels des espèces 1:2 sont très différents. Le contour de la bande A, caractéristique d'une toupie symétrique allongée, présente une structure en sous-bandes K, tandis que le contour de la bande B, celui d'une toupie assymétrique, possède une large branche Q non-structurée et des branches R et P de faible intensité. Le modèle des potentiels atome-atome suggère une symétrie C$_s$ pour l'isomère B dissymétrique formé d'un atome Ar au dessus du cycle benzénique et d'un second en position péripherique dans l'espace entre deux H voisins.

Les simulations Monte Carlo montrent l'existence d'au moins deux configurations stables pour les complexes Bz-Rg$_n$ (n>1) (Rg - Ar, Kr) à la température du jet supersonique. Leur stabilité et leurs propriétés thermodynamiques sont discutées.
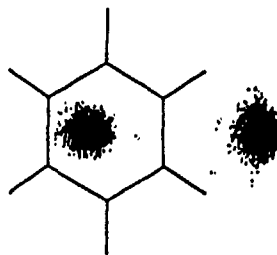
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/2/ M. Schmidt, M. Mons and J. Le Calvé, P. Millié and C. Cossart-Magos, Chem. Phys. Lett. in press.

Fig. : Simulation Monte Carlo à 5 K du complexe Bz-Ar$_2$.

LA REACTION PHOTOCHIMIQUE Cs(7P)+H$_2$ → CsH+H.

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La réaction a été étudiée en faisceaux croisés, avec un faisceau supersonique d'hydrogène, un faisceau effusif de cesium et deux faisceaux laser continus, monomodes et accordables. Le premier est utilisé pour compenser l'endoénergéticité de la réaction (≈2,7 eV) en excitant les atomes de cesium sur une transition de résonance $6S_{1/2}$ → $7P_{1/2,3/2}$ et le second pour sonder l'état des produits de réaction par la technique de fluorescence induite par laser (F.I.L.). L'analyse à haute résolution des profils de fluorescence de CsH conduit à la mesure des sections efficaces totales et différentielles pour tous les états rotationnels peuplés par la réaction.

-La mesure des sections efficaces totales donne: $\sigma(7P_{1/2})$ = 4.2 10^{-16} cm^2 et $\sigma(7P_{3/2})$ ≈ 1 10^{-16} cm^2. Elle permet de comparer l'efficacité du processus photochimique (Cs dans l'état 7P) à celle des processus inélastiques dus aux autres états excités (Cs dans l'état 6S, 6P, 5D et 7S). De plus, elle montre l'existence d'un "effet de structure fine", interprété dans le cadre d'un mécanisme de harponnage. Ce résultat est confirmé par l'existence d'un "effet de structure hyperfine" montrant que la section efficace varie lorsque l'on tourne la polarisation du faisceau laser qui excite les atomes de cesium.

-Les sections efficaces différentielles sont mesurées directement dans le centre des masses (technique Doppler). La forme des profils de fluorescence enregistrés quand le faisceau laser d'analyse est parallèle à l'axe de collision montre un fort piquage vers l'avant des produits CsH, le long de la vitesse initiale du cesium; l'angle de diffusion diminue avec l'énergie de collision mais est indépendant de la rotation de CsH. Ces résultats sont en accord avec des calculs semi-classiques et des calculs quantiques.

-Des expériences d'absorption saturée peuvent être menées sur ce système, la détection des produits se faisant en régime de saturation cohérente. En renvoyant le faisceau laser d'analyse sur lui-même au volume de collision, on observe un creux au sommet du profil de fluorescence; il correspond aux molécules qui diffusent dans le plan de collision. L'application de cette technique pourrait conduire à la sélection de produits de réaction dans un plan ou selon une direction.

THE $Cs(7P)+H_2 \rightarrow$ CsH+H PHOTOCHEMICAL REACTION.

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The title reaction is studied with a crossed-beam apparatus involving a supersonic beam of hydrogen, an effusive beam of cesium and two C.W. narrow-band tunable dye laser beams. The first one is used to compensate the endoergiticity of the reaction ($\approx$ 2.7 eV) by exciting Cs atoms on a $6S_{1/2}$ - $7P_{1/2,3/2}$ resonant transition and the second one to probe CsH product states through the laser-induced fluorescence technique (L.I.F.). High resolution analyses of CsH fluorescence profiles lead to the measurement of total and differential reactive cross sections for all rotational states populated by the reaction.

-Total reactive cross sections are: $\sigma(7P_{1/2}) = 4.2 \ 10^{-16}$ cm^2 and $\sigma(7P_{3/2}) = 1 \ 10^{-16}$ cm^2. They give a clear indication of the efficiency of the photochemical reactive process (Cs atoms in the 7P state) with respect to the inelastic processes associated with other excited states (Cs atoms in the 6S, 6P, 5D and 7S states). Furthermore, they show the existence of a "fine structure effect" which is interpreted in the frame of a harpooning mechanism. This result is confirmed by observing a "hyperfine structure effect", where the reactive cross section is a function of the polarization of the laser beam which excites Cs atoms.

-The differential cross sections are measured directly in the center of mass, by use of the Doppler technique. The shape of fluorescence profiles recorded when the analysis laser beam is parallel to the collision axis reveals a pronouced "forward" peaking of CsH products along the direction of incoming Cs atoms; it narrows with reagent collision energy but is independent of product rotation. These results are in agreement with semi-classical and quantal calculations.

-Saturated-absorption experiments can be conducted on this system, the L.I.F. detection being performed in a coherent saturation regime. By sending the analysis laser beam back to the collision volume (counterpropagating waves), one observes a narrow dip at the top of fluorescence profiles; under our experimental conditions, it corresponds to CsH products which scatter in the collision plane. Application of this technique could lead to the selection of products which scatter in a given plane or in a given direction.

LA PHOTOCHIMIE DU *cis*-PENTADIÈNE-1,3 EN PHASE GAZEUSE À 184,9 ET 147,0 nm.[1]

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La photochimie du *cis*-pentadiène-1,3 a été étudiée à 184,9 et à 147,0 nm en phase
gazeuse. Les produits majeurs observés à 184,9 nm, outre le *trans*-pentadiène-1,3, sont
le cyclopentadiène-1,3 et divers radicaux révélés par l'addition d'iodure d'hydrogène. Le
cyclopentadiène est formé très probablement via l'élimination successive de deux atomes
d'hydrogène avec isomérisation concurrente du radical pentadiènyle vers la structure cy-
clopèntenyle: Φ_0(cyclo-C_5H_6) $\simeq$ 0.25.

L'élimination du radical méthyle ($\Phi_0 \simeq 0.50$) est également importante. Il y a for-
mation concomittante des radicaux $CH_2=CHCH={}^\bullet CH^\bullet$ et dans une moindre mesure
des radicaux $CH_2=C=C^{\text{H}\bullet}CH_2^\bullet$. On n'a cependant pas pu établir si ce dernier radical
provient de l'isomérisation du précédent, ou s'il provient d'une molécule de pentadiène-
1,2** résultant de l'isomérisation de la molécule photoexcitée. On a pu enfin observer
une isomérisation conduisant vers la formation de pentadiène-1,4 ($\Phi_0 \simeq 0.03_5 \pm 0.01_5$).

À 147,0 nm, on retrouve les mêmes caractéristiques, avec une fragmentation plus poussée
des intermédiaires. L'énergie supérieure disponible à cette longueur d'onde explique
cette observation. Globalement, la photofragmentation du *cis*-pentadiène-1,3 s'apparente
beaucoup plus à la photochimie des alcènes acycliques et assez peu à celle du butadiène-
1,3 qui passe surtout par l'isomérisation vers la structure butadiène-1,2.[2]

[1] G.J. Collin, H. Deslauriers et G.R. De Maré, *Can. J. Chem.*, sous presse.

[2] G.J. Collin, H. Deslauriers, G.R. De Maré et R.A. Poirier, *J. Phys. Chem.*, **94** *(1990)* 134.

PHOTOCHEMISTRY OF GASEOUS cis-1,3-PENTADIENE AT 184.9 AND 147.0 nm.[1]

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The photochemistry of gaseous cis-1,3-pentadiene has been studied at 184.9 and 147.0 nm. Trans-1,3-pentadiene and 1,3-cyclopentadiene are the main products observed at 184.9 nm. The formation of radicals also occurs as is shown through the use of DI as a radical scavenger. Cyclopentadiene is the likely product of successive eliminations of two hydrogen atoms from the photoexcited molecule after rearrangement of the pentadienyl radical to the cyclopentenyl structure: $\Phi_0(\text{cyclo-}C_5H_6) \simeq 0.25$.

Elimination of a methyl radical ($\Phi_0 \simeq 0.50$) also occurs yielding $CH_2=CHCH=^\bullet CH^\bullet$ and, to a lesser extent $CH_2=C=CH^\bullet CH_2^\bullet$ radicals. However, it is not possible to identify properly the mechanism of the formation of the latter radical. It may be the result of the isomerisation of either the photoexcited molecules or the 1,3-butadien-1-yl radicals. A small amount of 1,4-pentadiene formation is also observed $\Phi_0(\text{cyclo-}C_5H_6) \simeq 0.25$.

At 147.0 nm, the same caracteristics are observed, together with higher fragmentation due to the higher energy content of the photoexcited molecules. It appears that the photofragmentation at both wavelengths is more in line with that of acyclic alkenes, contrary to that of 1,3-butadiene which involves an important isomerisation of the photoexcited molecules to the 1,2-butadiene structure.[2]

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[1] G.J. Collin, H. Deslauriers and G.R. De Maré, *Can. J. Chem.*, in press.
[2] G.J. Collin, H. Deslauriers, G.R. De Maré and R.A. Poirier, *J. Phys. Chem.*, 94 (1990) 134.

Reactivity of binary clusters
$N_2O - (Ar)_n$ with barium atoms

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Our group is involved in investigating the reactivity of homogeneous and binary van der Waals clusters with ground state and electronically excited metal atoms (barium at the present time).

Several experiments of our group have revealed that reactions that are normally chemiluminescent in the gas phase (e.g. $Ba(6s6p\,^1P_1) + H_2O \rightarrow BaOH^* + H$) are no longer chemiluminescent when taking place within large homogeneous clusters. The clusters studied so far are $(N_2O)_n$, $(H_2O)_n$, or $(CO_2)_n$ with n ranging from a few hundred to a few thousand.[1,2] This observation was interpreted as due to the solvation of the reaction product within the remaining of the cluster. The numerous non radiative couplings available in molecular clusters then account for the quenching of the chemiluminescence.

The new results that will be presented at the conference show that in contrast, chemiluminescence is not quenched when the reaction occurs within a binary cluster. One of the result presented concerns barium reacting with $N_2O - (Ar)_n$. The noble gas cluster $(Ar)_n$ in which the reactant N_2O was deposited plays to different roles: i) it is a "net" that catches the flying barium with a large cross section and ii) it is a solvent in which the reaction takes place, i.e. it allows the two reactants to migrate and to be close enough to react.

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Photodissociation Dynamics of Doubly Excited States of H$_2$

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We have applied photofragment ion imaging to investigate the dissociation dynamics of low lying doubly excited states of molecular hydrogen. Two-step, two-color multiphoton excitation of H$_2$, first via 201 nm, two-photon excitation into the E,F $^1\Sigma_g^+$ (v=0, J=1) state, followed by 563 nm, 1+m (m=1,2) excitation through the D $^1\Pi_u$ (v=2, J=1,2), B" $^1\Sigma_u^+$ (v=0, J=0,2), B' $^1\Sigma_u^+$ (v=4, J=0,2) and C $^1\Pi_u$ (v=11, J=1) states provides a ready means of populating several low lying doubly excited states of H$_2$ as a function of increasing internuclear distance. From these repulsive states, predissociation and autoionization are both possible. Because the excitation energy remains essentially constant as each intermediate state is accessed, differences in the photodissociation dynamics via each state can be ascribed directly to the effects of changing internuclear separation. H$^+$ fragments detected from each photodissociation pathway are distinguished by their differing velocities in an ion image. A typical image consists of concentric rings of H$^+$ fragment ions.

Image analysis of H$^+$ ions formed following photodissociation from the repulsive states has shown that several predissociation and autoionization channels are active. At smaller internuclear separations, absorption of two red photons in a resonant process through either the D (v=2) or B" (v=0) intermediate states leads to predissociation via the $^1\Pi_g$ (2pσ_u)(2pπ_u) repulsive state, resulting in H (n=1) and H (n=3) production. The electronically excited H atom absorbs a further red photon which leads to its ionization and detection.

Increasing the internuclear separation by excitation through the B' (v=4) or C (v=11) intermediate states shows dramatically different photodissociation behavior. 1+1 photon absorption via these state leads to H (n=1) and H (n=3) production as a result of predissociation via the $^1\Pi_g$ (2pσ_u)(2pπ_u) repulsive state. In addition, absorption of two red photons from the B' (v=4) or the C (v=11) state (which can be thought of as a 1+2 resonant absorption from the E,F state) leads to H$_2$ dissociation via the $^1\Pi_u$ (2pσ_u)(2pπ_g) state with concomitant production of H (n=1) and H (n=5). Competing with predissociation via the B' (v=4) intermediate state, autoionization from the $^1\Pi_g$ (2pσ_u)(2pπ_u) state leads to H$_2^+$ formation. Prompt absorption of an additional red photon from H$_2^+$ (v=2-5) leads to dissociation of the molecular ion.

Cage effect on the photodissociation of small molecules in rare gas matrices

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The first step in understanding photochemical reactions in condensed media goes via a microscopic description of the most elementary of such reactions: the photodissociation process on a purely repulsive potential surface and the resulting effect of the cage on it. In other words, what are the energy barriers for cage exit and what is the energy dependence of the photodissociation quantum yield? This problem has been studied by us on H_2O and Cl_2 trapped in rare gas matrices, by means of synchrotron radiation. Cage induced barriers for H atom escape have been determined for dissociation of H_2O in the first continuum in Ar, Kr and Xe matrices. Temperature as well as deuteration effects have also been investigated. Finally, absolute photodissociation quantum yields have been measured. Models accounting for the barrier energies and for the dependence of the dissociation efficiency above threshold with matrix, isotopic and temperature changes will be presented and discussed. Similar investigations were carried out for the case of Cl_2 and the discussion will focuss on the influence of the local structure and the distribution of final sites of the fragments on the dissociation energy barriers and efficiencies. Our results will also be compared to recent Molecular Dynamics simulations. These predict a direct and delayed cage exit mechanism for heavy (Cl) and light (H) fragments, respectively.

ON THE 193 NM PHOTODISSOCIATION OF ACETONE

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The 193 nm laser line has been used as an excitation source for investigating the photodissociation of acetone. Light of this frequency excites acetone in its 3s Rydberg <- X transition region. The understanding of the spectrum of this state is thus sought to assist in the interpretation of acetone 193 nm photodissociation.

The absorption spectra of acetone and acetone-d_6 around 193 nm were measured at several different temperatures, analyzed, and compared with those obtained for the 3p Rydberg and ion <- X transitions. Lifetimes were estimated from published spectra. The results were interpreted to demonstrate a comparable stability of acetone in its 3s and 3p Rydberg states but a significant alteration in the methyl end of the molecule in the 3s Rydberg state relative to either its ground, other Rydberg, or ion states.

PHOTOPHYSICS OF JET-COOLED AROMATIC AMINES

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Many aromatic amines typically exhibit in solution 'anomalous' fluorescence from TICT (Twisted Intramolecular Charge Transfer) states produced by rotation of the amine moiety in the molecule with respect to the aromatic framework. For many molecules, the mediation of a polar solvent in producing such emission is a requirement.

We have investigated dimethylamino benzonitrile (DMABN) and the related esters dimethylamino methyl benzoate (DMAMB) and dimethylamino ethyl benzoate (DMAEB) in supersonic nozzle expansions at varying partial pressures of fluorophore and polar and non-polar solvents. Although red-shifted fluorescence is observed in all cases, in no case can this be ascribed to TICT emission, being due instead to excitation of ground state dimers and self-complexes, and solvated clusters of these.

A comparison has been made of the laser-induced fluorescence of jet-cooled N-(4-phenyl)carbazole and the hydrogen-bonded complex between carbazole and benzonitrile. The electronic origin of the hydrogen bonded complex is shifted bathochromically to a greater extent than that of the covalently linked molecule. In both cases the conformation of the ring systems appears to be perpendicular in both ground and first excited electronic states. The spectroscopy can be explained in terms of a perturbed carbazole chromophore. Again, no evidence for TICT emission was found in the jet, in contrast to solution phase results.

Some results on the dynamics of decay of fluorescence, with emphasis on intramolecular vibrational redistribution, in 3 and 4 aminobenzonitriles, will be presented.

DETECTION OF THE HOCO RADICAL AND ITS LIFETIME IN GAS PHASE

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The HOCO radical has been inferred to be an intermediate of the important reaction OH + CO $\longrightarrow$ H + CO_2. Before the recent study of Ruscic et al.,[1] the radical had only been detected in a low-temperature matrix.[2] In the present study, the HOCO radical has been successfully detected by a photoionization mass spectrometry method in the gas phase. The HOCO radicals were generated by the reaction of Cl + HCOOH or the photolysis of acrylic acid (C_2H_3COOH). The HOCO radical produced by the reaction of Cl + HCOOH (with small excess energy; 13.1 kcal mol^{-1}) was found to be stale and its lifetime was confirmed to be very long (>10ms) at room temperature. On the other hand, the HOCO radical formed by 193-nm photolysis of C_2H_3COOH (with large excess energy; 55.8 kcal mol^{-1}) exhibits short and pressure dependent lifetime [Figure 1]. This is attributed to the competition of thermal decomposition and relaxation of 'hot' radicals. Further, this lifetime show an apparent isotope effect (HOCO/DOCO) [Figure 1] and this suggests that the decomposition mainly proceeds via 'tunneling' H-atom elimination. The rate of reaction of HOCO with O_2 was also determined.
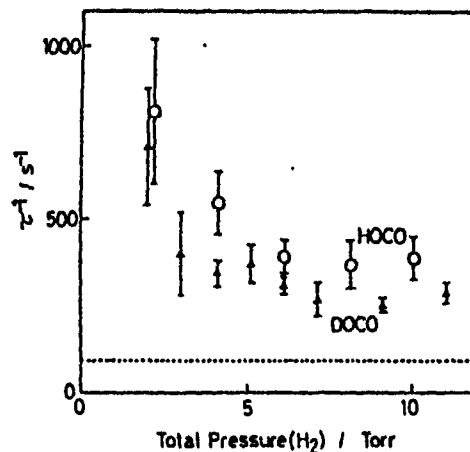
Figure 1. Lifetime of HOCO (DOCO) radical produced by the photolysis of acrylic acid.

References

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DIRECT INVESTIGATIONS OF ABSOLUTE REACTIVE CROSS SECTIONS AND PRODUCT
STATE DISTRIBUTIONS OF OH RADICALS PRODUCED BY VERY FAST
H ATOM – MOLECULE REACTIONS

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Using 193 nm photolysis of HBr, and HCl respectively, we have studied the hot H atom reactions

(a) $H + O_2$ ⟶ $OH + O$ σ_R (1.85 eV) = 0.37 ± 0.20 Å^2

σ_R (2.14 eV) = 0.15 ± 0.08 Å^2

σ_R (2.57 eV) = 0.10 ± 0.05 Å^2

(b) $H + NO$ ⟶ $OH + N$ σ_R (2.57 eV) = 0.01 ± 0.005 Å^2

(c) $H + CO_2$ ⟶ $OH + CO$ σ_R (1.86 eV) = 0.39 ± 0.20 Å^2

σ_R (2.57 eV) = 4.0 ± 1.0 Å^2

(d) $H + H_2O$ ⟶ $OH + H_2$ σ_R (2.52 eV) = 0.30 ± 0.10 Å^2
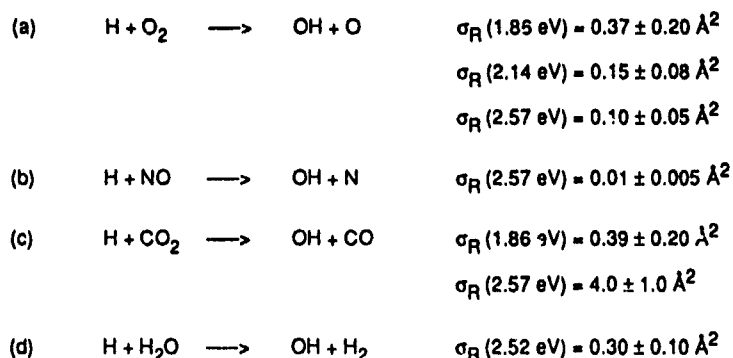
at different center of mass collision energies under single collision conditions. Laser induced fluorescence (LIF) was used to probe the nascent vibrational, rotational line structure distributions of the OH product molecules. Absolute reactive cross section σ_R (E_{trans}) for the reactions were obtained by calibrating the OH signals from the reactions against signals from well defined OH concentrations generated via photolysis of H_2O_2 at 193 nm.

We have compared our experimentally determined OH product state distributions to statistical distributions and in the case of reactions (a) and (d), to internal OH product state distributions obtained from trajectory calculations on *ab initio* potential energy surfaces. In the case of reactions (a), (c) and (d), we compare our experimental values of the absolute reactive cross sections to theoretical values obtained from quasi classical trajectory calculations. New results of absolute reactive cross sections and line structure resolved OH product state distributions for the reaction (d) are also presented.

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II- PHOTOPHYSICS
AND
PHOTOCHEMICAL KINETICS
IN CONDENSED PHASE

TRIPLET EXCIMERS INVOLVING CARBAZOLE

THE ROLE OF ION RECOMBINATION

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Both monomeric and excimer delayed luminescence may be observed from solutions of N-ethylcarbazole (NEC) photoexcited by 308 nm pulses from an excimer laser. The excimeric emission, recorded in the low microsecond time regime, is favored in solvents of high dielectric constant such as ethanol (EtOH) and N,N-dimethyformamide (DMF) whereas nonpolar solvents such as cyclohexane and paraffin oil favor the production of monomeric delayed fluorescence. A transient absorption band with a peak absorbance at 500 nm is also found as a prominent feature of transient spectra recorded in the higher dielectric solvents. This band has been assigned to the triplet excimer of NEC. It has been proposed that triplet excimers in this system arise by the geminate recombination of ion pairs consisting of carbazolyl radical cations and radical anions. The decay of the 500 nm band obeys a double exponential rate law. The rate constant attributed first order relaxation of the triplet excimer is 4.5×10^4 s^{-1}. The other component of the double exponential decay corresponds to decay of the precursor ion pair and has the value 5.0×10^5 s^{-1} in EtOH and 4.2×10^5 s^{-1} in DMF.

ELECTRONIC EXCITED STATE PROTON TRANSFER IN
2-(2'-HYDROXYPHENYL)IMIDAZO[1,2-a]PYRIDINE

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We present a picosecond time resolved transient absorption spectra of 2-(2'-hydroxyphenyl)imidazo[1,2-a]pyridine (HPIP) and its methoxylated derivative (OMePIP) in cyclohexane and dioxane.

HPIP   OMePIP
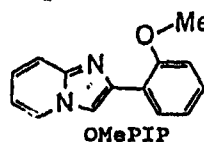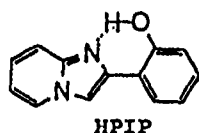
Due to the long lifetime, (on the nanosecond time scale), of the excited tautomer of HPIP (formed after proton transfer) [1], we are able to observe its transient absorption spectra without any contribution from the ground state tautomer (Fig. 1 a and b). OMePIP shows a stimulated emission with a maximum around 400 nm and different kinetics.
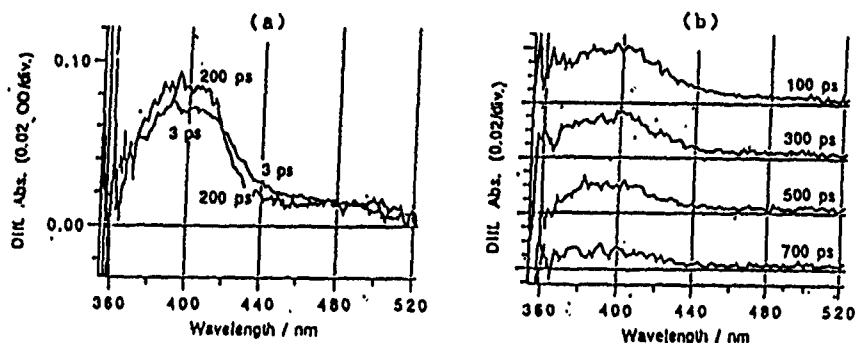
Fig.1: Transient absorption spectra of HPIP in cyclohexane (a) and dioxane (b) at different delay time.

Direct data from these spectra show that the rate constant for proton transfer in S_1 is greater than $(0.5 \text{ ps})^{-1}$. For the first time, we observed a cooling (picosecond regime) of the hot vibrational excited tautomer (Fig. 1-a). As we did not detect any absorption due to the ground state tautomer (Fig. 1-b), we suggest that the reverse proton transfer occurs within the hot molecule which easily passes over the low barrier on the potential energy surface of the ground state [2].

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VISIBLE-LIGHT INDUCED ELECTRON TRANSFER ON QUANTIZED CdS

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We perviously reported that quantized ZnS and CdS provide efficient photo-induced electron transfer systems, catalyzing two-electron transfer reductions of ketones to alcohols.[1,2] Here we report that visible-light induced electron transfer on quantized CdS is controllable by photochemical and sophisticated modification of the CdS.

Quantized CdS (CdS-0) catalyzes two-electron transfer photoreductions of aromatic ketones and electron-deficient olefins in methanol under visible light irradiation using triethylamine (TEA) as an electron donor, giving alcohols and dihydro compounds as exemplified by following two reactions.[2]
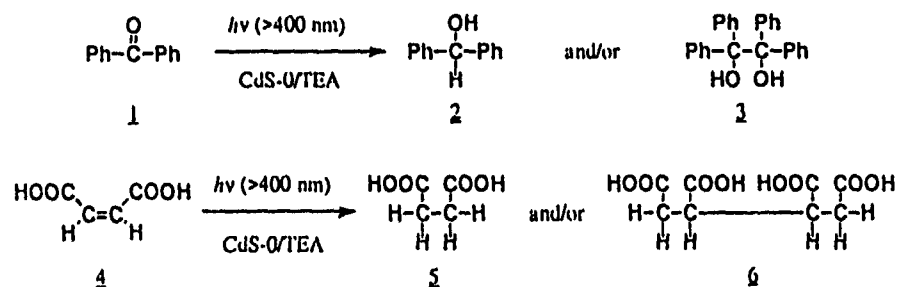
CdS-0 suspensions prepared at 0 °C from equal amounts of methanolic solution of $Cd(ClO_4)_2$ and Na_2S consist of 2-5 nm microcrystallites and their loose aggregates. Visible light irradiation of CdS-0 with TEA leads to the formation of the colored CdS-0 suspension (CdS-0-Cd) possibly due to the reduction of lattice Cd^{2+} near to sulfur vacancies. CdS-0-Cd has now been found to be much more selective for the formation of the alcohol (2) and the dihydro compound (5), whose formation is rationalized by sequential two-electron transfer reduction. However, the presence of excess S^{2-} in the reaction system suppress the formation of CdS-0-Cd and resulted in the exclusive formation of one-electron transfer reduction products, 3 and 6, respectively.

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PICOSECOND FLUORESCENCE STUDIES OF INTRAMOLECULAR CHARGE TRANSFER. A NEW VIEW AT TICT

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Intramolecular charge transfer has been studied, with a time resolution down to 20 psec, for several p-aminobenzonitriles and related compounds in solvents of different polarity and viscosity. By an analysis of double- and triple-exponential monomer and exciplex fluorescence decays (SPC), the rate constants of forward and backward charge transfer were determined as a function of temperature and solvent properties. This gives, for the first time, values for the activation energies of these processes and, hence, for ΔH and ΔS. Special attention was paid to the role of the longitudinal dielectric relaxation time in the charge transfer process.

It could be shown that for the aminobenzonitriles:

- A rotation of the amino group with respect to the benzonitrile moiety is not a prerequisite for charge transfer.[1]
- Longitudinal dielectric relaxation times cannot be related to the rate of charge transfer.
- Charge transfer and dual emission also occur in solvents such as toluene (no n-electrons), showing that 1:1 complex formation with the solvent is not a general mechanism for TICT.

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Photoinduced Electron Transfer Chemistry of Azoalkanes: Generation of 1,3-Cyclopentadiyl Radical Cations and their Transformations

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Azoalkanes give on photosensitized electron transfer products and/or product distributions that are different from those obtained in direct photolyses or thermolyses. In this context azoalkane 1 was examined, which yielded on direct photolysis (λ = 333 - 364 nm) and on thermolysis (T $\leq$ 300 °C) only housane 2. Thermolysis of 1 or 2 at T $\geq$ 500 °C led to cyclopentenes 3 and 4, of which the former was the thermodynamically favored product (Scheme 1). Also in the photosensitized electron transfer process with 9,10-dicyanoanthracene
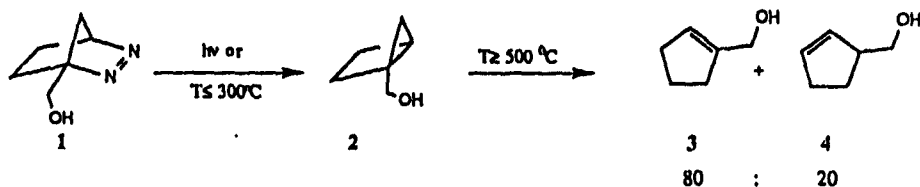
Scheme 1: Direct photolysis and thermolysis of azoalkane 1

(DCA) or 2,4,6-triphenylpyrylium tetrafluoroborate (TPT) as sensitizers, the cyclopentenes 3 and 4 were formed, however, now the latter was the major olefinic product (Scheme 2).

SENS = DCA or TPT

	2		3		4
DCA, CH$_3$CN:	42	:	16	:	42
TPT, CH$_3$CN:	16	:	14	:	70
DCA, CH$_2$Cl$_2$:	65	:	7	:	38
TPT, CH$_2$Cl$_2$:	35	:	6	:	59
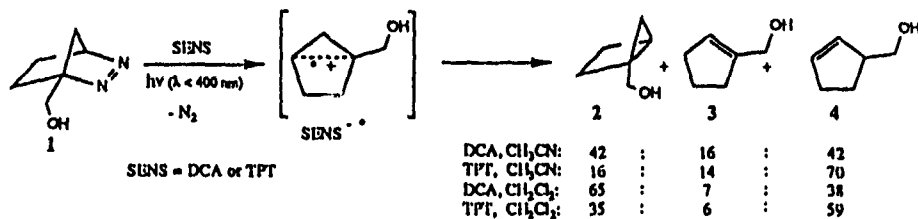
Scheme 2: Photosensitized electron transfer reaction of azoalkane 1

These contrasting results are rationalized in terms of diradical intermediates in the former (Scheme 1) and radical cations in the latter (Scheme 2). An unsymmetric charge/spin distribution in the radical cation intermediate favors rearrangement to the thermodynamic less stable cyclopentene 4. Photomechanistic implications, influence of solvent polarity and sensitizer and studies towards trapping of the radical cation intermediates will be discussed.

Acknowledgements:

SITE-SELECTIVITY AND SOLVENT DYNAMICS CONTROL IN ELECTRON-TRANSFER REACTION OF BIANTHYL IN POLAR SOLVENTS AND IN COMPLEXES WITH PROTEIN MOLECULES

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Statistical distributions of solute-solvent interaction energies and the rates of intermolecular relaxations may determine the pathways and rates of different charge-transfer reactions and therefore are especially important in polar solvents and in biological macromolecules. If the relaxations are slow, the high interaction energy part of the distribution can be photoselected by excitation at the red (long-wavelength) edge of absorption bands. We observe that intramolecular electron transfer in bianthyl molecule from the locally-excited (LE) to charge-transfer (CT) state, which requires solvent relaxations and is usually not observed in solid media, is dramatically facilitated in a number of low-temperature glassy solvents by the red-edge excitation. This allows to obtain the pure CT form spectroscopically and observe the dependence of its spectra upon the relaxational properties of the solvent which were modulated by changing the temperature. The strong correlation between the reaction rate and the rate of solvent relaxations was found in these experiments. A qualitative model of these effects describes the solvent dynamics control of ET rate by formation of optimal solvent-environment configurations rather than by direct involvement of these dynamics in electron transfer act. These configurations are rare in solid environments, and they can be photoselected only at the red-edge. In liquid solvents there exist the two steps of relaxation: one results in the dynamic formation of CT state, and the other is the relaxation of solvent dipoles to equilibrium with the high dipole moment of this state. The experiments with serum albumin-bianthyl complexes demonstrate that protein molecules may behave as microscopic solid bodies inhibiting the ET rate and displaying the red-edge effects.

PHOTOCHEMICAL REDUCTION OF CO_2 CATALYZED BY OLIGO(p-PHENYLENE)S

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Carbon dioxide fixation using light energy has attracted much interest in view of the global greenhouse effect. Photochemical reduction of CO_2 were extensively studied and novel photocatalysts or photosensitizer have been requisite for the purpose. Here, we report that p-terphenyl induces effective photoreduction of CO_2 to formic acid (HCOOH) and carbon monoxide (CO) in aprotic polar solvent.[1]

As shown in Table 1, the photoreductive formation of HCOOH and CO in anhydrous organic solvent systems was observed, where the photocatalysis of p-terphenyl in N,N-dimethylformamide (DMF) led to the most effective formation of HCOOH and CO (the quantum yield ($\Phi_{1/2HCOOH}$) was 0.072 at 313 nm.). A trace amount of H_2 was detectable. The turnover number of p-terphenyl for the formation of HCOOH in DMF is about 4, implying a cyclic activity of the system. On the other hand, o-terphenyl and m-terphenyl which are both very soluble in aprotic polar solvent showed much poorer activity than p-terphenyl, suggesting that p-phenylene unit is an important factor for the effective charge separation and electron transfer. It was previously reported that photocarboxylation of aromatic hydrocarbons such as phenanthrene, anthracene, and pyrene occurs in photolyses in the presence of various amines and CO_2 of their dimethyl sulfoxide and DMF solution.[2] In the present photolysis, however, no photocarboxylation was observed. In conclusion, the result in Table 1 indicates the first example of direct photoreduction of CO_2 catalyzed by organic sensitizer without an electron mediator. Further studies on the photoinduced charge separation and electron transfer in this system are in progress.

Table 1. Photochemical Reduction of CO_2 by Terphenyls in Anhydrous Organic Solvent[a]

Catalyst	Solvent	Photoproducts / μmol			Solubility in solvent[b]	
		HCOOH	CO	H_2	Catalyst/mg/cm^3	CO_2/M
p-Terphenyl	DMF	42	5.6	1.1	6.6	0.23
o-Terphenyl	DMF	1.9	0.1	0.4	670	0.23
m-Terphenyl	DMF	3.6	0.3	0.7	207	0.23
None	DMF	0	0.2	0.1	-	0.23
p-Terphenyl	CH_3CN	11	0.2	0.4	0.83	0.14
p-Terphenyl	CH_3OH	0	0	0.2	0.28	0.19
p-Terphenyl	THF	4.8	1.2	0.2	37.5	0.33

a) After irradiation at > 290 nm for 15 h. b) Solubilities of terphenyls and CO_2 in each solvent at 25 °C.

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ON THE MULTIPLE FLUORESCENCE EMISSION OF A CLASS

OF UNSYMMETICAL D-A-D' MOLECULES: UNSYMMETRICAL SQUARAINES

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Bis(4-dimethylaminophenyl)squaraine and derivatives, a class of D-A-D molecules, are shown to exhibit multiple emission bands from the Franck-Condon states of the squaraine and the squaraine-solvent complex, and a TICT state. In this paper, the multiple emission of unsymmetrical squaraines, 4-dimethylaminophenyl-4'-methoxyphenylsquaraine (1) and derivatives, is reported (Figure 1). Evidence is provided that the multiple emission bands are due to vibronic bands of the excited states of 1 and its solvent complex. The absence of any emission from the TICT state will be discussed.
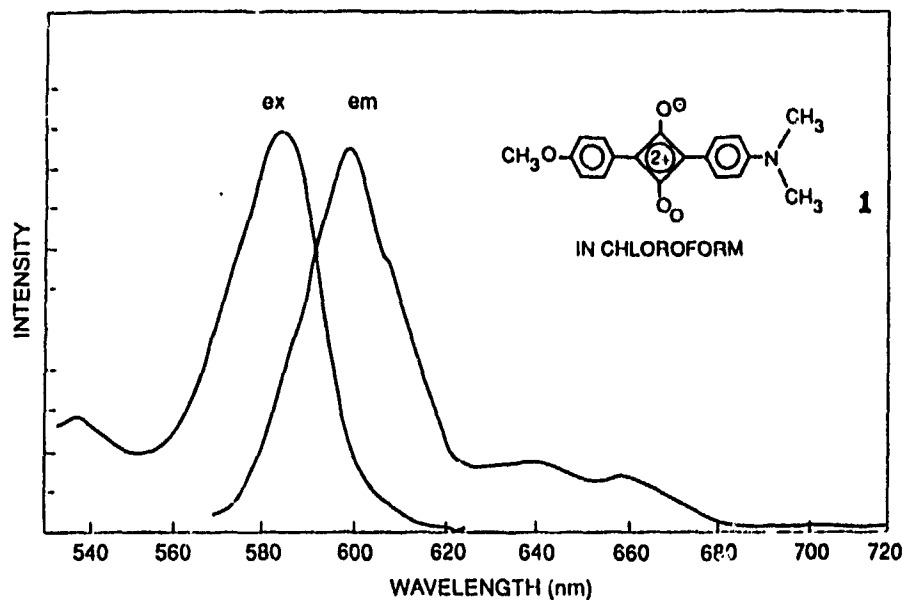
Figure 1 Excitation and corrected fluorescence spectra of 1

LES N-PHENYLAZA-15-CROWN-5: CHROMO ET FLUOROIONOPHORES POUR L'ETUDE DE LA COMPLEXATION DE DIVERS CATIONS PAR LES AZACOURONNES.

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La grande sensibilité des spectroscopies d'absorption électronique et de fluorescence a conduit à la conception et à la synthèse de Chromo et Fluoroinophores pour l'étude de la complexation des ions par les macrocycles[1]. Quand l'un des hétéroatomes de l'ionophore est partie intégrante du chromophore, la complexation des cations modifie les états électroniques en fonction de la valeur et de la direction des moments dipolaires à l'état fondamental μg et à l'état excité μe[1-3].

Nous décrivons les propriétés photophysiques de trois sondes (I-III) classées selon la densité électronique décroissante à l'état fondamental et la charge positive croissante à l'état excité, sur l'atome d'azote, près du cation complexé.

I   II   III
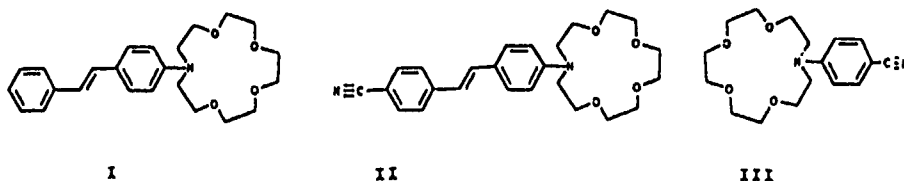
Dans les solvants polaires on pouvait s'attendre à ce que l'azacouronne analogue du DMABN (II) forme à l'état excité un transfert de charge intramoléculaire orthogonal (TICT) dans lequel l'azote porterait une charge positive[4]. Récemment nous avons montré que les dérivés du stilbène, tels que II, conduisent également à un état TICT mais avec le groupe dialkylaniline comme donneur sur lequel la charge positive est délocalisée[5].

Les constantes de complexations (log K) de divers cations par les trois sondes ont été déterminées spectroscopiquement dans différents solvants (CH_2Cl_2, CH_3OH, CH_3CN) et les caractéristiques de la fluorescence sont attribuées à l'interaction modulée entre la charge du cation et le dipôle du chromophore.

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3- S.A. JONKER, S.I. VAN DIJK, K. GOUBITZ, C.A. REISS, W.SCHUDDEBOOM, J.VERHOEVEN, Mol.Cryst.Liq.Cryst., 1990, 183, 273-282.
4- Z.R. GRABOWSKI, K.ROTKIEWICZ, A. SIEMIARCZUK, D. J. COWLEY, W. BAUMANN, Nouv.J.Chim., 1979, 3, 443.
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N-PHENYLAZA-15-CROWN-5 AS FLUORESCENT PROBES
OF THE DETAILED FEATURES OF IONS COMPLEXATION

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The recognized high sensibility of the absorption and fluorescence spectroscopies led recently to the design of Chromo- and Fluoroionophores for the study of ions binding by multidentate macrocyclic compounds[1]. When one of the heteroatoms of the ionophore is part of the mesomeric system of the chromophore, cations complexation influences the electronic states depending on the size and direction of the dipole moments μg and μe[1-3].

We report the photophysical properties of the three probes (I-III) classified according to increased charge localisation on the nitrogen atom, near the complexed cation, in the excited state.

I   II   III
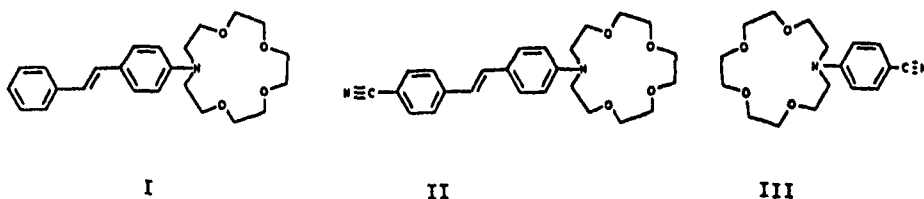
In polar solvents the azacrown ether analogue of DMABN (III) was expected to lead to an excited state with mutually perpendicular π-systems and complete charge separation between the azacrown donor, which consequently bear a positive charge on the nitrogen, and the benzonitrile acceptor group[4]. Recently we showed that in the stilbene serie, similar "Twisted Intramolecular Charge Transfer" (TICT) states are formed when the donor-acceptor strength of the substituents reaches a threshold as in II, but the dialkylanilino group is now the donor group where the positive charge is delocalized.

The cations binding properties (log K) of I-III were determined from spectrophotometric titration in solvents of various polarity (CH_2Cl_2, CH_3OH, CH_3CN) and the striking fluorescent characteristics were assigned to the modulated, cation charge-chromophore dipole, interaction.

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2- S. FERY-FORGUES, J. BOURSON, L. DALLERY, B. VALEUR, New. J.Chem. 1990, 14, 617-623 and ref therein.
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4- Z.R. GRABOWSKI, K.ROTKIEWICZ, A. SIEMIARCZUK, D. J. COWLEY, W. BAUMANN, Nouv.J.Chim., 1979, 3, 443.
5- R. LAPOUYADE, K. CZESCHKA, W. MAJENZ, W.RETTIG, E. GILABERT, C.RULLIERE, in preparation.

THE CHARGE-TRANSFER STATE AND SINGLET
OXYGEN PRODUCTION IN PHOTOEXCITED ORGANIC
MOLECULE-MOLECULAR OXYGEN COMPLEXES

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We examined charge-transfer (CT) state participation in
an excited state organic molecule(M)-molecular oxygen complex
by using a variety of spectroscopic probes. We showed
earlier that singlet oxygen ($^1\Delta_g O_2$) is formed upon
dissociation of the photoexcited CT complex ($M^+ \cdot O_2^{-} \cdot$) when the
CT state energy is lower than that of the triplet state
($^3M_1$).[1,2] We now examine a molecule whose CT state energy is
higher than that of $^3M_1$. Relative $^1\Delta_g O_2$ and $^3M_1$ yields were
determined upon 1) photolysis into the M-O_2 CT band of
1-methylnaphthalene and 2) $^3\Sigma_g^- O_2$ quenching of triplet
1-methylnaphthalene. In non-polar solvents, $^1\Delta_g O_2$ and $^3M_1$ yields
were independent of the *(M-O_2) production method, indicating
that relaxation of the ^{1,3}CT states to the $^{1,3}(^3M_1...^3\Sigma_g^- O_2)$
states is very efficient. In a polar solvent where the CT state
is more stable, the data indicate that direct coupling between
the CT and ground state surface $[^3(^1M_o...^3\Sigma_g^- O_2)]$ may increase.
CT mediated indirect coupling of the $^{1,3}(^3M_1...^3\Sigma_g^- O_2)$ and other
M-O_2 excited states to the ground state surface should also
increase in a polar solvent. $^1\Delta_g O_2$ quantum yields obtained upon
direct photolysis of six aromatic hydrocarbons support this
interpretation. Our data are consistent with a model for oxygen
induced intersystem crossing in which coupling between singlet
and triplet states is facilitated by mixing with a CT state.

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SWING ELECTRON TRANSFER ACTIVATION OF OXYGEN TOWARDS AROMATIC COMPOUNDS

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The reduction potential of oxygen vs. SCE range from - 0.57 V (H$_2$O) to - 0.82 V (CH$_3$CN). Theoretically, oxygen cannot oxidize by electron transfer substrates whose oxidation potential is less negative than approximately - 0.2 V (H$_2$O) or - 0.5 V (CH$_3$CN). Most of the neutral organic molecules do not have a negative enough oxidation potential to react spontaneously with oxygen. Nevertheless, photooxygenation may be performed using the concept of "swing electron transfer activation".
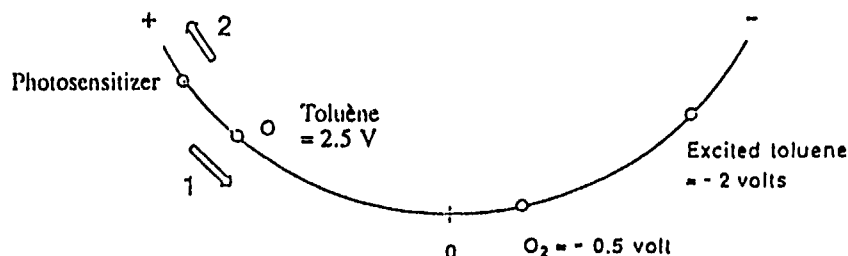
The figure illustrates why the word "swing" describes this activation. If the scale of redox potentials is represented globally as a curved arrow, only the zone situated on the right side of O$_2$ corresponds to a spontaneous reaction by electron transfer between substrates and ^{3}O$_2$. There are however two tricks to enlarge this reactivity : one is to swing the substrate from 1 to this zone by photoexcitation (case of toluene : E$^\circ_{fond.}$ = 2.5 V ; E$^\circ_{exc.}$ = -2 V) , the other one quite paradoxical consists in oxidizing the substrate (i.e. displace its redox potentials in the direction 2). The oxidized form then displays a good reactivity (not by electron transfer) toward ^{3}O$_2$.

As an example, when supported 2,4,6-trinitrobenzene is used to activate alkylaromatic hydrocarbons, the excited chromophore at the surface of the silica accepts an electron from the substrate and generates in the medium the substrate radical cation, species which is still more difficult to oxidize. This highly acidic radical cation (pKa $\simeq$ -10) is deprotonated and leads to a radical which reacts with ^{3}O$_2$ at a diffusion controlled rate.

Electron acceptors bound to silica act as photosensitizers. They can be reused after an easy separation from the medium by filtration or centrifugation. They are a way to improve the use of preparative photochemistry.
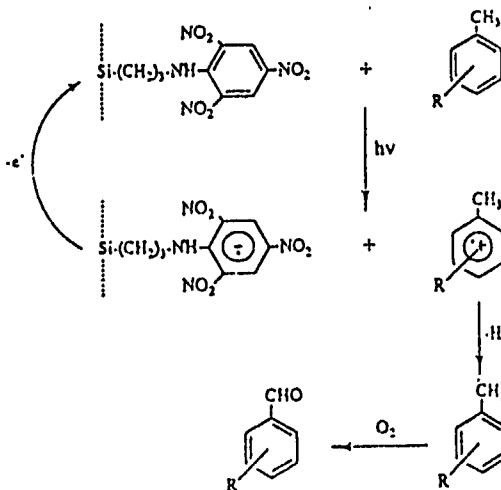
LE "PENDULE REDOX" OU COMMENT ACTIVER
L'OXYGENE VIS A VIS DES COMPOSES AROMATIQUES

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Le potentiel de réduction de l'oxygène (vs SCE) se situe entre - 0,57 V (H_2O) et - 0,82 V (CH_3CN). Théoriquement, l'oxygène ne peut oxyder par un transfert monoélectronique les substrats dont le potentiel d'oxydation est supérieur à - 0,2 V (H_2O) ou - 0,5 V (CH_3CN). La plupart des molécules organiques neutres n'ont pas un potentiel d'oxydation suffisamment faible pour réagir spontanément avec l'oxygène. Leur photooxygénation peut cependant être mise en oeuvre grâce au "pendule rédox".
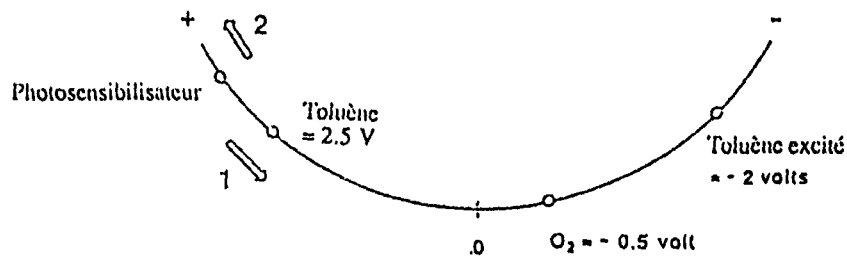
La figure illustre cette image de "pendule rédox". Si l'échelle des potentiels rédox est représentée globalement comme une flèche courbe, seule la zône située à droite de O_2 correspond à une réaction spontanée par transfert monoélectronique entre les substrats et $^3O_2$. Il existe cependant deux moyens pour élargir ce domaine de réactivité : l'un est de déplacer par photoexcitation le substrat depuis le point 1 jusque dans la zône de droite (cas du toluène E° fond = 2,5 V ; E° exc = -2 V) l'autre, quelque peu paradoxal, consiste à oxyder le substrat (c'est à dire déplacer son potentiel d'oxydation dans la direction 2). La forme oxydée présente alors une bonne réactivité (pas par transfert monoélectronique) vis à vis de $^3O_2$.

Quand le trinitrobenzène-2,4,6 est utilisé pour activer des hydrocarbures alkyl aromatiques vis à vis de $^3O_2$, le chromophore excité, lié à la silice, accepte un électron du substrat et crée dans le milieu un radical cation, espèce qui est encore plus difficile à oxyder. Néanmoins ce radical cation, très acide (pKa ≃ -10), est déprotoné et conduit à un radical benzylique qui réagit avec $^3O_2$ à une vitesse contrôlée par la diffusion. Les accepteurs d'électron liés à la silice peuvent être réutilisés après une séparation du milieu aisément réalisée par filtration ou centrifugation. Ils constituent une voie susceptible d'étendre le domaine de la photochimie préparative.
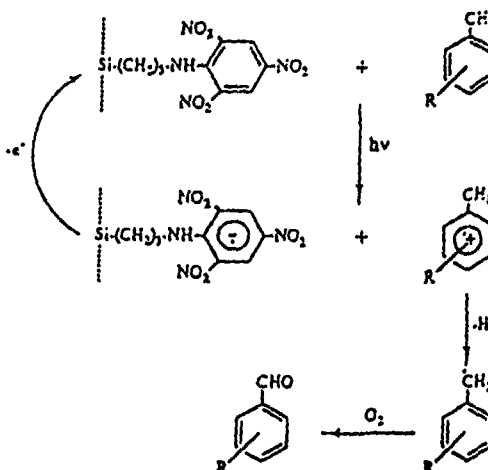
THE SOLVENT POLARITY DEPENDENCE OF TICT FORMATION RATES

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The dual fluorescence of dimethylaminobenzonitrile (DMABN) and its derivatives has been the subject of numerous kinetic studies because the adiabatic photoreaction populating the A* (or "Twisted Intramolecular Charge Transfer" (TICT) state) can be viewed as a prototype example of an electron transfer (ET) reaction which is strongly coupled to both intramolecular motion (twisting process, controlled by solvent viscosity) and the dynamics of dipolar solvent reorganization. In particular, the question arose, which of these factors is the most important one and whether there are still other factors important for the description of TICT formation dynamics /1/.

It will be shown that important factors are the dependence of the observed kinetics on initial conditions and the presence of a conical intersection for DMABN (Fig. 1). Additionally, the different time-scales for the twisting motion and the solvent relaxation have to be taken into account. It is shown that solvent-controlled electron transfer mainly occurs under conditions where solvent relaxation is slow as compared to the twisting motion.
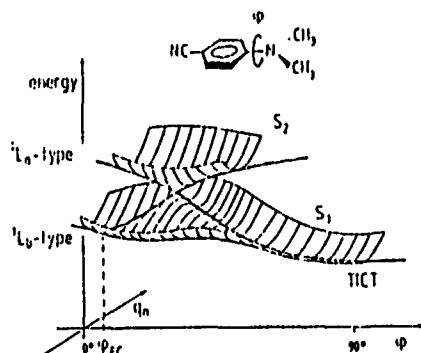
Fig. 1: Schematic representation of the conical intersection coupling S_1 and S_2 in DMABN. For conformations of reduced symmetry (coordinate q_n), the crossing between S_1 and S_2 is avoided creating a cone on S_1. This has strong kinetic consequences for the reaction kinetics towards the TICT state.

/1/ W. Rettig, Ber. Bunsenges. Phys. Chem. 95 (1991) 259

PARAMETERIZATION OF ELECTRON-TRANSFER QUENCHING IN THE FINITE SINK APPROXIMATION

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The finite sink modification of the Soluchowski-Collins-Kimball expression:-

$$1/k_Q(C) = 1/k^* + (1 - \rho/r_o)/k_D$$

provides a quantitative description of the dependence of the time-independent quenching rate constant $k_Q(C)$ on quencher concentration C in liquids if the sink radius r_o is assigned as the most probable nearest neighbour separation $(2\pi N'C)^{-\frac{1}{3}}$, and permits recovery of the relative diffusion coefficient D together with the limiting rate constant k_Q^* (C=0) $= k_D k^* /(k_D + k^*)$.

For electron-transfer quenching the parameter of interest is k^*, the intrinsic rate constant for electron transfer in the encountered donor/acceptor pair at separation ρ; this is available as k_Q^* in the reaction limit $4\pi N'D\rho = k_D > > k^* = k_Q^*$ but otherwise requires an independent estimate of ρ from the diffusion-limited condition $k^* > > k_D = k_Q^*$ when

$$k_Q^* /k_Q(C) = 1 - k^* (2\pi NC)^{\frac{1}{3}}\rho/(k^* + k_D) = 1 - (2\pi NC)^{\frac{1}{3}}\rho$$

For a particular donor/acceptor system this limit is established by an increase in solvent viscosity η until the experimental quantity $(1 - k_Q^* /k_Q(C)/C^{\frac{1}{3}}$ is independent of $D(\eta, T)$ as found for 9,10-dicyanoanthrene (DCNA) quenching by various electron donors in ethylene glycol over the temperature range 0° - 50°C.

Recovered estimates of $\rho(\pm 10\%)$ for DCNA quenching by benzylamine (4.1 Å, 1.2 V), aniline (7.4 Å, 1.02V), dimethylaniline(8.3 Å, 0.81V) and DABCO(7.8 Å, 0.57V) increase with reduction in quencher oxidation potential while the value for k^* in methanol at 25°C is a maximum for aniline indicative of a Marcus inverted region.

LIGHT-INDUCED ELECTRON TRANSFER AND CONFORMATIONAL DYNAMICS IN TRICHROMOPHORIC ELECTRON DONOR-ACCEPTOR MOLECULES.

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We have studied some of the photophysical properties of compounds 1 and 2, which can be viewed as trichromophoric $Donor_2$-$Donor_1$-Acceptor systems .

Fluorescence and time-resolved microwave conductivity (TRMC)[1] measurements indicate that in 2 a D_2-$D_1{}^+$-A^- state ($\mu \approx 24$ Debije) is formed upon excitation in solvents of medium solvating power. In contrast, compound 1 gives rise to a much more polar transient species ($\mu \approx 34$ Debije), best described as $D_2{}^+$-D_1-A^-. [1]
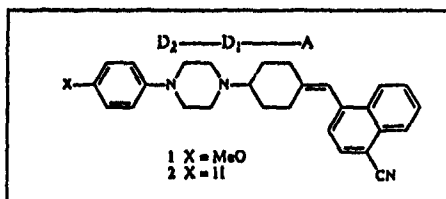
The positive charge in the asymmetric piperazine $Donor_2$-$Donor_1$ fragments appears to be mainly localized on one of the nitrogen atoms. A similar conclusion is drawn from a study of the optical absorption spectra of the radical cations of $Donor_2$-$Donor_1$ model systems. For a symmetric piperazine radical cation,[2] the optical absorption spectrum was recently taken as evidence for a delocalized structure, so it would seem that a small difference between the properties of the nitrogen sites is sufficient to switch from a delocalized to a localized structure.

In alkane solvents compound 1 displays a remarkable behaviour : three distinct fluorescence bands are seen, which can be assigned to a local emission of the initially excited acceptor chromophore, a charge-transfer emission from an extended conformation and another long-wavelength CT-emission from an exciplex-like conformation. The electrostatically driven conversion from one conformation to the other, a phenomenon recently demonstrated with simpler molecular systems in our laboratories,[3] could be monitored on a nanosecond timescale with fluorescence spectroscopy and TRMC.

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PHOTOINDUCED ACRIDINE FORMATION

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The irradiation of solutions of diarylamines (Ams) in chloroform or bromoform resulted in production of acridines with quantum yields about 0.1 and preparative yields up to 50%. The reaction was assumed to proceed *via* photoinduced electron transfer from amine to acceptor followed by recombination of amine cation-radical and $CHX_2^{\cdot}$ radical and intramolecular cyclization of intermediate (IM) formed.
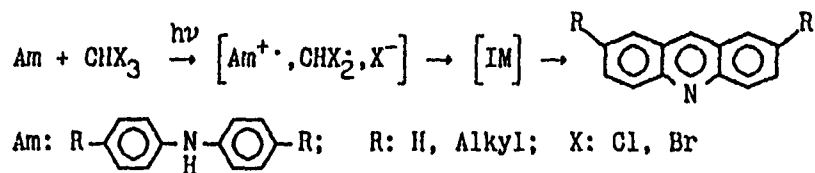
The photochemical reaction of di-p-tolylamine (DTA, $R=CH_3$) and $CHBr_3$ in toluene solution was studied in more detail.

The transient absorption spectrum ($\lambda_{max} \sim 700nm$), which was recorded $200\mu s$ following flash lamp excitation, corresponded with the spectrum of amine cation-radical $DTA^{+\cdot}$. The $DTA^{+\cdot}$ disappeared on second order kinetics, and the spectrum of intermediate ($\lambda_{max} \sim 540nm$) arose within time region to some seconds.

Both the rate constant of IM appearance (k^+) and the rate constant of IM decay (k^-) obeyed first order kinetics, but the k^+ value showed in turn first-order dependence on the concentration of DTA. Therefore, second amine molecule should take part in the IM formation reaction.

EXCITED STATE SOLVENT INTERACTIONS OF ALIPHATIC
AND AROMATIC AMINES

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Solvent effects on excited state properties were studies compara-
tively for a series of alipahtic and aromatic amines in various binary
solvent mixtures. Formation of fluorescent exciplexes of excited triethyl-
amine and 1-aza-bicyclo-2,2,2-octane (ABCO) with alcohols and ethers in
n-hexane solution were followed by nanosecond time and energy resolved
fluorescence spectroscopy. The results are discussed on the bases of a
successive association model. Structural features of these exciplexes
were obtained from ab initio calculations. Bonding interactions arise
essentially from an overlap of the lone pairs of the subunits.

The models for intermolecular interactions obtained from these
studies on aliphatic systems were applied to explain local solvent
effects in binary alcohol-hexane solvent on some aromatic amine systems
showing intramolecular charge transfer. These systems are essentially p-
cyano-N,N-dimethylaniline, commonly accepted as a model compound for the
phenomenon of "twisted intramolecular charge transfer", and N,N-dimethyl-
2-phenylethylamine.

Contrary to these systems, solvent effects upon fluorescence of N,N-
dimethylamine and related molecules can be explained by electrostatic
interactions with the molecular environment and are thus related to
macroscopic solvent parameters. Primary and secondary aromatic amines
(e.g. aniline) show, however, excited state complexation reactions in
amine-alcohol-hexane ternary systems which can be attributed to hydrogen
bonding interactions in the excited state. The influence of solvent on
various deactivation pathways is discussed in detail.

Intramolecular Triplet Excimers of Bridged Diaryl Compounds

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Formation and decay of intramolecular triplet excimers of bridged diaryl compounds, in fluid solutions at room temperature, have been investigated by time-resolved optical spectroscopy. The dependence of the excited-state dynamics on the nature of the bridging group, the nature of the aromatic moiety, the position of the linkage, and the nature of the solvent will be described.

ELECTRONIC RELAXATION IN 2-PYRIDONE VIA

HYDROGEN BONDED DIMERS

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The influence of donor-acceptor interactions on the lumi-
nescence properties of molecular systems can manifest itself
in many ways. We have investigated the fluorescence and phos-
phorescence behavior of 2-pyridone and our results indicate
the existence of a hitherto unrecognized intermolecular relax-
ation channel. This molecule has sustained continuing interest
in many laboratories due to its tautomeric equilibrium. A com-
parative study with 2-methoxypyridine, which does not involve
the keto/enol tautomeric equilibrium, is very revealing in im-
plicating a hydrogen bonded dimer in the excited state of 2-
pyridone, which most likely undergoes a double proton transfer
in the excited state. Of significant interest is the dramatic
increase in its fluorescence and phosphorescence yield ob-
served in alkaline media, which is in sharp contrast to the
enhanced luminescence observed for aromatic nitrogen heterocy-
clics upon protonation. Our interpretation is supported by
fluorescence and phosphorescence lifetime and quantum yield
data, which will be presented. Our semi-empirical MO calcu-
lations of this molecule illustrate the existence of close
n,π and π,π states, and the inversion of states occurring
with protonation of the nitrogen lone pair. Our data will
provide evidence for the existence of a hydrogen bonded dimer
in the excited state, which undergoes a double proton trans-
fer.

THE GROUND STATE BENZENE-OXYGEN COMPLEX

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Albuquerque, NM 87131 USA

The Drago-Rose[1]/Benesi-Hildebrand[2] spectrophotometric method
has been used to quantify ground state complex formation
between benzene and oxygen in the gas phase at 295 K.
Absorption to the benzene-oxygen charge-transfer state[3] was
the experimental parameter monitored. Assuming a 1:1
reaction stoichiometry, the data yield a free energy for
complex formation (ΔG_{295K}) of -1.2 ±0.3 Kcal/mole and a
complex extinction coefficient of 14 ±4 cm^{-1} M^{-1} at 218 nm.
Independent experiments based on Dalton's Law of partial
pressures, however, indicate that the Drago-Rose/Benesi-
Hildebrand results most likely overestimate the stability of
the benzene-oxygen complex and that a more accurate ΔG value
is --0.8 Kcal/mole. In an analogous experiment, the
methanol-oxygen charge-transfer absorption was quantified in
a series of aqueous solutions at 295 K. In this case, the
data do not indicate the presence of a weakly bound complex,
but rather are consistent with Mulliken's definition of a
"contact" complex.[4]

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PARTIALLY CONSTRAINED PROXIMATE CHROMOPHORES: EXCIMER STRUCTURE AND KINETICS IN DIANTHRACENE.

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During an investigation of a series of linked-anthracenes[1] and their photodimers (Fig. 1), it was found that some of the fluorescence decay curves were only fitted satisfactorily by a sum of two exponentials. Examination of the fluorescence emission by picosecond time-resolved spectroscopy indicated that it was actually composed of two overlapping bands. The possible formation of o-xylene excimers has been proposed.
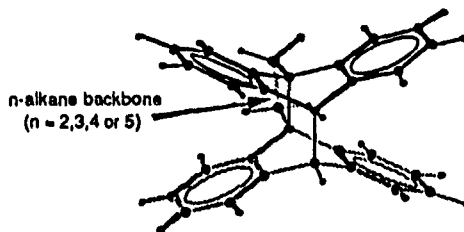
Figure 1

An inquiry is currently underway to examine:

(i) The kinetics of the excited state processes occurring in these molecules;

(ii) The consequence of apparently small structural perturbations in the σ-framework on the excimer minimum, and hence the photophysics;

(iii) The geometrical and electronic changes occurring upon excitation, using both *ab initio* and semiempirical calculations.

Recent workers have explored the kinetics of excimers formed from van der Waals dimers in the rotationally and vibrationally cold environment of a supersonic jet[2]. It is believed that the present study focuses on such phenomena occurring in the condensed phase, but in this case the chromophores are held in a closely overlapped configuration by a rigid "σ-framework". As a consequence, valuable insight is gained into the topology of the excited state hypersurface in the region of excimer formation.

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A photochemical and laser-flash-photolysis study on exciplexes of some diarylethylenes with electron donors and acceptors.

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Several papers in the last decade have shown that intersystem crossing and trans → cis photoisomerization of diarylethylenes (DAEs) can be enhanced by charge transfer (CT) interactions with electron donors or acceptors (1). In our laboratory a study on exciplexes of styryl-derivatives of phenanthrene and anthracene with amines (electron donors) has been carried out. The effect of the quencher on the fluorescence and photoisomerization quantum yields of the olefin has been investigated (2). Moreover, the transients originated by CT interactions have been characterized by pulsed techniques. In non-polar solvent the triplet is the main transient observed, while, in general, only radical ions are present in acetonitrile (3).

In order to extend this investigation, we undertook a photophysical and photochemical study of the exciplexes of the trans isomers of styrylnaphthalenes and their aza-analogues, 9-styrylphenanthrene and some arylthienylethylenes with dicyanobenzene, dimethylterephthalate and fumaronitrile (electron acceptors).

The fluorimetric measurements showed that the rate constants for the quenching of the olefin fluorescence by the electron acceptors increase with decreasing of the reduction potential of the quencher and reach the diffusional value for fumaronitrile (the strongest acceptor) in acetonitrile. The trans · cis photoisomerization is quenched or enhanced depending on the ethylenic compound and on the solvent.

Laser flash photolysis experiments showed that in non-polar solvents the main transient is the olefin triplet while in acetonitrile the CT interaction produces the corresponding radical ion pairs. The spectral and kinetic characteristics of the radical cations of diarylethylenes were obtained in terms of absorption spectra, lifetimes and formation quantum yields.

The laser flash photolysis investigation of these DAEs was also extended to the exciplexes with amines. Characterization of the radical anion and of the triplet state was also performed.

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PHOTOINDUCED INTRAMOLECULAR CHARGE SEPARATION IN PYRENE-DIMETHYLANILINE COMPOUNDS (PDMA). AN EXPERIMENTAL STUDY IN n-HEXANOL

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The intramolecular charge transfer (CT) reaction and solvation dynamics of the bichromophoric compounds 1-PDMA and 4-PDMA(s) have been studied in alcohols using picosecond emission spectroscopy and broadband picosecond time-resolved absorption spectroscopy. While fluorescence quenching and solvation in acetonitrile take place in ≤ 500 femtoseconds the processes are slowed down e.g. in n-hexanol by about a factor of 100, and can be followed spectroscopically at room temperature in the 10-500 ps range. The decay of the locally exited state (LE) is strongly nonexponential and in the case of 1-PDMA shorter than the low-frequency dielectric relaxation time (τ_L) of the alcohol solvent. The CT fluorescence spectra show an unstructured broad emission band which undergoes a very large bathochromic shift with increasing solvent polarity indicating a large dipole moment of the CT species. The complex fluorescence kinetics which depend on wavelength can in fact be explained in part by the time dependent red shift of the CT emission bands. Such kinetic behaviour has recently also been observed with a different class of bichromophoric molecules in alcohols.[1,2]

The results obtained with the model compounds PDMA provide the key for understanding the kinetics of linked molecules e.g. of the type $A-(CH_2)_n-D$, $n = 1$-4, in alcohols.

4-PDMA(s)   1-PDMA
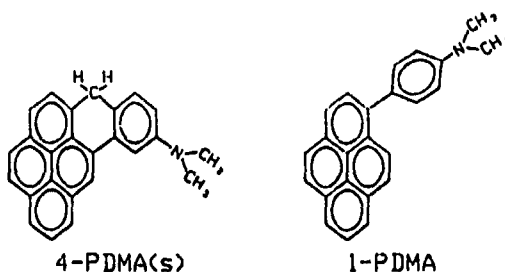
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SOLVATOCHROMISM IN ANILS

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The phenomenon of solvatochromism in anils[1,2] (development of a new absorption band in the spectral region near 440nm in polar hydrogen bonding solvents) appears much stronger in N-salicylidene-benzylamines and -ethylamino and-propylamino anilines in comparison to N-salicylideneaniline, because of the presence of the methyl groups between the C = N double bond and the neighbouring to the nitrogen aromatic ring which interrupts the resonance of the imino nitrogen lone pair electrons with the π system of the aromatic ring resulting in a more basic character of the imino nitrogen in the electronic ground state.

Solvatochromism of anils has been attributed to an enol-keto tautomerism[3].

(1)

enol   cis-keto

N-salicylideneaniline
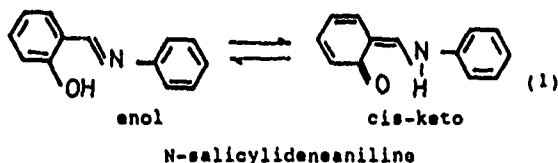
However, IR and Raman spectra of N-salicylideneaniline (1) in solvents less acidic than hexafluoroisopropanol have shown that the C = N double bond remains intact and thus no tautomerization occurs[4]. It appears therefore that the origin of the 440nm visible absorption band remains open for further research.

In the present work the above mentioned compounds have been studied comparatively in $CHCl_3$ and trifluoroethanol (TFE) by FT-IR spectroscopy. In all cases in TFE new absorption bands are observed in the region 1700-1500 cm^{-1} indicating the formation of the cis-keto tautomer. Kinetic studies in ethanol indicate also, that the cis-keto tautomer is connected by intermolecular hydrogen bond to one molecule of the solvent (2).

(2)
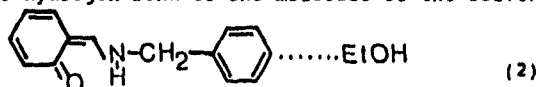
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DYNAMICS OF MULTICOMPONENT SOLVATION SHELL

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The solvation dynamics of a fluorescent probe (Coumarin 102) in the presence of an electrolyte ($LiClO_4$) was studied by varying the ion concentration at ambient and elevated pressure in acetone solution. Fluorescence decays were determined by time-correlated single photon counting as described previously[1]. They were analyzed by two different methods to yield the solvation correlation function $C(t)$ describing the solvation energy relaxation after initial photoexcitation: (i) reconstruction of the complete time-resolved emission spectra[2] and (ii) the time saving single-wavelength method.[3,4]

In the Coumarin $102/LiClO_4$/Acetone system a slow (ns) solvation shell relaxation component was observed that appeared to be similar to the one reported by Huppert et al.[5]. At ambient pressure, the relaxation time increased with decreasing ion concentration even under conditions where $LiClO_4$ was still in excess of coumarin. At high pressures (p = 300 MPa), however, this concentration dependence was found to be far less pronounced. At certain ion concentrations the reconstructed spectra first showed a rapid blue shift after excitation, followed by the expected red shift at later times. Similar phenomena have been observed for dansyl dissolved in pure glycerol at specific temperatures (viscosities)[6].

The applicability of the single-wavelength method is discussed in view of these experimental results, which are interpreted in terms of diffusive contributions to the mechanism of solvation shell relaxation.

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KETO-ENOL TAUTOMERISM IN THE METASTABLE TRIPLET STATE OF 2-(2'-DEUTEROXYPHENYL)BENZOXAZOLE AND 2-(2'-DEUTEROXY-4'-METHYLPHENYL)BENZOXAZOLE

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Due to intramolecular proton transfer 2-(2'-hydroxyphenyl)benzoxazole (HBO) can exist in two tautomeric forms, an enol form (E) and a keto (K) form. Accidentally, in the metastable triplet state of HBO, both forms have the same energy. For this reason HBO shows a dual phosphorescence[1], $^3K^* \to {}^1K$ and $^3E^* \to {}^1E$. In HBO the keto-enol equilibration $^3K^* \rightleftharpoons {}^3E^*$ is too rapid for its observation in an phosphorescence experiment. In its deuteroxy analogue DBO this equilibration is much slower than in HBO and strongly affects the initial time dependence of the dual phosphorescence.

In 2-(2'-hydroxy-4'-methylphenyl)benzoxazole (m-MeHBO) the energy of the keto triplet state is higher than the energy of the enol triplet state and, therefore, no keto phosphorescence is observed. In m-MeDBO, however, the $^3K^* \rightleftharpoons {}^3E^*$ equilibration is slower and time-resolved measurements show an initial keto phosphorescence.

In both cases the sum of the rate constants k_{KE} and k_{EK} has been obtained from the initial time dependence of the dual phosphorescence, in good agreement with results of transient-absorption experiments. It can be concluded from these phosphorescence experiments that $^3E^*$ is almost exclusively populated by $^3K^* \leadsto {}^3E^*$ and not by intersystem crossing $^1E^* \leadsto {}^3E^*$. Furthermore, a large isotope effect on the rate constants k_K and k_E has been found.
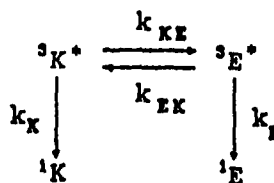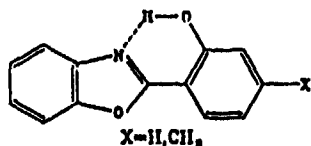
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EXCIMER AND EXCIPLEX INTERMEDIATES IN ANTHRACENE BUTTERFLIES

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Free radical synthesis of 1,2-(bis-9-anthryl)ethane (AEA) produces the isomer L as a side product [1]. It has been given the trivial name 'lepidopterene' on account of its suggestive shape.
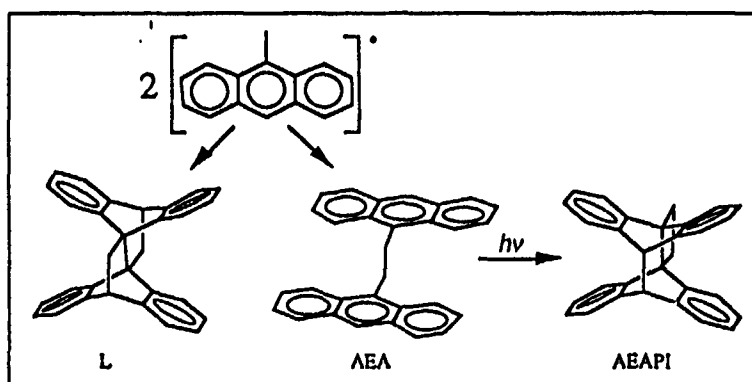
The remarkably different photophysics and photochemistry of lepidopterene, AEA and the photoisomer of AEA (AEAPI) have been examined using steady-state and time-resolved spectroscopy [2]. Temperature-dependent fluorescent spectra of AEA were numerically resolved into the contributions from various underlying components using Principal Factor Analysis. In addition the ground- and excited-state potential energy hypersurfaces were determined using the semi-empirical force field of Warshel and Karplus modified to take into account excimer interaction in the excited state [3].

The quite different behaviours of the isomers can be rationalized in terms of the theoretical ideas developed by Michl, based on the Woodward - Hoffmann rules for the conservation of orbital symmetry.

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NAPHTHYL-QUINOLYL-ETHYLENES CONFORMERS:

A PHOTOPHYSICAL STUDY.

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The presence of rotational conformers of trans diaryl-ethylenes in solution is a well extablished phenomenon[1,2]. In our laboratory, particular attention was devoted to the solvent dependence of the photochemical and photophysical properties of the rotamers of trans Styrylquinolines, both in neutral and protonated forms. In general, the behavior of these molecules depends on the position of the styryl residue with respect to the heterocyclic nitrogen[3]. The two conformers, when present, have quite different deactivation parameters so that a strong dependence of the photoisomerization and fluorescence quantum yields on the excitation wavelength was observed[4]. This effect is especially clear for the positional isomers bearing the styryl group linked to the benzenic ring of the quinoline, owing to high fluorescence yields and long lifetimes.

In order to study the conformational equilibrium of the compounds substituded on the pyridinic ring, we have synthesi-zed a series of naphthyl-quinolyl ethylenes, because the enlar-gement of the aromatic system generally increases the fluore-scence properties. As expected, the obtained compounds display a greater quantum yield of fluorescence and in this communica-tion we report a detailed study of the emission characteri-stics, studied by phase fluorometry technique, and their depen-dence on the excitation wavelength.

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EXCITED-STATE PROTON-TRANSFER PROCESSES
IN 2-PYRIDYLBENZIMIDAZOLES

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Ground- and excited-state acid-base behaviour of 2-(n'-pyridyl)benzimidazoles (n' = 2,3,4 called 2PBI, 3PBI and 4PBI respectively) in aqueous solution has been studied over a wide range of acidity. UV absorption and fluorescence emission spectra were measured as a function of pH in order to identify the various species that exist depending on acidity and the processes taking place between those species.

Absorption spectra reveal that the first protonation of 2PBI and 3PBI isomers takes place at the benzimidazole N3, whereas for 4PBI the N3-protonated species and the species protonated at the pyridyl N are present in roughly equal proportions due to the similarity of the basicities of these two N atoms.

Dual fluorescence is observed for 2PBI in acid media[1] and for 4PBI at any acidity in the pH range from 1 to 13, whereas a single band appears in the emission spectra of 3PBI. The high-energy emission band shown by all three compounds is due to emission of both neutral species and monocation protonated at the benzimidazole N3 as a function of acidity. For 2PBI and 4PBI, the low-energy emission band is attributed to the species protonated at the pyridyl N, which is formed by proton-transfer processes in 2PBI and also by direct excitation in 4PBI, due to an increase of basicity of that N atom in the excited state.
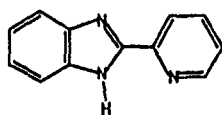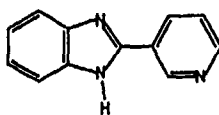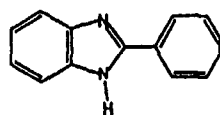
| 2PBI | 3PBI | 4PBI |

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WAVELENGTH AND TEMPERATURE EFFECTS ON
THE PHOTOCHEMISTRY OF VITAMIN D

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Ultraviolet irradiation of vitamin D produces six photoproducts S1 to S6[1]: two stereoisomeric bicyclo[3.1.0]hexene derivatives, suprasterols S1 and S2, two stereoisomeric allene derivatives, suprasterols S3 and S4, and two stereoisomeric cyclobutene derivatives, suprasterols S5 and S6. The two suprasterols S1 and S2 are formed as major photoproducts. The cis/trans isomerization product, trans-vitamin D, is only isolated after short-term irradiation in solution[2]. The formation of S1 and S2 has been related[3] to the occurrence of vitamin D in two cZt conformations that differ in the sense of helicity of the triene chromophore.

In order to investigate the relationship between the helicity and the possible influence of varying amounts of excitation energy on the photoproduct formation and in particular on the ratio S1/S2 we have studied the effects of wavelength, solvent and temperature on the photochemistry of vitamin D. Quantum yields of product formation in diethyl ether were determined. Crystalline vitamin D and vitamin D analogues were also irradiated.

When vitamin D is irradiated at room temperature at wavelengths longer than 302 nm all six photoproducts are formed. At shorter wavelengths the two allene derivatives S3 and S4 are not found in the irradiation mixture. The ratio of S1 and S2 does not reflect the ground state equilibrium. At lower temperature irradiation at 302 and 313 nm produces more S2 than expected from the temperature-induced change of the ground state equilibrium. At λ shorter than 302 nm the formation of S1 is favoured in the solvent isooctane; in ether and ethanol the proportion of S2 grows faster.

Irradiation of crystalline vitamin D and its analogues does not show a direct relation between the helicity in the ground state and the formation of S1 and S2 either.

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(2) R. Mermet-Bouvier, Bull. Soc. Chim. Fr. 1973, 3023
(3) J.W.J. Gielen, Ph.D. Thesis, Leiden 1981
(4) E.M. Vroom and H.J.C. Jacobs, Abstracts of the XIIIth IUPAC Symposium on Photochemistry, University of Warwick, Coventry 1990

ULTRAFAST CONFORMATIONAL RELAXATION PROCESSES IN SATURABLE DYES STUDIED BY TIME RESOLVED SPECTROSCOPY

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Photoinduced conformational relaxation such as photoisomerization involve large amplitude internal molecular motion which can be monitored by time-resolved spectroscopy. Extensive experimental studies have been reported on intramolecular rearrangements of olefines, polymethine and triphenylmethane dyes. In the recent years, particular attention was given to ultrafast photoisomerism processes in the latter three classes of compounds by picosecond and femtosecond studies [1-3 and references therein]. Polymethine and triphenylmethane saturable absorber dyes are used for laser applications such as passive mode-locking or short pulse amplifiers decoupling. More recently they have been applied to extracavity laser pulse shortening down to the subpicosecond level [4,5].

In order to understand the molecular processes responsible for the ultrafast absorption recovery of triphenylmethane saturable absorber dyes in fluid solutions, we measured their time-resolved transient absorption and gain spectra in the 320-750 nm wavelength range after subpicosecond laser excitation [6]. The observed transient spectra can be described by the superposition of the absorption and/or gain spectra of the ground and first excited states, and of a highly unstable transient state involved in the excited state relaxation process. The absorption cross sections of the transient state as well as the absorption and stimulated emission cross sections of the dye first excited S_1 state were extracted from these experiments and from stationary fluorescence measurements. The transient state absorption spectrum was found to be similar to that of S_1 but spectrally shifted to higher energies and attributed to a non fluorescent excited state conformer.

In order to characterize the photoinduced conformational change we undertook time-resolved anisotropy experiments. Pump-probe experiments with polarized light provide a mean to monitor changes in the direction of the transition dipole moment for the solution excited state electronic absorption during its relaxation process. The results obtained in time-resolved anisotropy measurements in the range of a few picoseconds will be presented.

[1] S. Abrash, S. Repinec, and R.M. Hochstrasser, J. Chem. Phys., 93, 1041, (1990)
[2] F. Heisel, J.A. Miché and J. Rachidi, Chem. Phys. Letters, 134, 379 (1987)
[3] A. Mokhtari, L. Fini and J. Chesnoy, J. Chem. Phys., 87, 3429, (1987)
[4] F. Nesa, M. M. Martin and Y. H. Meyer, Opt. Commun., 75, 294, (1990)
[5] N.D. Hung, Y. H. Meyer, M. M. Martin, F. Nesa, "Ultrafast Phenomena in Spectroscopy", Eds.E. Klose, B. Willhemi, Springer Proceedings in Physics 49, Springer-Verlag, 1990 p. 33
[6] M.M. Martin, P. Plaza, Y.H. Meyer, Chem.Phys.(1991) in press

RELAXATION CONFORMATIONNELLE ULTRARAPIDE DES COLORANTS SATURABLES ETUDIEE PAR SPECTROSCOPIE RESOLUE EN TEMPS

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La relaxation conformationnelle photoinduite, par exemple la photoisomérisation, met en jeu des mouvements moléculaires de grande amplitude qui peuvent être détectés par spectroscopie résolue en temps. Au cours de ces dernières années les réarrangements intramoléculaires ont fait l'objet d'un grand nombre d'études expérimentales à l'échelle des pico- et femtosecondes, dans les oléfines, les polyméthènes et les triphénylméthanes [1-3 et références incluses]. Les colorants appartenant aux familles des polyméthènes et triphénylméthanes sont des absorbants saturables très utilisés en technologie laser, pour le blocage en phase des modes d'une cavité ou pour découpler les amplificateurs des systèmes lasers à impulsions courtes et plus récemment, pour raccourcir les impulsions lasers par propagation résonnante *extracavité*, jusqu'au niveau subpicoseconde [4,5].

Dans le but de comprendre les processus moléculaires responsables du retour d'absorption ultrarapide des solutions de triphénylméthanes utilisées comme absorbants saturables, nous avons mesuré les spectres d'absorption transitoire et de gain de ces solutions, entre 320 et 750 nm, après une excitation laser subpicoseconde [6]. Nous avons montré que les spectres transitoires observés peuvent être décrits comme la superposition de spectres d'absorption et/ou de gain de l'état fondamental, du premier état excité S_1 et d'un état transitoire fugace mis en jeu dans le processus de relaxation non radiative de l'état S_1. Nous avons extrait de cette analyse les spectres de sections efficaces d'absorption de l'état S_1 et de l'intermédiaire. Le spectre de l'état intermédiaire est voisin de celui de S_1, mais déplacé vers les hautes fréquences. Nous avons attribué cet intermédiaire à un conformère non fluorescent de l'état excité.

Dans le but de caractériser le changement de géométrie de l'état excité, nous avons entrepris des mesures d'anisotropie. Les expériences pompe-sonde résolues en temps en lumière polarisée (en fixant les directions de polarisation des faisceaux pompe et sonde, orthogonales ou parallèles), permettent de suivre le changement de direction du moment dipolaire de transition d'absorption de l'état excité accompagnant le changement de géométrie. Nous présenterons les résultats obtenus dans l'étude de l'anisotropie à l'échelle de quelques picosecondes.

[1] S. Abrash, S. Repinec, and R.M. Hochstrasser, J. Chem. Phys., 93, 1041, (1990)
[2] F. Heisel, J.A. Miehé and J. Rachidi, Chem. Phys. Letters, 134, 379 (1987)
[3] A. Mokhtari, L. Fini and J. Chesnoy, J. Chem. Phys., 87, 3429, (1987)
[4] F. Nesa, M. M. Martin and Y. H. Meyer, Opt. Commun., 75, 294, (1990)
[5] N.D. Hung, Y. H. Meyer, M. M. Martin, F. Nesa, "Ultrafast Phenomena in Spectroscopy", Eds.E. Klose, D. Wilhemi, Springer Proceedings in Physics 49, Springer-Verlag, 1990 p. 33
[6] M.M. Martin, P. Plaza, Y.H. Meyer, Chem.Phys.(1991) in press

ETUDES PAR SPECTROSCOPIE LASER ULTRARAPIDE DU TRANSFERT DE CHARGE INTRAMOLECULAIRE ET DE L'ISOMERISATION TRANS-CIS. LE ROLE DU SOLVANT.

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Les molécules de colorant possédant un groupe donneur et un groupe accepteur d'électron reliés par un pont insaturé présentent un faible recouvrement entre leur spectres d'absorption et de fluorescence. Certaines ont d'excellentes propriétés laser: large accordabilité, fort taux de conversion, et faible seuil de pompage. Le composé DCM (4-(dicyanométhylène)-2-méthyl-6-[p-(diméthylamino)styryl]-4h-pyrane est un colorant laser styrénique largement utilisé. Cependant, des composés organiques connus comme rotors moléculaires, bien que présentant des structures chimiques et des spectres d'absorption et de fluorescence similaires, ont de mauvaises propriétés laser. Nous présentons dans ce papier une étude des propriétés photophysiques et photochimiques du DCM en tant que molécule modèle pour la détermination des caractéristiques de nouveaux colorants laser.

Les importantes modifications induites par le solvant sur les propriétés spectrales et la compétition entre les processus radiatifs et non radiatifs (conversion interne $S_1 \rightarrow S_0$, trans-cis isomérisation) ont été étudiées à l'aide de spectroscopies lasers nanoseconde et picoseconde. Nous avons déterminé quantativement l'efficacité des différents processus de désactivation du premier état singulet excité. Les rendements quantiques absolus de photoisomérisation du DCM ont été obtenus précisément au moyen d'un actinomètre au ferrioxalate. Plus que la viscosité, la polarité du solvant semble être un facteur déterminant. La photoisomérisation est limitée dans les solvants très polaires (méthanol, acétonitrile, diméthylsulfoxide, formamide, méthylformamide, diméthylformamide,...) mais très efficace dans les solvants faiblement polaires (chloroforme, dichlorométhane, tétrahydrofurane,....). Nous commenterons plusieurs modèles possibles de désactivation non radiative du premier état singulet excité.

ULTRAFAST LASER SPECTROSCOPY STUDIES OF PHOTOINDUCED INTRAMOLECULAR CHARGE TRANSFER AND TRANS-CIS ISOMERIZATION. THE ROLE OF THE SOLVENT.

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Dye molecules based on donor-acceptor chromogens constituted of an electron donor group and an electron acceptor group linked by an unsaturated bridge are remarkable as regards the weak overlap between the absorption and fluorescence spectra. Some of them present excellent laser properties: broad tunability, high conversion efficiency and low pumping threshold. The compound DCM or 4-(dicyanomethylene)-2-methyl-6-[p-(dimethylamino)styryl]-4H-pyran is a widely used styrene laser dye. However, organic compounds known as molecular rotors, although presenting similar chemical structures, absorption and fluorescence spectra, have poor fluorescing and lasing properties. The present paper is devoted to an extensive study of the photophysical and photochemical properties of DCM, as a model molecule in order to design new efficient laser dye molecules.

The dramatic effect of the solvent on the spectral properties and the competition between the radiative and nonradiative $S_1 \rightarrow S_0$ internal conversion and trans-cis isomerization processes is examined using picosecond and nanosecond laser spectroscopy. The various paths of the deactivation of the first excited singlet state are quantitatively determined. The absolute quantum yields of DCM trans-cis photoisomerization have been measured accurately with respect to the ferrioxalate actinometer. Besides viscosity, the solvent polarity is shown to play a more important role. Photoisomerization is inefficient in highly polar solvents (methanol, acetonitrile, dimethylsulfoxide, formamide, methylformamide, dimethylformamide,...) but very efficient in low polarity solvents (chloroform, dichloromethane, tetrahydrofuran,...). Possible models for the non radiative deactivation of the first singlet excited state are discussed.

Adiabatic *cis-trans* photoisomerizations of some bisstyryl compounds

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The traditionally accepted mechanism of Z-E photoisomerizations of olefins has been the diabatic mechanism: in the excited state the most stable geometry is such that the double bond is twisted 90°. From this geometry the excited molecule decays to the ground state where it isomerizes to either Z or E configuration[1]. However, Prof. K. Tokumaru and co-workers have found some antracenyl ethylenes where the plane geometry, in the excited triplet state, is more stabilized than the perpendicular one. This means that these substances, in the excited state, isomerizes according to an adiabatic mechanism. The adiabatic mechanism implies that the entire isomerization process occurrs on the excited energy surface, and that it is usually one-way (usually *cis* to *trans*)[2].

As a consequence of the adiabatic isomerization process, substances with more than one double bond, on a single excitation, might show Z-E photoisomerization of more than one double bond. A styryl stilbene (1), studied by K. Sandros, M. Sundahl et. al., shows adiabatic Z-E isomerization on both the excited singlet and triplet excited surfaces[3,4]. A few other bisstyryl compounds (2,3,4) have been studied with respect to isomerization quantum yields, photostationary states, and triplet life-times, determined with laser flash photolysis. In this series of bisstyryl compounds it seems that the adiabatic behaviour of the Z-E photoisomerization becomes increasingly pronounced as the triplet energy of the central aromatic unit drops.
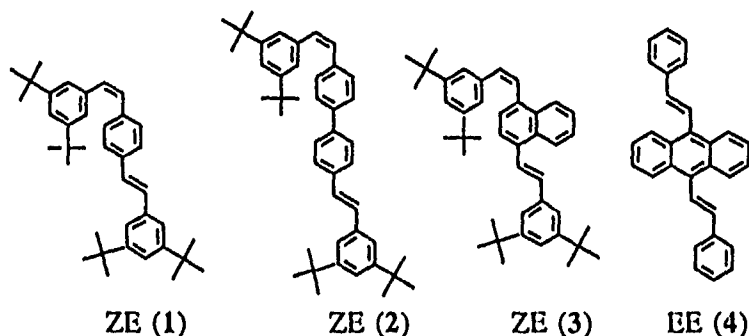
ZE (1)   ZE (2)   ZE (3)   EE (4)

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[4]Sundahl, M. *et. al. J. Phys. Chem.* 94 (1990) 6731.
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ETUDE THEORIQUE DU COLORANT STYRENIQUE DCM : EFFICACITE DE LA PHOTOISOMERISATION ET ETATS TICT. UNE ETUDE CS-INDO MRCI.

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Dans le but d'expliquer l'effet de la polarité du solvant sur l'efficacité de la photoisomérisation trans-cis et la structure électronique des états excités du colorant laser DCM, des calculs de chimie quantique MRCI (Multi. References. Configuration. Interaction) ont été effectués dans le cadre des approximations INDO. Nous présenterons ainsi, les courbes d'énergie potentielle, les moments dipolaires et la répartition des charges électroniques correspondant à l'état fondamental et aux premiers états excités singulets et triplets du DCM, obtenus lorsque l'on fait tourner la molécule autour de la double liaison centrale et de la liaison simple entre le groupe diméthylamino- et le noyau benzénique. Nous avons également envisagé les rotations autour des trois simples liaisons pouvant conduire à la formation d'états TICT (Twisted Intramolecular Charge Transfer). La méthode a été testée sur une molécule modèle le DMABN à partir de laquelle nous commenterons la validité des différents modèles de solvatation utilisés.

La courbe du premier état excité singulet du DCM, présente une faible barrière d'énergie potentielle à l'isomérisation trans-cis, qui n'est pas affectée par la polarité du solvant. Le seul état excité singulet présentant un large caractère de transfert de charge est l'état S2 dans une conformation où le groupe diméthylamino est perpendiculaire au noyau benzénique. La proposition d'une désactivation électronique de l'isomère trans dans l'état localement excité par formation d'un état TICT sera commentée en tenant compte des approximations de cette approche théorique.

THEORETICAL STUDY OF THE DCM STYRENE DYE : PHOTOISOMERIZATION EFFICIENCY AND TICT STATE. A CS-INDO MRCI STUDY.

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The solvent-induced changes upon the trans-cis isomerization efficiency and electronic structure of the excited states of the DCM styrene dye (4-(dicyanomethylene)-2-methyl-6-[p-(dimethylamino) styryl]-4H-pyran) , have been considered by means of CS INDO MRCI calculations (Conformations. Spectra, Intermediate. Neglect of Differential. Overlap, Multi. References. Configuration. Interaction). Potential energy curves, dipole moments and atomic charge densities as a function of two internal coordinates, namely, the rotation angle about the central "double" bond and the twisting of the dimethylamino group, have been obtained for the ground state and the lowest excited states. Structural requirements for the existence of ICT (Intramolecular Charge Transfer) excited states has been investigated by considering internal rotations about three single bonds. The reliability of the potential energy surfaces and of the solvation models has been discussed from test-calculations on the DMABN molecule.

In the first excited singlet state of DCM, the low energy barrier to the trans-cis isomerization, has been found unaffected by the solvent polarity. The only singlet excited state, presenting a large ICT character, has been found to be the S_2 state for a perpendicularly twisted conformation of the dimethylamino group (TICT state). The assumption of a deactivation of the trans-isomer in the locally excited state, through the TICT funnel has been largely discussed with reference to the simplifications of the present theoretical approach.

HYDROGEN TUNNEL EFFECTS IN THE METASTABLE TRIPLET STATES OF 2-(2'-HYDROXYPHENYL)BENZOXAZOLE AND 2-(2'-HYDROXY-4'-METHYLPHENYL)BENZOXAZOLE

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2-(2'-hydroxyphenyl)benzoxazole (HBO) and 2-(2'-hydroxy-4'-methylphenyl)benzoxazole (MHBO) can exist in two tautomeric forms, the enol-tautomer E, and the keto-tautomer K.

| R = H : | HBO | E |
| R = CH₃ : | MHBO | E_m |

K

K_m
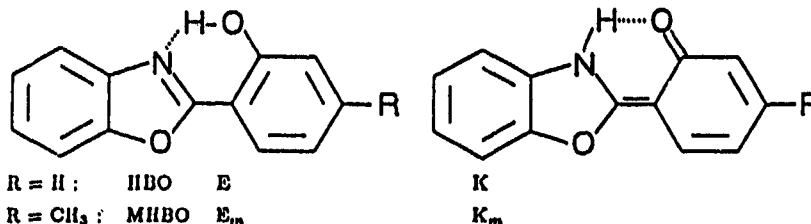
Flash exitation of HBO leads to the exclusive formation of the keto triplet state $^3K^*$ within a few nanoseconds. This state then rearranges to the enol triplet state $^3E^*$, whereby an equilibrium $^3K^* \underset{k_{ek}}{\overset{k_{ke}}{\rightleftharpoons}} {}^3E^*$ is established within microseconds. During this equilibration a hydrogen atom migrates between the N- and the O-atom of HBO.

The temperature dependence of the rate constants k_{ke} and k_{ek} is soleley determined by hydrogen tunnel effects. Replacement of the migrating hydrogen by deuterium (DBO) reduces the equilibration rate by a factor of 1000, i.e. due to this isotope effect the equilibrium between the two triplet states of DBO is established within milliseconds. Below ≈70 K the equilibration reaction of HBO and DBO becomes temperature independent.

Since the observed lifetimes have values which can easily be determined experimentally, the couple HBO and DBO is the first example where rate constans of hydrogen tunneling could be determined for both isotopomers between 30 K and 250 K in a variety of alkane solvents with drastically different viscosities. This made it possible to explore the important question how solvent friction influences hydrogen tunnel effects.

After introduction of a methyl group in 4'-position of HBO, the two triplet states $^3K_m^*$ and $^3E_m^*$ are no longer isoenergetic, with the result that the equilibrium is shifted towards $^3E_m^*$, because $^3K_m^*$ lies ≈300 cm^{-1} above $^3E_m^*$. The influence of this shift on the hydrogen tunnel effects has been investigated at different temperatures between 30 K and 250 K and the results are compared with those obtained with the unsubstituted compound HBO.

The Oxenium Ion, an Intermediate formed by Protonation of Aromatic Ketones in the Triplet State ?

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Although the photochemistry of aromatic ketones has been studied extensively, little is known about the reactivity of their excited states in water.[1,2] Protons quench $n\pi^*$ triplets,[2] but it is not known what the nature of the quenching is. To address this question we have studied acetophenone and related aromatic ketones.

Upon photolysis of acetophenone with an excimer laser or a conventional flash lamp, a long-lived intermediate I with absorption maximum at 280 nm is formed in acidic aqueous solution. The lifetime of I, $\tau=0.5$ s, at room temperature does not depend on oxygen or proton concentration. Stern-Volmer analysis shows that the intermediate I is a product of the protonation of the triplet. For acetophenone this intermediate I is formed within the 20 ns laser pulse, but for benzophenone a new intermediate II leading to I is formed with the same rate as the decay of the triplet. The lifetime of II is 50 ns and does not depend on the proton concentration.

No stable products are formed under conditions where the intermediates I and II are detected. Also, no H/D exchange in the phenyl ring is found.

The scheme represents our current working hypothesis to explain the observations. Suggestions for critical experimental tests or alternative hypotheses are welcome.

Scheme
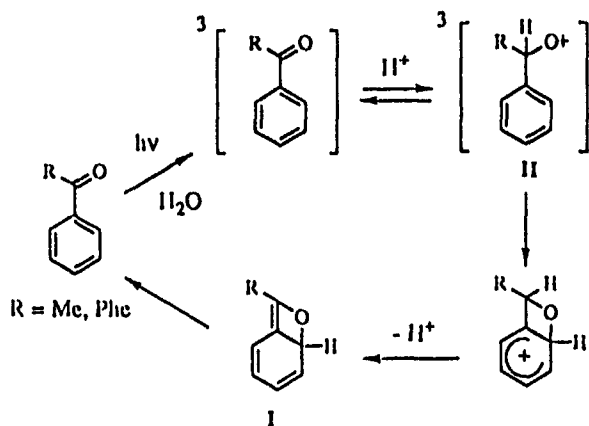
(1) J. F. Ireland, P. A. H. Wyatt, *J.C.S. Faraday I*, 1973, 69, 161
(2) M. B. Ledger, G. Porter, *J.C.S. Faraday I*, 1972, 68, 539

PHOTOLYSIS OF MATRIX-ISOLATED NH₃ :
MODEL-ASSISTED IDENTIFICATION OF TRAPPING SITES
IN ELECTRONIC SPECTRA OF THE PRODUCTS

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It has been generally assumed in the literature that doping of
rare gas matrices with ammonia yields NH_3 on single substitu-
tional sites in an fcc environment. In situ photolysis of
matrix-isolated NH_3 in the VUV yields NH_2 and NH. While the
visible absorption spectrum of NH_2 in Ar, Kr, and Xe exhibits
only one site, two sites are resolved in approximately equal
proportions in Ne, separated by about 50 cm⁻¹. We have recently
shown[1], by analysing a substructure superimposed on each rota-
tional line of the forbidden $a^1\Delta$ <-> $X^3\Sigma^-$ transition that NH
actually occupies two nearly degenerate sites in Ar, Kr, and
Xe, in approximately equal proportions. We assign these to NH
in single substitutional sites in fcc and hcp environments.
Site-selective detection on the spectrally resolved substruc-
ture components of the $a^1\Delta \to X^3\Sigma^-$ rotational lines has enabled
us to resolve excitation spectra of either site on the $A^3\Pi$ <-
$X^3\Sigma^-$ transition, but not on the $c^1\Pi$ <- $a^1\Delta$ transition, which
was studied in a two laser experiment. Local modes can be
observed in the phonon sidebands of the gas phase forbidden
$b^1\Sigma^+ \to a^1\Delta$ transition, which is vibronically induced by the
matrix. Comparison of the local mode frequency in argon with
model calculations strongly supports the assignment to a single
substitutional site. The calculations confirm the degeneracy of
the sites in fcc and hcp, and predict local modes of conside-
rably higher frequency on interstitial sites. A careful search
of the $a^1\Delta$ <-> $X^3\Sigma^-$ spectrum, while exciting different portions
of the $A^3\Pi$ <- $X^3\Sigma^-$ transition region, confirms the existence of
another non-rotating NH with local modes in the expected fre-
quency range, which is tentatively assinged to interstitial NH.

[1] C. Blindauer et al., Chem. Phys. 150 (1991) 93-108

Generation and Transformation of Excited Hydroxydiphenylmethyl Radicals in the Benzophenone-Ethanol System

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The chemistry of the hydroxydiphenylmethylradical **1** in ethanol was examined. Radical **1** was prepared by hydrogen abstraction of triplet benzophenone from ethanol. At low photon intensities (lamp), radical **1** combines with a solvent-derived radical to form pinacol **2** or it dimerizes to benzpinacol (**4**). At high photon densities (laser jet) excitation of radical **1** yields much higher amounts of the substituted benzophenone **3** and benzhydrol (**5**).

	rel. yield [%] of products[a]			
Photolysis mode	2	3	4	5
Laser Jet	20	51	11	18
Lamp	1	30	65	3

a) Normalized to 100%; error ca. 5 % of stated value
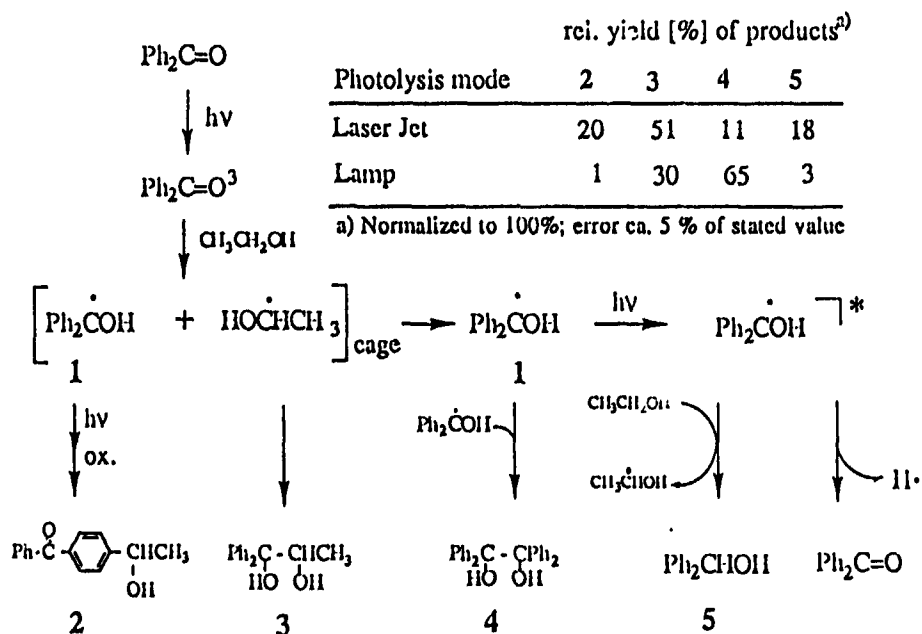
Scheme 1

Formation of **2** is rationalized by combination of radical **1** with an ethanol derived radical and subsequent in situ oxidation. The intensity dependent formation of benzhydrol speaks for the ability of the excited radical **1** to abstract hydrogen from ethanol, a hitherto unknown reactivity of this excited radical species.

THE PHOTOCHEMISTRY OF SOME 2-HALO-1,3-DIENES

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Irradiation of vinyl halides in solution affords both products derived from vinyl radical- and from vinyl cation-intermediates The mechanism of formation of these intermediates is still a subject of discussion. Homolytic bond cleavage of the carbon-halogen bond and subsequent electron transfer as well as direct homolysis and heterolysis have been suggested[1].

In order to get more insight in the mechanism and as part of our quantitative study of structure-photoreactivity relations in vinyl halide photo-chemistry we have studied a series of β-halo,-β-(methyl-substituted) ethenyl-styrene systems such as I, II and III (X = Cl, Br).
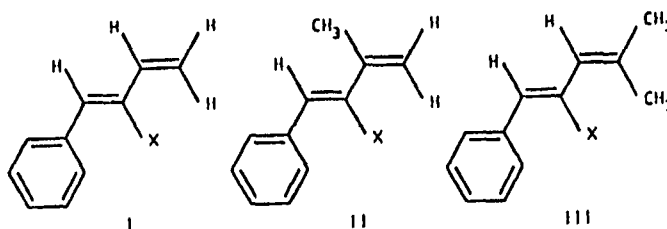
Quite efficient dehalogeration (from S_1) and formation of (i.a. allylic rearranged) ionic products are observed. No radical products were detected.

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CIDNP and CIDEP Studies on Intramolecular Hydrogen
Abstraction Reaction of Polymethylene linked
xanthone and xanthene.

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Intramolecular hydrogen abstraction reaction of a polymethylene
linked xanthone and xanthene is investigated by using chemically
induced dynamic nuclear and electron polarization (CIDNP and CIDEP)
methods. The reaction scheme is determined from the CIDNP and CIDEP
spectra of unlinked xanthone and xanthene system. The exchange
integral J between the two terminal radicals of the polymethylene
linked system is obtained from both of the simulation of the radical
pair CIDEP spectrum and the magnetic field effect of the low field
CIDNP respectively.

In the simulation process of the CIDEP, we used the spin
correlated CIDEP theory modified with (a) the fast population
relaxation between the central $S-T_0$ mixed state[1], (b) the
contribution from the triplet mechanism, and (c)hyperfine line
dependent line width[2]. The J values obtained from this method
depend on the polymethylene chain length and the temperature. The
magnetic field effect of the CIDNP is simulated by the stochastic
Liouville method, and the effective J value is obtained from the
peak position of the magnetic field effect. The tendency of the
chain length and the temperature dependence of the effective J
values is same as the results of CIDEP. But the quantitative value
is larger than that of the CIDEP. We conclude that the isomers of
the biradicals which have shorter interradical distance can be
measured by the CIDNP method than that of CIDEP.

[+] Present address: Department of Chemistry Faculty of Science,
Kyoto University, Kyoto   , Japan.
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SPECTROSCOPIE LASER DE PHOTOAMORCEURS SOUFRES :
LES COMPOSES S-PHENYL THIOBENZOATES

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Le photoamorçage d'un processus de photopolymérisation radicalaire dépend de l'efficacité du photoamorceur. De nombreux photoamorceurs efficaces existent, mais on recherche de nouveaux composés possédant à la fois une meilleure photosensibilité et une plus grande réactivité. Les composés S-phényl thiobenzoates de part la faiblesse de la liaison C-S génèrent facilement des radicaux benzoyls. Nous avons montré que les radicaux benzoyl et thiyl étaient formés par coupure de la liaison C-S dans le premier état excité triplet [1].

Les expériences de spectroscopie laser résolue dans le temps nous ont permis de mettre en évidence le radical benzoyl ainsi que d'étudier la désactivation de l'état triplet. L'étude de la photopolymérisation amorcée par les composés S-phényl thiobenzoates a montré que le rendement est directement lié à l'efficacité du photoamorceur. Ces expériences nous amènent à conclure que certains de ces composés peuvent être plus efficaces que les composés de type benzoïne éther. Ceci est vraisemblablement lié à une meilleure absorption de la lumière. Les radicaux benzoyl et thiyl agissent respectivement dans l'étape d'amorçage et de terminaison.

Références :

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LASER FLASH PHOTOLYSIS AND THE PHOTOPOLYMERIZATION STUDY ON SULPHUR CONTAINING PHOTOINITIATORS: S-PHENYL THIOBENZOATE.

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The photoinitiation of radical chain polymerization depends on the efficiency of the photoinitiator. Many efficients photoinitiators are available, but improved systems which exhibit faster curing speed and better photosensitivity are required. S-phenyl thiobenzoate compounds can easily generate benzoyl radicals due to the weak C-S bound. We show that both benzoyl and thiyl radicals arise from the α cleavage of the C-S bound in the first excited triplet state. (1)

Laser flash photolysis experiment allow us to observe benzoyl radical and to study the deactivation of the triplet state. The yield of polymer from the photopolymerization initiate by S-phenyl thiobenzoate is directly related to the photoinitiator reactivity. These experiments lead us to conclude that these photoinitiators are more reactive than benzoin ethers. The benzoyl and thiyl radicals act as initiator and terminator agents.

References:

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D. Ruhlman, J. Photochem. Photobiol. A: Chem 53 (1990) 359.

Diffusional Kinetics of Bimolecular Photoreactions on Solid Surfaces

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Bimolecular chemical reactions on solid surfaces require some mobility of the adsorbed species. In the following, the kinetics of diffusion controlled deactivation processes $T_1 + T_1 \rightarrow S_1 + S_0$ and $D^+ + e^- \rightarrow S_0$ are quantified by time-resolved fluorescence and transient absorption spectroscopy after pulsed laser excitation. The first type of reaction is investigated with polycondensed aromatic nitrogen heterocycles, the second one with phenylenevinylenes and diphenylpolyenes, all adsorbed on aluminas and silicas with pore sizes from 4-100 nm and very different hydroxyl coverages. Depending on the latter parameters, the diffusional rate constants of triplet-triplet annihilation and radical-electron recombination vary by several orders of magnitude. Both reactions are thermally activated with diffusional barriers of $5-10$ kcal mol^{-1}.

The decay kinetics was analysed in detail with conventional second order and geminate first order rate equations in limited and unlimited compartments, and with the fractal approach. The first method is reliable on adsorbents with large pore diameters. We found diffusional coefficients depending strongly on the masses and sterical requirements of the adsorbates. The second method was used with a spectral dimension of $d_s = 4/3$. Then this method is quantitatively applicable to adsorbates with very small pore sizes, where interporal diffusion is necessary for bimolecular collisions. Since one of the aims of the fractal approach is the quantification of "irregularity" and since the approach can be successfully applied to our results of interporal diffusion but not to the intraporal ones, we conclude that only the pore distribution in the oxides is irregular, whereas the pores themselves are formed by regular, smooth surfaces.

CIDEP GENERATED IN THE S_1 AND T_1 MOLECULES-RADICAL INTERACTIONS

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It is well known that the lowest excited singlet (S_1) or triplet (T_1) states are quenched by free radicals. Kinetic studies have been done about these phenomena by laser flash photolysis and the quenching mechanisms have been discussed based on these works. Time resolved ESR (TR-ESR) is useful to study intermediate paramagnetic species, but few[1,2] works were carried out on quenching mechanisms by TR-ESR.

We applied TR-ESR to study quenching mechanism and found out the chemically induced dynamic electron polarization (CIDEP) on free radicals generated through the S_1- and T_1 molecules-radical interactions. The rules of the CIDEP generation are summarized as follows,

S_1 molecule-radical   A + A/E, T_1 molecule-radical   E + E/A,

where A and E mean total microwave absorption and emission, respectively, and E/A means emission in low and absorption in high magnetic fields. Total absorptive and emissive polarizations are explained by the avoided crossing of $|Q-3/2>$ and $|D1/2>$ states of triplet-radical pair through the zero-field-splitting interaction of triplet molecule. The hyperfine dependent polarization is interpreted by the mixing of $|Q\pm1/2>$ and $|D\pm1/2>$ states in the region of non-zero exchange interaction due to hyperfine interaction followed by the exchange interaction by the reencounter.

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PHOTOCHEMICAL PRIMARY PROCESSES OF POLY(ETHYLENE TEREPHTHALATE) SOLID POWDERS: A DIFFUSE REFLECTANCE LASER PHOTOLYSIS STUDY

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Three photo-excited species of poly(ethylene terephthalate) (PET) solid powders were observed with diffuse reflectance laser photolysis and their assignment was discussed.

The transient absorption spectra are shown in Fig. 1. A broad peak around 430nm was quenched by oxygen at nearly diffusion controlled rate, but not quenched by N_2O. As N_2O is a good electron acceptor, an anion radical is excluded as a possible intermediate. Doping PET with several molecules of known triplet energy, we performed T-T energy transfer experiments. In the case of p-terphenyl-doped powders, an absorption peak at 460nm which is assigned to the triplet of p-terphenyl was observed instead of the 430nm band of PET. These results indicate that the latter band is due to the triplet state of PET powders. From kinetical studies, we found that the transient absorption around 430nm consists of two components. An absorption band around 520nm was observed additionally when the sample was excited with 308nm pulse. Examining various possibilities, the band was assigned to a precursor of the above triplet (430nm) species. The band (around 520nm) could be assigned to the triplet state of PET powders from the consideration of temporal behavior.

These primary processes will be discussed in terms of inhomogeneity of polymer structure.
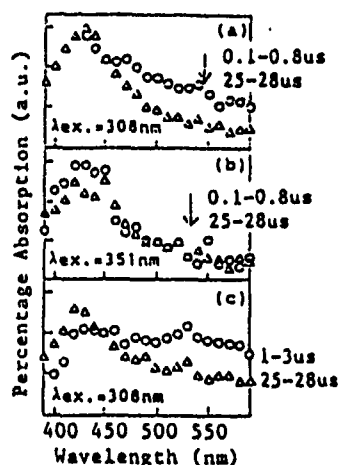
Fig.1. Transient absorption spectra of PET powders at room temperature (a), (b), and 77K (c). The excitation wavelength is given in the figure.

THE GENERATION OF α,α-DIMETHYLBENZYL CATION IN THE PHOTOLYSIS OF 2,3-DIMETHYL-2,3-DIPHENYLBUTANE. PROTONATION INDUCED SIDE-CHAIN FRAGMENTATION.

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The photofragmentation of 2,3-dimethyl-2,3-diphenylbutane was studied by nanosecond 248 nm laser flash photolysis. In the course of our investigation, we observed the formation of α,α-dimethylbenzyl radical from the parent molecule in deoxygenated 1,1,1-trifluoroethanol (TFE) solutions and found that its generation requires more than one photon. This finding is consistent with the formation of the 2,3-dimethyl-2,3-diphenylbutyl radical cation by biphotonic ionization followed by fragmentation of the C_2-C_3 bond to yield both α,α-dimethylbenzyl radical and cation, the latter being too short lived to be observed.

When the polarity of the solvent was decreased by going to dichloromethane, only the radical was observed. This time, its generation is monophotonic which is consistent with homolytic photocleavage of the central C-C bond.

In order to observe the expected cation, a solvent of high polarity and low nucleophilicity is required. 1,1,1,3,3,3-Hexafluoroisopropanol (HFIP) fulfills these requirements[2]. However, in this solvent the predominant product, from the 248 nm laser excitation, is the α,α-dimethylbenzyl cation while the corresponding radical is not observed. To explain this observation, we propose the initial generation of a cyclohexadienyl type cation by photoprotonation of the substrate. This carbonium ion undergoes heterolytic side-chain cleavage to yield the α,α-dimethylbenzyl cation and isocumene.
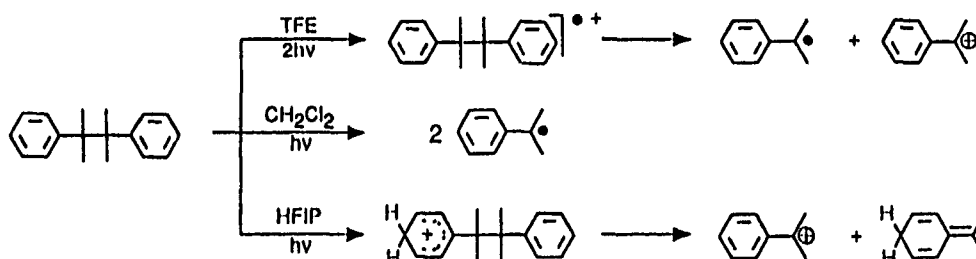
In order to test the generality of this novel method with respect to generation of carbonium ions, the photochemistry of 1,1-dimethyl-2-phenylethyl alcohol in HFIP was studied. Product analysis after 254 nm photolysis revealed the formation of toluene and acetone as major products, which is in support of the photoprotonation mechanism.

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SEPARATIONS EN CHAMP NUL DES SOUS-NIVEAUX DU TRIPLET FLUORESCENT
DES CARBENES AROMATIQUES

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Les carbènes aromatiques tels que le dibenzocycloheptadiénylidène (DBC) sont des intermédiaires réactionnels possédant deux électrons non appariés localisés sur le même atome de carbone. Ces espéces se forment par photolyse UV "in situ" de composés diazotés en matrice d'hexane-n ou heptane-n à 15-20 K. Ils sont détectés par leur fluorescence triplet-triplet. Les études de RPE[1] ont montré que le triplet fondamental T_0 du DBC a une séparation entre sous-niveaux D = 0.3932 cm^{-1}.

La fluorescence du DBC piégé en matrice à 15-20 K décroit suivant une loi non exponentielle. Ceci est expliqué par une émission à partir de sous-niveaux distincts de T_1, plus rapide que la relaxation spin-réseau, dans nos conditions expérimentales[2]. En présence d'un champ magnétique, la durée de vie $\tau_{\parallel}$ de la composante lente du déclin est raccourcie. En suivant la même démarche que pour le m-xylylène,[3] nous calculons la dépendance de $\tau_{\parallel}$ en fonction d'un champ magnétique faible pour différentes valeurs du paramètre D à l'état excité T_1 d'une molécule supposée plane. Pour le DBC, la courbe théorique qui traverse au mieux les points expérimentaux correspond à D = (0.07 ± 0.01) cm^{-1}. Puisque la valeur de D est essentiellement contrôlée par l'interaction spin-spin, la décroissance de D entre l'état fondamental T_0 et l'état excité T_1 montre que les deux électrons non appariés localisés sur le carbone central divalent à l'état T_0, tendent à se délocaliser sur les noyaux aromatiques à l'état T_1.

Alors que les séparations des sous-niveaux triplets des carbènes à l'état fondamental sont mesurées par RPE, le paramètre D dans un état excité de durée inférieure à la microseconde se trouve atteint pour la première fois, grâce à l'effet d'un champ magnétique sur les déclins de fluorescence.

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(1) I. Moritani, S.I. Murahashi, M. Nishino, Y. Yamamoto, K. Itoh and N. Mataga, J. Am. Chem. Soc. 89, 1259 (1967).
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ZERO-FIELD SPLITTING OF THE FIRST EXCITED TRIPLET STATE IN AROMATIC CARBENES ESTIMATED FROM MAGNETIC EFFECTS ON FLUORESCENCE DECAYS

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Matrix-isolated aromatic carbenes such as dibenzocycloheptadienylidene (DBC) are generated "in situ" by UV photolysis of the corresponding diazo precursors dispersed in n-hexane or n-heptane at 15-20 K. They are detected by their triplet-triplet fluorescence spectra. ESR experiments[1] indicate that DBC has a triplet ground state T_0 with a ZFS parameter $D = 0.3932$ cm^{-1}.

The fluorescence decay of DBC in n-hexane or n-heptane at 15-20 K is nonexponential and significantly modified in the presence of a magnetic field. As the field increases the lifetime $\tau_{||}$ of the slow component decreases drastically. The nonexponential decay is attributed to the fluorescence from different sublevels of the emitting triplet T_1 at a rate faster than the spin-lattice relaxation between the different sublevels[2].

As for m-xylylene, the dependence of $\tau_{||}$ as a function of a weak magnetic field can be calculated for different values of the ZFS parameter D,[3] assuming a planar molecule. For DBC, the best fit between the calculated curve and the experimental points corresponds to $D = (0.07\pm0.01)$cm^{-1}. This shows that the D value decreases by a least an order of magnitude by excitation from the ground triplet state T_0 to the first triplet T_1. Since the D value is mainly controlled by spin-spin interaction, our result suggests that the unpaired electrons which are mainly localized on the central divalent C atom in the T_0 state, become largely delocalized on the aromatic rings in the T_1 state.

Whereas the ZFS parameter D is currently measured by ESR for matrix-isolated carbenes in the ground state T_0, this parameter has been determined, for the first time, in the first excited triplet T_1 of these species by using the above-described method.

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ETUDE SPECTROCINETIQUE DE LA DEGRADATION UV
DE SYSTEMES PHOTOCHROMIQUES

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Le photochromisme orange/bleu du dithizonate de mercure a été étudié par une nouvelle méthode spectrocinétique qui permet l'évaluation complète du spectre UV/Visible de l'isomère bleu thermiquement instable[1]. En solution dans le tétrachlorure de carbone, il se produit une photodécoloration progressive. L'origine de cette dégradation provient de la catalyse du retour thermique bleu ----> orange par des produits de photodégradation. Parmi ces produits, l'effet de la dithizone libre a été étudié[2]. Après repos dans l'obscurité, l'effet de fatigue a tendance a disparaître et le photochromisme est récupéré. Un mécanisme a été établi et les paramètres cinétiques et spectroscopiques les plus importants ont été déterminés. La participation d'un complexe monodithizonate de mercure est proposée.

D'un autre côté, le cas du TPID/CHCl$_3$ (TPID = triphenylimidazolyle dimère) illustre un système expérimental relativement différent (jaune pâle/violet) où la dégradation augmente même après repos à l'obscurité. L'origine de cette dégradation fortement accélérée réside dans un mécanisme réactionnel peu commun qui fait du système TPID/CHCl$_3$ le seul exemple connu où un tel effet non linéaire a été mis en évidence[3]. Une boucle autocatalytique apparaît lorsque les radicaux triphenylimidazolyle (TPI·), qui initialement font écran et empêchent la photolyse du chloroforme, commencent à être décolorés sous l'influence des ions H· produits justement par la photodécomposition du CHCl$_3$. Cette boucle est responsable de la forte accélération du processus de décoloration sous irradiation UV en continu.
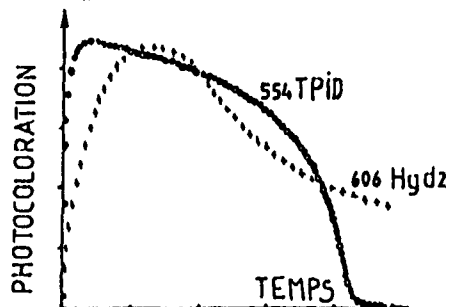
La Figure 1 compare les cinétiques de photodégradation des deux systèmes:
a)-ralentissement (dithizonate de mercure /CCl$_4$);
b)-accélération (TPID/CHCl$_3$).

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3)-B.Borderie, D.Lavabre, G.Levy, J.C. Micheau and J.P. Laplante
J.A.C.S. 112(11), 4105-9, (1990).

SPECTROKINETIC INVESTIGATION OF THE UV DEGRADATION OF PHOTOCHROMIC SYSTEMS

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The orange/blue photochromism of mercury dithizonate has been investigated using a new spectrokinetic method[1] allowing the complete evaluation of the UV/Visible spectrum of the thermally unstable blue isomer. In carbon tetrachloride solution, a gradual photofading occurs. The origin of this decay must be related to the catalysis by photodegradation products of the blue ---> orange thermal return. Among these photoproducts, the effect of the free ligand dithizone was investigated[1]. After several hours in the dark, the fatigue phenomenon disappears and the photochromic effect is recovered. A reaction mechanism was established, and the relevant kinetic and spectroscopic parameters were determined. The involvement of a monodithizonate mercuric complexe is assumed.

On the other hand, the case of the TPID/CHCl$_3$ (TPID = triphenylimidazolyl dimer) illustrates a rather different experimental system (pale yellow/violet) where the fading increases even after a rest in the dark. The origin of this strong accelerating decay lies in a very special mechanism making the TPID/CHCl$_3$ system the only example so far where such a non linear kinetic effect has been recognized[1]. A feedback loop occurs when the triphenylimidazolyl radicals (TPI*), which initially have a screening effect and prevent photolysis of chloroform, start to be bleached by the H* ions produced by CHCl$_3$ photodecomposition. This loop is responsible of the strong acceleration of the fading process during continuous UV irradiation.
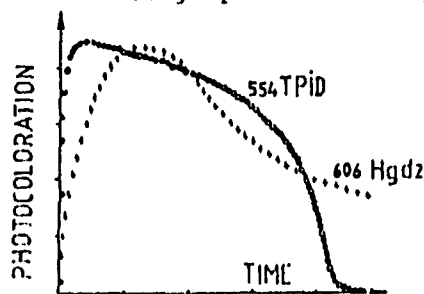
Figure 1 compares the kinetics of the photodegradation of the two systems:
a)-slowing down (mercury dithizonate/CCl$_4$);
b)-accelerating (TPID/CHCl$_3$).

References:
1)-H. Rau and G. Greiner, EPA Newsletters 41, March 1991, 40-55.
2)-A.E. Goodwin and H. Mottola, Anal.Chem. 55, 329-34 (1983).
3)-B.Borderie, D.Lavabre, G.Levy, J.C. Micheau and J.P. Laplante J.A.C.S. 112(11), 4105-9, (1990).

HIGH STABILIZATION OF COLORED SPIRONAPHTHOXAZINES
BY PHOTOCHROMIC CHELATE FORMATION

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So far, spironaphthoxazines have been used for several commercial applications such as light filters, ophthalmic lenses, sunglasses, and ski goggles[1]. This is mainly due to their excellent fatigue resistance and rapid color changes both in the light and in the dark. The colored merocyanine form generated upon exposure to the light is thermally unstable, recovering colorless spiro form immediately after the offset of the light. Our effort has been focused on keeping the colored form more stable in the dark. This report demonstrates that the chelate formation with di- and trivalent metal ions is quite suitable for this purpose, if the compound has a coordinating group adjacent to the oxazinyl oxygen which acts as another coordinating group in the merocyanine form. The reaction scheme is shown below[2].

Methoxy, hydroxy, and sulfonyl groups were used as the coordinating group (R_2) and the metal ions employed were inorganic salts or mixed complexes with acetylacetonate and ethylenediamine. The half lifetime of the colored form in the dark was $10 - 10^5$ times longer in the presence of metal ions than in their absence. This stability effect was dependent on metal ions, ligands, and/or matrices. Generally, it increased with the increase in the electron negativity of metal ions and in the donating ability of ligands. The excess stabilization was greater in polymer films than in solutions. The bathochromic shift to the near infrared region was also observed.
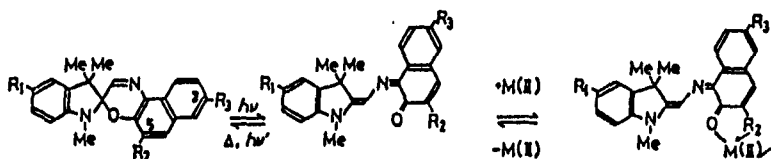
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A PHOTOCHROMIC SYSTEM BASED ON THE FORMATION OF FLAVYLIUM DYES

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Flavylium ions can react with hydroxid ions to form different products [1]. In a glycerol-borax class of high viscosity obviously the pseudo base B is formed. On irradiation B can be transformed back to the flavylium ion F':
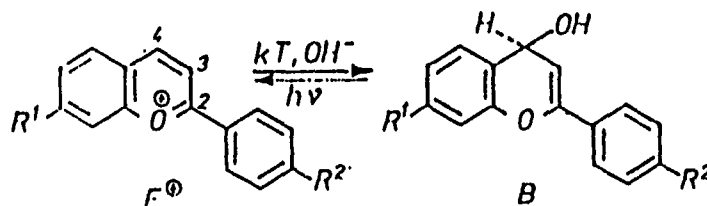
The dependence of the photochemical and the thermal reaction on structural and environmental effects has been studied. Both reactions depend strongly on structural and environmental effects (viscosity, pH). In particular, the effect of the donor strength of the substituents R^1 and R^2, the effect of bridging the 2-phenyl group to the benzopyrylium moiety (position 3) and the role of substituents in 4-position has been studied.

Spectral data and reaction rate parameters (quantum yield, decay time, rate constants, activation energy) were determined.

[1]   R.A. McClelland and S. Gedge, J. Am. Chem. Soc. 102
      (1980) 5838

PHOTOCHEMISTRY AND PHOTOPHYSICS WITHIN CYCLODEXTRIN CAVITIES

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In studies of solid-state photochemistry, it has been recognized
that the topochemical relations among neighboring molecules and atoms
dictate the outcome of photochemical excitation[1]. However, photochemistry
within CD cavities involves features quite distinct from those of
crystalline solids since the interior of the cavity constitutes an
isolated environment. Also, since included species are usually present
only as single molecules within the cavity, photochemistry is restricted
to intramolecular events, except in cases of multiple occupation of
cavities or such occupences that intermolecular interaction is possible.
These features offer opportunities to the photochemist to use the CD
cavity as a vehicle to focus experiments only on certain specific aspects
of a mechanistic problem and to use it as a microvessel to carry out
selective phototransformations. Thus, we will examine photochemical and
photophysical processes that occur in molecules complexed within CD's and
we will compare the output to that which occurs in solution and in the
solid state. Such, more ol less systematic studies, may help in under-
standin the chemical and physical properties of organic molecules
included in CD's.

In the present wotk we present two examples : the photochemical
dimerization of p-MeO-cinnamic[2] acid and the photochromism[3] of
N-5-Cl-salicylideneaniline insite the cyclodextrin cavity.

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POLYMER MATRIX EFFECT ON THE PHOTOCHROMISM OF SPIROPYRAN

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In relation to the photochromism of 1,3,3-trimethylindolino-6'-nitro-8'-substituted-benzospiropyran derivatives (SP), polymer matrix effect on the decoloration accompanying the reaction of merocyanine (MC) to SP in polymethylmethacrylate (PMMA, $M_n = 7 \times 10^3 - 1 \times 10^6$), a copolymer of MMA and a monomer having a SP group (CP, $M_n = 6.3 \times 10^4$), and polystyrene (PSt, $M_n = 7.8 \times 10^4$) films was studied by flash photolysis using Nd:YAG laser (355nm) at various temperatures.

The decoloration rate is characterized by non-homogeneous distribution of the free volume in polymer films and analyzed based on a kinetic matrix effect. The dispersive parameter in the kinetic matrix effect (β) was obtained: $\beta = 0.5$ in PMMA and CP films and $\beta = 0.37 - 0.45$ in PSt film. Arrhenius plots of the matrix response function time constant (α) versus inverse of temperature change significantly at T_g (370-390K) corresponding to the glass transition, $T\beta$ (240-270K), and $T\beta'$ (310-330K). $T\beta'$ is observed in MC-PMMA films, when MC has a ester group at 8' position of MC. On the other hand, $T\beta'$ is observed neither in PMMA film dispersed with MC having no ester groups nor in CP and PSt films. Therefore, the distribution of the free volume in polymer films depends significantly on onset of segmental motions, onset of motions of side groups, and the interaction between two ester groups of MC and PMMA, respectively.

Fast and slow processes are found in the decoloration of MC having a ester group at 8' position below 273K in PMMA and CP films. The fast decay rate is constant at 183-273K. The ratio of MC undergoing the fast process to MC doing the slow one increases with decreasing temperature. Stable MC and unstable MC below 273K correspond to trans-MC and cis-MC isomers in PMMA and CP films, while only trans-MC isomer forms in PSt film. It is suggested that cis-MC is stabilized in polar matrix (PMMA) through the interaction between two ester groups of MC and PMMA.

TRANSFERT DE PROTON INTRAMOLECULAIRE PHOTOINDUIT PRESENTE PAR LA METHYL-4 OMBELLIFERONE

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La méthyl-4 ombelliférone (4-MU) est un indicateur fluorescent et un colorant laser au domaine d'émission exceptionnellement large (360-590 nm). Ceci est dû à l'existence de quatre formes fluorescentes éventuelles, qui peuvent être sélectionnées selon le solvant et le pH: la forme neutre ($\underline{N}$*), et les formes: anionique ($\underline{A}$*), cationique ($\underline{C}$*) et tautomère ($\underline{T}$*), dérivant de $\underline{N}$* par transfert de proton à l'état excité, suivant le schéma général:
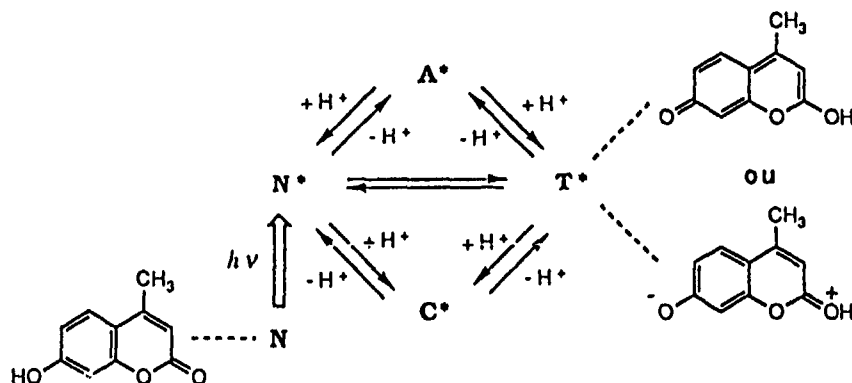
Le mécanisme de la réaction de tautomérisation photoinduite n'a pas encore été totalement élucidé. La question de savoir si $N^* \rightleftharpoons T^*$ peut se produire par transfert de proton intramoléculaire (assisté par des molécules de solvant), ou obligatoirement par l'intermédiaire des espèces A* ou C*, demeure un sujet de controverse. En fait ce problème est lié à la nature de T*, éventuellement zwitterionique.

L'étude présentée ici a pour but de contribuer à l'élaboration du modèle réactionnel en mettant à profit des mesures cinétiques réalisées par fluorimétrie de phase multifréquence. Les résultats portent sur le comportement de la méthyl-4 ombelliférone dans un solvant hydroxylique tel que le n-butanol particulièrement adapté à l'observation des seules formes N* et T*. L'ajout graduel d'eau au système a été étudié, et, en parallèle avec les mesures cinétiques, l'examen des spectres de fluorescence permet d'approfondir le rôle des molécules "relayant" le transfert de proton lors de la tautomérisation de 4-MU.

PHOTOINDUCED INTRAMOLECULAR PROTON TRANSFER
IN 4- METHYLUMBELLIFERONE

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4-Methylumbelliferone (4-MU) is a fluorescent indicator and a laser dye whose
emission range is exceptionally broad (360-590 nm). This is due to the existence of four
possible fluorescent species, which can be selected depending on solvent and pH: the neutral
form (N*), and the anionic (A*), cationic (C*) and tautomeric (T*) forms stemmed from N* by
excited-state proton transfer, according to the general scheme :
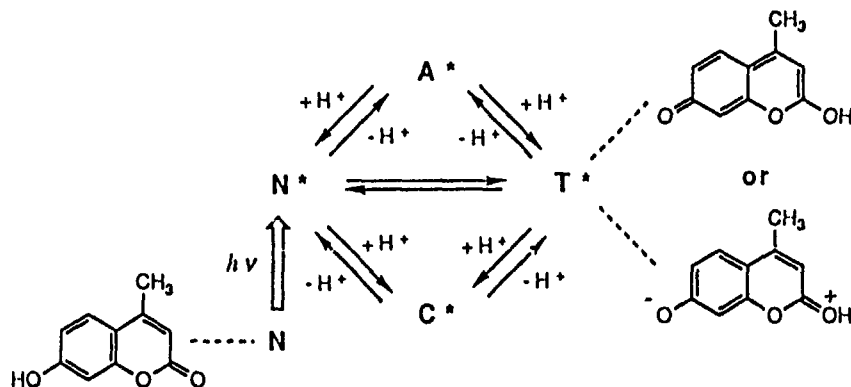
The mechanism of photoinduced tautomerization has not been cleared up yet. A debated
question remains whether N* $\rightleftharpoons$ T* may occur directly by intramolecular proton transfer, or
necessarily via A* or C* intermediates. In fact, this problem is related to the possible
zwitterionic nature of T*.

The present study aims at bringing the contribution of time-resolved measurements
using multifrequency phase fluorometry to an elaboration of the reaction model. The presented
results focus on 4-MU behavior in a hydroxylic solvent such as n-butanol which turns out to be
a convenient medium for isolating the only emission from N* and T* forms. The effect of
gradual addition of water is investigated, and in conjunction with kinetic measurements,
fluorescence spectra studies allow us to point out how water molecules may relay proton
transfer in 4-MU tautomerization.

TRANSFERT D'ENERGIE PHOTOINDUIT DANS UNE SUPERMOLECULE COUMARINIQUE. DETERMINATION DE LA DISTRIBUTION DE DISTANCE INTERCHROMOPHORE ET EFFET DE LA COMPLEXATION PAR UN CATION

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Le transfert d'énergie électronique au sein d'une supermolécule constituée de deux coumarines liées par une chaîne très flexible (pentaoxyéthylène), a été étudié par spectroscopie de fluorescence stationnaire et par spectroscopie d'absorption résolue dans le temps.

DONNEUR   ACCEPTEUR
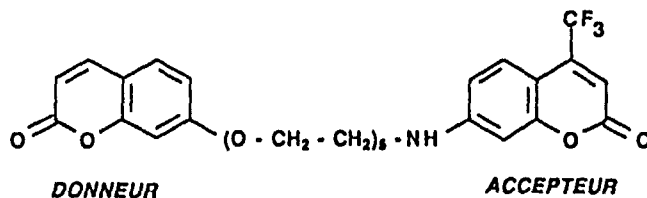
Des mesures dynamiques par la technique "pump-probe" à l'échelle sub-picoseconde montrent que le transfert se produit en quelques picosecondes, et les résultats peuvent être interprétés par un modèle du type interaction dipôle-dipôle impliquant une distribution Gaussienne des distances entre les deux coumarines. La distribution Gaussienne déduite des résultats expérimentaux est en bon accord avec celle obtenue par des calculs conformationnels.

La chaîne liant les deux coumarines est capable de complexer certains cations. Une complexation efficace a été observée avec du perchlorate de plomb dans le carbonate de propylène et l'acétonitrile. Il en résulte une modification importante des propriétés photophysiques de la supermolécule; en particulier le rendement de transfert est augmenté de façon significative lors de la complexation. La stoechiométrie du complexe a pu être déterminée à partir de l'évolution du spectre d'absorption lors de l'addition de cation.

PHOTOINDUCED ENERGY TRANSFER IN A DONOR-ACCEPTOR COUMARIN SUPERMOLECULE. RECOVERY OF THE DISTRIBUTION OF INTERCHROMOPHORIC DISTANCES AND EFFECT OF CATION BINDING

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Electronic energy transfer in a supermolecule consisting of two coumarins linked by a highly flexible chain (pentaglyme) has been studied by steady-state fluorescence spectroscopy and time-resolved absorption spectroscopy.

Sub-picosecond time-resolved excite-and-probe measurements show that energy transfer proceeds on a time scale of several picoseconds and that the results can be well described by a dipole-dipole interaction model involving a Gaussian distribution of distances between the two coumarins. The recovered Gaussian distribution agrees fairly well with the distribution derived from conformational calculations.

The chain linking the two coumarins is able to complex cations. Efficient complexation by lead perchlorate has been observed in propylene carbonate and in acetonitrile, which induces changes in photophysical properties of the supermolecule; in particular, the efficiency of energy transfer is significantly increased upon complexation. The stoechiometry of the complex can be determined from steady-state absorption data.

DEPOLARISATION DE FLUORESCENCE PAR TRANSFERT D'ENERGIE DANS DES PAIRES DE CHROMOPHORES IDENTIQUES OU DIFFERENTS

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Nous présentons une étude théorique de la dépolarisation de fluorescence par transfert d'énergie du type Förster dans des paires de chromophores identiques ou différents, situés à une distance fixe et sans corrélation d'orientation.

Dans le cas de chromophores différents, le déclin d'anisotropie de l'accepteur $r_A(t)$ peut présenter trois types de comportements extrêmes. Dans l'un d'entre eux (Figure a, $\tau_D = 1$ ns, $\tau_A = 0.01$ ns, $R_0/r = 1.5$) $r_A(t)$ passe par un maximum puis décroît et tend vers une valeur limite négative (- 0.034).

Lorsque les deux chromophores sont identiques, le déclin d'anisotropie $r(T)$, où $T = (R_0/r)^6(t/\tau)$, a été calculé de façon rigoureuse (———, Figure b) et comparé à celui obtenu par une méthode approchée (- - - - -). Nous avons montré également que l'anisotropie du chromophore excité indirectement (······) dépend du temps et tend vers 0 aux temps longs, alors qu'il était assimilé à une constante dans des travaux antérieurs.
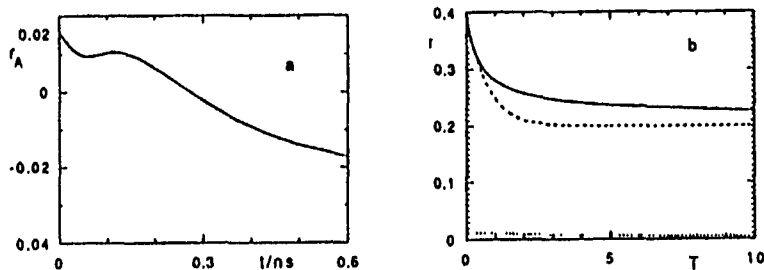
FLUORESCENCE DEPOLARIZATION BY ELECTRONIC ENERGY TRANSFER IN DONOR-ACCEPTOR PAIRS OF LIKE AND UNLIKE CHROMOPHORES

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Fluorescence depolarization by dipolar energy transfer is theoretically studied in donor-acceptor pairs of like and unlike chromophores at a fixed distance and with random and uncorrelated static orientations.

For unlike chromophores, the acceptor anisotropy decay $r_A(t)$ is shown to display three different types of extreme behaviour. In one of these (Figure a, $\tau_D = 1$ ns, $\tau_A = 0.01$ ns, $R_0/r = 1.5$) it passes through a maximum and then decays towards a negative limiting value (- 0.034).

For like chromophores, the exact pair anisotropy decay $r(T)$, where $T = (R_0/r)^6(t/\tau)$, (———, Figure b) is obtained and compared with that given by an approximate treatment (- - - - -). It is also shown that the anisotropy of the indirectly excited partner (·······) is time-dependent and tends to zero for long times, in contradiction with previous works where it is reported to be constant.
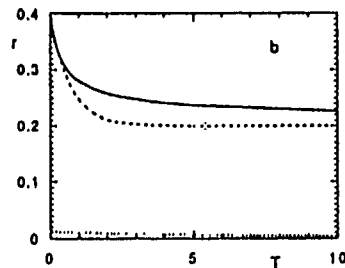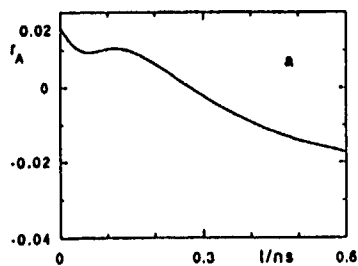
MOLECULAR INTERACTIONS IN THE SYSTEM:

ZINC-TETRAPHENYLPORPHYRIN / POLY-4-VINYLPYRIDINE / METHYL VIOLOGEN

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Metalloporphyrin compounds have been used for a long time as potencial sensitizers for photochemical and photoelectrochemical processes[1]. More recently there has been increasing interest to explore the effects of suitable axial ligands coordinated to the porphyrin[2].

In our studies we are using zinc-tetraphenylporphyrin (ZnTPP) coordinated with poly-4-vinylpyridine (PVP). All the results reported there in have been achieved in methanol solutions.

We have previously reported[3] the measurement of the equilibrium constant for the reversible ground-state complexation of ZnTPP with PVP, using absorption spectroscopy data. This value ($K \approx 88$ M^{-1}), besides being much lower than that observed for complexation to pyridine[4], is also rather smaller than that observed by others authors in a different solvent[5].

Using fluorescence spectroscopy data we have observed that the species ZnTPP-PVP has an emission spectrum similar to the emission of ZnTPP, although red shifted. The fluorescence quantum yield of the complex (ZnTPP-PVP) is found to be the same of the free porphyrin .

We have also measured transient state fotoluminescence spectra in order to obtain the lifetimes of the species in solution.

Moreover, we have been interested in studing the molecular interactions in the three component system ZnTPP-PVP-MV (MV = methyl viologen).

We observed the formation of a ground-state complex between ZnTPP and MV, that has been caracterized using absorption spectroscopy data.

We have investigated the deactivation mechanism of the two-component(ZnTPP-MV) and three component (ZnTPP-PVP-MV)system.Our results are compatible with a kinetic mechanism that includes, besides the unimolecular processes, the bimolecular quenching of ZnTPP and ZnTPP-PVP by MV. The fluorescence quenching constants are $K_1\tau_1 = 30.4$ (for the quenching of ZnTPP) and $K_2\tau_2 = 12.3$ (for the quenching of ZnTPP-PVP) .

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Adiabatic Photoreactions as Fluorescence Probes for Polymers

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Relaxation processes observable in polymers, are named in sucession of their appearance at different temperatures as α, β and γ process. The α relaxation is better known as the glass transition (T_g) of polymers. At T_g the segment mobility is frozen. β and γ relaxations are related to the freezing of the side group motions of the polymer main chain. In recent years, luminescence probes have been used to explore the molecular mobility in highly viscous media, especially in polymers at temperatures above T_g. But only few luminescence probes are available for the region below T_g[1,2]. Two different approaches can be used: a) the probe is covalently attached to the main chain or to the side group, b) the probe is dissolved in the polymer. Because of the high macroscopic viscosity of a polymer below T_g ($\eta \geq 10^{13}$ Pas) the luminescent probe must be sensible to react on small changes of the local viscosity (local free volume) of the surrounding medium. We used 9-tert-butyl-10-cyanoanthracen (TB9ACN) as a fluorescence probe for the mobility of polymers below their glass transition temperature[2]. In the excited state, TB9ACN relaxes through a funnel on the S1 hypersurface halfway between the anthracene and the Dewar anthracene structure. This leads to shortened fluorescence lifetimes (measured by Single Photon Counting). Various Polymethylacrylesters below the glass transition will be discussed.

TB9ACN
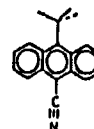
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DUAL FLUORESCENCE IN NOVEL CAROTENOID-LIKE CHROMOPHORES

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This contribution presents fluorescence spectra of a new class
of carotenoid-like compounds. These compounds exhibit dual flu-
orescence whose quantum yields are in the range of 10^{-5}. The
higher energetic fluorescence is originated from the second ex-
cited singlet state while the lower energetic luminescence is
achieved from the first excited singlet state whose excitation
is symmetry-forbidden. S_1-fluorescence additionally contains
hot luminescence which has been identified by fluorescence ex-
citation spectra obtained from the direct excitation of the
S_0-S_1 transition. Hot luminescence is generated from a vibro-
nic state in which one of the C=C stretching vibrations is in-
volved. The spectra reveal that the vibrational energy of that
C=C stretching vibration in the S_1 state is considerably large
(approx. 1750 cm^{-1}). This is in accordance with Raman spectra
from the first excited singlet state of ß-carotene /1/ and
theoretical considerations including diabatic states /2/.
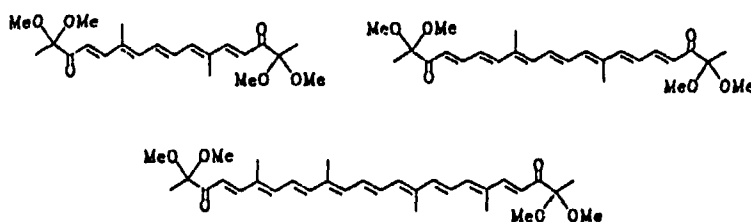
/1/ T. Noguchi, S. Kolaczkowski, C. Arbour, S. Aramaki,
    G.H. Atkinson, H. Hoyaski and M. Tasumi
    Photochem. Photobiol. 50, 603 (1989)
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    J. Chem. Phys. 89, 3681 (1988)

HIGH EFFICIENCY LIGAND-TO-METAL ENERGY TRANSFER. UV SENSITIZED
RED LUMINESCENCE OF EUROPIUM(III) CHELATES.

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Lanthanide ions (f elements) form with β-diketoenolates
neutral complexes soluble in organic media. In acetonitrile,
tris(6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5,-octanedionato)-
Europium (III) presents a 294 nm absorption band ($\Delta\lambda$=50nm FWHM)
due to a ligand $S_0 \rightarrow S_1$ electronic transition. When exciting the
complex in this band, no ligand fluorescence is observed but
narrow intense fluorescence lines are emitted at 590, 614, 650
and 700 nm, corresponding to radiative transitions of the
Eu(III) ion.

The energy transfer involves the following mechanism:
- Intersystem crossing $S_1 \rightarrow T_1$ to the triplet state of the
ligand. It is favoured by the small energy difference between
the two states, characteristic of the conjugated ketonic
systems and by the presence, close to the carbonyl groups, of
the Eu ion which increases the spin-orbit coupling by the
"heavy atom effect" (Z value).
- Energy transfer from the triplet donor ligand to an
isoenergetic excited state of Eu(III).
- Rapid relaxation of Eu(III) to the fluorescent $^5D_0$ and $^5D_1$
excited states.

The high fluorescence quantum yield (Φ=0.80±0.05)
indicates the remarkable efficiency of the ligand-to-metal
energy transfer and the low efficiency of the non radiative
deactivation processes of EU(III) as confirmed by the long
lifetime of the $^5D_0$ level, (τ=800±20 μs). The $^5D_1$ fluorescence
decay time, τ=650±70 ns , identical to the $^5D_0$ fluorescence
risetime indicates that the latter is populated from the
former.

The β-diketoenolate ligands thus constitute a cage around
the Eu(III) ion and protect the fluorescent excited state from
the deactivating vibrational modes of the solvent. This is
confirmed by the absence of isotopic effect in CH_3CN and CD_3CN.
However, a H_2O molecule can approach the Eu(III) ion and
induce radiationless deactivation via the O-H vibrations.

Other effects have been investigated: deuteration of the
ligands, electron donor $Fe(CN)_6^{2-}$ effect.

TRANSFERT D'ENERGIE LIGANDE-METAL A HAUT RENDEMENT: SENSIBILISATION UV DE LA LUMINESCENCE ROUGE DE CHELATES D'EUROPIUM(III).

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Les ions lanthanides (éléments 4f) forment avec les anions β-dicétoénolates des tris complexes neutres, solubles en milieu organique. En solution dans l'acétonitrile, le chélate tris(6,6,7,7,8,8,8-heptafluoro-2,2-diméthyl-3,5-octanedionato) europium (III) présente à 294nm une bande d'absorption (largeur à mi-hauteur $\Delta\lambda=50$nm) due à une transition électronique $S_0 \rightarrow S_2$ localisée sur le ligande. En excitant le complexe dans cette bande, on n'observe pas de fluorescence du ligande mais des raies fines et intenses à 590, 614, 650 et 700 nm, correspondant à des transitions radiatives de l'ion Eu(III).

Le transfert d'énergie qui conduit à cette émission s'accomplit selon le mécanisme suivant:

- Conversion interne $S_2 \rightarrow S_1$
- Croisement inter-système $S_1 \rightarrow T_1$ (via T_2) vers l'état triplet du ligande. Il est favorisé par la faible différence d'énergie entre ces deux états, caractéristique des systèmes cétoniques conjugués, et par la présence, à proximité des groupements carbonyle, de l'ion europium, qui accroît le couplage spin-orbite par effet d'"atome lourd interne" (valeur élevée de Z).
- Transfert d'énergie du triplet donneur à un état iso-énergétique excité de Eu(III).
- Relaxation rapide de Eu(III) vers les niveaux excités luminescents $^5D_0$ et $^5D_1$.

La valeur élevée ($\Phi=0,80\pm0,05$) du rendement quantique d'émission démontre la remarquable efficacité du transfert d'énergie du ligande vers le métal, et la faiblesse des processus de désactivation non radiative de Eu(III), confirmée par la longue durée de vie de l'état $^5D_0$ ($\tau=800\pm20\mu$s). Le temps de déclin de la fluorescence de $^5D_1$ ($\tau=650\pm70$ns), identique au temps de montée de la fluorescence de $^5D_0$, indique que ce dernier est peuplé à partir de $^5D_1$.

Les ligandes β-dicétoénolates constituent ainsi une cage autour de l'ion Eu(III) et protègent l'état excité luminescent des modes vibrationnels désactivateurs du solvant. Ceci est confirmé par l'absence d'effet isotopique entre CH_3CN et CD_3CN. Cependant, une molécule H_2O peut s'approcher de l'ion Eu(III) et induire une désactivation non radiative via les vibrations O-H.

D'autres effets ont été étudiés: deutération des ligandes, effet d'un donneur d'électron $Fe(CN)_6^{4-}$.

PRESSURE EFFECT ON THE RADIATIONLESS DEACTIVATION OF SINGLET OXYGEN IN SOLUTION

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Lifetimes of $^1\Delta_g$ singlet oxygen ($^1O_2$) have been determined in 12 solvents in dependence of pressure and in part of temperature using time resolved phosphorescence techniques, see Fig. 1. Experimental activation volumes for the deactivation of $^1O_2$ by solvent molecules vary between -11.9 (pentane) $\le \Delta V^*_{obs} \le$ -4.1 ml mol^{-1} (formamide) at 298 K. The increase of ΔV^*_{obs} with temperature was measured in toluene and CH$_3$CN. The data are analyzed by means of a kinetic scheme assuming a preequilibrium of $^1O_2$ and solvent molecule to form a singlet contact complex ^1C. Deactivation of $^1O_2$ occurs by energy transfer between the collision partners of C converting ^1C to ^3C, which subsequently splits into the deactivation products. A statistical model developed by Yoshimura and Nakahara is used to calculate the reaction volume ΔV_C of the preequilibrium. It is revealed that the major part of ΔV^*_{obs} consists of ΔV_C. Activation volumes ΔV^*_E of the actual deactivation of $^1O_2$ by oscillators X-Y of the solvent molecule depend neither on the polarities of solvent nor of X-Y. Independent of oscillator they are estimated to be $\Delta V^*_E \approx$ -2 ml mol^{-1} if X-Y is C-H, C-Cl, C-F, N-H or C=S.
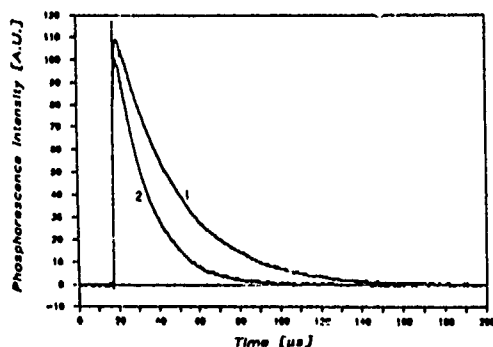
Fig. 1: $^1O_2$ phosphorescence in toluene at 298 K at (1) 1 bar and (2) 1500 bar; sensitizer RUB, λ_{exc} = 512 nm; pulse energy 2 mJ; $\tau_\Delta(1)$ = 29.2 µs; $\tau_\Delta(1500)$ = 15.7 µs; curves are averaged over 32 laser shots.

PATHWAYS OF PHOTOCYCLOADDTION OF ARENES TO ALKENES AND DIENES

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For the photocycloaddition of arenes to alkenes and to the terminal C atoms of
1,3-dienes three modes of addition are possible, i.e. ortho, meta and para addition. In
each of these addition modes there are several possibilities for the location of the newly
formed σ bonds between the reactants with respect to the position of substituents at the
benzene nucleus.

The photochemical additions of arenes to alkenes are highly selective for the
mode of addition and their regioselectivity is quite strong. In the photocycloaddition of
arenes to dienes the selectivity in the mode of addition is less pronounced.

The pathways of the reactions are investigated from the preferred conformations
in the early stage of the reaction to the funnels in the potential energy surface of the
first excited state of the complex between arene and alkene or diene. The presence of
energy barriers in these pathways and their relative values determine the selectivity of
the photocycloaddion.

The favoured conformations of the complex of reactants at the start of the
reaction are determined by first order perturbation of the zero order wave functions and
the position of the funnels is found by simple semi-empirical calculations.

Isomerization Reaction and Excimer Formation Kinetics of DBMBF$_2$

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Isomerization kinetics and excimer formation of a polar molecule (dibenzylmethine)-borondifluoride (DBMBF$_2$) in solutions have been studied. In dilute n-alcohols, DBMBF$_2$ exhibits temperature and solvent dependent fluorescence lifetimes from 0.3 to 2.0 ns in the blue region of the spectrum. This behavior arises most probably from an isomerization reaction taking place in the excited state. Our *ab initio* -calculations of the ground state suggest, that the most probable isomerization coordinate is the phenyl torsion motion of the molecule. The observed isomerization kinetics is clearly non-Kramers type: the hydrodynamic viscosity overestimates the friction experienced by the reaction at high viscosities. Using rotation correlation times as a measure of friction[1,2] results much better agreement of the experiment and theory. However, a slight underestimation of the reduced rates is still observed at high values of friction. We think, that the remaining descrepancy arises from a slow response of the solvent to the reaction coordinate at low temperatures[3].

In polar, non-hydrogen bonding solvents at concentrations exceeding 0.01 M, a second emission band arises in the green part of the spectrum. This band does not have a counter part in the absorption spectrum and has a lifetime of 50 ns. Both observations are typical of excimer formation in solution. In the monomer region, two-exponential decay is observed as concentration is increased. The new, slower component has a lifetime of 2-3 ns which is ascribed to an unstable transition state of the excimer or to trimer formation.

1. Ben-Amotz, D. & Scott, T. W., J. Chem. Phys. 87(1987) 3739-48.

2. Lee, M., Haseltine, J. N., Smith III, A. B., & Hochstrasser, R., J. Am. Chem. Soc. 111(1989) 5044-51.

3. Grote, R. F. & Hynes, J. T., J. Chem. Phys. 74(1981) 4465-75.

PHOTOCYCLISATION INTRAMOLECULAIRE DE p-BENZO-QUINONES SUBSTITUEES : MECANISME DE LA REACTION ET SON INHIBITION PAR TRANSFERT D'ELECTRON INTRAMOLECULAIRE.

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Nous avons étudié par photolyse-éclair laser la photocyclisation intramoléculaire de la phényl-p-benzoquinone et de composés apparentés, réction qui donne des dérivés du dibenzofurane selon le mécanisme suivant :
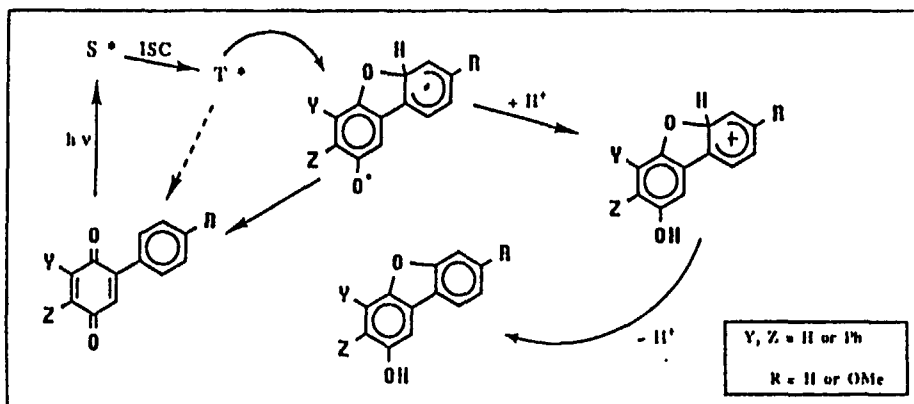
Quand -R est un groupement méthoxy, le rendement quantique de formation de l'état triplet et, par suite, le rendement quantique de la réaction de photocyclisation diminue fortement lorsque la polarité du solvant augmente. Ceci s'explique par une compétition entre le passage intersystème S-T et un transfert d'electron intramoléculaire au niveau des états singulet excités.

Cette inhibition de la photoréactivité de benzoquinones substituées par un transfert d'électron intramoléculaire est un résultat tout à fait inattendu : en effet, l'espèce zwitterionique résultant d'un tel transfert d'électron a souvent été proposée comme intermédiaire réactif des réactions de cyclisation. Cet effet de photostabilisation semble être très efficace lorsque des groupements dialkylamino ou methoxy sont fixés directement sur le cycle p-benzoquinone et pourrait être important pour expliquer la stabilité de certaines quinones naturelles telles que les ubiquinones.

INTRAMOLECULAR PHOTOCYCLIZATION OF SUBSTITUTED BENZOQUINONES : MECHANISM AND INHIBITION OF THIS REACTION BY INTRAMOLECULAR ELECTRON TRANSFER

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The mechanism of the intramolecular photocyclization of phenyl-p-benzo-quinone and related compounds to give dibenzofuran derivatives was investigated by laser-flash photolysis and shown to be the following :
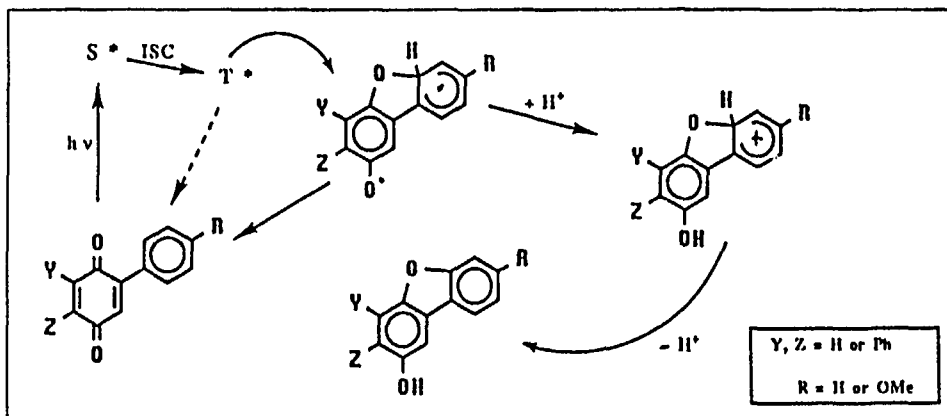
With the -R substituent being a methoxy group, the quantum yield of triplet formation and, consequently, the quantum yield of the photocyclization reaction strongly decrease when the solvent polarity increases. This is explained by a compe-tition between intersystem-crossing and intramolecular electron transfer in the excited singlet states.

This inhibition of the photoreactivity of substituted benzoquinones by intramolecular electron transfer is a quite unexpected result : a zwitterionic species resulting from such an electron transfer has often been proposed as a reactive inter-mediate for the photocyclisation reactions. This photostabilisation process seems to be very effective in the case of compounds where dialkylamino or methoxy groups are directly attached to the p-benzoquinore ring. It could be important to explain the stability of some natural quinones such as ubiquinones.

EXCITED STATE PROPERTIES OF PORPHYRIN HETERO-AGGREGATES

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Studies on excited state properties of metalloporphyrin dimers have been prompted in connection with the electron transfer function of the special pair in the photosynthetic reaction center. We have recently shown that electron-attracting gold porphyrins and electron-releasing zinc porphyrins form the hetero-aggregates with charge transfer interaction in preference to the self-aggregates in aqueous solution.[1] The hetero-aggregates are suitable for the systematic investigation not only on the excited dimer with unsymmetrical electronic distribution[2] but also on the fundamental features in the electron transfer of tightly stacked donor-acceptor complex.[3] We wish to report the excited state properties and the photo-induced electron transfer reactions of the porphyrin hetero-aggregates.

From the pico-second time-resolved absorption measurements, it was assured that the singlet radical ion pair was formed within the laser pulse duration (fwhm=24ps) by the direct photo-excitation of the hetero-aggregate with lower charge recombination energy ($-\Delta G^0$) than the triplet excitation energy (E_T). The singlet radical ion pair returned to the ground state through the single exponential decay without any dissociation process. The rate constant of the charge recombination (k_{CR}) of a series of hetero-aggregates with various $-\Delta G^0$ decreases with increasing the exothermicity like as the 'inverted region' as shown in Figure.
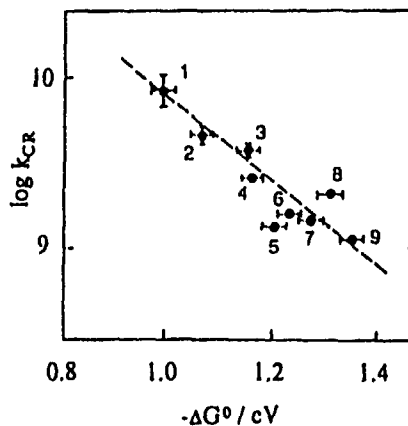
Figure. Energy gap dependence of charge recombination rate constant (k_{CR}) of radical ion pair formed by the photo-excitation of the porphyrin hetero-aggregate in aqueous solution. 1: ZnTCPP-AuTMPyP(4), 2: ZnTSPP-AuTMPyP(4), 3: ZnTSPP-AuTMPyP(3), 4: ZnTCPP-AuTSPP, 5: ZnTCPP-AuTCPP, 6: ZnTSPP-AuTSPP, 7: ZnTSPP-AuTCPP, 8: ZnTAPP-AuTSPP, 9: ZnTAPP-AuTCPP.

(1) H. Segawa, H. Nishino, T. Kamikawa, K. Honda and T. Shimidzu, Chem. Lett., 1917 (1989).

(2) D. G. Johnson, W. A. Svec and M. R. Wasielewski, Isr. J. Chem., 28, 193 (1988).

(3) T. Asahi and N. Mataga, J. Phys. Chem., 93, 6575 (1989); ibid. 95, 1956 (1991).

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ETATS EXCITES DE COMPLEXES TOLYL-TERPYRIDINIQUES DE Fe(II), Ru(II), Os(II). TRANSFERT D'ELECTRON INTRAMOLECULAIRE DANS UNE DIADE A BASE DE Os (II).

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Le nombre d'études photophysiques et photochimiques de complexes polypyridiniques de métaux de transition a augmenté d'une manière impressionnante en raison de l'aptitude de ces complexes à donner des processus de transfert d'électron ou d'énergie. En effet, ils servent de photosensibilisateurs dans les systèmes modèles de conversion photochimique de l'énergie solaire, et sont des candidats potentiels en tant que composants de dispositifs d'électronique moléculaire. Contrairement aux complexes bipyridiniques de Ru(II) qui ont fait l'objet de nombreux travaux, très peu d'études photophysiques ont été consacrées aux complexes terpyridiniques de métaux de transition, probablement parce qu'à température ambiante $[Ru(tpy)_2]^{2+}$ (tpy = 2,2' : 6',2"-terpyridine) et ses dérivés sont considérés comme non-luminescents et qu'ils ont un état excité de courte durée de vie (1). Cependant, ces complexes présentent une symétrie axiale qui est préservée par substitution sur la position 4' du ligand. Cette structure semble bien adaptée à la réalisation de systèmes linéaires pour des transferts d'électron dirigés.

Dans ce travail, nous avons examiné les propriétés spectroscopiques et photophysiques de complexes tolyl-terpyridiniques de Fe(II), Ru(II) et Os(II). Nous avons, en particulier, déterminé par spectroscopie par éclair laser les durées de vie et les spectres des états excités, et nous avons trouvé que $[Os(CH_3-ptpy)_2]^{2+}$ (CH_3-ptpy = 4'-(p-tolyl)-2,2' : 6',2"-terpyridine) est un chromophore intéressant pour construire des systèmes supramoléculaires de type diade. Nous avons, par conséquent, étudié la diade $[(CH_3-ptpy) Os(II) (MV^{2+}-ptpy)]^{4+}$ (2) comprenant ce chromophore lié de façon covalente au méthylviologène MV^{2+} (1,1'-diméthyl-4,4'-bipyridinium) et examiné l'éventualité d'un transfert d'électron intramoléculaire photoinduit.

(1) E. AMOUYAL, M. BAHOUT, G. CALZAFERRI and I. KAMBER
   J. Phys. Chem., in press

(2) J.P. COLLIN, S. GUILLEREZ and J.P. SAUVAGE
   Inorg. Chem. 29, 5009 (1990)

EXCITED STATES OF TOLYL-TERPYRIDINE COMPLEXES OF Fe(II), Ru(II),Os(II). INTRAMOLECULAR ELECTRON TRANSFER IN AN Os(II)-BASED DIAD.

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The number of photophysical and photochemical studies of polypyridine complexes of transition metals has grown impressively, particularly because of the ability of these complexes to undergo electron or energy transfer processes. Indeed, they are used as photosensitizers in model systems for photochemical conversion of solar energy, and they are potential candidates as components of molecular electronics devices. Contrary to bipyridine complexes of ruthenium (II), which have been extensively studied, only very few photophysical studies have been devoted to terpyridine complexes of transition metals, probably because $[Ru(tpy)_2]^{2+}$ (tpy = 2,2' : 6',2"-terpyridine) analogues are considered as non-luminescent, and because of a very short excited state lifetime at room temperature (1). However, these complexes exhibit an axial symmetry which is preserved by substitution at the 4- position of the ligand. Such a structure seems well adapted for constructing linear devices for directed electron transfer.

In the present work, we have studied spectroscopic and photophysical properties of tolyl-terpyridine complexes of Fe(II), Ru(II) and Os(II). In particular, we have determined by laser flash spectroscopy the lifetimes and spectra of the excited states and find that $[Os(CH_3-ptpy)_2]^{2+}$ is an interesting chromophore for constructing and studying supramolecular systems of diad type. We have therefore examined the diad $[CH_3-ptpy)Os(II)(MV^{2+}-ptpy)]^{4+}$ (2) containing this chromophore covalently linked to methylviologen MV^{2+} (1,1'-dimetyl-4-4'bipyridinium) and are considering the possibility of a photoinduced intramolecular electron transfer.

(1) E. AMOUYAL, M. BAHOUT, G. CALZAFERRI and I. KAMBER
J. Phys. Chem., in press

(2) J.P. COLLIN, S. GUILLEREZ and J.P. SAUVAGE
Inorg. Chem. 29, 5009 (1990)

EFFECTS OF SUBSTITUENTS AND SALTS ON ISOMERIZATION OF STILBENE CATION RADICALS

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The efficiency of unimolecular cis→trans conversion of cation radicals of stilbene derivatives depends upon the substituents on the phenyl rings, and the cation radicals of cis-4,4'-dibromo- and cis-4,4'-dimethylstilbene were, when generated by secondary electron transfer, converted unimolecularly to those of the corresponding trans-stilbenes in high quantum yields at ambient temperature.[1] However, the stilbene cation radicals have been reported not to undergo cis→trans conversion in the 100 μs range.[2] We now wish to report the effects of salts on the cis→trans conversion of stilbene cation radicals, as observed by transient spectroscopy and on steady irradiation.

The cation radicals of cis- and trans-stilbenes were generated by 9,10-dicyanoanthracene/biphenyl co-sensitization in acetonitrile with 425-nm laser pulse in the absence and presence of salts such as $LiClO_4$, $NaClO_4$, $Mg(ClO_4)_2$, and Et_4NClO_4. In the absence of salts cis-stilbene cation radicals decayed with bicomponent kinetics of the first and second order, as monitored at 515 nm, and no absorption band ascribable to trans-stilbene cation radicals was observed. However, in the presence of $LiClO_4$, the decay followed bicomponent first-order kinetics, and an absorption band due to the resulting trans-stilbene cation radicals appeared at 475 nm. Activation energies for the decays of the fast and slow components were determined to be 4 and 2 kcal mol^{-1}, respectively. The former value is in the same range as those for unimolecular cis→trans conversion of the cation radicals of the 4,4'-disubstituted stilbenes in the absence of salts, and the latter value is similar to that of the decay of trans-stilbene cation radical in the presence of $LiClO_4$. The activation energies for cis→trans conversion of cis-4,4'-dibromostilbene cation radicals were 7 and 4 kcal mol^{-1} in the absence and presence of $LiClO_4$.

These results suggest that the cis→trans conversion of stilbene cation radicals emerges on account of the effect of salts reducing the rate of back electron transfer. Detailed isomerization mechanisms will be discussed.

1) Y. Kuriyama, T. Arai, H. Sakuragi, and K. Tokumaru, *Chem. ~ 's. Lett.*, 173, 253 (1990).

2) F. D. Lewis, R. E. Dykstra, I. R. Gould and S. Farid, *J. Phys. Chem.* 92, 7042 (1988).

DETERMINATION EXPERIMENTALE DE LA CONSTANTE APPARENTE
DE FORMATION DE L'EXCIMERE DU 1,2-BENZANTHRACENE.

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Le cas des réactions avec formation et dissociation d'excimères intermoléculaires a fait l'objet d'un grand nombre d'études lorsque la constante de dissociation k_{-1} est petite devant la constante de formation k_1. Selon la valeur du coefficient de diffusion, la constante apparente de formation est alors soit une fonction décroissante du temps (modèle de Smoluchowski), soit une véritable constante (modèle cinétique de Birks). Nous nous intéressons ici au cas du 1,2-benzanthracène dans des solvants visqueux, pour lequel la constante de dissociation n'est plus petite par rapport à la constante de formation (elle-même grossièrement proportionnelle au coefficient de diffusion).

Un modèle récent[1] a montré que la constante apparente de formation de l'excimère est alors une fonction complexe du temps, décroissante aux temps très courts, puis croissante. Le but de ce travail étant d'obtenir, sans a-priori, la constante apparente, nous avons développé une méthode de déconvolution à partir de séries d'exponentielles et des multiplicateurs de Lagrange[2]. Les déclins expérimentaux de fluorescence du monomère et de l'excimère ont été obtenus par la technique de comptage de photon unique, en utilisant un laser comme source picoseconde. Après déconvolution, une méthode analytique nous a permis de calculer la durée de vie de l'excimère et la constante apparente. Comme on peut le constater sur la figure ci-dessous, l'évolution temporelle de cette dernière est sensiblement identique à celle prévue par le modèle.
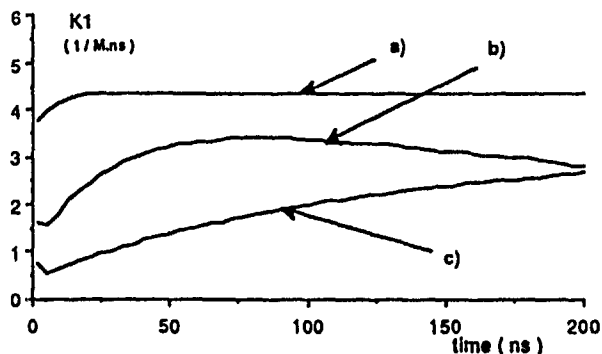
Constante apparente de formation de l'excimère du 1,2-benzanthracène dans divers solvants .
a) cyclohexane, b)paraffine/cyclohexane, c)paraffine

(1) J.C. Andre, F. Baros et M.A.Winnik, J.Phys.Chem. 1990 94 2942-2948.
(2) J.C. Andre, M. Bouchy, J. Duhamel, F. Baros et W. Dong, Modelling and Simulation Int. Symp., Grindelwald (1989), 414-417.

EXPERIMENTAL DETERMINATION OF THE APPARENT RATE CONSTANT
IN THE CASE OF THE FORMATION OF EXCIMER OF 1,2-BENZANTHRACENE.

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The case of reactions with excimer formation and dissociation has been widely studied when the rate of back-reaction is negligible compared with the rate of formation. Then, according to the value of the diffusion coefficient, the apparent rate constant is a decreasing function of time (model of Smoluchowski) or an actual constant with respect to the time (kinetic model of Birks). We examine here the case of 1,2-benzanthracene in viscous solvents, for which the rate constant of dissociation k_{-1} is no more negligible compared with the rate constant of formation k_1 (roughly proportional to the diffusion coefficient).

A recent model [1] has shown that the apparent rate constant of excimer formation is now a complex function of time, decreasing at short time and then increasing. The aim of this work was to get, without any a-priori, the apparent rate constant. Thus, we have developped a deconvolution method based on multiexponential series and Lagrange multipliers[2]. Experimental determination of the fluorescence decays of both monomer and excimer was made using the single photon counting technique with a picosecond laser as a source. After deconvolution, an analytical method allows us to compute the lifetime of excimer and the apparent rate constant . As seen on the following figure, the recovered apparent rate constant has the same behaviour in time as the one predicted by the diffusional model.
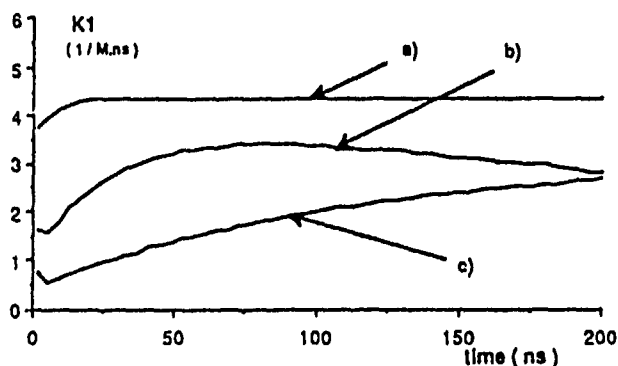
Apparent rate constant of formation of excimer of 1,2-benzanthracene in different solvents :
a) cyclohexane, b)paraffin/cyclohexane, c)paraffin

(1) J.C. Andre, F. Baros and M.A.Winnik, J.Phys.Chem. 1990 94 2942-2948.

(2) J.C. Andre, M. Bouchy, J. Duhamel, F. Baros and W. Dong, Modelling and Simulation Int. Symp., Grindelwald (1989), 414-417.

PHOTOTRANSFORMATION de l'HYDROQUINONE en SOLUTION AQUEUSE

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Il est bien connu que l'irradiation de l'hydroquinone (QH_2) en solution aqueuse aérée conduit à la formation de benzoquinone (Q), alors qu'il se forme du 2,2',5,5'-tétrahydroxybiphényle (THBP), avec un rendement quantique très faible ($\leq 2.10^{-3}$), lorsque QH_2 est excitée en solution dégazée. Le travail présenté ici a permis d'établir que :

*   *en absence d' oxygène*, QH_2 peut être photo-oxydée en Q par les ions nitrate et que la formation de THBP résulte d'une photoréaction de QH_2 avec Q, réaction qui est favorisée par une augmentation de pH . L'effet de concentration et l'inhibition par l'oxygène permettent de penser que la formation de THBP et la majeur partie de l'oxydation par NO_3^- fait intervenir l'état excité triplet de l'hydroquinone ($^3QH_2^*$). Cette conclusion est confirmée par l'effet inhibiteur du 3-chlorophénol (ClP). En effet, lorsque QH_2 est excitée en présence de ClP, la principale réaction observée est la formation de résorcinol, et cette réaction est expliquée par un transfert d'énergie de $^3QH_2^*$ vers ClP.

*   *en solution aérée*, QH_2 est transformée en Q et en hydroxybenzoquinone (QOH), le rapport Q/QOH étant voisin de 2. De l'eau oxygénée (H_2O_2) se forme également, et sa concentration est analogue à celle de Q. Aucune influence significative de ClP sur la vitesse d'oxydation de QH_2 n'a été observée, ce qui amène à conclure que cette oxydation se produit à partir de l'état excité singulet et que l'oxygène agit principalement comme capteur d'électron (ou de H·). L'oxydation de $^3QH_2^*$ par l'oxygène et la capture d'électron par les ions NO_3^- peuvent cependant intervenir dans une faible mesure.
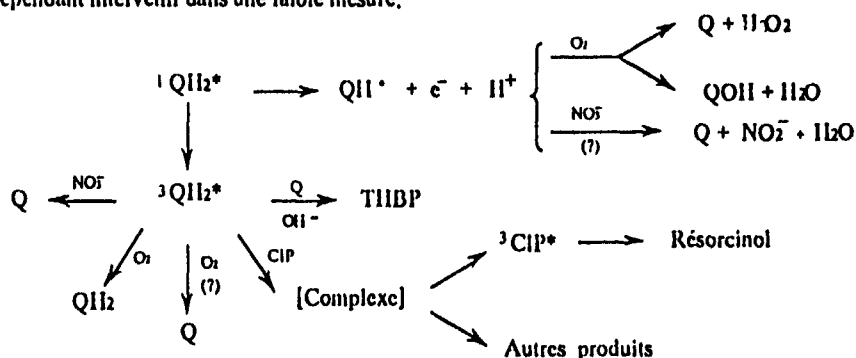
PHOTOTRANSFORMATION of HYDROQUINONE in AQUEOUS SOLUTION

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It is well known that the irradiation of hydroquinone (QH_2) in air saturated aqueous solutions leads to benzoquinone (Q), whereas 2,2',5,5'-tetrahydroxybiphenyl (THBP) is formed with a very low quantum yield ($\leq 2.10^{-3}$) when QH_2 is excited in degassed solution. In the present work it is established that :

• *in the absence of oxygene*, QH_2 can be photo-oxidized into Q by nitrate ions and that the formation of THBP results from a photoreaction of QH_2 with Q favoured by increasing pH. From the concentration effect and the inhibition by oxygene, it can be suggested that the formation of THBP and the major part of the oxidation by NO_3^- involve the excited triplet state of hydroquinone ($^3QH_2^*$). This conclusion is confirmed by the inhibiting effect of 3-chlorophenol (ClP). When QH_2 is excited in the presence of ClP, the main reaction observed is the formation of resorcinol and this reaction can be explained by an energy transfert from $^3QH_2^*$ to ClP,

• *in air saturated solution*, QH_2 is converted into Q and hydroxybenzoquinone (QOH). The ratio Q/QOH ≈ 2. Hydrogen peroxide (H_2O_2) is also formed and its concentration is similar to the concentration of Q. No significant influence of ClP is observed on this reaction and it can be assumed that this oxidation involves a photo-ionisation of the excited singlet state and that O_2 mainly reacts as an electron (or H^+) quencher. Oxidation of $^3QH_2^*$ by O_2 and electron quenching by NO_3^- as minor pathways cannot be excluded.
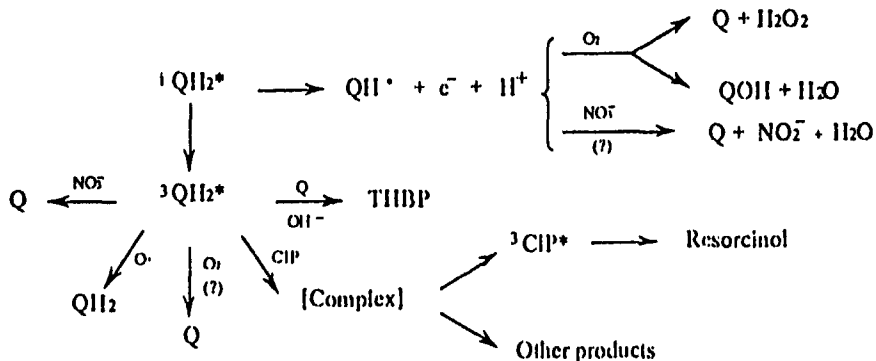
PHOTO-CIDNP DE COMPOSES PHOTOCHROMES.

Françoise Rietsch, Jean Marko, Jean-Marie Aubry et Gaston Vermeersch

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Les endoperoxydes d'hydrocarbures aromatiques constituent des systèmes photochromes hautement réversibles. Deux types de réactions sont généralement impliquées dans la photochimie de ces dérivés : une photocycloréversion selon un processus concerté et une fragmentation résultant d'une rupture homolytique du pont peroxyde, impliquant un intermédiaire de courte durée de vie[1].

Nous avons étudié par photo-CIDNP (^{1}H et ^{13}C) le comportement photochimique d'un composé modèle : l'endoperoxyde du 9,10-diphénylanthracène(DPAO$_2$). La photodégradation de ce dernier est parfaitement décrite dans la littérature. Les différents photoproduits ont été isolés et caractérisés[2]. Notre but était de mettre en évidence les intermédiaires radicalaires suggérés par les auteurs et d'apporter des éléments nouveaux au mécanisme de la photodégradation.

Nos expériences ont été effectuées dans des tubes RMN de 5 mm avec des solutions dégazées de DPAO$_2$ (10^{-2} M) dans l'acétonitrile. Nous avons constaté par CLHP que tous les photoproduits décrits par Rigaudy et coll.[2] étaient présents dans notre mélange réactionnel après l'irradiation lumineuse. Les effets de CIDNP observés nécessitent la présence d'eau ($\geq 1\%$) dans le solvant et ne concernent, cependant, que deux composés : le phénol et la 9-hydroxy 9-phénylanthrone (HPA). D'autre part, les polarisations sur HPA sont inversées lorsque les radiations de longueur d'onde inférieures à 350 nm sont filtrées.

Nos résultats conduisent aux conclusions suivantes :
- Les formations du phénol et de HPA résultent du piégeage de radicaux par une molécule d'eau.
- Le mécanisme de formation de ces deux dérivés dépend de la longueur d'onde d'irradiation.
- Nous n'avons pu obtenir aucune preuve directe d'un précurseur biradicalaire. Cependant, lors de l'irradiation avec le filtre nous avons détecté transitoirement les signaux RMN d'un bisépoxyde.
- L'application de la règle de Kaptein relative à l'effet net nous permet de proposer l'intervention de deux paires radicalaires différentes. Ainsi HPA serait formé à partir, soit d'un radical 9-phénylanthrone 9-yl, soit d'un radical 9,10-dihydroxy 10-phenylanthrone 9-yl. Le phénol, quant à lui, serait formé dans les deux cas à partir du même radical phénoxy. La première paire résulterait du réarrangement d'un biradical issu d'une rupture homolytique du pont peroxyde de DPAO$_2$ dans un état excité singulet. La seconde paire pourrait provenir d'une réaction secondaire entre le phénol et HPA.

Ces effets de CIDNP ne sont pas observés dans le cas d'endoperoxydes aromatiques possédant un rendement élevé de photocycloréversion.

(1) Jesse K., Markert R., Comes F.J., Schmidt R. et H.D. Brauer, Chem. Phys. Letters 166, 95-100 (1990).- (2) Rigaudy J., Scribe P. et C. Brelière, Tetrahedron 37, 2589-93 (1981).

PHOTO-CIDNP OF PHOTOCHROMIC COMPOUNDS.

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Endoperoxides of aromatic hydrocarbons are known to be components of highly reversible photochromic systems. Photochemistry of these endoperoxides generally proceeds through a dual pathway: a concerted cycloreversion and a fragmentation which should involve a short-lived reaction intermediate, probably resulting from homolytic cleavage of the peroxide bridge[1].

We have reinvestigated, by means of photo-CIDNP, the photochemical behaviour of a model compound, the endoperoxide of 9,10-diphenylanthracene ($DPAO_2$). The photodegradation of the latter compound is a well-documented reaction[2]. All the photoproducts have been isolated and characterized by different analytical techniques. Our aim was to provide some evidence for the radical intermediates, which were tentatively proposed, and to get a deeper insight on the mechanism of the photodegradation.

Typically, ^1H and ^{13}C CIDNP spectra of $DPAO_2$ (10^{-2} M) were run in degassed, wet (1% H_2O) acetonitrile solutions. As checked by HPLC, all the derivatives described by Rigaudy et al. [2] were present in the NMR sample after irradiation. Among them, nevertheless, only phenol and 9-hydroxy 9-phenylanthrone (HPA) exhibit strong nuclear polarizations. The latter are not longer observed when dry acetonitrile is used. When the solutions are irradiated through a glass filter cutting off the wavelengths under 350 nm, the polarizations on HPA were inverted.

Our present results can lead to the following conclusions:

- The formations of phenol and HPA result from trapping of a radical pair by a molecule of water.

- According to the irradiation wavelength, two different pathways are implicated.

- No direct evidence is found for a biradical precursor. Nevertheless the NMR spectrum of an intermediate bisepoxide was observed during the irradiation through the filter.

- Considering the magnetic parameters (g-factors, hyperfine coupling constants) of the different radicals that could be involved in the reaction, in agreement with the Kaptein rule and the relative intensities of the polarized signals, two radical pairs are proposed depending on the irradiation wavelength. In both cases a phenoxy radical is the precursor of phenol. HPA is formed either from a 9-phenylanthrone 9-yl radical or a 9,10-dihydroxy 10-phenylanthrone 9-yl radical. The first pair would result of the rearrangement of a biradical due to an homolytic cleavage of the peroxide bridge in $DPAO_2$ in its singlet excited state. The second pair could be generated by a secondary reaction between phenol and HPA.

A similar study was done with two other endoperoxides and we have noted that no CIDNP effect was observed for the derivatives with a high rate of photocycloreversibility.

- (1) Jesse K., Markert R., Comes F.J., Schmidt R. and H.D. Brauer, Chem. Phys. Letters 166, 1, 95-100 (1990).- (2) Rigaudy J., Scribe P. and C. Brelière, Tetrahedron 37, 2589-93 (1981).

REACTION PRODUCTS AND POSSIBLE TRANSIENTS FROM PHOTOLYSIS OF MATRIX-ISOLATED FURAN-2,3 DIONE DERIVATIVES

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5-phenyl-furan-2,3-dione **1** and benzofuran-2,3-dione **2** trapped at low temperature (T< 30 K) in rare gas matrices or in KBr matrices (78 $\leq$ T $\leq$ 300 K) were irradiated at $\lambda \geq$ 335 nm or $\lambda \geq$ 230 nm. The reaction products were monitored by high resolution FT-IR spectroscopy.
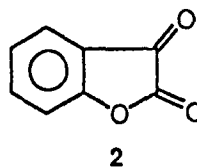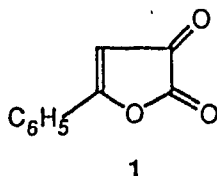
Each photolysis experiment at $\lambda \geq$ 335 nm (15 $\leq$ T $\leq$ 78 K) gives carbon dioxide (ν = 2377 cm^{-1}) and a product presenting an absorption band at 2140 cm^{-1} assigned to a ketene stretching vibration (νC=C=O) ; this product disappears when temperature raises up to 200 K (KBr matrices). Both reactant concentrations obey a first order kinetic law (k= 2.3-2.8.10^{-5} s^{-1}).

Further irradiation at $\lambda \geq$ 230 nm increases the rate of photolysis (k = 4-6.10^{-5} s^{-1}) and leads to IR absorption appearance in the range 2148-2132 cm^{-1} ; the new bands are assigned to carbon monoxide. In the case of **2**, a competitive process occurs (lost of CO) and transient species **3** and **4** were identified in the reaction mixture (ν = 2112-1650 and 1900 cm^{-1} respectively). The assumption of transient **5** (benzyne) is supported by observation of a band at 2080 cm^{-1} which grows during photolysis.

These photochemical results will be compared with thermolysis mechanism.
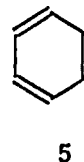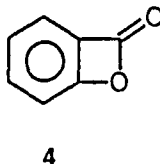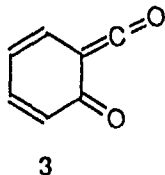
ON THE ELECTRONIC SPECTRUM AND PHOTOPHYSICS
OF MICHLER'S HYDROL BLUE (MHB)

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MHB, which is the most typical diphenylmethane dye,
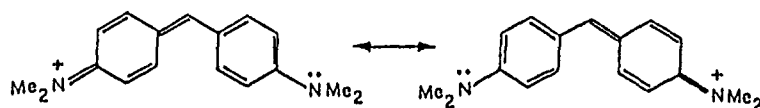
has long been studied with special reference to its structural
and spectroscopic properties. Certain bridged analogues of MHB,
in which the aryl groups are not free to twist about the
central bonds, are known to be intensely fluorescent unlike the
"non-fluorescent" unbridged compound. The absorption spectrum,
on the other hand, is very little affected by bridging. From
these observations MHB is expected to be nearly coplanar in the
ground state, while in the first excited singlet state out-of-
plane twisting of the six-membered rings should occur quite
easily, thus providing an efficient channel for the non-
radiative relaxation. In an attempt to verify the reliability
of these hypotheses we have carried out a theoretical CS INDO
study on MHB concerning the ground-state conformation, the
electronic S_0-S_n and S_0-T_n transitions and the potential energy
curves for the torsion about one central bond in the ground
state and the lowest excited states (T_1, T_2, S_1). The
intersystem crossing was also investigated by calculating the
pertinent spin-orbit coupling terms between S_1 and the nearest
triplet (T_2) at different values of the twisting coordinate.
The calculation results show that both the spectroscopic
properties and the photophysical behaviour of MHB can be
explained by its near relationship with the simple nonamethine-
cyanine chromophore.

An experimental investigation on the emission properties
and the triplet formation quantum yield of MHB is in progress,
aiming to better discriminate between the intersystem crossing
and the internal conversion from a twisted conformation as the
preferred excited-state deactivation pathway.

FLUORESCENT PHOTOCHROMIC SYSTEMS

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Fluorescent photochromics, *i.e.* non-fluorescent materials which reversibly produce highly fluorescent materials upon irradiation, may offer some advantages over absorption photochromics because of the ease of detection of fluorescence.

We have shown that this can be achieved using two very different photochromic systems, and in this report we provide details of the photochemistry and thermal chemistry of these systems.

PROTONATION AND PHOTOCHEMISTRY OF A

PYRAZOLOTRIAZOLE AZOMETHINE DYE

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Pyrazolotriazole azomethine dyes are image forming materials in conventional colour photography, and as such, the colour of the dye is of critical importance. The behaviour of the azomethine dye shown in figure 1 has been studied over a wide range of acidity in non-aqueous solvents using UV absorption, flash photolysis, ^1H NMR and ^{13}C NMR. Absorption studies (figure 2) reveal the formation of both a monocation and a dication, with absorption maxima at ≈ 600 nm and 640 nm respectively, as the acidity is increased. Analysis of the NMR spectra of the dye in $CDCl_3/CF_3COOH$ mixtures suggests that the nitrogen of the imine group is protonated first at an acid concentration of $\approx 10^{-2}$ M, with the second protonation at the amino group evident at an acid concentration of ≈ 1 M. Flash photolysis of the dye solution produces a mixture of syn and anti isomers which thermally back reacts to give the initial isomer composition over a period of ≈ 1 s in neutral solvents. The rate of this first order process is very dependent upon the proton concentration, and increases by about three orders of magnitude as the proton concentration is increased from 10^{-7} to 10^{-4} M in an ethanol/water mixture (9/1 v/v). The dicationic form of the dye is unstable to hydrolysis in hydroxylic solvents.
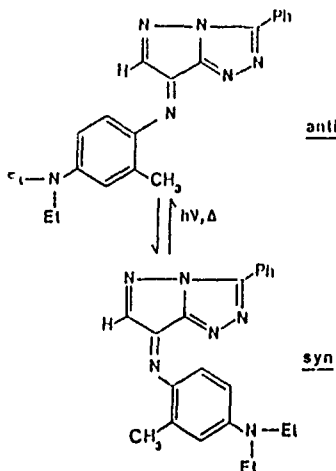
Figure 1
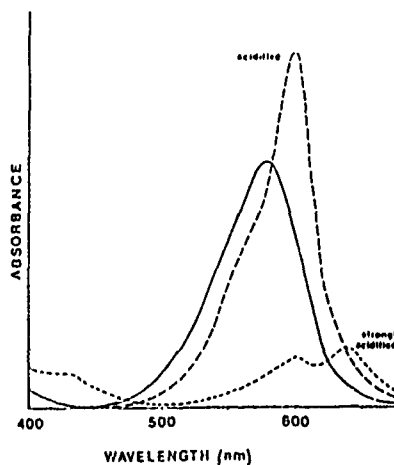
Figure 2

EVIDENCE FOR TWO GROUND STATE CONFORMERS OF
TETRABENZO[a,cd,f,lm]PERYLENE

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Two isomeric tetrabenzo derivatives of perylene, tetrabenzo[a,cd,f,lm]-perylene (1) and tetrabenzo[a,cd,j,lm]perylene (2) were studied by electronic spectroscopy in solutions, glasses and Ar matrices. The analysis of absorption, fluorescence, fluorescence excitation and magnetic circular dichroism (MCD) spectra suggests that in room temperature solutions two different conformations of 1 are present, of which only one is fluorescent. For 2, only one form is observed.

The results of molecular mechanics calculations are consistent with these findings, predicting for 1 two conformers with similar energies. In 2, the computed energy separation between two low energy forms is higher. All of the calculated structures are strongly non-planar.
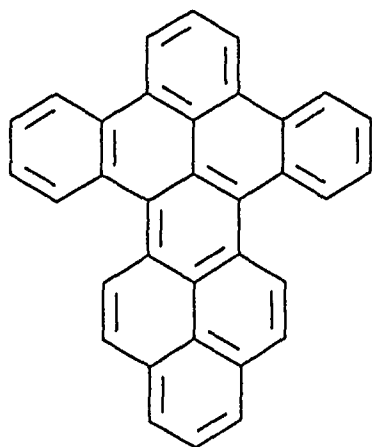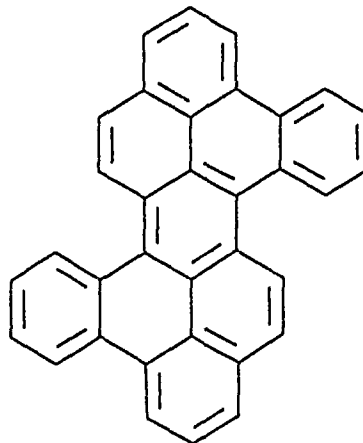
1   2

ETUDE PAR SPECTROSCOPIE RESOLUE EN TEMPS D'UN TRANSFERT DE PROTON INTRAMOLECULAIRE DEPENDANT DU SOLVANT : CAS DE DERIVES DU BIS-OXAZOLE

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Parmi les composés donnant lieu à un transfert de proton intramoléculaire à l'état excité (ESIPT), certains dérivés du bis-oxazole constituent des exceptions pour lesquelles l'observation d'une fluorescence duale (primaire et tautomérique) a été rapportée dès 1983[1], ce qui a donné lieu à différentes controverses. Nous avons étudié, par spectroscopie stationnaire et résolue en temps, l'influence du solvant et de la température sur les propriétés photophysiques du 2,5-bis-(benzoxazolyl)-4-méthoxyphénol. Deux bandes d'émission ont toujours été observées, celle présentan. un important déplacement de Stokes et due à l'état de transfert de proton étant la plus intense et se déplaçant légèrement vers le rouge pour des polarités croissantes du solvant.

Dans d s solvants aliphatiques (méthylcyclohexane, pentane, 2-méthylbutane, 1-2 dichloroéthane), les courbes de déclin relevées dans les deux bandes indiquent qu'un équilibre s'établit entre les deux états excités : les constantes de déclin sont de l'ordre de 5 ns à 22°C et augmentent si on refroidit la solution. De la variation avec la température du rapport des intensités émises par les formes tautomérique et initiale, on a déduit le changement d'enthalpie à l'état excité ($\approx 1,6\,\mathrm{kcal\,M^{-1}}$ dans le méthylcyclohexane). Dans le 1-2 dichloroéthane ($\epsilon = 10,3$), la reversibilité est fortement réd ite (fluorescence de l'état ESIPT ≈ 70 fois plus élevée à 22°C que celle émise dans la bande "bleue", ce rapport étant voisin de 2 dans le méthylcyclohexane) et le déclin de la bande "bleue" présente une importante composante rapide ($\approx 1,2\,\mathrm{ns}$). Une telle composante est également clairement visible dans les autres solvants à basse température.

Dans le n-butanol, les constantes de déclin des deux émissions sont nettement différentes, ce qui est attribué à l'existence dans l'état fondamental de deux espèces, dont l'une conduit à un transfert de proton irréversible.

La substitution du groupe méthoxy par un groupe acétique entraîne une forte diminution de la fluorescence "normale", le rendement quantique de l'état de transfert du proton restant pratiquement inchangé.

(1) A. Mordziński, A. Grabowska, W. Kühnle, A. Krówczyński, Chem. Phys. Lett. 101(1983)291.

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TIME RESOLVED KINETIC STUDY OF SOLVENT DEPENDENT INTRAMOLECULAR PROTON TRANSFER IN BIS-OXAZOLE DERIVATIVES

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Among the compounds exhibiting excited-state intramolecular proton transfer (ESIPT) reaction, H-bonded bis-oxazole derivatives are exceptions for which a dual fluorescence (primary and tautomeric) has firstly been reported in 1983[1], that led to numerous controversial work. We have studied the influence of the solvent and the temperature on the photophysical properties of the 2,5-bis-(benzoxazolyl)-4-methoxyphenol (stationary and time resolved fluorescence measurements). Two emission bands were always present, the strongly Stokes-shifted one due to the ESIPT state being the most intense and the shift increasing with the solvent polarity.

In aliphatic solvents (methylcyclohexane, pentane, 2-methylbutane, 1,2-dichloroethane) the decay curves recorded in both bands show the presence of a backward reaction and of an equilibrium; the decay constants are near to 5 ns at RT and increase upon cooling. From the temperature dependence of the ratio of the tautomeric and the normal (primary state) emissions, the excited state enthalpy change has been determined (≈ 1.6 kcalM^{-1} in methylcyclohexane). In 1,2-dichloroethane ($\varepsilon \approx 10.3$), the reversibility is strongly reduced (proton transfer state fluorescence is ≈ 70 times greater than the "blue" band at RT while this ratio is ≈ 2 in methylcyclohexane) and an important short component (≈ 1.2 ns) in the "blue" emission is observed. Such a component becomes also clearly visible in the other solvents at low temperatures.

In n-butanol both fluorescence bands decay exponentially with different time constants, that can be attributed to the existence in the ground state of two different species, one giving rise to an irreversible ESIPT reaction.

The substitution of the methoxy by an acetic group leads to an important decrease of the normal fluorescence, the proton transfer state quantum yield being practically unchanged.

(1) A. Mordziński, A. Grabowska, W. Kühnle, A. Krówczyński, Chem. Phys. Lett. 101(1983)291.

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ETUDE PHOTOPHYSIQUE ET PHOTOCHIMIQUE DE COLORANTS LASER RHODAMINE

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Nous avons étudié les propriétés de solutions concentrées (10^{-3} M) de Rhodamine 6G (R6G) et comparé sa photostabilité en solution aqueuse micellaire de dodécylsulfate de sodium (SDS) et en solutions alcooliques, sous irradiation continue UV-visible, et sous pompage laser XeCl à 308 nm (à 250 Hz).

Sous irradiation continue, la R6G se photodécompose rapidement en solutions alcooliques. Le mécanisme fait intervenir la réaction de transfert d'électron entre l'état triplet et l'état fondamental de deux molécules de colorant ($T + S_0 \rightarrow R^{+\cdot} + R^{-\cdot}$). En solution micellaire de SDS, le colorant cationique est inséré dans la phase hydrophobe de la micelle, au voisinage de la couche externe anionique, ce qui le protège de toute décomposition.

Par contre, sous pompage laser à 308 nm, la photodécomposition est plus importante en solution micellaire. Elle fait intervenir une excitation à deux photons en deux étapes $S_0 \rightarrow S_1^* \rightarrow S_n^*$, due à un accroissement de l'absorbance au cours du pompage. L'ionisation qui s'ensuit ($S_n^* \rightarrow R^{+\cdot}+e^-$) est plus efficace en solution micellaire qu'en solution alcoolique. De plus, la répulsion de l'électron hydraté par la micelle chargée négativement empêche sa recombinaison avec le radical cation.

Nous avons montré d'autre part, qu'en irradiation continue, une faible concentration de DABCO (10^{-5} M) ajoutée à une solution de R6G pouvait considérablement améliorer sa stabilité. Parmi les nombreuses propriétés du DABCO ("quencheur" de triplet, donneur d'électron, base), son rôle de donneur d'électron provocant la réduction du radical cation $R^{+\cdot}$ est très efficace.

A PHOTOPHYSICAL AND PHOTOCHEMICAL STUDY OF RHODAMINE LASER DYES

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The photodecomposition of concentrated (10^{-3} - 3.10^{-3} M) rhodamine 6G (R6G) alcoholic and aqueous sodium dodecylsulfate (SDS) micellar solutions has been investigated under continuous UV-visible illumination and in high repetition rate (250 Hz) XeCl laser pumped dye laser.

Under UV-visible illumination, the R6G photodegrades rapidly in alcoholic solutions. The mechanism involves the electron transfer reaction of the triplet excited state with a ground state dye molecule (T + $S_0 \rightarrow R^{+\cdot} + R^{-\cdot}$). In SDS micellar solution, the R6G cation is embedded in the hydrophobic interior of the micelle close to the negatively charged end groups and is therefore protected from any possible degradation.

Under XeCl laser pumping at 308 nm, the contrary is observed. The photodegradation is higher in the micellar solution. We conclude to a sequential two photon excitation at 308 nm, $S_0 \rightarrow S_1^* \rightarrow S_n^*$, due to a strong increase of the absorbance during the laser pumping. We believe that the S_n^* ionization ($S_n^* \rightarrow R^{+\cdot} + e^-$) of R6G is more efficient in SDS aqueous solution and that the recombination of the radical $R^{+\cdot}$ with the resulting hydrated electron is prevented by the repulsive electrostatic surface potential of the SDS negative interface.

We found that under continuous illumination, a rather small concentration of DABCO (10^{-5} M) added to an alcoholic solution of R6G could ensure a strong decrease of the photodegradation. Among the various properties which are recognized to DABCO (triplet quencher, electron donor,base), the role of electron donor providing the reduction of the $R^{+\cdot}$ radical cation and the R6G regeneration is very efficient.

THE WOLFF REARRANGEMENT OF α-DIAZOKETONES

Otto Strausz, Elizabeth Lown, Ratnakar Gosavi and Manuel Torres

A central problem in the photochemistry of α-diazoketones is the question of the concertedness of their Wolff rearrangement (WR) – decomposition sequence. Using the isotopic labelling technique we have shown some years ago that in the photolysis of many, but not all α-diazoketones, oxygen scrambling occurs to varying extents indicating the intervention of oxirenes, which in turn are manifestations of the presence of ketocarbenes and therefore the non-concertedness of the WR:
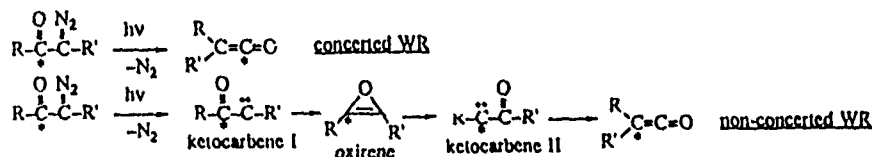
Kaplan has demonstrated the importance of the diazoketone conformation vis-à-vis product distribution on the example of the conformer pair
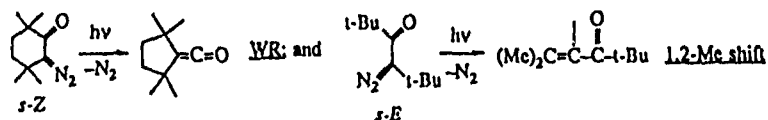
Since early molecular orbital (MO) calculations predicted the lowest singlet state of the parent ketocarbene, formylmethylene, to have a non-planar geometry precluding the possibility of conformational isomerism, the difference in the mode of decomposition was explained in terms of a concerted process for the WR and a ketocarbene mechanism for the 1,2-Me shift. This has led to the general belief that the WR is a concerted process. However, subsequently it was shown that the photolysis of vinylene thioxocarbonate with locked s-Z conformation also yielded the WR product even though a concerted step here is inconceivable:
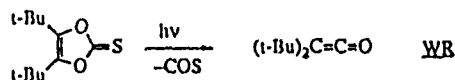
Also, multiconfiguration MO calculations predicted a planar geometry for the lowest singlet state of formylmethylene permitting geometrical conformationalism. Current results will be presented in support of the non-concertedness of the WR of simple alkyl and aryl diazoketones via ketocarbenes and the conformational control of the reactivity in the ketocarbene, the s-E conformation favoring WR and the s-Z conformation oxirene formation,
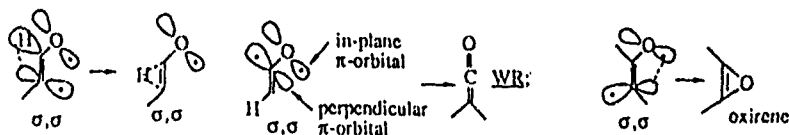
Multiple Adiabatic *Cis-Trans* Photoisomerizations

Mikael Sundahl*, Tatsuo Arai**, Kjell Sandros***, Katsumi Tokumaru**, Olof Wennerström*

Cis-trans photoisomerizations of olefins have been studied for more than 50 years. The mechanism usually suggested for *cis-trans* photoisomerizations has been a diabatic mechanism. In a diabatic *cis-trans* photoisomerization, on excitation of either a *cis* or a *trans* isomer, concomitant to excitation an excited state conformer, p*, with approximately 90° twist of the double bond is formed. This conformer decays to the ground state, and then gives a mixture of *cis* and *trans* isomers. An example of a molecule which undergoes this kind of isomerization is stilbene[1]. In contrast to this diabatic mechanism, Prof. K. Tokumaru and co-workers have found that some anthracenyl ethylenes undergo adiabatic one-way isomerization: on sensitized excitation of a *cis* isomer (or direct excitation via intersystem crossing) the formed $^3cis*$ undergoes isomerization on the triplet excited state surface to give the $^3trans*$, which then decay to its ground state[2].

For molecules with more than one double bond an adiabatic isomerization mechanism implies that it should be possible to isomerize more than one double bond with a single excitation. We have several examples of molecules undergoing such multiple adiabatic *cis-trans* photoisomerizations. A styrylstilbene (1) shows adiabatic isomerization on both the singlet and triplet excited state surfaces[3,4]. Evidence for the suggested mechanism will be presented in terms of quantum yields of isomerizations, fluorescence spectra (steady-state and time resolved) and T-T absorption observed on laser flash photolysis. An orthoparacyklophane (2) shows an adiabatic one-way six-fold isomerization from the all-Z to the all-E isomer[5]. The isomerization proceeds on the triplet excited state surface, and the product is formed in its excited state. Some preliminary results on a bisstyrylstilbene (3) will also be presented.
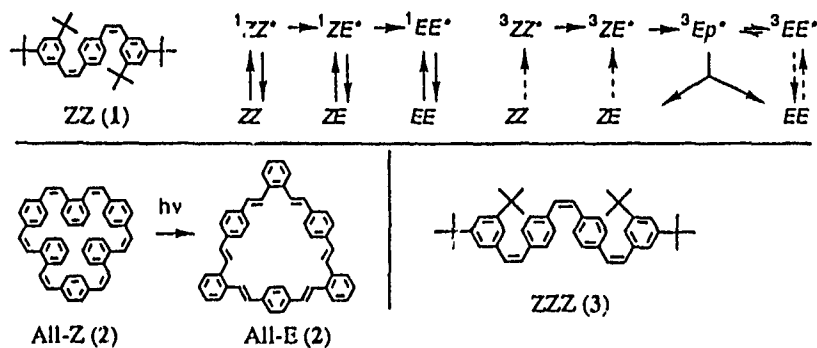
ZZ (1)   All-Z (2)   All-E (2)   ZZZ (3)

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CHEMILUMINESCENCE OF THE T.I.C.T. STATES

POPULATED BY INTER-MOLECULAR ELECTRON TRANSFER

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Population of the highly polar "twisted" intramolecular CT states (TICT) is achieved by electron transfer between the opposite radical ions of the parent molecule:

$$D^+ - A + D - A^- \longrightarrow (D^+ - A^-)^* + D-A \qquad (1)$$
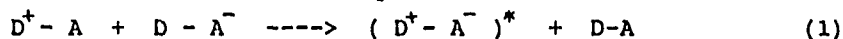
Radical ions are generated at the electrode, by subsequent pulses of reduction and oxidation of the parent molecule, D-A. With the beginning of the second pulse, the reaction (1) starts, and the chemiluminescence appears - with the spectrum identical to that of the TICT fluorescence.

In a series of acridine, anthracene, and other arene derivatives of N,N-dialkylanilines the yields of the excited state are high: they result from a competition between (1) and the formation of the lower lying triplet (locally excited in the A moiety) - and can be estimated with the modern theory of the electron transfer kinetics (Marcus; Jortner; Onuchic).

The chemical generation of the TICT state offers a chance to observe the emissions from a system with two minima - populating it at the other minimum than in the radiative excitation; to study the "photochemistry without light"; or to search for the processes otherwise appearing only under high excitation density conditions.

EXCIMER LASER-INDUCED C-C BOND FORMATION OF BICHROMOPHORIC COMPOUNDS VIA A DIRADICAL INTERMEDIATE

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In the course of our research on the application of lasers for organic synthesis, we have assessed the efficiency of photochemical diradical generation. In this context compound 1 was used for the quantitative studies, because the product 2 is directly proportional to the amount of diradicals and therefore can be used for monitoring quantitatively the process.

Three kinds of excimer lasers were used for the reaction, namely XeCl (308 nm), KrF (248 nm),[1] and ArF (193 nm) lasers. In the case of irradiation with the KrF laser, the product 2 was obtained in higher yield by using a focussed laser beam. The reaction showed considerable wavelength dependence, so that the best yield was obtained by KrF laser photolysis, the best conversion by a XeCl laser, and the best mass balance by an ArF laser.

The reactions of the derivatives 1 c-e with KrF laser were also conducted. They gave higher yields of 2 compared to those of 1 a and 1 b.

a X = Br   b X = Cl
c X = PhO   d X = PhS   e X = PhSe
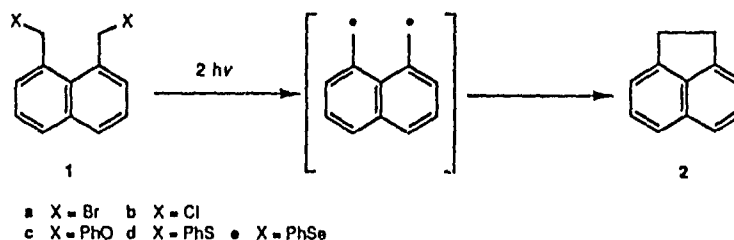
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THIN LAYERS OF NOVEL ELECTRON RELAY COMPOUNDS
ON CONDUCTIVITY GLASS AND PHOTOSENSITIVE PAPER

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The properties of two novel electron relay compounds R7B = 1,1'',1'''-tribenzyl[4,2';4',4'';6',4''']quaterpyridinium trichloride and R7D = 1,1'',1'''-tridodecyl[4,2';4',4'';6', 4''']quaterpyridinium trichloride have been studied. Both compounds could be reduced to blue radicals as with methyl viologen (= MV).

The radicals of R7B were insoluble in water and much more stable against oxygen than those of MV. Moreover the colours of these radicals were dependent on pH. They were reversible colourless in acidic and blue (λ_{max} = 590 nm) in alkaline solutions. If R7B was reduced electrochemically its radicals strongly adsorbed on electrodes (conductivity glass, glassy carbon).

Thin colourless films of R7B and agar-agar on paper resulted in blue-dyeing (λ_{max} = 590 nm, reflexion photo-spectrometry) of the irradiated parts (near UV). Addition of EDTA to the light-sensitive mixtures intensified this effect.

Furthermore, R7B could act as an electron transfer substance and as a sensitizer in aqueous photolytic hydrogen producing systems with added sensitizer (> 400 nm) and without added sensitizer (> 300 nm). The hydrogen production rates and quantum yields have been determined in systems containing sensitizer S, relay R7B, EDTA, colloidal platinum catalyst and without added sensitizer and compared with those of MV.

Not only the reduced (λ_{max} = 600 nm) but also the oxidized form of R7D was insoluble in water. Thin films of R7D on conductivity glass could reversibly be reduced in electrolyte solutions. Adsorbed R7D is able to work as an electron transfer and a sensitizing agent.

NEW EVIDENCE FOR THE PROXIMITY OF THE LOWEST ^{1}nπ* and ^{1}ππ* STATES AS THE CAUSE OF THE DUAL FLUORESCENCE OF 4-N,N-DIALKYLAMINOALKYLBENZOATES IN SATURATED HYDROCARBONS

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The dual fluorescence of the compound 4-N,N-diethylaminoethylbenzoate (DEAEB) is considered by some authors to be governed by essentially the same mechanism, which operates in the case of the dual fluorescece of 4-N,N-dimethylaminobenzonitrile (DMABN) in polar solvents. From this point of view, the anomalous fluorescence band (F_A) is regarded as emission from a twisted intramolecular charge transfer state (TICT-state) [1]. An alternative explanation assigns the band F_A of solutions of the two compounds in polar solvents to emission by solute-solvent exciplexes [2]. The fact that solutions of DEAEB in alkanes also exhibt dual fluorescence, is considered to be strong evidence against the emitting solute-solvent exciplexes [1]. It has been pointed out previously that this is no evidence, because the the replacement of the CN group in DMABN by an ester group introduces low lying nπ* electronic states and that the dual fluorescence of DEAEB might be related to the proximity of the lowest ^{1}nπ* and ^{1}ππ* states [3].

The results of a study concerning the photophysical and photochemical behaviour of solutions of several 4-N,N-dialkylamino(alkylbenzoates) in alkanes will be presented. Stationary fluorescence, time resolved fluorescence and triplet - triplet absorption of these solutions have been studied as a function of temperature and viscosity. If the viscosity is kept constant, the temperature dependence of the decay rate constants k_N and k_A of the normal (F_N) and anomalous fluorescence respectively reveals Arrhenius behaviour with different parameters for the two rate constants. It is concluded that the N and A emitting states decay predominantly respectively via a temperature dependent non-radiative process and a temperature dependent radiative process. The photochemical behaviour can be switched from nπ*-character to ππ*-character.

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PHOTOINDUCED REDOX REACTIONS OF 1-NITRONAPHTHALENE AND 2-NITROTHIOPHEN

WITH METHOXYBENZENES : A Flash Photolysis Study

By

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Abstract : One-electron oxidation of methoxy-substituted benzenes (Q) was
achieved by reaction with the lowest excited triplet state of either
1-nitronaphthalene (^3NN) or 2-nitrothiophen (^3NT), in 35% (v/v) ethanol-
-water. This was shown from the observation of the corresponding radical
ions ($Q^{\cdot+}$ and $NN^{\cdot-}$ or $NT^{\cdot-}$) following laser flash photolysis of solutions
of NN (or NT) and Q . In both cases a correlation was found between the
logarithm of the second-order rate constant (k_2), for the quenching
of the triplet state by Q, and the reduction potential of the quencher
radical cation. The greater reactivity of ^3NT compared with ^3NN, is
explained within the framework of the Rehm-Weller model by the higher
ground-state reduction potential and triplet excitation energy of the
former. Increasing the acidity of the medium increased the rate constant
for one-electron oxidation of methoxybenzene by ^3NN ; thus a value of
$k_2 = 7.07 \times 10^7$ dm^3 mol^{-1} s^{-1} was measured in neutral solution, whereas
in acid (1 mol dm^{-3} H_2SO_4) a value of $k_2 = 2.22 \times 10^9$ dm^3 mol^{-1} s^{-1}
was obtained.

THE INTERMEDIATE RADICALS AND ABNORMAL PHOTOREACTION
BEHAVIOUR OF O-SUBSTITUTED NITROBENZALDEHYDES

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The Photoreaction mechanism of o-Nitro- and 2-4-Dinitrobenzaldehyde have been studied by ESR and optical spectroscopy techniques. Results show that, markedly different from other aromatic aldehydes, the photochemical processes of o-substituted benzaldehydes are rather complicated and unusual. The observed ESR spectra are overlapped signals consisting of three and two types of radicals for o-Nitrobenzaldehyde and 2-4-Dinitrobenzadehyde respectively. The overlapped ESR spectra were entirely distinguished through decaying processes based on the much different lifetimes of these free radicals. It is therefore believed that the title compounds not only,as is well known, photorearrangement to o-Nitroso-benzoic acid but also photolysis reactions take place simultaneously. As a results, rearrangement product o-Nitrosobenzoic acid act as spin trap to react with active radicals in photolysis to form the stable nitroxyl radicals.It is obvious that the ESR signals in photochemical reaction do stem from the products of secondary reaction processes via post-photoisomerization. At the same time, the measured absorption spectra also indicate the existence of three kinds of spin-adducts for o-Nitrobenzaldehyde. Reaction mechanism is proposed for the UV photochemical processes of o-substituted nitrobenzaldehydes.

FOTOGENERATION, REACTIVITY AND COMPLEXATION OF
DIVALENT SILICON (SILYLENE) USING STATIC AND
LASER FLASH PHOTOLYSIS TECHNIQUES.

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One of the transients observed during the
photodecomposition of compounds containing the Si-Si bond
is the divalent silicon $:Si(R_2)$. The silylene like its
singlet carbene analog, is unusually reactive and
participate in insertion reaction into OH, SiH, SnH, C=C
and C≡C bonds. The relative rate constant of insertion
of silylene into SiH and OH using static photolysis is in
a very good agreement with the relative rate constant of
the same reactions using flash photolysis technique.
Laser flash photolysis of compounds containing Si-Si bond
·in the presence of reagents containing a lone pair of
electron such as ethers, amines etc. reveal that the
silylene disappears with a pseudo first order kinetics
and a new transit appears concomitantly. The transient
proves to be a complex between the empty orbital on the
silylene and the lone pair of electron. The reactivity of
the complex was found to be much lower than the
reactivity of the free silylene. The relation between the
reactivity of the free and complexed forms of silylene
and the structure of different reagents will be
discussed.

PHOTOPHYSICAL PROPERTIES OF PORPHYRINOID COMPOUNDS

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The photophysical properties of the [22 π] porphyrinoids acetylene-cumulene-porphycene 1 [1] and its tetrahydro derivative 2 [2], as well as the [26 π]homologue 3 [3] were studied in benzene solutions. Near-IR fluorescence spectra were recorded with a home-made emission spectrometer equipped with a Ge diode and lock-in detection. Absolute fluorescence quantum yields were determined for 1 and 2 by steady-state thermal lensing. Triplet-triplet (T-T) absorption spectra, triplet lifetimes, and quantum yields (Φ_T) were obtained by direct irradiation of 1 and 2.

1   2   3
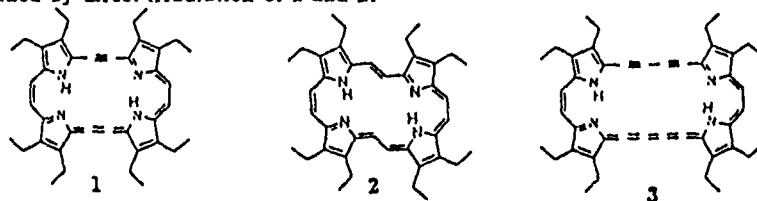
Only 2 sensitized the generation of singlet molecular oxygen, $O_2(^1\Delta_g)$, detected by steady-state and time-resolved near-IR emission. Since the triplet energy of 2 is near that of $O_2(^1\Delta_g)$, its value (21.7 kcal/mol) was determined by the analysis of the biexponential triplet decay at several O_2 concentrations. Laser-induced optoacoustic (LIOAS) experiments with 2 combined with the triplet energy yielded the Φ_T value.

Φ_T of 1 was determined by the method of Medinger and Wilkinson [4] using bromobenzene to enhance the triplet yield. LIOAS and flash photolysis experiments at various O_2 concentrations, combined with Φ_T, yielded a triplet energy of 1 3 kcal/mol lower than that for 2.

Energy transfer from various donors was used in order to record the T-T spectrum of 3 and to estimate the maximum Φ_T as well as the triplet state absorption coefficient. Taking the measured difussional quenching constant of $O_2(^1\Delta_g)$ by 3, and using $O_2(^1\Delta_g)$ as donor and 3 as acceptor in energy transfer experiments, the triplet energy of this compound was estimated to be lower than 19.5 kcal/mol.

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[3] Unpublished compound. We thank Prof. E. Vogel, Köln, for a generous sample of 3.

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FLUORESCENCE BEHAVIOUR OF
DIAZONAPHTHOQUINONE-TYPE PHOTORESIST MATERIALS

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In the convential photo-lithographic process for manufacturing integrated micro-electronic circuits (IC's) the photoresist material is illuminated with light, having a wavelength of 435 nm or 365 nm and coming from a mercury lamp. The commercial photoresist materials being used for this purpose, consist of novolac (a mixture of cresol/formaldehyde polymers) and compounds of the 2-(diazo)1-naphthoquinone (I) type, as the basic primary photoactive system, and some additives known only to the manufacturer. Photo-excitation of I in the presence of water, leads predominantly to the formation of indene-carboxylic acid or its esters (IV). However, several other products can be formed also (V-VII, Yield 4-16%), depending on the nature of the environment of the photo-excited molecule[1,2].
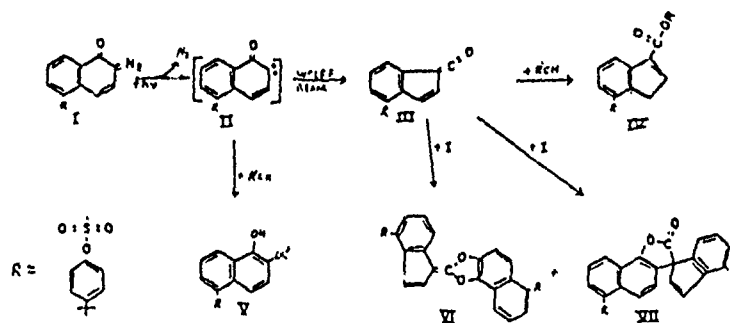
Higher packing densities of elements in a IC, require a spatial resolution exceeding the maximum achievable resolution in the conventional photo-lithographic process. There is a tendency in the modern developments to try to meet this requirement by choosing the wavelength of the light shorter than 365 nm.

Photoresist materials of known composition have been prepared by introducing the diazonaphtoquinone type compounds into either a novolac or a polyphenylphenol matrix and have then been investigated by stationary and time resolved fluorescence spectroscopy as well as by time resolved u.v / vis. absorption spectroscopy. These sytems show a strong and broad fluorescence (maximum 425 nm) when irradiated with wavelengths shorter than 400nm. This fluorescence light can be absorbed by the diazonaphtoquinone and can initiate photochemistry in regions, where this is not desired. Novolac and Polyvinylphenol, both used frequently as the matrix in diazoquinone resists, also show fluorescence when irradiated with light of wavelength shorter than 320 nm. It will be shown that the diazonaphthoquinone's are converted into fluorescing species via a monomolecular reaction and via a dimerization. The sum of the fluorescence quantum yields of these species amounts to ca. 10%. Based on their fluorescence spectra they are considered to be a mixture of the compounds V to VII. Since the quantum yield of the formation of the mixture is ca. 20%, the photochemical side reactions of the diazonaphthoquinone's may be very harmful in the lithographic process.

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Efficient Electron Exchange Chemiluminescence
of a Dioxetane Initiated by
8-Hydroxypyrene-1,3,6-Trisulfonic-Acid Tetrasodium Salt

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Several examples of peroxide chemiluminescence via intermolecular electron exchange have been reported to date but with low chemiluminescence quantum yields.[†]

We have found that 8-hydroxypyrene-1,3,6-trisulfonic acid tetrasodium salt or pyranine 1 catalyses the chemiluminescent decomposition of dioxetane 2 with a quantum yield of 0.042 einstein / mole of dioxetane.
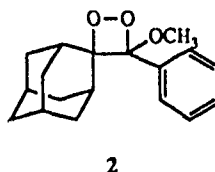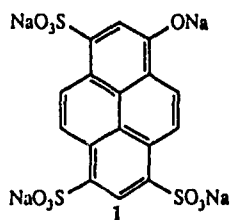
The reaction conditions differ markedly from other electron exchange chemiluminescence processes. Due to the very different solubility properties of the reactants, the reaction is carried out in aqueous buffer and cationic micelles. The dioxetane resides in the micellar core with the fluorescer at the Stern layer. The resulting chemiluminescence spectrum matches the fluorescence spectrum of 1. A significant difference in activation energies as well as kinetic properties clearly distinguishes this reaction from simple thermal dioxetane decay coupled to energy transfer to the fluorescer.

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The Electronic Structure Computation and Electron Paramagnetic Resonance
Spectroscopy of the Matrix-Isolated Mono(1,3,5-Trifluorobenzene) Vanadium(0)
Half-Sandwich Complex.

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The (1,3,5-trifluorobenzene)vanadium(0) half-sandwich complex is
isolated in an Ar matrix and its EPR spectrum recorded. In addition, its
electronic structure is computed and the V-C distance is optimized using the
LDF-LCAO method. The theoretical computations predict that the molecule is
metastable in the gas phase with the ^2E and $^2A_1$ states being nearly
degenerate. Consequently the influence of the trapping matrix is a decisive
factor in determining: a) Its ground state and b) If it may be isolated in a
stable form. The resonance field positions, the g, ^{51}V, ^9F and ^1H hyperfine
tensors for this molecule, in its $^2A_1$ state, are derived as a function of its
molecular orbital coefficients. The hyperfine resonance positions derived
for the three ^9F spatially equivalent atoms are not the same. The detailed
expressions that give rise to this magnetic inequivalency are identified. The
simulation of the experimental EPR spectra and the comparison of the
experimental and computed spin Hamiltonian tensor components reveal that the
complex, when trapped in an Ar matrix at 12 K, has a Jahn-Teller ^2E ground
state.

III- MODIFICATION OF MOLECULAR ASSEMBLIES

PHOTOPHYSICS OF UV STABILIZERS IN SOLUTION
AND IN POLYMER SUBSTRATES

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Despite many investigations, there remains considerable uncertainty concerning the mechanisms of excitation energy dissipation in compounds which act as UV absorbers and photostabilizers of polymeric materials[1]. In particular the role of excited state intramolecular proton transfer (ESIPT) in accounting for the exceptional photostability of those compounds which contain intramolecular hydrogen bonding has been questioned. This paper reviews a number of absorption, fluorescence and picosecond spectroscopy studies recently carried out in our laboratories aimed at investigating the photophysics of o-hydroxyphenylbenzotriazole (HPB) and o-hydroxyphenyl-s-triazine (HPT) based photostabilizers in a range of solvents and polymer substrates.

For the compounds studied the spectral contributions made by various ground state species (i.e. planar and non-planar) to light absorption have been resolved and quantified. Both the contributions of these ground state species and the mechanisms of energy relaxation are found to depend markedly on the polarity and hydrogen bonding properties of the surrounding medium. In certain aprotic hydrogen bonding solvents and polymer substrates the ESIPT process is effectively disrupted, while for HPB derivatives in hydroxylic solvents there is evidence for solute-solvent complexation mediating the proton transfer process.

In some HPT derivatives and in polymer films of HPB compounds which can be copolymerized with methyl methacrylate and styrene, emission from the proton-transferred species is observable at room temperature and picosecond fluorescence measurements indicate the rate constant for ESIPT exceeds 10^{11} s^{-1}. Temperature dependence studies of this highly Stokes-shifted emission suggest the activation energy for ESIPT is negligible. In copolymers of 2-naphthylmethacrylate with incorporated HPB, efficient non-radiative energy transfer to HPB occurs from both 2-naphthyl monomeric and excimer species resulting in the effective photostabilization of the polymer.

The results of these photophysical studies suggest possible means of optimizing the performance of UV photostabilizers.

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PHOTOCHEMISTRY OF POLY(BIS(4-BENZYLPHENOXY)PHOSPHAZENE).

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In this paper we report the direct and the benzophenone sensitized photochemistry of poly[bis(4-benzylphenoxy)-phosphazene], $[NP(O-C_6H_4-CH_2-C_6H_5)_2]_n$, (PBPP), in solution and in film, in the presence of air or in inert atmosphere.

It has been found that the direct irradiation of the polymer, both in CH_2Cl_2 solutions and in solid state, results in the splitting of the C-H bond of the methylene group of the side benzylphenoxy residues on the polyphosphazene skeleton to produce the $-O-C_6H_4-\overset{\bullet}{C}H-C_6H_5$ radical. The same species are formed also in the benzophenone sensitized photochemistry of PBPP.

In air-equilibrated, dilute, solutions, the radicals evolve towards chain scission and degradation, while in solid state they couple giving rise to extensive crosslinking. This last reaction, moreover, was found to be largely prevailing in the benzophenone sensitized process.

POLYMER CHARACTERIZATION USING SINGLET OXYGEN
PHOSPHORESCENCE AS A SPECTROSCOPIC PROBE.

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NM 87131, USA
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Sandia National Laboratories, Albuquerque, NM 87185, USA

Singlet molecular oxygen ($^1\Delta_g O_2$) can be produced in solid
organic polymers by a variety of different methods including
1) energy transfer from a photosensitizer dissolved in the
polymer matrix,[1] 2) energy transfer from the polymer itself,[2]
and 3) photolysis into the polymer-oxygen charge-transfer
absorption band.[3-5] The phosphorescence of singlet oxygen can
be monitored in both steady-state and time-resolved
experiments, yielding valuable information on the structure
and properties of 1) the polymer and 2) solutes dissolved in
the polymer. We are also able to comment on processes that
can have important practical ramifications including, for
example, polymer degradation. In addition, this
spectroscopic probe can be used to rapidly quantify oxygen
diffusion/permeation coefficients in polymer films over a
wide temperature range.

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PHOTO-OXIDATION OF POLY[BIS(4-BENZYL)PHENOXY]PHOSPHAZENE

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In recent years there has been a growing interest in polymer bearing reactive groups, which can undergo easily chemical modification by thermal and photochemical methods. In this work we report the results concerning the photo-oxidation of poly[bis(4-benzyl)phenoxy]phosphazene films by irradiation with UV light ($\lambda > 300 nm$) in presence of warm air ($50°C$).

FTIR and UV-visible techniques were used to follow the formation of photoproducts and to suggest a detailed photodegradation mechanism.

In particular, we show that the decrease of a band at 1460 cm^{-1} and a simultaneous formation of new peak at 3400 cm^{-1} in the FTIR spectra is a clear evidence that the hydroperoxidation sites are the $-CH_2-$ groups belonging to benzyl moieties. Besides the decomposition of hydroperoxides generates two different mechanisms of β-scission processes of alkoxy-radicals leading to the formation in the FTIR spectra of new bands at 3550, 1725, 1702 and 1660 cm^{-1} attributed at alcohols, aromatic esters, benzaldehydes and benzophenone groups, respectively. Accordingly, the detection by GC of benzene vapour as main volatile products and the formation of an intense band at 340 nm in UV-vis. spectra strongly support the suggested mechanism. The high photoreactivity of photogenerated groups is mainly responsible for the extensive crosslinking reactions and yellowing of photooxidated films.

ABNORMAL CHANGES OF FLUORESCENCE SPECTRA OF PYRENE IN Si-Ti BINARY SYSTEMS
DURING THEIR SOL- GEL- XEROGEL TRANSITION PROCESSES

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So-called "sol-gel method" is expected to be one of the most promising approaches to produce useful composite materials such as optical media and molecular devices. We have investigated the characteristics of fluo-rescence spectrum and thermal stability of pyrene and rhodamine B encapsulated into SiO_2 networks during sol--gel--xerogel transition processes.[1] In this paper, we report characteristic changes in fluorescence spectra of pyrene in Si-Ti binary systems during sol--gel-- xerogel transition processes of ethanol solutions containing mixtures of tetra- ethoxy silane (TEOS) and titanium tetrabutoxide (TTBO), and pyrene (0.01 mol/dm^3).

Fig. 1 shows the characteristic changes of fluorescence spectra of pyrene in Si-Ti binary systems during various stages of their sol--gel--xerogel transition processes of ethanol solution containing TEOS, TTBO, and pyrene at 298 K. At an initial stage of sol--gel process, two characteristic fluorescence spectra are observed at around 372-392 nm and 430-540 nm. The former shows the 0-0 band at 372 nm, being attributed to the fluorescence of pyrene monomer. The latter structure- less emission is assigned to the excimer of pyrene dimer. It is seen that the intensity of excimer emission decreases with progrssion of sol--gel transition, and the excimer emission disappears at the point of gelation of the system. The excimer emission reappears in the gel--xerogel transition process. The fluorescence spectra

of pyrene monomer scarcely change, however, their excitation spectra were found to change in the sol--gel transitions of the systems.

These observed changes in pyrene dimer and monomer emissions were not observed in TEOS-alone systems without Ti compositions. In the presentation, a possible mechanism for the observed changes in Si-Ti binary systems is discussed considering the role of Ti com- position as coordination sites for pyrene.
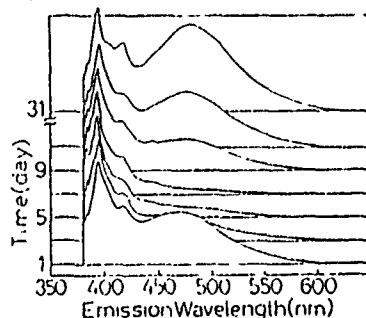
Fig. 1. Fluorescence spectra of pyrene in Si-Ti binary system at various stages of the sol--gel--xerogel transitions.

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THE PHOSPHORESCENCE OF 2,3,7,8-DIBENZOPYREN-

1,6-DIQUINONE IN SOLUTIONS AND FABRICS

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2,3,7,8-Dibenzopyren-1,6-diquinone (DBPQ) is known to be an efficient photosensitizer of fabrics decomposition. The photodestruction processes of fabrics are supposed to be initiated by the dye triplet state. However, up to recent time the triplet state of DBPQ was not detected experimentally.

In this work we managed to observe the phosphorescence, accompanying the radiation deactivation of DBPQ triplet state in solutions, cellulose films and fabrics. The phosphorescence was registered at -196^{0}C. The phosphorescence spectrum of the monomolecular form of DBPQ consists of three major bands at 750, 845 and 935 nm. The relative intensities of these bands are 1:0,6:0,1. The phosphorescence lifetime is $1,6\pm0,1$ ms, the exitation spectrum coincides with the absorption spectrum of the monomolecular form of the dye. In addition to this phosphorescence the short wavelength low temperature delayed luminescence was measured. The spectrum of this luminescence is presented by the broad band at 680 nm, the lifetime is about $5,3\pm0,5$ ms. The exitation spectrum coincides with the absorption spectrum of the aggregated dye molecules.

Phosphorescence measurements show that the triplet molecules of monomeric DBPQ are always present in coloured films and fabrics. Thus, it is not excluded, that there monomeric triplet are the main initiators of photodestructive reactions in textile materials.

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PRIMARY PHOTOCHEMICAL PROCESSES OF ORGANIC DYES ADSORBED ON SURFACES

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The properties of molecules adsorbed at surfaces are modified to a greater or lesser extent depending on the nature of the adsorbate-adsorbent interaction. We have investigated the ground and excited state absorption and emission properties for oxazine and acridine dyes when they are adsorbed on the surface of microcrystalline cellulose. Ground state absorption and fluorescence measurements provide evidence for aggregation of these dyes on the surface, often in marked contrast to their behaviour in dilute fluid solution. Monomer and dimer spectra have been elucidated and the equilibrium constants for dimerisation measured for several systems. Both fluorescent and non-fluorescent dimers have been detected.

The absorption spectra of the triplet states of acridine orange and other dyes adsorbed on cellulose surfaces have been measured, using the technique of diffuse reflectance laser flash photolysis. Triplet lifetimes which are often considerably longer than in fluid solution have been measured. Triplet-triplet energy transfer, with triplet benzophenone as sensitizer, has been used to allow relative triplet extinction coefficients to be obtained for the first time. Both static and dynamic quenching mechanism pertain and the determining parameters controlling dynamic aspects of light induced heterogeneous reactions are discussed.

Photophysics of Benzoquinolines Along the Sol-Gel Transition

- A Probe of Structural Changes of the Transition

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The advantages, uniqueness, and potentiality of the sol-gel process have already well known. The fluorescence and fluorescence-excitation spectra of three benzoquinolines(BQs) during the sol-gel-xerogel transition of tetraethyl-orthosilicate(TEOS) have been observed as a function of time. Three conclusions were obtained. First, BQs show two fluorescences(FN and FA) originated from neutral form and anionic form during the transition. Secondly, BQs form a hydrogen-bonded complex with silanol groups of surface of cage in xerogel state. Thirdly, change of ratio of the fluorescence intensity of FN to that of FA occurred in four stages, being reflected the change of chemical and physical circumstances around the doped BQs.

Fig. 1 shows the weight change of the reaction system and ratio of the fluorescence intensity of FN to that of FA. The change of the ratio is divided into four stages. In the first stage, the ratio increases rapidly, owing to the increase of the silanol groups by hydrolysis of TEOS. In the second stage, gelation occurred and the unchanged ratio was observed. In the third stage, the formation of pores is completed until this stage is ended. As the distance of the hydrogen bond becomes shortened due to shrinkage of the gel, the ratio gradually increases with enhancement of increased formation of the hydrogen-bonded complex. In the last stage, the residual solvent molecules around the doped BQs are gradually evaporated. Therefore, the ratio gradually approach a definite value. In the presentation, a possible interpretation for the individual stages is discussed.
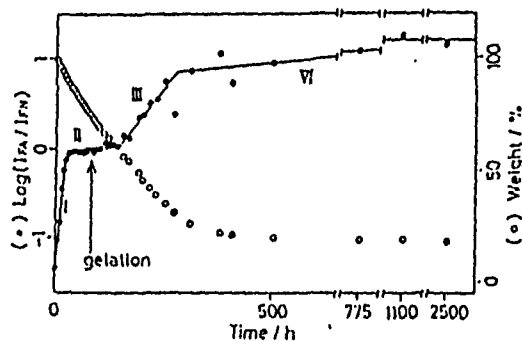
Fig. 1. The weight change of the reaction system and the ratio of the fluorescence intensity of FN to that of FA for 5,6-BQ.

NANOSECOND TIME-RESOLVED SPECTROSCOPY AND NANOSECOND
DYNAMIC PHOTOGRAPHY OF POLYMER FILMS JUST UPON
LASER ABLATION

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High density photo-excited molecules embedded in a polymer film can cause morphological change of the surface[1]. The mechanism is, however, still unclear from a molecular point of view. In the present work, we have studied biphenyl-doped poly(methyl methacrylate) films using a KrF excimer laser (248nm, 18ns) to correlate photochemical primary processes with ablation. A nanosecond streak camera system was utilized to measure fluorescence and transient absorption spectra of the films just upon laser ablation. Fragment ejection from the surface was directly monitored under a microscope using rhodamine-dye fluorescence as a nanosecond flash lamp.

The lowest triplet state of biphenyl was generated and decayed rapidly during the laser pulse, and subsequently a continuum absorption spectrum covering the whole visible wavelength region appeared. The latter may be ascribed to morphological changes. Any transient species other than S_1 and T_1 were not observed. The film seemed to remain transparent and have not been ablated during the pulse. Actually, fragment ejection was confirmed to occur at 50ns after excitation by nanosecond dynamic photography. It is, therefore, considered that it takes a few tens ns for absorbed energy to disperse in the film and to induce its ablation.

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Optical Electrochemistry : Real-time Spectroscopy of Conduction Band Electrons in a Metal Oxide Semiconductor Electrode.

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Use of optically transparent TiO_2 membranes has permitted electrons present in the conduction band of a semiconductor electrode to be monitored spectroscopically in real-time. It has also been possible, for the first time, to correlate real-time absorbance changes assigned to Faradaic processes occurring at the electrode surface with the real-time behavior of the charge carriers in the electrode, also monitored spectroscopically. The purpose of this paper is to communicate the results of some initial studies which demonstrate the usefulness of such an approach [1,2].

Transparent TiO_2 membranes (thickness 4μm) were prepared by sintering 15 nm colloidal anatase particles on a conducting glass support. Potentiostatic control of the Fermi level within the colloidal-like particles of the semiconductor membrane is possible [3]. Visible, and near infrared spectra have been measured for membrane biased at potentials between -1.500 V and +1.000 V (SCE) and indicate formation of an accumulation layer at negative potentials. Spectral data is presented in a manner which permits determination of the flatband potential of the semiconductor membrane. The growth and decay behavior of the accumulation layer have been studied and can be seen to be controlled by filling of deep trap states [4]. It has also been possible to monitor in real-time the Nernstian shift of the membrane flatband potential following reduction of adsorbed H^+ ions under acidic conditions. Finally, Faradaic processes of methylviologen at the TiO_2 membrane, following application of a potential step, were investigated by real-time measurement of absorbance changes associated with both the transport of charge carriers in the membrane and the redox processes occurring at the surface of the membrane.

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RELATIONSHIP BETWEEN THE GEOMETRY OF THE EXCITED STATE OF VANADIUM OXIDES
ANCHORED ONTO SiO_2 AND THEIR PHOTOREACTIVITY TOWARD CO MOLECULES

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When a metal oxide is dispersed on a support surface both its
physical and chemical nature are seriously modified, often resulting in
high catalytic and photocatalytic activities and selectivities.
Fortunately, metal oxide catalysts such as vanadium oxide supported on
SiO_2 exhibits photoluminescence in the visible region.

In this paper we report the Franck-Condon analysis of the well
resolved phosphorescence spectra at 77K of vanadium oxide catalysts
anchored onto SiO_2 with different vanadium concentrations. The
photoreactivities of these catalysts toward CO molecules have been
measured and a good linear relationship between the yields of photo-
formed CO_2 and the phosphorescence yield is obtained. A comparison of
the theoretical Franck-Condon analysis and the experimental results
indicate that an elongation of the internuclear distance between vanadium
and oxygen ions in the excited state of the vanadyl groups may be
associated with the easy photoreduction of the catalyst with CO.
Further, the results of the analysis of the well-resolved
photoluminescence spectrum of powdered ZnO and its small photoreactivity
toward CO are compared with those for vanadium oxides anchored onto SiO_2.
This analysis gives useful information about the lowest excited states of
the different catalysts and especially about the primary processes of
photocatalysis on a molecular scale.

THE INFLUENCE OF METAL(II) SALTS AND SOLID SUPPORTS ON THE NATURE OF THE PHOTOCHEMICAL REACTION OF 1,1-DIPHENYL-2-HALO-SUBSTITUTED ETHENES

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Photolysis of 1,1-diphenyl-2-haloethene in methanol solution in the presence of copper(II) acetate, copper(II) triphlate or cadmium(II) acetate resulted in the formation of ionic and radical products. The ratio of ionic and radical products depended on the halogen atom bonded and also slightly on the salt used. The effect of the solid support (silica gel, silica gel impregnated with copper(II) or cadmium(II) salts) was studied and it was determined that the product distribution as well as the ratio of ionic to ionic and radical products changed in comparison to the results obtained when irradiation was carried out in solution.
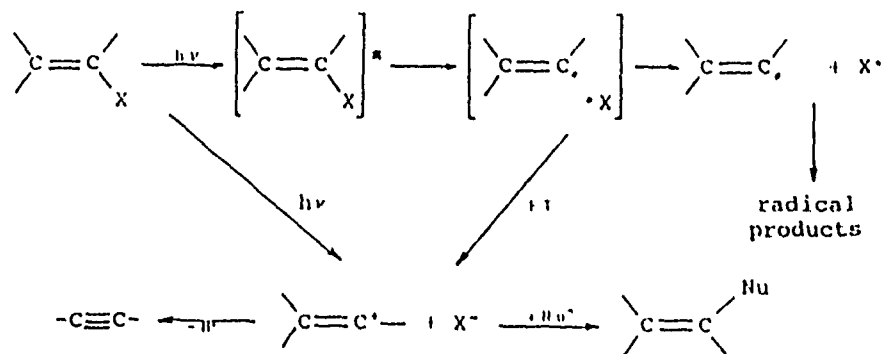
EFFETS DES ETHER-COURONNES SUR LA STRUCTURE INTERFACIALE DES MICELLES ET VESICULES.

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Les ether couronnes(EC) sont des composés capable d'encapsuler les contre ions au voisinage des interfaces micellaires et vesiculaires. L'effet d'addition de quelques EC sur la structure interfaciale de micelles de laurylsulfate de sodium (NaLS) et de vésicules de dihexadecylphosphate (DHP), est étudié par l'intermédiaire de deux réactions de transfert d' électrons: la photoionisation de la tetramethylbenzidine (TMB) et le déclin du photocation (TMB$^+$).

Les études précédentes avaient montré une relation linéaire entre le rendement d'ionisation et le potentiel électrique interfacial ($\Delta\Psi$) [1]. D' autre part, la constante de vitesse de déclin du photocation TMB$^+$ est une fonction exponentielle de $\Delta\Psi$ [2].

Au cours de ce travail, nous avons observé des modifications de $\Delta\Psi$, consécutives aux additions d' ether couronnes. Dans des conditions particulières, une augmentation de la séparation des charges a pu être mise en évidence.

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EFFECTS OF CROWN-ETHERS ON THE INTERFACIAL STRUCTURE OF MI-CELLES AND VESICLES.

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Crown ethers (CE) compounds are able to capture the counter ions near the micellar or vesicular interfaces. The effect of various CE addition on the interfacial structure of sodiumlaurylsulfate (NaLS) micelles and dihexadecyl-phosphate (DHP) vesicles, is studied through two electron transfer reactions, the N,N,N',N', tetramethylbenzidine (TMB) photoionization and the photocation (TMB$^+$) decay.

Previous studies had shown a linear dependence of the photoionization yield vs the interfacial electrical potential ($\Delta\Psi$) [1]. A relationship between TMB$^+$ dark decay rate and $\Delta\Psi$ was also demonstrated [2].

In the present study, photoionization yield and TMB$^+$ decay rate display an opposite variation vs CE concentration. The results are discussed in terms of $\Delta\Psi$ variations.

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EXCITED-STATE PROTON-TRANSFER REACTIONS
IN LIPID BILAYER MEMBRANES OF VESICLES

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Investigation of excited-state proton-transfer reactions in organized molecular assemblies supplies very important information on the structure and dynamics of such systems. These data are necessary to understand mechanisms of the proton transport in biomembranes and to design artificial systems for solar energy conversion, etc.

Proton transfer photoreactions of some hydroxyaromatic compounds ArOH (1- and 2-naphthol, chlorosubstituted naphthols) in vesicles prepared from egg lecithin (EL) or dipalmitoylphosphatidylcholine (DPPC) were investigated. Fluorescence spectra and kinetics of ArOH in vesicles suspension depend on the lipid concentration. Almost all molecules of the hydroxyaromatics are solubilized in the bilayer membranes at the concentration of EL greater than 3 mM. Further increasing the lipid concentration do not change the parameters of the decay curves and the ratio of the fluorescence quantum yields of ArO^- (φ') and ArOH (φ).

In contrast to the homogeneous aqueous solution the decay curve of ArOH in lipid bilayers at pH$\approx$7 can be fitted only by the sum of two exponentials. The lifetime of the fast decaying exponential term coincides with the rise time of ArO^- fluorescence. This give a possibility to suggest the existence of at least two different localization sites of ArOH in the bilayer. Only the molecules of ArOH located in more hydrophylic region can dissociate in the excited state. The fraction of these molecules can be calculated from the ratio of two preexponential factors. The temperature dependence of φ'/φ for various naphthols in DPPC vesicles has a minimum near the temperature of gel-liquid crystal phase transition.

General dependence of the protolytic photodissociation rate constants on the equilibrium constants was obtained for vesicular, micellar and homogenious aqueous solutions.

EXCITED STATE DIFFUSION OF TICT MOLECULES IN DHP SUSPENSIONS

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We have studied the diffusions and quenching of the excited state of some TICT molecules, dialkoxy-1,4 anthracene (Ant1,4) and bi9,9'(ethyl12-hexyl10)anthryl (BOA), which are entrapped in the bilayer membrane of dihexadecyl phosphate (DHP). The time-resolved fluorescence decays are obtained with a streak camera in the picosecond time scale. Our purpose is to get a better understanding of the structure of bilayer membrane formed from artificial surfactants.

(1) The DHP suspensions were obtained by the standard sonication protocol[1]. The influence of the ionisation of DHP polar groups on structure was investigated by adding NaOH to the suspensions prior sonication. Quasi elastic light scattering (QELS) and encapsulation of paramagnetic or fluorescent probes have been used to investigate the organization of bilayer membrane in DHP suspensions during preparation. By the encapsulation measurements we show that more than 80% of DHP molecules are organized in membrane fragments with the flat disk shape. The electron paramagnetic resonance (EPR) spectra of n-doxyl stearic acid (nNS) show that a phase segregation of the nitroxide probes occurs in the bilayer membranes and that the added probes are localized in the border of the disks.

(2) The isosbestic points observed from transient fluorescence spectra show the existence of the two population in the DHP bilayer membrane, a polar and a non polar site. By monitoring the decay of the fluorescence intensity, we measure the excited state diffusions of BOA and Ant1,4 from the core to the surface of neutral DHP bilayer. The decay of the inner population is more rapid for Ant1,4 (t_{in}=0.235ns) than for BOA (t_{in}=6ns). The quicker diffusion of Ant14 agrees with a ground solubilization of Ant14 at the interface. The diffusion of the two molecules may be controlled by the surface of potential originating from the variation of the chemical affinity of the probe across the membrane.[2] In the case of charged DHP membranes the fluorescences of two molecules have the same decay rates in the red region (470nm) as in the blue one(410nm). No diffusion of the excited states has been observed for the two molecules.

(3) The efficient quenching of Ant1,4 by nNS indicates that the fluorescent molecule is solubilized at the border of the disks. No dependence of the quenching rate on the position of the nitroxide group was observed. The isosbestic point on the quenching spectra confirms the existence of only two population in the neutral DHP membrane.

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Diffusion de l'Etat Excité de Molécules TICT dans les Membranes de Dihexadecylphosphate

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Nous avons étudié la diffusion et le quenching de l'état excité de dérivés de l'anthracène, soit dialkoxyl-1,4 anthracène(Ant1,4) et bi9,9'(ethyl12-hexyl10)anthyl(BOA) qui sont encapsulés dans les bicouches membranaires de dihexadecylphosphate (DHP). Les déclins de fluorescence résolus dans le temps ont été mesurés avec une caméra à balayage de fente picoseconde. Le but du travail est de montrer l'existence de fragments membranaires et de mieux comprendre leur structure.

(1) Les vésicules et les fragments de membrane ont été préparés par sonication[1]. L'influence de l'ionisation des têtes polaires du DHP sur la structure a été étudié en neutralisant par la soude les échantillons avant sonication. Nous avons utilisé la diffusion de la lumière et l'encapsulation de sondes paramagnétiques et fluorescentes pour l'étude de l'organisation des bicouches membranaires au cours de la préparation. La mesure de l'encapsulation montre que plus de 80% de molécules DHP sont organisées en fragments membranaires qui ont la forme de disques plats. Les spectres de n-doxyl acide stéarique(n-NS) enregistrés par RPE montrent qu'il existe une ségrégation de phase des sondes dans les disques et que ces sondes rajoutées sont localisées au bord des disques.

(2) Les points isosbestiques observés sur les spectres de fluorescence résolus dans le temps montrent l'existence de deux populations dans les bicouches membranaires de DHP, correspondant à deux environnements polaire et apolaire. En analysant les déclins de l'intensité de fluorescente nous mesurons les diffusions de l'état excité de l'Ant1,4 et du BOA du coeur vers la surface de la membrane. Le déclin de la population interne est plus rapide pour l'Ant1,4 que pour le BOA (voir tableau1). La diffusion rapide de l'Ant1,4 montre bien une solubilisation initiale de ces molécules proche de l'interface. Dans le cas du DHP sous la forme basique la population rouge est plus favorable par rapport la population bleue.

tableau 1

DHP	τ_{in} (ns) in 0%NaOH	τ_{in} (ns) in 50%NaOH
Ant1,4	1,46	3,38
BOA	6,63	6,75

(3) Le quenching de l'Ant1,4 et le BOA par les n-NS indique que les molécules fluorescentes sont dissoutes au bord du disque. La vitesse de quenching est indépendante de la position du groupe nitroxide. Les points isobestiques dans les spectres de quenching stationnaire confirment qu'il existe seulement deux localisations des solutés dans les membranes DHP.

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TRANSFORMATION EN SOLUTION AQUEUSE DU CYCLOHEXADIENE-1,3 DIETHANOATE-1,4

DE SODIUM ET DE L'ACIDE PHENYLENE-1,4 DIACETIQUE PHOTOCATALYSEE PAR ZnO

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Les transformations photocatalytiques du cyclohexadiène-1,3 diéthanoate-1,4 de sodium (CHDDE) et de l'acide phénylène-1,4 diacétique (PDA) ont été étudiées[1].
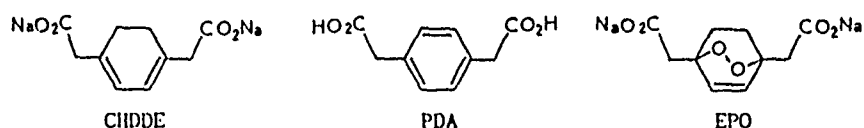
CHDDE a été choisi comme substrat car il permet de mettre en évidence l'intervention ou non de $^1O_2$ dans la réaction, puisqu'il réagit facilement avec $^1O_2$ en donnant un endoperoxyde spécifique :

$$CHDDE + {}^1O_2 \longrightarrow EPO$$
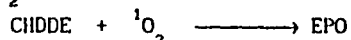
La formation de EPO n'étant pas observée lors de la transformation de CHDDE photocatalysée par ZnO, on peut conclure que $^1O_2$ n'intervient pas dans la réaction. Des mesures cinétiques ont été faites à plusieurs concentrations de substrats, à différents pH et en l'absence ou en présence d'alcool isopropylique, utilisé comme capteur d'OH$\cdot$. A pH = 7, pour une concentration de substrat de 10^{-3} M, les rendements quantiques de transformation sont égaux à 0,31 et 0,15 pour CHDDE et PDA respectivement. En présence de 1% de iPrOH, ils tombent à 0,24 et 0,08. A pH = 11, ils sont égaux à 0,19 et 0,17. De plus, les disparitions sont complètement inhibées par iPrOH.

On peut conclure qu'en milieu basique, l'oxydation par OH$\cdot$ est la principale voie de transformation. En milieu neutre, d'autres espèces interviennent. Une oxydation du substrat par les trous positifs est proposée.

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PHOTOCATALYTIC TRANSFORMATION OF SODIUM 1,3-CYCLOHEXADIENE 1,4-DIETHANOATE AND 1,4-PHENYLENEDIACETIC ACID, IN AQUEOUS ZnO SUSPENSION

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The photocatalytic transformations of sodium 1,3-cyclohexadiene 1,4-diethanoate (CHDDE) and 1,4-phenylenediacetic acid (PDA) have been studied[1].
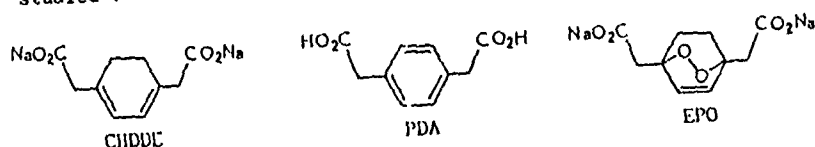
CHDDE was chosen as a probe molecule for $^1O_2$ involvement. It easily reacts indeed with $^1O_2$ giving rise to a specific endoperoxide :

$$CHDDE + {}^1O_2 \longrightarrow EPO$$
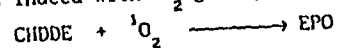
In the photocatalytic transformation of CHDDE on ZnO, no formation of EPO was observed, and it can be concluded that $^1O_2$ is not involved.

The initial rates of CHDDE and PDA transformation have been measured as functions of the initial substrate concentration in the absence and in the presence of iPrOH, an OH· scavenger. At pH=7, with a substrate concentration equal to 10^{-3} M, quantum yields of conversion are 0.31 and 0.15 respectively for CHDDE and PDA. In the presence of iPrOH, 1% v/v, the quantum yields were reduced to 0.24 and 0.08. At pH=11, they are respectively equal to 0.19 and 0.17, and iPrOH inhibits almost completely the consumption of the two substrates.

It can be deduced that in basic solution, the oxidation by hydroxyl radicals is the main route of substrate conversion. In neutral medium, it competes with one or several other pathways. Oxidation by positive holes is most likely one of them.

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PHOTOPHYSICAL PROPERTIES OF
TRIARYL PYRYLIUM SALTS

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The photophysical properties of a homologous series of 2,4,6-triaryl pyrylium tetrafluoroborates substituted by six alkoxy chains[1,2,3] (fig.1) are investigated in dilute solutions and in their columnar liquid crystalline and solid phases. Both oriented and non oriented liquid crystalline samples are studied.

The influence of lateral chain length on the absorption, fluorescence and excitation spectra and on the fluorescence lifetimes and quantum yields is examined in various solvents.

Fig.1
Triaryl pyrylium salts
$R=C_nH_{2n+1}$; $n=2,3,4,5,8,12$

In the organized phases the steady-state fluorescence spectra are red-shifted with respect to those observed with dilute solutions. The presence of two emission bands has been revealed by time resolved spectroscopy. These bands are attributed to the existence of different energy sites within each column, due to the relative orientation of neighbouring chromophores. The decay kinetics which greatly depend on the lateral chain length, consequently on the distance between the column axes, indicate that both intracolumnar and intercolumnar transfer processes are involved.
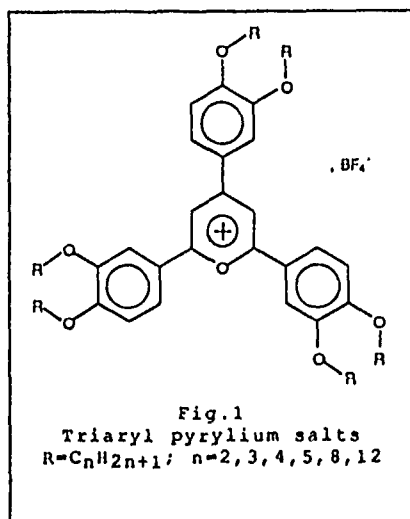
(1) STRZELECKA, H., JALLABERT, C. and VEBER, M., 1988, Molec. Crystals Liq. Crystals, 156, 355.
(2) DAVIDSON, P., JALLABERT, C., LEVELUT, A.M., STRZELECKA, H., VEBER, M., 1988, (a) Liq. Crystals, 3, 133. (b) Molec. Crystals Liq. Crystals, 161, 395.
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DIFFUSION DU BIANTHRYL DANS LES MILIEUX MICRO-HÉTÉROGENES.

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La diffusion et le piégeage de l'état excité du Bianthryl (BA) a été étudiée dans divers milieux micro-hétérogènes afin de déterminer la localisation de la molécule sonde. Le BA est une molécule apolaire mais sont son spectre de fluorescence dépend de la polarité du solvant. Dans les micelles, la molécule excitée diffuse vers l'interface aqueuse où elle est piégée. Cette diffusion a lieu sur la surface de potentiel constituée par les variations de l'affinité de la molécule pour les différents cite du milieu micro-hétérogène. Le cinétique de la diffusion reflète la forme de la surface de potentiel. La dynamique des populations libre et piégée a étée mesurée par fluorescence. Les milieux étudiés inclus les vésicules de DMPC (dimeristoyl-phosphatidyl-choline) , les membrane de DODAC (Dioctadecyl-dimethyl-ammonium chloride), les micelles de CTAC (Cethyl-trimethyl-ammonium chloride) et de SDS (Sodium dodecylsulfate) et des suspensions de microcristaux de bianthryl. Les suspensions de tensio-actifs ont été obtenues par sonication et filtration en suivant le protocole standard[1] Le courbes de déclin de fluorescence ont étées obtenues en comptage de photon unique (IMS) ou avec une camera à balayage de fente (Orsay). Des simulation des déclins ont été effectuées par résolution numérique de l'équation de Smolukovsky afin de déterminer la forme du profil de potentiel. .

Dans les micelles, le temps caractéristique de dépolarisation de fluorescence indique que la diffusion browniène a lieu. Dans les micelles de SDS, le bianthryl rencontre une barrière énergétique sur son chemin vers la surface. Dans les micelles de CTAC, le bianthryl apparait comme proche de la surface.

Dans les milieu membranaires (DMPC, DODAC), la dépolarisation de l'émission que le temps caractéristique de rotation browniène. Le déclin de la population "libre" est de la forme $\exp(-k\sqrt{t})$. Ce type de déclin est typique d'un procéssus de diffusion vers des piéges distribués aléatoirement. Les deux observations montrent que le BA forme des micro-domaines dans la membrane et qu'une diffusion résonante de l'excitation a lieu.

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DIFFUSION OF BIANTHRYL EXCITED STATES IN MICROHETEROGENEOUS MEDIA.

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The diffusion and trapping of bianthryl excited state has been studied in various microheterogeneous media in order to determine bianthryl localisation. Bianthryl is an apolar molecule but its excited state emission depends on the polarity of the solvent. In micelles, the excited molecule diffuses and reaches the water phase where it is trapped. The diffusion of the excited state occurs on the potential surface and barriers originating from the variation of the chemical affinity of the probe across the microdomain. The dynamics of the diffusion depends on the shape of the chemical potential profil. The inner and superficial population have been measured by monitoring the fluorescence intensity. The media studied include DMPC (dimeristoyl-phosphatidyl-choline) vesicles, DODAC (Dioctadecyl-dimethyl-ammonium chloride) membranes, CTAC (Cethyl-trimethyl-ammonium chloride) and SDS (Sodium dodecylsulfate micelles and bianthryl microcristal suspensions. The surfactant suspensions were obtained by sonication and filtration using standard preparation protocols[1] The fluorescence decay curves where registered with the picosecond time correlated single photon counting method (IMS) or with a streack camera (Orsay). Simulation of the decays where performed using the numerical solutions of the Smolukovsky diffusion equation, in order to determine the shape of the chemical potential profil.

In micellar systems the fluorescence depolarisation lifetime indicates that physical diffusion occurs. In SDS micelles, bianthryl encounters a barrier on its way to the surface. In CTAC micelles bianthryl appears to be close to the surface but no diffusion of the water inside the micelle is observed.

In membrane systems (DMPC, DODAC), the depolarisation of the emission is much shorter than the expected rotational relaxation time. The decay of the membrane population has the form of $\exp(-k\sqrt{t})$. This decay shape is typical of a diffusion process to randomly distributed traps. Both observations shows that bianthryl molecules form micro-domains in the membrane and that exciton diffusion and trapping occurs.

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Pansu R.B. Yoshihara K J.Phys.Chem. in press (1991)

PHOTOCHEMICALLY SWITCHED PHASE TRANSITIONS
IN LYOTROPIC LIQUID CRYSTALLINE SURFACTANT SYSTEMS

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In concentrated aqueous surfactant solutions (> 20 % by weight) interactions of micellar aggregates lead to the formation of lyotropic liquid crystalline phases. Phase transition temperatures (pT) in these systems may be increased or decreased by several degrees upon addition of small amounts of certain aromatic compounds while other aromatic compounds do not show this effect. In some cases it is possible to transform photochemically compounds of the former class to compounds belonging to the latter[1] Thereby in-situ changes of pT become possible simply by exposing the samples to a suitable radiation field. This allows reversible swichting of phases when samples containing photochromic solubilizates are irradiated under conditions near pT, provided the isomeric forms of these solubilizates have different influences on pT. In principle, the observed effects are of interest for photochemical information storage.

We want to report on light induced phase transitions between liquid crystalline phases and (optically) isotropic phases, obtained using cationic (cetyltrimethylammonium bromide) and non-ionic (Triton X-100) surfactants and stilbene as well as azobenzene derivatives as photochromic solubilizates. The results indicate an influence of the geometry of the respective photoisomers, i.e. longish isomers of solubilizates stabilize the isotropic phase rather than corresponding globular isomers.

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THE NATURE OF THE EXCITED STATES OF CdS SEMICONDUCTOR PHOTOCATALYSTS

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Interest in semiconductor systems, such as CdS, ZnS and TiO_2 has increased rapidly in recent years due mainly to their potential use as solar harvesting systems. The compounds have also found an important utility in the photosynthesis of organic molecules. Many of the studies employ colloidal dispersions of the semiconductor materials and in order to maximise their photocatalytic activity it is clearly important to characterise the nature of the excited states involved. In this work the luminescences of CdS colloidal dispersions has been investigated using a combination of steady-state and time-resolved absorption and emission spectroscopies. Fluorescence was found to originate with two main chemical surface states whose emission properties are also susceptible to particle size effects.

Colloidal dispersions of nanometre-sized cadmium sulphide particles (R < 1nm) were prepared in AOT/heptane/water reversed micelles (microemulsions). These solutions give a strong emission centred around 470 nm but includes shoulders at 425, 450, 500 and 530 nm. The profile is found to be sensitive to the ratio of cadmium to sulphide used in the preparation, with the sulphide-rich species being responsible for the longer wavelength emission. Interestingly this type of emission is rapidly quenched as a function of time (*ca.* 2 hours) presumably due to chemical changes within the system. Two types of CdS dispersion with 1:1 stoichiometry (cadmium:sulphide) were also prepared to give an initial surface excess in either one of the species. Again it was shown from our measurements that the preparation which has the more sulphide-enriched surface gives the lower energy luminescence. However, all the emission profiles become similar as a function of time presumably because the colloidal surfaces evolve towards formal 1:1 stoichiometry. This information coupled with our further observations on the rapid fluorescence quenching which occurs on the addition of water points to the over-riding importance of surface sites in the emission of CdS.

Fluorescence lifetime measurements of the systems reveals complicated multi-exponential character in all cases. However, by investigating the system using time-resolved emission spectroscopy, we have shown for the first time that only two species give rise to the observed luminescence. One type decays rapidly ($\tau \sim 5$ ns) and emits at short wavelengths (425 nm); the second, longer-lived species ($\tau \sim 50$ ns) emits at lower energy (475 nm). We believe that these two main components are responsible for the emission in all of the CdS species we have produced. The low energy species can be assigned to surface cadmium vacancies (sulphide excess) whilst the high energy species are surface sulphide vacancies (cadmium excess).

On production of larger sized CdS particles (R = 2nm) we find that the emission profile is red-shifted (530 nm) in accord with a concomitant decrease in the uv absorption band gap energy.

Quantum-sized HgS in Contact with Quantum-sized CdS-Colloids

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It has been accomplished to grow differently sized HgS nanocrystallites in a controlled manner on the surface of CdS-nanocrystallites, thus forming a so-called sandwich colloid.

The charge carrier dynamics in colloidal CdS are reasonably well understood (1,2). Now we investigate a more complex system exhibiting both electron and hole transfer from CdS to Q-sized HgS, the recombination of which gives rise to remarkable fluorescence properties. The maximum of the fluorescence band of Q-HgS can be shifted according to its size (quantum-size effect) between 580 nm and 770 nm. Hence, it is possible to prepare solutions showing exquisite green, yellow, orange or red fluorescence (fig. 1).

We confirmed the existence of these sandwich particles by chemical and spectroscopic methods and traced the opto-electronic properties by means of static and time-resolved fluorescence spectroscopy at temperatures between room temperature and liquid helium temperature. A fluorescence mechanism will be proposed.
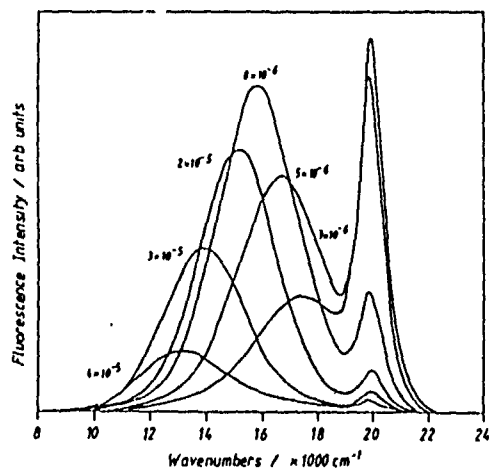

Figure 1: Fluorescence spectra of CdS in contact with HgS of various size.

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PHOTOREDOX PROCESSES ON MIXED TiO_2/Fe_2O_3 COLLOIDS

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Photocatalytic properties of aqueous solutions of mixed
TiO_2/Fe_2O_3 colloids (Fe^{III}-content between 0.02 and 5%) have
been studied by laser flash photolysis (λ_{exc} = 355 nm) and
transient absorption spectroscopy. Reduction of methyl
viologen (MV^{2+}) in alkaline solution (pH 11.6) and oxidation
of SCN^- in acid solution (pH 1.7) have been examined in
detail. Laser-induced formation of transients (MV^+ or $(SCN)_2^-$)
depends on the Fe^{III}-content of the colloid. Application of
a model developed previously[1] shows that quantum yields of
MV^{2+} reduction, as well as concentrations of adsorbed MV^{2+},
decrease with increasing Fe^{III}-content; the opposite is true
for SCN^- oxidation. In contrast to what is obtained in pure
TiO_2 colloids, the dependence of the concentration of SCN^-
adsorbed on the particle surface on bulk SCN^- concentration
does not conform to a single adsorption isotherm. Formation
of $(SCN)_2^-$ is observed even at very low bulk SCN^- concentration
($< 10^{-5}$ M), indicating the contribution of specific complexa-
tion of SCN^- with surface Fe^{3+} ions.

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THE PHOTODEGRADATION OF LIGNIN MODELS IN SOLID MEDIA

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The photodegradation of ether models of lignins included in PMMA polymer matrices or absorbed on low density polyethylene films has been studied using flash photolysis and steady state irradiations. Reaction products were identified by chromatography, ir and uv-vis spectroscopy. The models included α- and β-O-4 ethers, which may contain OH, OCH_3, and CO groups at various positions on the chain or the rings.

The transient spectra observed by flash photolysis of all ether models in solid media showed the presence of phenoxy radicals, similar to those found in solution[1], indicating primary photochemical steps corresponding to the cleavage of the α or β ether bonds, or when present phenolic O-H bonds. In general, α-O-4 bonds cleave easier than β-O-4 bonds. Also, the presence of carbonyl groups at the α position increases the rate of this reaction, possibily due to energy transfer.

On the other side, no ketyl radicals were detected, indicating that abstraction of hydrogen atoms by excited carbonyl groups is not as efficient as in solution, as expected from the lower mobility of the species in these media. Similarly, in the absence of oxygen, no coupling products leading to coloured species[2] were observed. Under these conditions, no formation of carbonyl groups could be detected.

These results show that great care has to be taken when trying to extended the reaction mechanisms of photodegradation of models in solution to those for the lignins in their natural environment.

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OBSERVATIONS DURING THE EXPOSURE OF A Ce-Pd INTERFACE TO WATER VAPOR AND SOLAR LIKE LIGHT

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Reduced CeO_{2-x} is known to be oxydized at room temperature with water under hydrogen release. If palladium is added to this system the reaction rate is increased by more than two orders of magnitude.[1] A photo reduction of Ce would allow further hydrogen generation by this process. After the observation that water dissociates on a Ce-Pd interface and a large portion of the released hydrogen penetrates into the palladium substrate,[2] further hydrogen can be generated in illuminating such a system consisting in a Ce-Pd interface and water vapor in the gas phase with solar like light. The reaction was studied in ultra high vacuum by means of a hydrogen sensitive metal insulator semiconductor (MIS) device.[3] After the passivation of the metallic interface by water vapor the hydrogen detector indicates at water pressures of 10^{-5} Pa hydrogen generation.
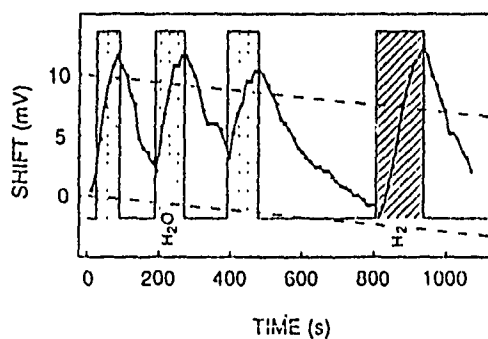
Figure 1   Response of Ce-Pd MIS detector under light exposure to gas burst dosages. A clear effect is observed if such a structure is exposed to 10^{-5} Pa water vapor. The effect is compared with a 10^{-5} Pa hydrogen gas burst. The dashed lines correspond to the shift decrease before the bursts which indicates the hydrogen depletion of the detector.

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DESORPTION D'IONS POSITIFS INDUITE PAR IMPACT DE PHOTONS
SUR LES MOLECULES CONDENSEES (CH_4-H_2O)

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L'excitation entre 20 et 100 eV de molécules condensées en multicouches peut produire différents processus électroniques comme la simple ou la multiple ionisation, l'excitation d'états satellites ou de Rydberg. Ces processus primaires et les réactions secondaires induites à la surface de tels systèmes par impact de photons peuvent être sondés par l'analyse en masse des ions positifs désorbés.

Cas de H_2O :

1) Par impact de photons sur la glace en multicouches, seule la désorption de H^+ est observée avec un seuil à 25 eV. Ce seuil correspond probablement à la formation d'états satellites de H_2O^+ et la désorption de H^+ peut certainement s'expliquer par un mécanisme comparable à celui proposé pour expliquer la désorption d'ions dans l'argon condensé[1].

2) Quand une submonocouche de H_2O, déposée sur un film formé de multicouches de krypton est photoexcitée entre 20 et 150 eV la désorption d'ions est dominée par la désorption d'agrégats $(H_2O)_n H^+$ (n = 1 à 10). L'intensité de la désorption de ces agrégats suit exactement la variation de la désorption de Kr^+ dans le krypton pur en fonction de l'énergie d'excitation. Dans ce cas l'énergie d'excitation absorbée par le substrat, en l'occurence le krypton, est transférée aux agrégats d'eau $(H_2O)_n$ en surface où la désorption a lieu.

Cas de CH_4 :

La photoexcitation du méthane condensé entre 15 et 60 eV induit la désorption d'un grand nombre d'ions positifs dont la masse est comprise entre 1 et 40. Il y a deux grandes familles d'ions : l'ion parent CH_4^+ et les ions provenant de sa fragmentation (H^+, CH_2^+, CH_3^+, ...) et ceux provenant de réactions ion-molécule en surface (CH_5^+, $C_2H_3^+$, $C_2H_5^+$...). L'ion parent lui-même est observé avec un rendement très faible, un seuil à 25 eV et une augmentation brutale vers 35 eV. Les ions fragments apparaissent à des énergies comparables à celles de la phase gazeuse[2]. Il faut remarquer que le rendement de tous les ions primaires et secondaires augmentent brutalement aux environs de 35 eV qui est le seuil de double ionisation de CH_4 en phase gazeuse[3].

Conclusion :

Comme nous l'avons démontré pour les rares gaz condensés[1], la désorption des ions simplement chargés est principalement gouvernée par un acte primaire qui implique l'excitation de deux électrons (formation d'états satellites ou double ionisation) suivie par un échange de charge intermoléculaire ou une ionisation. Ensuite, la répulsion coulombienne entre les 2 charges positives produit l'éjection des espèces chargées positivement. Ces résultats mettent en évidence le rôle de mécanismes supplémentaires (fragmentation, réaction ion-molécule, formation d'agrégats en surface) pour la désorption d'ions quand les molécules sont concernées.

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DESORPTION OF POSITIVE IONS INDUCED BY PHOTON IMPACT ON CONDENSED MOLECULES (CH$_4$ - H$_2$O)

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The excitation in 20-100 eV energy range of molecules condensed in multilayers can produce different electronic processes as single ionization, multiple ionization, excitation of satellites states or Rydberg states. Those primary processes and the secondary reactions induced at the surface of such systems by photon impact can be probed by the mass analysis of desorbed positive ions.

H$_2$O case :

1) By photon impact on ice in multilayers, only the desorption of H$^+$ is observed with a threshold energy at 25 eV. This threshold corresponds probably to the formation of satellites states of H$_2$O$^+$ and the desorption of H$^+$ can certainly be explained by similar mechanism as those involved for ion desorption in condensed argon[1].

2) When a sub monolayer of H$_2$O on a multilayer film of Kr is photoexcited between 20 and 150 eV the ion desorption is dominated by the desorption of clusters (H$_2$O)$_n$ H$^+$ (n = 1 to 10). The intensity of the ion desorption follows exactly the variation of the desorption of Kr$^+$ in pure krypton as a function of excitation energy. In this case the excitation energy absorbed by the substrate (Kr) is transfered to the clusters of H$_2$O at the surface where the desorption occurs.

CH$_4$ case :

The photoexcitation of condensed methane between 15 and 60 eV induces the photodesorption of positive ions dispersed on a large mass spectrum (m = 1 to 40). There are two main families of ions, those issued of the fragmentation of the parent ion CH$_4^+$ (H$^+$, CH$_2^+$, CH$_3^+$,....) and those resulting from a ion-molecule reaction (CH$_5^+$, C$_2$H$_3^+$, C$_2$H$_5^+$...). The parent ion itself is observed with a much lower yield. The threshold for the desorption of CH$_4^+$ is measured at around 25 eV with a sudden increase of the yield at around 35 eV. The fragment ions appear at energies which are similar to those observed in gas phase[2]. Nevertheless it should be noticed that the yield of all ions (primary and secondary), increased suddenly at 35 eV, double ionization threshold of CH$_4$ in gas phase[3].

Conclusion :

As we have demonstrated for the rare gases[1], the desorption of singly charged ions is mainly gouverned by a primary act which involved the excitation of two electrons (formation of satellites states or double ionization) followed by intermolecular charge exchange or ionization leading to a Coulomb repulsion between positive charges. In addition the present results emphasize the role of additional mechanismes (fragmentation, ion-molecule reaction and cluster formation at surface...) of ion desorption when molecules are concerned.

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     Phys. Rev. Lett. 64, 1289 (1990).
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SYNTHESIS OF $(Cr_{1-x}Ti_x)_2O_3$ SOLID SOLUTION
BY LASER-IGNITED VAPOR-PHASE REACTION.

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Recently, much attention has been paid to the fine ceramic powders prepared by chemical vapor deposition: the fine powders produced by a vapor-phase reaction have a low impurity level and a narrow size distribution. In the present work we have obtained a monodispersed fine powder of $(Cr_{1-x}Ti_x)_2O_3$ in a single phase by igniting a chain reaction in a gas mixture of CrO_2Cl_2-$TiCl_4$-H_2 with a TEA CO_2 laser.

The explosive reaction induced by irradiation of the gas mixture with a focused single laser pulse was accompanied by a strong orange emission. The reaction products were HCl and dark-green particles. The distribution of particle sizes was relatively uniform with a mean particle size of $0.25\mu m$. For all the experiments the P(26) line of the $10.6\mu m$ branch at $939cm^{-1}$ was used, corresponding to the Cr-O stretching mode of CrO_2Cl_2. The X-ray diffraction patterns of the powders produced are almost identical to that published for Cr_2O_3,[1] although the peaks are shifted to lower an... s. Lattice constants were calculated by the method of WPPD.[2] The lengths of the a-and c-axes of the hexagonal unit cell of the oxide produced increase linearly with increasing $TiCl_4$/CrO_2Cl_2 ratio in the gas mixture. The differences in lattice constants are due to the different ionic radius between Cr^{3+}(0.63Å)and Ti^{3+}(0.76Å). From the experimental results, we consider that because of the small difference in the ionic radius of titanium, it can occupy the regular cation position giving a substitutional solid solution. Compositional changes result in the color of the particles varying from light-green to dark-green.

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PHOTOPHYSICS AND PHOTOCHEMISTRY OF COMPOUNDS WITH MULTIPLE PATHWAYS, W(CO)₄phen

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The compound W(CO)₄phen (phen = 1, 10 phenanthroline) is photochemically interesting as it has been established that ligand substitution processes occur from a metal-to-ligand charge transfer (MLCT) excited state[1]. Pressure dependence studies[1] have revealed that ligand substitution follows an associative mechanism upon irradiation into the MLCT band. However, upon excitation into the ligand field (LF) band, ligand substitution follows a dissociative pathway[2]. Furthermore, non-equilibrium multiple luminescence has been observed for W(CO)₄phen[3], thereby indicating rather unusual photophysics. Thus, we have initiated a time-resolved absorption study using picosecond laser flash photolysis. The system uses a mode-locked Nd/YAG laser with a 2.5 mJ, 30 ps pulse with wavelength of 355 nm or 532 nm for excitation and a 425-675 nm probe pulse for detection. The excited state absorbance was observed within 20 ps of excitation into the LF or the MLCT band, but there is a time dependence in the excited state absorbance following MLCT excitation which is missing following excitation into the LF band. Solvatochromic shifts evaluated for the excited state absorbance are similar to those observed in the ground state absorbance. Alternative models for photophysical events will be considered.

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THE PHOTOCHEMISTRY OF AMINO SUBSTITUTED 1,4-NAPHTHOQUINONES

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It has been shown[1] that photolysis of 2-amino-1,4-naphthoquinone in acetic anhydride leads to the formation of the trimeric 6-[3'-amino-2'-(1,4-naphthoquinonyl)]-dibenso[b,h]carbazole-5,13:7,12-diquinone as well as 3,3'-diamino-2,2'-bi-1,4-naphthoquinonyl and dibenso[b,h]carbazole-5,13:7,12-diquinone.

We now wish to report that substitution in the 3-position of 2-amino-1,4-naphthoquinone, with groups such as methyl, phenyl, halogen or amino, tends to cause photochemical autoxidation leading mainly to the formation of phthalic acid. The reaction probably proceeds via epoxidation followed by hydrolysis and subsequent ring cleavage. A reaction mechanism which explains this phenomenon will be discussed.

The photolysis of 3,3'-diamino-2,2'-bi-1,4-naphthoquinonyl surprisingly took quite a different course to produce a product with a molecular mass of 654 ($C_{40}H_{18}O_8N_2$) and which contains only two secondary amino groups. The photochemical condensation of the two biquinonyl molecules is unique in the sense that it incorporates the loss of two primary amino groups. The structure of this unusual photoproduct as well as a possible explanation for its formation will be discussed.

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THE INTRAMOLECULAR PHOTOCYCLIZATION OF N-[(2-HALOARYL-
ALKYL]PYRIDINIUM AND N-ARYLALKYL-2-HALOPYRIDINIUM SALTS.

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Various N-arylethyl-2-halopyridinium, N-arylmethyl-2-halopyridinium, N-[(2-halo-aryl)ethyl]pyridinium and N-[(2-haloaryl)methyl]pyridinium salts were synthesized and their photochemical and photophysical properties studied. Upon irradiation the aqueous solutions of N-arylethyl-2-chloropyridinium salt and N-arylmethyl-2-chloro pyridinium salt are cyclized to give isoquinolium salt and isoindolium salt, respectively. In contrast to the pyridinium salts, the aqueous solution of N-(2-halobenzyl)isoquinolium salt appear not to undergo photocyclization. In the photocyclization of N-(2-chlorobenzyl)-2-chloropyridinium salt, pyrido[2,1-a]-4-chloroisoindolium salt is formed by the cleavage of chlorine atom of pyridinium ring. This indicates that the excited moiety is not the phenyl ring, but the pyridinium ring. The triplet state of the pyridinium salts are involved in the photocyclization, since oxygen retards most of reaction. Some assistance of a π-complex between the excited chlorine moiety of the salts and the phenyl plane of the same molecule is required to explain the reactivity of the salts. The reactive pyridinium salts have a low fluorescence quantum yield(Φ_f < 0.01) and a higher triplet energy(E_t > 63kcal/mole) than the unreactive quinolinium salt. The unreactivity of isoquinolinium salt can be understood in relation to its high fluorescence quantum yield and its low triplet energy(E_t 61kcal/mole).

PHOTOCHEMICAL REACTIVITY OF 2,4,6-TRINITROPHENYL N-SUBSTITUTED
AMINO ACIDS AND PEPTIDES.

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The photochemistry of N-2,4-dinitrophenyl substituted amino
acids have been subject to several investigations[1-4], but only
a single short-communication has appeared on the light-induced
reactions af N-2,4,6-trinitrophenyl(TNP) amino acids and pep-
tides.[5] According to this, 2,4,6-trinitroanilin (picramid) is
the main product when TNP-amino acids or TNP-dipeptides are
irradiated in dilute acid.

We have reinvestigated the photodegradation of a series of
TNP-amino acids (glycin, alanin, valin, leucin, isoleucin, phe-
nylalanin and 2-amino-octanoic acid) in weakly basic solution.
The products are identified as 2-nitroso-4,6-dinitroanilin (2),
carbondioxide and the aldehyde (4) with one carbon less than the
amino acid (see scheme). TNP-tryptophan is not photoactive. By
irradiation of TNP-dipeptides, the unsubstituted aminoacid is
set free.
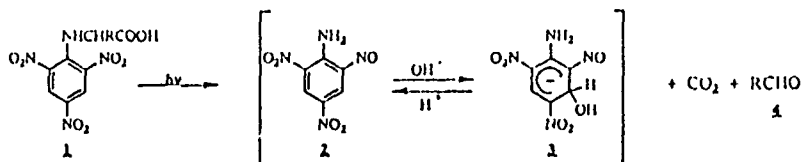
Irradiation of N-2,4-dinitrophenyl substituted aminoacids
does also lead to reduction of the ortho-nitrogroup,[1-4] but
light-sensitivity is higher in case of TNP-substitution. These
features make the TNP-group a potential light-removable protec-
tion group for solid phase peptide syntheses.

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Single-Photon Timing Data Analysis of the Probe

Migration Kinetics in Micellar Systems

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Global analysis with the reference convolution method[1] is applied
to study the effect of the probe migration on the fluorescence quenching in
micellar system. Analysis of synthetic single photon timing data based on a
multiexponential decay function to the probe migration kinetics[2] is used
to search the recovery of the model parameters and to test its model
testing capability. The results of such analysis clearly indicate that the
model parameter recovery can only be obtained under simultaneous analysis
of various decay curves. The simultaneous analysis of four or more decays
at diverse quencher concentrations including the monoexponential decay of
the probe in the absence of quencher is suggested as a standard procedure
to search this more complex kinetics involving the quenching of a probe in
micelles.

The applicability of this simultaneous analysis is extended to real
experimental data obtained for the quenching of the probe sodium 1-pyrene
sulfonate by the quencher N-tetradecylpyridinium chloride in aqueous
hexadecyltrimethylammonium chloride (CTAC) micelles. Values of the rate
constant of quenching and probe migration as well as the mean aggregation
number of CTAC are determined as a function of the surfactant
concentration.

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PHOTOOXYGENATION CATALYTIQUE DU 1,8-CINEOLE PAR L'OXYGENE MOLECULAIRE CATALYSEE PAR (Bu4N)4 W10 O32.

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L'irradiation (λ >280nm) de solutions dans l'acétonitrile de 1,8 cinéole 1 saturées d'oxygène moléculaire et contenant des quantités catalytiques de $(Bu_4N)_4$ $W_{10}O_{32}$ conduisent à l'oxygénation de ce produit naturel, la CGL indique la formation de quatre produits principaux. Le rendement total de ces produits monooxygénés de 1 (voir plus loin) et la proportion n'ayant pas réagi sont donnés dans le tableau 1.

Table 1

Produits Total	% et Recovered	Total Poid et Converting second product %
1	68	7
2	70	11
3	48	17

Comme on le voit, après 2 heures de photolyse une quantité relativement grande des produits monooxygénés de même qu'une bonne correspondance du bilan de masse (94%) sont obtenus Une photolyse prolongée conduit à une quantité de produits monooxygénés et à un bilan de masse plus mauvais, certainement dû à la formation du produit di-et polyoxydé (le même effet a été observé dans la photooxygénatio 1 de l'adamantane dans ces systèmes.

Nous nous attendions à ce que la composition du mélange réactionnel peut-être considérablement simplifié si on oxyde tous les alcools secondaires en cétones correspondantes.

En fait, nous avons trouvé que le traitement du mélange réactionnel avec un excès de chlorochromate de pyridinium dans le CH_2Cl_2 à température ambiante, conduit à la disparition de deux des quatres produits oxygénés, tandis que la quantité des deux produits restant s'accroit. Après ce traitement l'analyse par C G L -MS, montre que ces deux produits sont des dérivés monocétoniques de 1 (m/e = 168). La proportion relative de ces produits était de 2,5/1 L'expérience de contrôle a montré que ces produits ne sont pas formés à partir de 1 après traitement avec le chlorochromate de pyridinium mais seulement par transformation d'alcool secondaires formés dans la photooxydation des cétones correspondantes Nous avons pu isoler une petite quantité de produits purs et nous avons trouvé que le composé majoritaire est le 1,3,3-triméthyl-2-oxabicyclo-[2.2.2] octan-5-one 2 tandis que le composé mineur était le 1,3,3 triméthyl-2-oxabicyclo[2 2.2] octane-6 one 3.

PHOTOOXYGENATION OF 1,8-CINEOLE BY MOLECULAR OXYGEN CATALYSED BY (Bu4N)4 W10O32.

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The irradiation (λ>280nm) of oxygen-saturated solutions of 1,8 cineole 1 in acetonitrile containing catalytic amount of (Bu4N)4W10O32 leads to oxygenation of this natural product; the GLC showed formation of four principal products. The total yield opf these products, assumed to be monooxygenated derivatives of 1 (see later) as well as the yield of recovered are given in the Table 1.
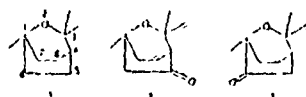
Photolysis Time (h)	% of Recovered 1	Total yield of monooxygenation products (%)
1	53	7
2	0	24
4	4	15

As is seen after 2 hrs of photolysis a relatively high yield of monooxygenation products as well as a good mass balance (94%) was obtained. More prolonged photolysis makes mass balance and total yield of mono oxygenation products worse, presumably as a result of the formation of di- and more oxygenated products (the same effect was observed in photooxygenation of adamantane by this system.

We expected that composition of the reaction mixture may be considerably simplified if we oxidize all secondary alcohols formed to the corresponding ketones. In fact we have found that treatment of the reaction mixture with an excess of pyridinium chlorochromate in CH2Cl2 at r. t; results in disappearance of two from four oxygenation products, whereas the amount of two remaining products increases. After this treatment, GLC-MS analysis showed that these two products are monoketo derivatives of 1 (m/e= 168). The ratio of these products was 2.5:1. Control experiment has shown that these products are not formed from 1 upon the treatment with pyridinium chlorochromate and only transformation of secondary alcohols formed in photooxygenation to corresponding ketones takes place. We have been successful in isolation of small samples of pure compounds. We fave found that the major product was 1,3,3-trimethyl-2-oxabicyclo-[2.2.2]octan-5-One 2 whereas the minor one was the 1,3,3-trimethyl-2-oxabicyclo[2.2.2]octan-6one 3

# ION FORMING PROCESSES UPON 248 nm LASER EXCITATION OF BENZOPHENONE IN AQUEOUS SOLUTION

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Benzophenone (B) under UV irradiation is known to undergo efficient isc and the lowest n,π^* triplet state is responsible for most of its photochemistry[1]. We have studied B in aqueous solution by time-resolved absorption and conductivity techniques. T–T annihilation, being almost unavoidable upon pulsed 248 nm laser excitation (especially at high intensity), is now attributed partly to an electron transfer reaction leading to the cation and anion radicals.

$$^3B^\bullet \quad + \quad ^3B^\bullet \quad \rightarrow \quad B^{+\bullet} \quad + \quad B^{-\bullet} \tag{1}$$
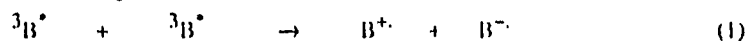
Disproportionation (1) plus reactions (2) and (3)

$$B^{+\bullet} \quad + \quad H_2O \quad \rightarrow \quad B\text{-}OH \quad + \quad H^+ \tag{2}$$

$$H^+ \quad + \quad OH^- \quad \rightarrow \quad H_2O \tag{3}$$
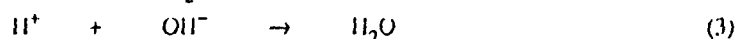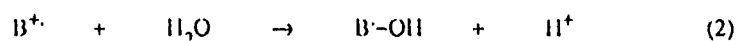
may account for the observed negative transient conductivity signal in the 1–100 μs range at pH >9. It is likely that reaction (2) of the radical cation with water, forming the OH-adduct radical and H^+, is faster than the 20 ns pulse width.

A second ion forming process (4), leading to $B^{+\bullet}$ and hydrated electrons, is photoionization as a consecutive two-photon process.

$$B \quad \xrightarrow{\;2\;h\nu\;} \quad B^{+\bullet} \quad + \quad e^-_{aq} \tag{4}$$
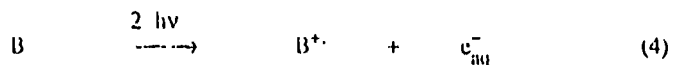
Furthermore, secondary reactions involving e^-_{aq} and the protolytic ketyl-radical/anion-radical equilibrium (5),

$$B^{-\bullet} \quad + \quad H_2O \quad \rightleftharpoons \quad \cdot BH \quad + \quad OH^- \tag{5}$$

$pK_a = 9.2$, were observed and are discussed.

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PHOTOCHEMISTRY OF CONJUGATED POLYACETYLENES

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The photoreaction of 1,4-diphenyl-1,3-butadiyne(DPB) with an electron deficient olefin, dimethyl fumarate(DMFu), yields 1:1 and 1:2 photoadducts. The 1:1 photoadduct was produced by [2+2] photocycloaddition reaction of DPB with DMFu and the 1:2 photoadducts were produced by the addition reaction of photo-rearranged intermediate of 1:1 adduct and DMFu. One of the 1:2 photoadducts possessed a cyclopropane and an oxirane moieties and the other two cyclopropyl groups.
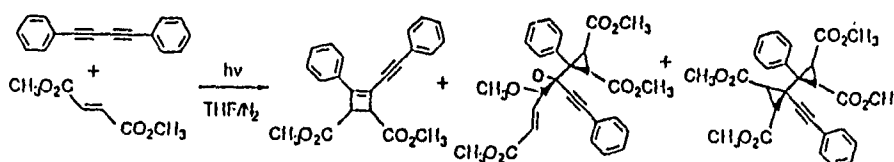
Irradiation of DPB(4 mmol) with two unsymmetrical olefins, acrylonitrile, (AN) and ethyl vinyl ether, (EVE), at 300 nm yields regiospecific 1:1 photoadducts(1 and 2) and 1:2 photoadducts(3-6).
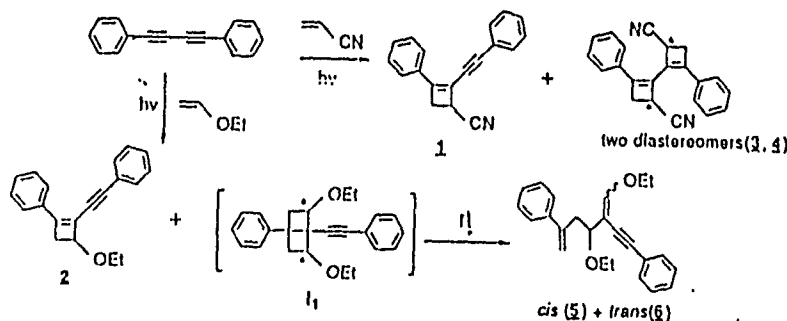
Characterization of the photoproducts and a plausible reaction mechanism will be discussed.

PHOTOPHYSICAL PROPERTIES OF ACRIDINE ORANGE IN REVERSED
MICELLES OF DODECYL AMMONIUM PROPIONATE

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Acridine Orange aggregates in water and fluorescence emission are observed from both monomer and dimer[1]. Also, the formation of dye aggregates at premicellar surfactant concentration has been detected[2]. However, in Dodecyl Ammonium Propionate reversed micelles, only monomers are observed in concentrations ranging from 10^{-6}-5.10^{-4}M for acridine orange. The absorption and emission properties are strongly dependent on the water content, and surfactant concentration. Indeed two monomeric species emitting at 480 nm and 530 nm are detected, their ratio varying in the range of W_o=0-7. A well defined isosbestic point at 448 nm is observed in the absorption spectra, in the same range.

Fluorescence quantum yield (Table 1) and lifetimes, as well as time-resolved-spectra were determined for this system, in order to evaluate the equilibrium of species present.

	$\phi_f^{430\,b)}$	$\phi_f^{448\,b)}$	$\phi_f^{475\,b)}$
$W_o^{a)}$=0	0.12	0.14	0.20
$W_o^{a)}$=7	0.16	0.22	0.31
H_2O	-	-	0.16

Table 1: Fluorescence quantum yields at different excitation wavelength and water content. a) W_o=[H_2O]/[surfactant] ; b) Excitation wavelength

The possibility of FORSTER energy transfer occuring between the two forms will be discussed in order to explain the data observed.

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PHOTOINDUCED ELECTRON AND ENERGY TRANSFER REACTIONS IN
OIL-IN-GELATIN EMULSION FILMS

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Photochemistry in heterogeneous systems has been an active area of research for a number of years. However the oil-in-gelatin emulsion films which are used extensively in photographic materials have received relatively little attention.

We wish to report results from investigations of such systems involving a) steady-state and laser flash photolysis room temperature emission studies of oil soluble, and water soluble lumophores, contained in emulsion films a few tens of micron thick composed of a gelatin matrix with a 0.5-9% (w/w) n-dibutylphthalate oil phase; and b) studies of the generation, mobility, and reactions of singlet oxygen in swollen gelatin emulsions composed of 5% (w/w) gelatin in water with a 0.5% (w/w) dibutylphthalate oil phase.

Emission Studies in Thin Films   At low oil phase concentrations the luminescence decay of the oil insoluble $Ru(bipy)_3^{2+}$, is non monoexponential. However, the decay kinetics can be fitted to two components, one of which has a lifetimes comparable to that of $Ru(bipy)_3^{2+}$ in degassed water, (610 ns) while the other major component is significantly longer lived with $\tau \approx 1.5$ μs. This lifetime decreases as the oil phase concentration is increased from 0.5 to 9%, perhaps as a result of the overall higher O_2 concentration in oil rich films. The phosphorescence lifetimes of two Pd^{II} porphyrins, one oil soluble, one water soluble, have also been determined. For the water soluble Pd^{II} porphyrin τ_P was comparable to that in degassed water, as expected for a gel phase of very low oxygen permeability. Surprisingly, the oil soluble Pd^{II} porphyrin also showed a long lifetime, inconsistent with its location in the oxygen rich oil phase droplets. This may be due to complexation of a fraction of the porphyrin by the gelatin matrix.

Singlet Oxygen Studies   The degree of phase separation and singlet oxygen mobility in swollen gelatin emulsions has been probed by comparing the rate of loss of an oil soluble $^1O_2$ acceptor (rubrene) in the presence of either an oil or water soluble photosensitiser. Preliminary studies indicate that the rate of rubrene loss is $\approx$ 6 X faster in the presence of the oil soluble sensitiser, but rubrene loss is still significant with a water soluble sensitiser, suggesting partial spatial separation of the reaction components.

ETUDE PHOTOPHYSIQUE DE COMPLEXES DU RUTHENIUM (II) D'UNE QUATERPYRIDINE " TWISTEE "

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Les complexes bipyridiniques de métaux de transition, tels que $[Ru(bpy)_3]^{2+}$ (bpy = 2,2' -bipyridine), sont très étudiés en raison de leur intérêt fondamental et appliqué. Ils sont, en effet, souvent utilisés pour initier des processus de transfert d'électron ou d'énergie photoinduits. Mais à notre connaissance, les complexes quaterpyridiniques de métaux de transition n'ont fait l'objet d'aucune étude photophysique.

Dans ce travail, on décrit les propriétés spectroscopiques et photophysiques de deux nouveaux complexes de Ru(II) d'une quaterpyridine (qpy) "twistée", l'un est mononucléaire $[Ru(bpy)_2 (tmqpy)]^{2+}$ et l'autre dinucléaire $\{[Ru(bpy)_2]_2 (tmqpy)\}^{4+}$ (tmqpy = 5,5', 3", 5'''-tetramethyl-2,2' 6',2" : 6", 2'''-quaterpyridine). Ces propriétés sont comparées à celles du complexe $[Ru(bpy)_2 (dmbpy)]^{2+}$ (dmbpy = 5,5' dimethyl-2,2'-bipyridine) qui peut être considéré comme le "monomère" du complexe dinucléaire. En effet, le ligand qpy substitué a été concu de manière à ce que les deux groupements méthyls en position 5' et 3" imposent une torsion à la molécule autour de la liaison C-C centrale. Les deux sous-unités dmbpy sont alors dans des plans perpendiculaires (conformation dite "twistée"), ce qui favorise la formation de complexes dinucléaires. Les résultats montrent, en particulier, que le déclin de fluorescence du complexe mononucléaire est bi-exponentiel avec une composante rapide et une composante plus lente. Cette dernière a une durée de vie voisine de celle du "monomère" alors que la composante rapide a une durée de vie similaire à celle du complexe dinucléaire. Ce comportement suggère l'existence de deux familles de conformères dans le complexe mononucléaire à l'état excité.

PHOTOPHYSICAL STUDY OF TWISTED QUATERPYRIDINE
COMPLEXES OF RUTHENIUM (II)

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Bipyridine complexes of transition metals, such as $[Ru(bpy)_3]^{2+}$ (bpy = 2,2'-bipyridine), have been extensively studied particularly because of their ability to undergo photoinduced electron or energy transfer processes. But, to our knowledge, no photophysical results have been reported concerning quaterpyridine (qpy) complexes of transition metals.

In the present work, the spectroscopic and photophysical properties of a mononuclear and a dinuclear Ru(II) complex of a twisted quaterpyridine, $[Ru(bpy)_2(tmqpy)]^{2+}$ and $[[Ru(bpy)_2]_2(tmqpy)]^{4+}$ (tmqpy = 5, 5', 3", 5"'-tetramethyl-2,2' : 6', 2" : 6", 2"'-quater-pyridine) respectively, are described and compared with those of $[Ru(bpy)_2(dmbpy)]^{2+}$ (dmbpy = 5,5'-dimethyl-2,2'-bipyridine) which can be considered as the "monomer" of the dinuclear complex. Indeed, the substituted qpy ligand has been devised so that the presence of two methyl groups at 6' and 2" position maintains the two dmbpy subunits of this ligand in a twisted conformation around the central C-C bond, which favors the formation of dinuclear complexes. The results show, in particular, that the fluorescence decay of the mononuclear complex is biexponential with a short-lived and a long-lived component. The long-lived component has a lifetime close to that of the "monomer" whereas the short-lived component is similar to that of the dinuclear complex. This behaviour suggests the exis-tence of two families of conformers in the mononuclear complex excited state.

Electroluminescence des ions de terre rare trivalents (TR^{3+})
à l'interface ZnO semiconducteur / H$_2$O sous forte polarisation anodique

D. Kouyaté, J. C. Ronfard-Haret et J. Kossanyi
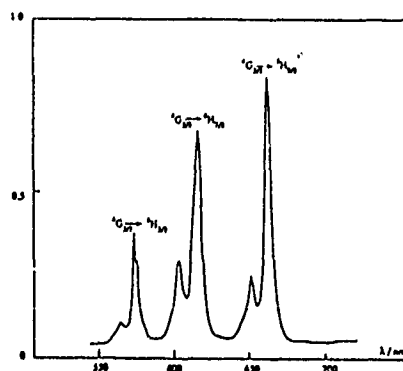
C.N.R.S., 2-8 rue Henry Dunant, 94320 THIAIS (France)

Sous forte polarisation anodique (env. 10 V/ECS), des électrodes d'oxyde de zinc polycristallin, dopé par des ions de terre rare trivalents (TR^{3+}), en contact avec un électrolyte aqueux, sont le siège d'une émission lumineuse intense.

Les spectres de ces émissions lumineuses sont caractéristiques des ions TR^{3+}, et leur intensité suit la relation d'Alfrey-Taylor.

Un modèle d'interface ZnO/électrolyte aqueux sous forte polarisation anodique est proposé:

des électrons provenant de la réduction d'un couple redox à l'interface ZnO/H$_2$O sont injectés par effet tunnel dans le semiconducteur à travers la bande interdite. Ces électrons, accélérés par le champ électrique intense régnant dans le semiconducteur, viennent exciter par impact les ions TR^{3+} qui y sont insérés, en provoquant leur luminescence.

Spectre de l'ion Sm^{3+}
enregistré sur une électrode
ZnO:Sm^{3+} (Sm/Zn ≈0.9 %)
sous polarisation anodique
(9.88 V/ECS)

Electroluminescence of rare earth trivalent ions (RE^{3+})

at the semiconducting-ZnO/H_2O interface under anodic polarization

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Under anodic polarization (c.a. +10 V/SCE), polycrystalline zinc oxide electrodes, doped with trivalent rare earth ions (RE^{3+}), in contact with aqueous electrolyte, show an intense light emission.

The spectra of this light emission is typical of the RE^{3+} ions, and its intensity follow an Alfrey-Taylor-type relationship.

The following pattern for the ZnO/aqueous electrolyte interface under anodic polarization is proposed:

électrons originating from the reduction of ZnO surface defects at the ZnO/H_2O interface are injected through the gap, into the semiconductor by a tunnelling process. These electrons, accelerated by the high electric field in the electrode, can impact-excite the RE^{3+} to their upper states which undergo intrinsic radiative deactivation process.

Emission spectrum of Sm^{3+} ion recorded with an $ZnO:Sm^{3+}$ (Sm/Zn =0.9 %) electrode under anodic polarization at +9.88 V/SCE.
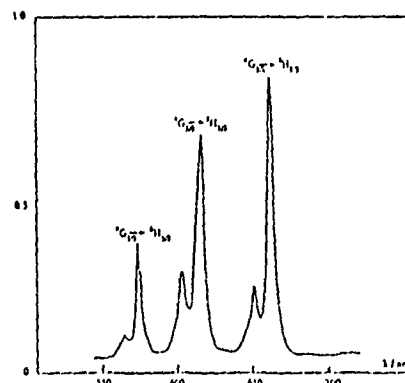
COMPUTER SIMULATIONS OF PHOTOCATALYSIS ON POROUS SUBSTRATES

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Leonardo da Vinci claims in his "Notebooks" note No. 394 that "All the branches of a tree at every stage of its height, when put together, are equal in thickness to the trunk (below them)". This statement is now being widely used as an early example of order in ramified structures that can be characterized in terms of critical exponents such as fractal dimension [1]. This is understood in terms of the simultaneous need to pass nutrients from the roots to the leafs and expose the leaf area to sunlight. The issue can be summarized in terms of power output optimization that requires a compromise between at least two vastly different length scales in the morphology of the tree (catalyst). If one regards the photosynthetic apparatus as the most important natural manifestation of a photoelectrochemical system, da Vinci's statement and its functional interpretation provides the earliest manifestation of the correlation between morphology and activity in photoelectrochemical systems.

The issue of chemical reactions in restricted geometries is not new and there is now a considerable experimental [2] and theoretical [3] activity in this area. The possible correlations between morphologies of catalytic structures and fractals was reviewed by Van Damme [4].

We will demonstrate some of these issues on a computer simulation of photodegradation of organic materials in aqueous environment on porous semiconductors. We will explore the scaling properties of such simulation and compare kinetic models that apply for different operating conditions.

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   b. K. Lindenberg, B.J. West and R. Kopelman; Phys. Rev. Lett., 60, 1777 (1988).
4. H. Van Damme in "Photocatalysis - Fundamentals and Applications, Wiley-Interscience, New York (1989), p. 175.

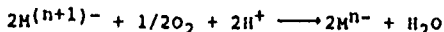# PHOTOCATALYSIS BY POLYOXOMETALLATES

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Polyoxometallates, among other things, are redox catalysts, in a variety of important industrial processes[1] They function as: a. Electron and/or hydrogen carriers, and b. oxygen carriers. The first case addresses, mainly, homogeneous solution reactions, whereas, the second case takes place, mostly, in heterogeneous media.

The oxygen to metal charge transfer (CT) band, responsible for the photochemistry of these compounds, causes a charge separation ($e^- + h^+$), that results in oxidation by h^+ of a great variety of organic compounds, and reduction of polyoxometallate according to the condensed scheme:

$$M^{n-} \rightleftharpoons {}^*M^{n-}(e^- + h^+)$$

$$2{}^*M^{n-}(e^- + h^+) + Me_2CHOH \longrightarrow 2M^{(n+1)-} + Me_2CO + 2H^+$$
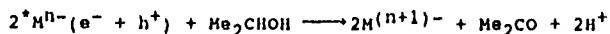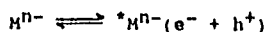
Electrons accumulated on polyoxometallates may be delivered to H^+ (evolution of H_2), or may be transferred to dioxygen, thus restoring the polyoxometallate to its original form[2].

$$2M^{(n+1)-} + 2H^+ \longrightarrow 2M^{n-} + H_2 \text{ or}$$

$$2M^{(n+1)-} + 1/2O_2 + 2H^+ \longrightarrow 2M^{n-} + H_2O$$

Key to the effective photocatalytic oxidation of various organic compounds is the regeneration (reoxidation) of reduced polyoxometallate by dioxygen. The mechanism of reoxidation by dioxygen is discussed for a series of polyoxometallates. The results suggest the formation of a polyoxometallate-dioxygen adduct prior to CT from polyoxometallate to dioxygen.

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DYNAMIC ENERGY AND ELECTRON TRANSFER ON SURFACES

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Dynamic energy and electron transfer on solid surfaces provides an insight to the behaviour of adsorbed molecules, particularly regarding diffusional mobility.
We have been investigating several energy and electron transfer systems adsorbed onto silica in order to acquire information on adsorbate interactions with the surface.

Dynamic energy transfer on silica is observed, for example, from ^{3}eosin to anthracene. In this case it has been established that anthracene is the mobile partner in the quenching process.
Electron transfer studies have been less conclusive, however. Excited state quenching by electron donors or acceptors is observed although radical products have yet to be detected possibly due to rapid back electron transfer. For example, we have yet to observe the products of the electron transfer between ^{3}anthracene and methyl viologen on silica, although the triplet state of anthracene is quenched efficiently. ' Data for other energy/electron transfer systems will also be presented.

TEMPERATURE AND SOLVENT EFFECTS ON POLYSTYRENE CYCLIZATION

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The cyclization of a polystyrene chain ($M_n = 4500$; $M_w/M_n = 1.07$) both ends labelled with a pyrenyl group (structure 1)
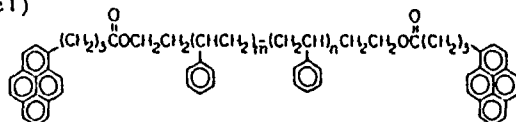
1

was studied in toluene, cyclopentane and cyclohexane at different temperatures. Upon electronic excitation, an intramolecular excimer can be formed at the encounter of both chain ends, following the kinetic scheme
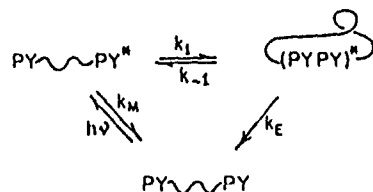
The cyclization rate coefficient (k_1), the rate coefficient of excimer dissociation and ring opening process (k_{-1}) and the reciprocal of the excimer lifetime (k_E) were obtained from the monomer and excimer fluorescence decay curves[1], once known the monomer lifetime ($\tau_M = 1/k_M$) from the decay of a dilute solution of a polystyrene chain one end labelled.

From the Arrhenius plots of k_1 and k_{-1} the activation energies E_1 and E_{-1} were calculated. E_1 is close to E_η (viscous flow activation energy) showing that the cyclization process is diffusion influenced.

The Arrhenius plot of k_{-1} for cyclohexane is not linear. However, two straight lines that intercept each other at 39ºC, close to the θ temperature of polystyrene in cyclohexane (34.5ºC), can be plotted through the experimental points. A binding energy of the excimer ($\Delta E = E_{-1} - E_1 = 9.0 \pm 1.0$ Kcal.mol.$^{-1}$) was obtained irrespective of solvent if temperatures above the θ temperature are considered in the Arrhenius plots of k_{-1}. The binding energy agrees with the published values for the intermolecular pyrene excimer[2], showing that the dissociation process is not strongly influenced by the polymer chain.

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PHOTOCHIMIE DE α-DI- ET TRICETONES.

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Le comportement photochimique de quelques di-et tri-cétones a été analysé par différentes techniques : spectroscopie d'absorption et d'émission, irradiation continue et photolyse laser.

L'irradiation d'une solution déaérée d'acénaphtènequinone (1) dans l'acétonitrile (E_T= 52kcal/mol) conduit à l'observation d'un transitoire présentant un spectre d'absorption avec des maxima à 330, 570 et 630 nm. Ce transitoire, attribué au triplet de 1, présente une durée de vie de 4,8 µs et est inhibé par le cyclohexadiène-1,3 (k_q = 2×10^9 $M^{-1}s^{-1}$) et le β-carotène (k_q= 1×10^{10} $M^{-1}s^{-1}$).

En présence de donneurs d'hydrogène, une diminution de la durée de vie du triplet de 1 est observée, du fait de la réaction rapide d'abstraction d'hydrogène par le carbonyle excité. Des valeurs de $k_{H-abstraction}$, variant entre 6.2×10^5 $M^{-1}s^{-1}$ (propanol-2) et 7.5×10^9 $M^{-1}s^{-1}$ (p-méthoxyphénol) ont été obtenues. L'acéanthrènequinone (2) (E_T= 42 kcal/mol) présente un comportement similaire à celui de 1 ; une valeur de $2.3 \times 10^6 M^{-1}s^{-1}$ a été obtenue pour $k_{H-abstraction}$ dans le cas du cyclohexadiène-1,4. Les dicétones 1 et 2 sont photochimiquement stables sous irradiation prolongée.

Par contre, l'indanetrione-1,2,3 (3) (E_T= 42 kcal/mol ; τ_T= 6.5 µs et λ_{T-T}= 360 et 570 nm dans l'acétonitrile anhydre) donne lieu sous irradiation à une coupure en α suivie par une décarbonylation lente. L'état triplet de 3 présente également une remarquable réactivité vis à vis des donneurs d'hydrogène ; par exemple $k_{H-abstraction}$= $1.4 \times 10^6 M^{-1}s^{-1}$ avec le cyclohexadiène-1,4.

PHOTOCHEMISTRY OF VICINAL DI- AND TRIKETONES.

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The photochemistry of some vicinal di- and triketones was investigated combining the techniques of steady state and laser flash photolysis with emission and absorption spectroscopy.

Irradiation of a degassed acetonitrile solution of acenaphthenequinone (1) (E_T= 52 kcal/mol) leads to the formation of a readily detectable transient with absorption at 330, 570 and 630 nm. This transient decays by a clean first order kinetics with a lifetime of 4.8 μs and is quenched by 1,3-cyclohexadiene (k_q= 2×10^9 $M^{-1}s^{-1}$) and β-carotene (k_q= 1×10^{10} $M^{-1}s^{-1}$).

In the presence of typical hydrogen donors, a dramatic shortening of the triplet lifetime for 1 is observed, consequence of the relatively fast hydrogen abstraction process from the triplet of 1. Values for $k_{H-abstraction}$ ranging from 6.2×10^5 $M^{-1}s^{-1}$ (2-propanol) to 7.5×10^9 $M^{-1}s^{-1}$ (p-methoxyphenol) were obtained. Similar behavior was observed for aceanthrenequinone (2) (E_T= 42 kcal/mol). For this diketone, in benzene, we obtained a $k_{H-abstraction}$ = 2.3×10^6 $M^{-1}s^{-1}$ using 1,4-cyclohexadiene as a hydrogen donor. Both of these diketones are photochemically stable even under irradiation for a long term period.

On the other hand, 1,2,3-indanetrione (3) (E_T = 42 kcal/mol ; τ_T = 6.5 μs and λ_{T-T}= 360 and 570 nm in dry acetonitrile) reacts preferentially via an α-cleavage process followed by a considerably slow loss of carbon monoxide. Similarly to 1 and 2, triplet 3 shows remarquable fast hydrogen abstraction constant in presence of 1,4-cyclohexadiene ($k_{H-abstraction}$= 1.4×10^6 $M^{-1}s^{-1}$).

SOLVATOCHROMISM AND SOLVATOKINETIC BEHAVIOR OF CIS-TRANS
ISOMERIZATION FOR MEROCYANINES IN MICELLAR AGGREGATES

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b)Faculty of Science, Tanta University ,Tanta, Egypt.
c)Fakultät für Chemie, Universität Konstanz, Konstanz , Germany.

Merocyanines of the stilbazolium betaine type are charac-
terized by their extreme negative solvatochromic effect, which permits
their use as sensitive probes of solvent polarity. We recently
reported[1] that the first transition energy ΔE in different solvents of
varying polarity and the free activation enthalpy $\Delta G'$ of thermal cis-
trans isomerization for stilbazolium type merocyanines are linearly
correlated with each other and with Dimroth's solvent polarity para-
meter E_T .

The present study investigates the relationship between the
solvatochromic and solvatokinetic behavior of cis-trans isomerization
of a simple merocyanine dye and its amphiphilic analogue in aqueous
and in reversed micelles of two differently charged detergents (CDBA
and AOT) . The results show that there is a linear correlation bet-
ween solvatochromic and solvatokinetic behavior in micellar systems.
However the free activation enthalpy $\Delta G'$ in microemulsion systems is $3\frac{1}{2}$
- 5 k.cal. lower than the corresponding value obtained in homogeneous
solutions having the same value of spectroscopic polarity . The
results obtained offer further insight into the nature of the aqueous
microphase located in the interior of the inverted micellar systems.

A particularly interesting aspect of this study is the utili-
zation of two different, medium - dependent, functions in one mole-
cule, which serves as a structural probe for organized assemblies.

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ELECTRONIC ABSORPTION, FLUORESCENCE AND PHOSPHORESCENCE SPECTRA OF
SELECTED METHOXYNITRONAPHTHALENES-SOLVENT EFFECTS.

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The photohydrolysis of methoxynitronaphthalenes has been proposed as a
model for the mechanism of aromatic photosubstitutions (1). Because of our
interest in the photophysical properties of these compounds, we investigated
the room-temperature electronic absorption and fluorescence, and low-tempe-
rature phosphorescence spectra of several selected methoxy nitronaphthalenes.
The electronic absorption and fluorescence spectra were determined in va-
rious solvents of different polarities (cyclohexane, dioxane, chloroform,
ethylacetate, acetonitrile, DMSO, DMF, methanol, butanol, 2-propanol). The
variation of the Stokes shift with the solvent dielectric constant-refrac-
tive index term was studied. The solvatochromic method (Bakhshiev and
Chamma-Viallet equation) was used in an attempt of determining the diffe-
rences in the ground and first excited singlet state dipole moments of
these compounds.

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KINETIC STUDY OF THE PHOTOISOMERIZATION OF ACETOXYISOPIPERITENONE.

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The photoisomerization of carvone and the photolysis of carvone hydra-zone derivatives have been studied recently, but several drawbacks prevent their application to the photochemical storage of light energy (1,2). In this work, we have investigated the direct and sensitized photoisomerization reactions of acetoxyisopiperitinone (AIP) at room temperature (293K).

AIP
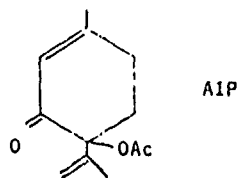
Solvents of different polarities (cyclohexane, dioxane, alcohols, aceto-nitrile) were used. The direct photoisomerization overall first-order rate constants (k_1) and quantum yields (ϕ_p) were found to depend markedly of the polarity of the solvent. k_1 values ranged between 0.13 and 0.30 min^{-1} and ϕ_p values between 0.06 and 0.11. The structure and yield of the photo-products were elucidated by as chromatography-mass spectrometry. The kine-tic of sensitized photoisomerization of AIP was studied, using acetophe-none and benzophenone as photosensitizers. The existence of a triplet-triplet energy transfer mechanism was demonstrated. The usefulness of photoisomerization of AIP as a system for the photochemical storage of light energy was evaluated.

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Coventry , England, July 1990.

SUB-PICO AND NANOSECOND TRANSFER PROCESSES IN MIXED "ELECTROSTATIC" PORPHYRIN-PHTHALOCYANINE DIMERS. FROM THE LIQUID PHASE TO ORGANIZED MEDIA.

Thu-Hoa Tran-Thi[a,d], Jean-François Lipskier[a,d], Serge Palacin[b], Serge Gaspard[c], Daniel Houde[d], Claude Pépin[d], Ernö Keszei[d], Jean-Paul Jay-Gerin[d]

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c : Institut de Chimie des Substances Naturelles, CNRS, 91190 Gif sur Yvette , France.
d : Groupe CRM en Sciences des Radiations et Dépt. de Médecine nucléaire et de radiobiologie, CHUS de Sherbrooke, Sherbrooke, Québec, J1H5N4 Canada.

Abstract.

"Electrostatic" dimers can be easily obtained by pairing cationic (or anionic) porphyrins with anionic (or cationic) phthalocyanines. The face-to-face geometry resulting from the coulombic attraction of the charged substituents and the donor-acceptor character of the complexe, induce a drastic change of the optical absorption spectrum of these complexes in comparison with that of a 1/1 mixture of the corresponding neutral monomers.

$M = Cu^{II}$
$M = Al^{III}Cl$
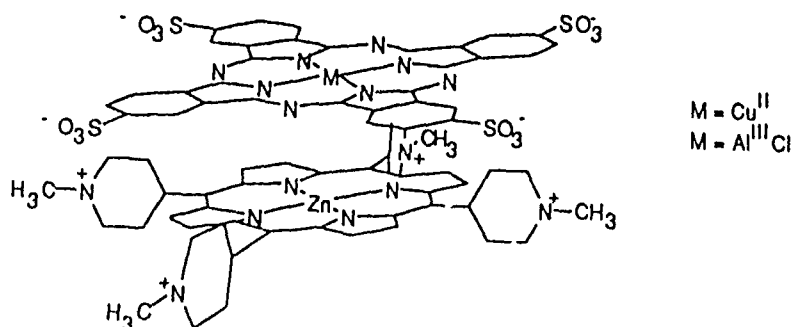
The optical and photophysical properties of two systems (see figure) are investigated as functions of
- the nature of the donor-acceptor complexes
- the nature of the medium (from liquid phase to organized media).

PHOTOINDUCED ELECTRON WIRE PROPERTIES OF FACE TO FACE TRI AND TETRAPORPHYRINS EMBEDDED IN ULTRATHIN MEMBRANES

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The recent developments of supramolecular chemistry have emphasized the interest of molecular assemblies for their future possible applications in molecular electronics and more generally for signal processing.

For this purpose, supramolecular devices have to be designed by assembling molecular components having various functions such as diodes, transistors..... and linked by elements such as electron wires [1]. Towards this direction we report a study of the electronic conduction of molecules showing this ability. Face to face free base and metallated porphyrins were synthesized and incorporated into artificial membranes (planar lipid bilayers) separating two aqueous phases containing an electron acceptor and an electron donor respectively. Upon light absorption a transmembrane electrical flux was recorded between two electrodes dipped in both aqueous redox phases.

In order to propose a mechanistic schema, electrical data (photocurrents and photopotentials) as well as spectroscopic data (absorption and fluorescence spectra) were recorded and analysed. The problem of the orientation and location of the face to face porphyrins inside the membrane is discussed on the basis of data obtained on mixed chromophore-lipid surface monolayers, and of chromophore concentration effects on both the amplitude of the photocurrents and the light energy saturation levels.

The mechanism we suggest, involves an intramolecular electron transfer, following the photoinduced oxidization of the tetrapyrrole ring of the porphyrin facing the oxidizing aqueous phase. Ion coupling due to the electrical polarization of the membranes as the result of the light conversion process is shown to enhance the electric fluxes.

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PROPRIETES PHOTOINDUITES DE FIL MOLECULAIRE CONDUCTEUR,
CONSTITUE DE TRI ET TETRAPORPHYRINES FACE-FACE INCORPOREES A
DES MEMBRANES ARTIFICIELLES ULTRAMINCES

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Philippe Maillard**, Geneviève Miquel* et Michel Momenteau**
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(France)

Les récents développements de la chimie supramoléculaire montrent un intérêt
croissant pour les assemblages moléculaires en direction d'applications futures dans le
domaine du traitement de l'information.

Cette ligne de recherche a conduit à concevoir diverses molécules qui représen-
tent des éléments actifs ou passifs de circuits de l'électronique : diodes, transistors...et
des connecteurs de composants tels des fils moléculaires conducteurs [1]. En ce qui
concerne l'élaboration de ces éléments de connection, nous présentons une étude
photoélectrochimique de molécules qui présentent cette propriété. Des porphyrines
face-face (formes bases libres ou métallées) ont été synthétisées et incorporées à des
membranes lipidiques bimoléculaires, interposées entre deux milieux aqueux, l'un
étant accepteur et l'autre donneur d'électron. Sous excitation lumineuse, un flux élec-
trique transmembranaire a pu être détecté entre deux électrodes plongées dans les
milieux aqueux adjacents à la membrane.

Afin de proposer un mécanisme du transfert d'électron intramoléculaire, des
photopotentiels et photocourants ont été mesurés. Les spectres d'absorption, d'excita-
tion et d'émission de fluorescence ont été enrégistrés en complément des mesures
électriques. Le problème de la position et de l'orientation des chromophores dans la
membrane sera discuté aux vues de résultats acquis avec des monocouches mixtes
lipide-chromophore, et sur les membranes ultraminces (effet de concentration de por-
phyrines sur l'amplitude des photocourants, et sur les valeurs des intensités lumineuses
de saturation).

Le mécanisme proposé est basé sur un déplacement intramoléculaire d'électron
entre noyaux tétrapyrroles, déplacement qui résulte de la photooxydation des porphy-
rines à l'interface aqueuse oxydante. Le phénomène de couplage ions-électrons a été
mis en évidence : il contribue à une exaltation du flux électrique membranaire.

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PHOTOPHYSICS AND PHOTOPOLYMERIZATION OF THIN SOLID FILMS OF 1,4-DISTYRYLBENZENE AND 2,5-DISTYRYLPYRAZINE

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The photopolymerization, molecular arrangement, stability, electronic structure and (photo)conductivity of thin solid films are investigated by UV/VIS absorption, fluorescence , photoaction spectroscopy, and laser light scattering. The organic materials 1,4-distyrylbenzene (DSB) and 2,5-distyrylpyrazine (DSP) are sublimed in high vacuum or deposited from solution on the surface of a silicon wafer or of fused silica.

At submonolayer coverages, DSP is adsorbed as single molecules, with weak interactions to the surface similar to DSP in an unpolar solution. DSB molecules are only detected as aggregates down to the lowest concentration observable. Samples with films a few monolayers thick show red shifted absorption and fluorescence spectra. In these films intermolecular interactions yield in state-splitting and exciton absorption and fluorescence bands of low energy.

Light scattering of the organic film increases with time as well as the exciton absorption and the fluorescence intensity especially of DSB films by about a decade. Microcrystals are formed on the surface by rearrangement of the organic molecules, but the absorption threshold is still shifted hypsochromic compared to polycrystalline samples of the pure material. Scanning Electron Microscopy shows flat rhombic microcrystals with ca. 0.5 µm length.

The photopolymerization in the solid state produces oligomers by irradiation with the energy of the exciton absorption. The electronic spectra of the oligomer are blue shifted compared to the spectra of the educt. Irradiation with light of higher energy, which both the monomer and oligomer absorb, yields the polymer. The polymerization rate is determined and the reaction rate for irradiation with light of shorter wavelenght is found to be faster than for irradiation with longer ones. The stability of the DSP-film is improved and the photoconductivity is strongly reduced by polymerization.

PHOTOELECTRODECAPAGE DU SILICIUM DE TYPE n.

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Science, 76100 Rehovot, Israel.

Une nouvelle technique de passivation des centres de recombinaison à la
surface du silicium utilisé dans des jonctions de type solide/liquide ou Schottky, est
presentée dans cette communication. Il s'agit d'un décapage par voie
photoélectrochimique (photoélectrodécapage ou PED) qui correspond à une
photocorrosion contrôlée du Si en milieu 5% HF sous polarisation anodique. Il est
toujours effectué après un traitement classique de décapage chimique du Si qui
inclut l'utilisation de HF concentré.

Le traitement PED modifie la topographie de la surface du Si qui devient
rugueuse, matte et plus sombre. Les analyses de microscopie à balayage montrent la
présence de nombreux cratères microscopiques. Le PED modifie aussi
considérablement les propriétés photoélectrochimiques en milieu 57% HI. Le
potentiel de circuit ouvert est décalé de -0,25 V et un photocourant important (>35
mA/cm^2 sous éclairement extrapolé de 100 mW/cm^2) est couramment observé. Un
rendement quantique externe de 80% est obtenu dans une large gamme spectrale. Le
photocourant correspond principalement à l'oxydation de I⁻ ainsi que le montre la
formation d'iode à proximité de l'électrode. Alors que le Si decapé chimiquement est
photocorrodé immédiatement en présence de HI, la stabilité du Si après traitement
PED est considerablement augmentee.

La vitesse de dépôt chimique d'une couche d'or sur Si à partir d'une solution
aurique est augmentée après PED. La réponse spectrale des diodes
Si(photoélectrodécapé)/Au est considérablement améliorée.

La surface rugueuse produite par PED conduit à une diminution des pertes
dues à la reflection de la lumiere. Toutefois l'effet principal de ce traitement serait
de réduire la densité des états de surface comme semble le montrer l'augmentation
du photopotentiel et les expériences de photoluminescence à 2,8K.

Le photoélectrodécapage apparaît être un traitement très prometteur pour le Si
multicristallin.

PHOTOELECTROETCHING OF n-SILICON

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A new technique for the passivation of surface recombination centers in Si based PEC's and Schottky junctions is presented in this communication. Photoelectrochemical etching (PECE) is a controlled photocorrosion of Si in diluted HF solutions.

n-type Si was first chemically etched by alternate oxidation of Si and dissolution of Si-oxide films formed. PECE was carried out in 5% HF under reverse bias. After PECE the Si surface became less shiny and darker, the surface roughness increasing with the charge passed. SEM analysis shows the presence of etch pits.

The (photo)current-potential curves of n-Si ($N_D = 10^{15}/cm^3$) in 57% HF exhibit a small anodic d. c current for the chemically etched Si which disappears after photoetching and a photocurrent onset at -0.2 V vs. SCE. The PECE treatment dramatically affects the i-E curve: the onset potential is shifted by -0.25 V and a high photocurrent (> 35 mA/cm^2 when extrapolated to 100 mW/cm^2) is observed. The charge passed across the interface corresponds mainly to the oxidation of I$^-$, as indicated by the darkening of the solution in the vicinity of the electrode. The initial plateau current decreased by only 5% after 45 min. This is in contrast with previous observations of strong photocorrosion of illuminated n-Si/aqueous electrolyte junctions, even in concentrated HI. Chemically etched n-Si exhibits external quantum efficiencies of 60% in 57% HI, while for PECE-Si quantum efficiencies reach 80% over a broad spectral range.

Electroless deposition of Au on n-Si ($N_D = 10^{18}/cm^3$) after chemical etching leads to an enhanced rate of electroless Au plating and improved spectral response of the so formed Schottky junctions.

The rough surface produced by the PECE process minimizes reflection losses. However, the main effect of this treatment is to reduce the density of surface states as indicated by the shift of -0.25 V of the onset potential of the photocurrent, and also by photoluminescence measurements PECE seems to be promising also for the treatment of polycrystalline Si.

Sur la formation d'un exciplexe comme intermédiaire possible
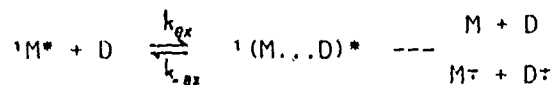dans un transfert électronique photo-induit.

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Nous avons montré que la fluorescence des N,N'diacyl indigo est inhibée par les donneurs et accepteurs d'électrons, dans les solvants polaires, selon un mécanisme de type transfert d'électron. Dans les solvants apolaires (PhMe, PhH) la fluorescence est aussi inhibée mais le mécanisme dépend du potentiel d'oxydation du donneur E_D^{ox}. Si $E_D^{ox} > 0,8V$ la constante d'inhibition k_q^F varie de la façon suivante:
k_q^F dépend de la longueur d'onde et diminue pour les grandes longueurs d'onde; cet effet est d'autant plus marqué que E_D^{ox} est élevé
k_q^F croit lorsque la température décroit.
Ces effets ne sont pas observés dans les solvants polaires (MeCN) ou dans les solvants apolaires si $E_D^{ox} < 0,5V$.

Ces résultats peuvent s'expliquer par la formation réversible et exergonique d'un exciplexe selon le schéma:
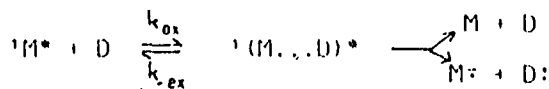
L'émission de l'exciplexe n'est observable directement car elle est faible et recouverte par l'émission du monomère. L'étude de k_q^F en fonction de la température, entre 250 et 330K et en supposant que dans ce domaine $k_{-ex} \gg k_d$, permet d'estimer ΔG_{ox}^0 et de le comparer à ΔG_{el}^0 comme l'indique le tableau ci-dessous pour le N,N'dibenzoylindigo.

D	$E_D^{ox}(V)$	$\Delta G_{el}^0(eV)$	$\Delta G_{ox}^0(eV)$
PhH	0.8	-2.1	-1.6
1,2diméthoxybenzene	1.45	+0.6	-0.2

Plus E_D^{ox} est élevé plus l'exciplexe est favorisé comparativement au transfert d'électron. Dans les solvants apolaires l'hypothèse du transfert d'électron repose essentiellement sur la mise en évidence d'espèces paramagnétiques analogues aux radicaux anions des dérivés d'indigo M·. Nous suggérons que la formation de l'exciplexe permette le transfert d'électron lorsque l'échange direct s'avère thermodynamiquement défavorisé.

On the Exciplexe Route in the Electron Transfer
between N,N' diacylindigo derivatives and Electron Donors

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We have shown that the fluorescence of the N,N'
diacylindigos is quenched by electron donor or acceptor in
polar solvent via an electron transfer process. In apolar
solvent (PhH, PhMe) the fluorescence is also quenched but the
mechanism depends on the oxydation potential of the donor
E_D^{ox}. If $E_D^{ox} > 0.8V$ the fluorescence quenching rate constant
k_q^F changes as follows:

k_q^F depends on the wavelength and decreases at long
wavelength; this effect becomes more important as E_D^{ox} grows.

lowering the temperature increases k_q^F.
These effects are not obsrved in polar solvent (MeCN) or in
apolar solvent with donor having $E_D^{ox} < 0.5V$

These results can be understood on the basis of an
exciplexe, the formation of which is reversible and exergonic.

$$^1M^* + D \underset{k_{-ex}}{\overset{k_{ex}}{\rightleftarrows}} {}^1(M...D)^* \quad --- \quad \begin{array}{c} M + D \\ M^{\overline{\cdot}} + D^{\overline{\cdot}} \end{array}$$

The exciplexe emission occurs on the red side of of the
monomer's one, is very weak and consequently is not directly
detectable. From the study of Logkq versus the temperature and
assuming that in the temperature range 250-330K $k_{-ex} >> k_d$
ΔG^o_{ex} can be estimated and compared to ΔG^o_{et}. The higher E_D^{ox}
the more favored is the exciplexe formation compared to the
electron transfer as shown below for NN'dibenzoylindigo.

D	$E_D^{ox}(V)$	$\Delta G_{et}^o(eV)$	$\Delta G_{ex}^o(eV)$
Ph$_3$N	0.8	-2.1	-1.6
1,2dimethoxybenzene	1.45	+0.6	-0.2

In non polar solvent the electron transfer
hypothesis is substantiated by the detection of a paramagnetic
species which is believed to to be the radical anion of the
indigo derivative $M^{\overline{\cdot}}$. Thus we suggest that the exciplex
formation can provide an alternative mechanism for the
electron transfer when the direct route is thermodynamically
disfavored.

PHOTOCHEMICAL FORMATION OF [Re(bpy)(CO)ₓ{P(OEt)₃}₂]+
AND PHOTOSENSITIZED CO$_2$ REDUCTION

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The photoredox chemistry of [fac-Re(L)(CO)₃X]⁺ ⁰⁺ ⁰ (L = diimine ligand; X = neutral or anionic monodentate ligand) in the presence of an aliphatic tertiary amine is of interest associated with a variety of photosensitized reactions, which are thought to proceed through the loss of X or CO following electron transfer from an amine to the luminescent state of the Re(I) complexes.' However, little has been reported on the electron transfer photosubstitution of a CO ligand.

In the present investigation, we have found that visible-light irradiation of [fac-Re(bpy)(CO)3Br] and P(OEt)3 in the presence of tri-ethylamine results in the double substituion of both Br⁻ and CO ligands to give [Re(bpy)(CO)₂{P(OEt)3}₂]⁺·Br⁻ (1) in ~ 90% yield along with 0.6 – 0.8 equivalent CO in a variety of solvents. On the other hand, no other substituted Re(I) product such as mono-substituted compounds was not detected at all. The quantum yields for the formation of 1 at 405 nm are 0.71 for a degassed acetonitrile solution and 5.3 10⁻² for a degassed tetrahydrofuran solution.

The product 1 reveals a relatively strong emission at 603 nm with a fairly long lifetime (223 ns) in acetonitrile. The luminescence of 1 is not quenched by triethylamine but significantly by 1-benzyl-1,4-dihydro-nicotinamide (BNAH), a typical NADH model, at 6.8 10¹⁰ M ⁻¹ s ⁻¹. The reduction of CO2 to CO is photocatalyzed by [Re(bpy)(CO)₂{P(OEt)3}₂]⁺·X (X = BF4, PF6, ClO4, and BPh4) in the presence of both BNAH and triethylamine, but not at all by 1. Photocatalytic activities of the bis-phosphito complexes will be discussed.

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PULSED LASER PHOTOCHEMISTRY OF PENTANAL AT 355 NM

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ABSTRACT

We perform a comparative study of the pentanal reactivity upon the irradiation with a continuous wave laser and a pulsed one at wavelengths around 350 nm.

The results obtained are qualitatively and quantitatively different. With the CW laser one observes the 8 products classically obtained with a lamp at 313 nm. With the pulsed laser two only of these species are present (α dione and α ketol); the quantum yield for these two products is much higher and is an increasing function of the intensity (in the field explored 0.1 MW. cm^{-2} - 4.2 MW.cm^{-2}). It should be underline that concomitantly the absorbance is much higher than that expected for a $S_0 \rightarrow S_1$ transition and, moreover, is an increasing function of intensity. These results are compatible with a two-photon excitation process.

Laser Absorption Spectroscopy of Excimer Laser Ablation Process

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Important informations of the mechanism of ablation processes and of following reactions in the gaseous phase have been obtained by the analysis of the plasma plume. The methods are emission spectroscopy and mass spectroscopy. But these established methods obtain certain limitations concerning the quantitative time resolved detection of the ablated species like atoms, molecules, ions or molecular fragments or relating to the experimental expense.

In this work it is reported on the absorption spectroscopic analysis of plasma plumes produced by KrF-laser ablation of ceramic material. The measurements have been made with a spectroscopic arrangement by use of a broadband ns-dye laser.

Some time resolved absorption spectra are shown in Fig.1. The extreme line broadenings of the different ion- and atomic states at short time delays are hints of the high temperatures and high pressures during the ablation process. The density of the atoms and ions inside the spectroscopic channel have been determined and discussed in dependence of the time delay and of the distance to the surface of the target.

With this investigations we demonstrated the practical use of the time resolved absorption spectroscopy to get more informations of the ablation process. Of speciall importance is the possibility of the direct time resolved particle determination very near at the interaction area without influence of the environment.

By this the time resolved absorption method is very well qualified to investigate the actual ablation, of the origin of the plasma plume during the laser pulse and shortly after that.
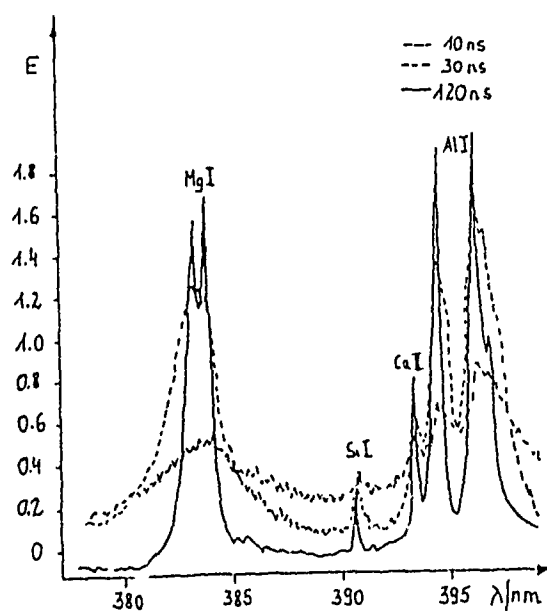
Fig.1: Time resolved absorption spectra of KrF laser ablation of MgO-ceramic

Optical Emission Spectroscopy of Excimer Laser Ablation Process at Ceramic Material

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Processing of ceramic material by excimer laser ablation is a state-of-the-art methode in science and technology. Despite of that, the basic ablation process and its dependence on radiation and surroundings parameters are understood insufficiently.

We carried out ablation experiments with intense radiation of XeCl and KrF excimer lasers. Time resolved fluorescence measurements with spectral resolution ≤ 1 Å in different regions of the ablated plasma cloud allowed us to get informations about produced intermediates, population of excited states in the plume and about the interaction of radiation with the sample material.

The basic emission phenomena after irradiating a piece of MgO-ceramic with a 20 ns XeCl laser pulse of 10 J/cm² are demonstrated in the figure:
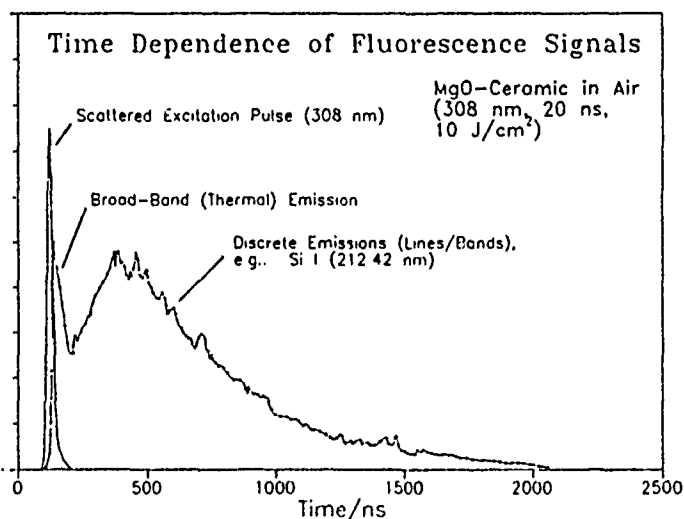
Starting some nanoseconds after the laser pulse, a very structureless spectrum with nearly a thermal energy distribution is emitted from a region some micrometers above the interaction area on the surface. We attribute these emissions to a rather highly excited plasma state. Some 10 ns later, we observed a strong decrease of this thermal radiation in favour of rising discrete emissions that can be explained by plasma recombinatin processes. In air, their peaking can be found after some 100 ns.

Further experiments will allow us to discuss as well the influence of irradiating wavelength and power as different environment conditions on the optical phenomena of the plume.

EVANESCENT WAVE-INDUCED FLUORESCENCE OF POLYMERS

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Evanescent wave induced fluorescence spectroscopy and time-correlated single-photon counting have been combined to provide a method of studying the fluorescence decay profiles of fluorophores at a solid/solution interface. Using these techniques the photophysical properties of tetrasulphonated aluminium phthalocyanine (AlS_4Pc) in methanol and water solution have been studied at fused silica interface. In a poor solvent, such as methanol, AlS_4Pc is shown to form an adsorbed monolayer on the fused silica surface and exhibit a fluorescence decay profile that deviates from the simple, first-order, single-exponential kinetics of the bulk solution. By changing the solvent to water, which is a good solvent for AlS_4Pc, the surface/bulk differences are not observed.

The ability of time-resolved fluorescence spectroscopy to distinguish between concentration and quantum-yield effects on evanescent wave induced fluorescence intensity, is clearly demonstrated.

The technique has been used to investigate interactions between synthetic polymers in solution and surfaces.

When a disordered 'Y' form of a soluble poly(diacetylene) poly-4BCMU encounters a fused silica surface, a time-dependent chromism occurs, where an ordered R form of the polymer rapidly forms and then decays away. After ≈4 hours equilibrium is reached and the fluorescence from the surface is seen to be enhanced by a factor 4C over the identical spectroscopic species in free solution. This enhancement can be attributed to a restricted molecular motion reducing the non-radiative deactivation pathway, and hence increasing both the fluorescence quantum yield and lifetime.

These results indicate that the preparation of thin films, for optical waveguiding, may have anomalous guiding properties as a result of the ordering effect at the surface. This effect has been observed previously in thin films of poly-9BCMU prepared by the dip-coating technique.

Change in Surface Chemical Structure of Polyethersulphone
by Excimer Laser Irradiation

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The change in surface chemical structure of polyethersulphone (PES, $+\bigcirc SO_2 \bigcirc O\}_n$) induced by excimer laser irradiation in vacuum and in air have been studied by X-ray photoelectron spectroscopy(XPS) and Fourier transform infrared spectroscopy(FTIR).

After the PES film(100 µm) washed with supersonic waves in ethanol was irradiated with ArF laser(193 nm, 260 mJ/pulse) at 10^{-7} Pa, the change in surface chemical structure of the PES film was measured by XPS(Shimadzu ESCA 850S). Both oxygen 1s XPS peak(533 eV) and sulphur 2p XPS peak(170 eV) assigned to sulfonyl group were decreased remarkably after irradiation. On the other hand, a new sulphur 2p XPS peak(164 eV) assigned to sulfide was appeared and was increased with irradiation time. Oxygen 1s XPS Peak (535 eV) assigned to ether bond was little affected by ArF-laser irradiation. In addition, it was found from mass analysis of gas evolved from PES by ArF-laser irradiation that oxygen was generated mainly with small amounts of sulphur oxide and sulphur dioxide gases. These results indicate that sulfonyl structure of PES was decomposed selectively with ArF-laser irradiation and oxygen was released from sulfonyl group[1]. Similar change in XPS spectra was observed by KrF-laser irradiation(248 nm, 450 mJ/pulse) of PES. The irradiation effect induced by ArF laser was larger than that by KrF laser. These results were compaired with that irradiated in air. When PES film irradiated with ArF laser in vacuum was exposed to ammonia gas, it was found that nitrogen atom was introduced onto surface of PES.

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SENSITIZATION OF PHOTOPOLYMERIZATION PROCESS BY EXCITATION ENERGY TRANSFER

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During transformation of monomers into polymers (in mass polymerization) the efficiency of photoluminescence, radio-luminescence and excitation energy transfer change. This was explained differently by various authors [1-3].

In this paper, we investigated the influence of several monomers (styrene, α-methyl styrene, methyl methacrylate and buthyl methacrylate) on the quantum yield of luminescence of some aromatic hydrocarbons (benzene, toluene, p-xylene, ani-sole). The obtained results indicate that the polymerizable compounds act as quenchers. It means that the excitation energy of solvents is transferred to monomers and thus intensifies the efficiency of photopolymerization process in solutions. Moreover, our investigations show that the sensitizing of photopolymerization by excitation energy transfer from solvents is more distinct for weakly absorbing monomers.

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CONDUCTIVE ORGANIC THIN FILMS AND MEMBRANES
THEIR SCIENTIFIC FOUNDATIONS AND INDUSTRIAL APPLICATIONS (part 34)

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The significance of organic conjugated and nonconjugated electroactive polymers in science and industry, such as solar radiant energy conversion and storage systems, various type of batteries primarily lithium cells, sensors, microelectronics, corrosion controling processes and the like are well established concepts. All the vast application choices require a deeep understanding of their physicochemical properties, primarily investigations steming from the well known theoretical methods such as extended Hückel, valence effective Hamiltonian, ab initio calculations etc with respect to design, preparation & processesing of the products which has become an essential issue. Eventhough broad interest is focused on the concept of electrical conductivity and the associated problems in conducting polymers, however, the fundamental mechanism by which electricity transports in such systems is still far from clear. This uncertainty even spans the application of models which are applicable to inorganic semiconductors or their corresponding conductors. By taking into account the concept of solitons and polarons as the major carriers, the one dimensionality behavior of conductive conjugated polymers, as compared with three dimensionally bonded usual semiconductors, alters strongly the behaviors of charges added to the macromolecule backbone, i.e. local reorganization in the electron bonding nearby the added charges on the polymer chain. Conjugated and non-conjugated conductive polymers can usually be excited by chemical- & photochemical doping as well as by charge injection into the space charge or surface regions. The spectral sensitization of the macromolecules can be realized employing specific dyes. Based on these aspects, several photo- & electrically conducting polymers have been prepared by chemical, electrochemical and plasma assisted techniques, characterized well, and their applications primarily in solar cells and lithium batteries tested. The laboratory scale miniature PEC & PVC were fabricated and the operational parameters under optimum conditions are monitored. The results are promissing and computer simulations are carried out. In certain cases, polymeric thin films were utilized in the form of chemically modified electrodes. As the substrates, ITO, TiO_2, SiO_2, SnO_2, PbO_2, MnO_2,..... and as the sensitizers, MB, Th, RhB & ... were tested.All these steps were taken inorder to catalyze the fuel production and to evaluate the whole cell parameters. Recent advances in outdoor application of polymers in solar energy conversion systems, commercialization of such devices, requirements for finding proper redox couples.... are the main motivations for investigating various features of the polymer bulk, the mechanism of electrical conductivity (on the bases of Marcus-Dogodnaze-Mulliken-Gerischer theories) and charge transfer proceses as well as the electrode & electrolyte properties. In this paper, my new findings with respect to the afore-mention d concepts-criteria- & problems will be reported.

POSTWORDS: The author as a victim is fully responsible for the entire financio-scientific aspects of the work in this series since 1979.

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PHOTOSENSITIVE CHEMICALLY MODIFIED ELECTRODES ON THE BASIS OF FLUOROCARBON POLYMERIC MEMBRANE MF-4SK

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Photogalvanic cells are the devices for conversion of solar energy to electric or chemical. Presented report is dealing with usage chemically modified electrodes (CME)in photogalvanic devices. This leads to decrease of reagent's outlay and to lowering of mass and sizes of cells. Photogalvanic systems on the basis of known sensitizers as thionine and $[Ru(bipy)_3]^{2+}$ and quenchers- Fe(II) and $[PtCl_6]^{2-}$ ions relatively, impregnated to solid polymeric electrolyte MF-4SK[*] are discussed.

- Electrochemical behavior of thionine in MF-4SK membrane was studied, and it was shown that redox pair thionine/leucothionine works reversibly in it. Charge diffusion coefficient for thionine in membrane was determined and its value points at diffusion mechanism of charge transport in membrane.

- Electropolymerization of thionine in MF-4SK matrix was studied, and main kinetic laws of this process and electrochemical characteristics of polythionine in membrane were determined.

- Photosensitive CME on the basis of polythionine and Fe(II) ions as quencher in MF-4SK is discussed. The influence of photoexcitation on the potential of such electrode was studied.

- Photosensitive CME on the basis of $[Ru(bipy)_3]^{2+}$, impregnated in solid polymeric electrolyte MF-4SK is reported.

- Quasi-solid phase photogalvanic cells for light energy conversion on the basis of discussed CMEs modified electrodes were suggested and studied.

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[*]MF-4SK - analogues to Nafion (trade mark of Du Pont)

SPECTROSCOPY AND PHOTOCHEMISTRY OF NITROGEN DIOXIDE
AN AB-INITIO MRD-CI STUDY

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Ab-initio MRD-CI electronic structure calculations have been carried out on NO_2. An extended basis set of DZ + POL quality augmented with s- and p-type Rydberg functions has been employed, together with an extensive treatment of electron correlation. Cuts of the potential energy surfaces along the O–N–O bending and ON–O stretching coordinates are reported for the lowest ten doublet ($5^2A',5^2A''$) and six quartet ($3^4A',3^4A''$) states. Dipole moment functions and transition moment properties were computed. The present ab-initio study provides a considerable amount of new information on the excited states which is employed to discuss key aspects of the spectroscopy and photochemistry of NO_2. The following topics, among others, are addressed: the visible and UV absorption spectrum and photodissociation, the "anomalous" radiative lifetime and the *air-afterglow* chemiluminescence. The computed vertical ionization potentials are compared with the available experimental data.

PHOTOPHYSICS AND PHOTOCHEMISTRY OF HYDROXY- AND METHOXYBENZENES COMPLEXED TO CYCLODEXTRINS

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Photophysical and photochemical properties of phenols are strongly dependent on solvent environment[1,2]. We have now studied by fluorescence and transient absorption spectroscopy, the influence of the inclusion of hydroxy- and methoxybenzenes into the hydrophobic cavity of cyclodextrins (CDx's) in aqueous solution. In agreement with earlier work[3] the quantum yield of fluorescence ($\emptyset_F$) was found to increase upon inclusion. The increase is strongest for those compounds which have the shortest fluorescence lifetime (τ_F) in aqueous solution. In the case of 2,4,6-trimethyl phenol (TMP), $\tau_F \approx 0.7$ ns in aqueous solution. Upon addition of ß-CDx, a component with $\tau_F \approx 3.6$ ns appears which is assigned to the TMP-CDx complex; this is to be compared to $\tau_F \approx 5.6$ ns in ethanol. Addition of 0.01 M ß-CDx causes increase of $\emptyset_F$ by a factor of 2.5 and increase of the intersystem crossing yield ($\emptyset_{ISC}$), by a factor of 1.8. Analysis of photophysical data shows that all singlet deactivation rate constants decrease upon complexation of TMP with ß-CDx, but slowing down of internal conversion is most pronounced. The efficiency of one-photon electron ejection from TMP is reduced by complexation, owing to the more hydrophobic environment; in contrast, two-photon electron ejection is enhanced, probably because of the longer S_1 lifetime.

The decay of e^-_{aq} is found to be accelerated in the presence CDx's which form complexes with hydroxy- and methoxybenzenes.

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PHOTOSTABILIZATION MECHANISMS OF HALS: INTERACTION
WITH SINGLET AND TRIPLET ANTHRACENE

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Photooxidation of polyolefins largely occurs by the classical scheme developed for rubber and oils thermal oxidation[1]:

$$R' + O_2 \longrightarrow ROO' \; ; \quad ROO' + RH \longrightarrow ROOH + R' \; ; \quad 2R' \longrightarrow Products$$
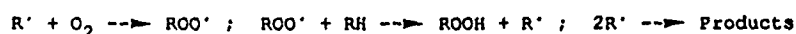
A key question in polyolefin photooxidation is the origin of the primary radical (R') shown in the scheme. It is now generally accepted that different chromophoric impurities are active in generating R'. Among the impurities polynuclear aromatic hydrocarbons (PNA), in particular anthracene, are believed to be photoinitiators of non minor importance [2,3]. The accumulation of these compounds in polyolefins is now well established: they are absorbed by the polyolefins from the polluted urban athmospheres.

To contrast the action of the different photoinitiators various classes of light stabilizers have been developed, the most efficient being that of of Hindered Amine Light Stabilizers (HALS). HALS are derivatives of 2,2,6,6-tetramethylpiperidine which undergo oxidation to hydroxylamine derivatives and to N-oxyl free radicals during the processing and the photooxidation of polyolefins. HALS are active on various initiators of photooxidation: their interaction with hydroperoxides, aliphatic carbonyls and singlet oxygen have been already studied.

To investigate the probable role of HALS as quenchers of the electronically excited PNA, we studied the interaction of various piperidines, hydroxylamines and piperidine N-oxyl radicals with the singlet and triplet excited states of anthracene. In this communication we report the results of such a study.

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A LASER PHOTOLYSIS STUDY of the ALKALIDE Na$^+$C222.Na$^-$

by

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Alkalides are compounds containing alkali metal ions at the unusual valence state -1. They can be prepared in amines (like methylamine) in the presence of a cryptand molecule, according to a reaction such as :

$$2\,Na + C222 \rightarrow Na^+C222.Na^-$$

The subsequent removal of the solvent leads to a solid compound (sodide), whose aspect is bright, shiny, gold-like. The compound Na$^+$C222.Na$^-$ is non-metallic. It behaves as a semiconductor having an apparent band gap of 2.4 eV.

Thin films of solid Na$^+$C222.Na$^-$ have been studied by using laser photolysis at two different wavelengths. When excited at 605 nm (within the main absorption peak, centered at 650 nm), above a given power threshold, there is a rapid bleaching of the spectrum, followed by a fast but partial recovery of the absorption spectrum. At 308 nm, even though the absorption of the sodide is very low, the effect is the same, but in this latter case, the recovery of the spectrum is almost complete.

This phenomenon is interpreted in the following manner : at 308 nm, the sodide is excited directly into the conduction band. The relaxation of the excited species correspond to a simple hole-electron pair recombination. At 605 nm, when the laser power applied is low, the sodide undergoes a 3s^2 $\rightarrow$ 3s3p transition, followed by a fast, non-radiative process. When the power is increased, two processes occur : (1) a bi-photonic mechanism promotes the sodide ion first into the 3s3p state, then partly into the conduction band. (2) The recovery can therefore take place both from the conduction band (hole-electron pair recombination) and from the 3s3p excited state. In the former case, since the conduction band is a continuum of delocalized states, the recovery is ideal and is similar to what happens with UV light. In the latter case, the 3s3p orbitals may overlap, thus leading to decomposition reactions such as :

$$Na^{-*} + Na^{-\,\prime} \rightarrow products\ (Na, e^-...)$$

This work shows the interest of testing two different wavelengths in order to elucidate the photochemistry of Na$^+$C222.Na$^-$. Temperature dependance measurements will subsequently be made on this sodide and extended to other alkalides.

IV- BIOLOGICAL ASPECTS OF
PHOTOCHEMISTRY

THE PRIMARY CHARGE SEPARATION IN PHOTOSYSTEM TWO.

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Transient absorption spectroscopy has been used to study the primary charge separation in reaction centres isolated from the photosystem two of higher plants. The experimental apparatus allowed excitation of the reaction centres at wavelengths between 600nm and 685nm with a time resolution of 150fs. Absorption kinetics are observed with lifetimes between 1ps and 20ps, using low energy excitation pulses and stabilised reaction centres. The transient species involved are identified from their spectral and excitation wavelength dependence. The primary charge separation is observed, with a lifetime of approximately 1ps. At certain excitation wavelengths additional, relatively slow, kinetics are observed and assigned to energy transfer from accessory pigments to the primary electron donor, P680. These processes are included in a kinetic model of the electron and energy transfer pathways active in the isolated photosystem two reaction centre, based on experiments conducted over a time range from femtoseconds to milliseconds.

PHOTOLYSE LASER DU COMPLEXE HISTIDINE-HEME-CO

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Dans les hémoprotéines, le fer de l'hème est lié avec un atome d'azote de l'imidazole d'une histidine, ce qui confère à l'hème un rôle important tel que la fixation reversible de l'oxygène (dans les myoglobines et hémoglobines), la catalyse de la réduction de l'hydrogène peroxide (catalases et peroxidases), le transport d'électrons (cytochromes), l'oxycation de substrats organiques (oxygénases et dioxygénases) et la réduction de l'O_2 en eau (oxydases terminales).

L'interaction hème-globine dans les hémoprotéines a déjà été très largement étudiée, cependant le rôle joué par l'histidine proximale n'est pas encore complètement élucidé. Afin de mieux comprendre l'effet de la liaison fer-histidine sur la réactivité de l'hème, la photodissociation du complexe histidine-hème-CO a été entreprise, suivie de mesures de spectroscopie d'absorption de la picoseconde à la milliseconde. Les deux ligands du groupement hémique, l'histidine et la molécule de CO sont dissociées après excitation. On n'observe pas de phase de dissociation de l'histidine ce qui signifie que les deux ligands doivent être dissociés dans les premières pico-secondes.

Les cinétiques de recombinaison indiquent qu'après photodissociation, une molécule d'eau se recombine en premier à l'hème puis la molécule de CO et enfin H_2O est remplacée par l'histidine.

LASER PHOTOLYSIS OF THE HISTIDINE-HEME-CO COMPLEX

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In hemoproteins, the heme is usually bonded by its iron atom to an imidazole nitrogen of a histidine residue, which permits many important functions such as the reversible binding of oxygen (in myoglobins and hemoglobins), catalysis of the reduction of hydrogen peroxide (catalases and peroxidases), electron transport (the cytochromes), oxidation of organic substrates (oxygenases and dioxygenases) and the reduction of dioxygen to water (the terminal oxidases).

The interaction of heme with globin in hemoproteins has been extensively studied but the role of the proximal histidine residue is not yet fully understood. In order to understand the effect of the iron histidine bond on the reactivity of the heme, photodissociation of the histidine-heme-CO complex has been investigated with picosecond to millisecond absorption difference spectra. Both ligands of the heme group, histidine and carbon monoxide, are apparently released after excitation. No independent phase for the dissociation of the histidine was observed, indicating that both ligands are dissociated within the first picosecond.

The recombination rates and kinetic difference spectra indicate that after photodissociation, the heme group recombines successively with water, carbon monoxide and finally the water molecule is replaced by histidine.

THE TRIPLET STATE OF TRYPTOPHAN IN KERATIN
AND ITS REACTION WITH OXYGEN

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Tryptophan is a key primary chromophore involved in the photochemistry of protein. As such, tryptophan and related indoles have been the subject of intensive photochemical investigation both *in vitro* and within proteins.

In the work described in this paper the fluorescence and phosphorescence of tryptophan residues in the solid protein, keratin from wool has been studied.

From determinations of the tryptophan fluorescence maximum as a function of temperature it is concluded that there is a very effective, thermally induced mixing of the ^1L_a and ^1L_b excited singlet states which results in enhanced internal conversion[1] and, at least in part, could be responsible for a relatively low triplet state yield. The triplet state yield of tryptophan in keratin at 77K was determined to be 0.11 whereas values of 0.37[1] and 0.50[2] have been measured in PVA and ethylene glycol respectively at 77K.

Laser flash photolysis measurements on the phosphorescence excited by 265 nm excitation have shown that there is a very rapid rate of reaction of oxygen with many of the triplet states of tryptophan produced in keratin. This implies that the observed phosphorescence is due to tryptophan residues at the surface of the sample which react principally with gas phase oxygen molecules impinging on the surface.

Despite this rapid reaction with oxygen, no singlet oxygen could be detected by its characteristic chemiluminescence at 1270 nm following excitation of tryptophan triplet states. It is estimated that if singlet oxygen is produced, its yield <0.05.

The absence (or low yield) of singlet oxygen could arise from either the low yield of tryptophan triplet states discussed above or inefficient energy transfer from the tryptophan triplet to molecular ground state oxygen.

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EXALTATION DE LA PHOTOACTIVITE DE MOLECULES HYBRIDES "ZINC-PORPHYRIN-ELLIPTICINE" PAR ADDITION D'ADN

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De nombreuses équipes travaillent actuellement au développement d'agents thérapeutiques qui sont activés sélectivement par leur cible biologique. Les dérivés de l'hématoporphyrine habituellement utilisés en photothérapie anticancéreuse présentent un manque de sélectivité qui entraine simultanément une réponse phototoxique. Dans le cadre des recherches réalisées sur de nouvelles porphyrines synthétiques, il a été récemment montré que la zinc-tetrakis(4-N-methylpyridiniumyl)porphyrine (ZnTMPyP) peut induire des altérations de l'ADN sous irradiation.[1]

Nous présentons ici de nouvelles molécules hybrides "zinc-porphyrine-ellipticine" qui présentent deux propriétés particulièrement interessantes en vue de leur utilisation en photothérapie. La première est que la présence dans leur structure d'un agent intercalant augmente fortement leur affinité pour l'ADN.[2] La seconde est que leur photoactivité qui est très faible en solution homogène, est fortement exaltée en présence d'ADN.

Deux hybrides ont été étudiés[3]: Porph-O(CH$_2$)$_3$NHCO(CH$_2$)$_5$-Ellip, 1, et Porp-NHCO(CH$_2$)$_4$-Ellip, 2. L' excitation de la bande Q de la porphyrine provoque une luminescence très faible de ces composés: Leur rendement de fluorescence est de l'ordre de 8×10^{-4} alors que la fluorescence de ZnTMPyP est de 2.5×10^{-2}. Le rendement de fluorescence des molécules hybrides complexées par l'ADN est 22 fois plus grand dans le cas de 1 (ou 8 fois dans le cas de 2) que celui des hybrides libres alors que le rendement de fluorescence de ZnTMPyP est très peu modifié par la présence d'ADN. Dans le même temps, les propriétés de l'état triplet sont aussi fortement modifiées: La luminescence de l'oxygène singulet généré par les molécules hybrides a son rendement fortement augmenté (11 à 4 fois) par addition d'ADN.

Notre hypothèse est que la faible photoactivité des molécules hybrides seules est le résultat d'un stacking intramoléculaire dû à leur conformation repliée qui entraine un quenching des propriétés des états singulet et triplet. L'augmentation de leur photoactivité lors de l'addition d'ADN résulterait d'un changement concomitant de la conformation de ces molécules. L'ADN sert ici d'activateur pour ces molécules.

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DNA AS A SWITCH FOR THE PHOTOACTIVITY OF HYBRID MOLECULES "ZINC-PORPHYRIN-ELLIPTICINE"

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Numerous teams are currently working on the development of therapeutic agents which are selectively activated by their biological target. The hematoporphyrin derivatives usually used in cancer phototherapy exhibits a lack of selectivity which leads to a concomitant phototoxic response. Searching new photoactivable synthetic porphyrins, it has been recently shown that zinc-tetrakis(4-N-methylpyridiniumyl)porphyrin (ZnTMPyP) may induce DNA damage under irradiation.[1]

We report here on new water-soluble hybrid molecules "zinc-porphyrin-ellipticine" which exhibit two properties particularly interesting for their potential use in phototherapy: First, the presence of an intercalating agent highly increases the affinity of the molecule for DNA.[2] Secondly, their photoactivity which is very low in homogeneous solution is dramatically enhanced in the presence of DNA.

Two hybrid compounds[3] have been studied: Porph-O(CH$_2$)$_3$NHCO(CH$_2$)$_5$-Ellip, **1**, and Porph-NH-CO(CH$_2$)$_4$-Ellip, **2**. Upon excitation in the Q-band of the Zn-porphyrin the luminescence of these compounds was very low: Their fluorescence yield was about 8×10^{-4} while the fluorescence of ZnTMPyP as 2.5×10^{-2}. The fluorescence yield of hybrid molecules complexed with DNA was 22 times for **1** (or 8 times for **2**) that of free hybrids while the fluorescence yield of ZnTMPyP was only poorly modified in the presence of DNA. In the same time, the properties of the triplet state were also dramatically changed: the yield of singlet oxygen emission generated by the hybrid molecules was highly enhanced (11 or 4 times) upon addition of DNA.

Our hypothesis is that the low photoreactivity of hybrid molecules alone is the result of a strong intramolecular stacking due to their folded conformation leading to a quenching of the properties of both singlet and triplet states. Addition of DNA changes the conformation of the molecule and consequently their photoreactivity, making then DNA as a switch for photoactivable molecules.

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THE PHOTOCHROMIC EQUILIBRIUM BETWEEN BACTERIORHODOPSIN (BR) AND ITS K INTERMEDIATE STUDIED BY LASER-INDUCED OPTOACOUSTIC SPECTROSCOPY (LIOAS) WITH NS AND SUB-PS LASER PULSES

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LIOAS was used to measure the heat stored by the intermediate K, produced in 5 ps after excitation of BR and living for ca. 2 μs, i.e., longer than the heat integration time of the experiment, which is determined by the acoustic transit time (between 150 and 670 ns depending on the laser diameter)[1]. Using $<$ 500 femtosecond pulses a lower limit for $\Phi_{BR \rightarrow K} = 0.5$ was derived.

Through variation of the acoustic transit time the lifetime of K was determined to be $\tau_K = 1.5$ μs, in agreement with the literature value [2].

With 6-ns pulses a photochromic equilibrium was established within the pulse between BR and K. The dependence of the heat released promptly on the excitation energy fluence was modeled for each of the six excitation wavelengths (532-630 nm; ϵ_K/ϵ_{BR} varied between 0.7 and 2.7 [2]). The best fit of the experimental points was obtained for a quantum yield of formation BR from K, $\Phi_{K \rightarrow BR} = 0.41$, and a lifetime of K*, $\tau_{K*} = 39$ ps ($\tau_{K*} > \tau_{BR*} \approx 0.7$ ps is consistent with the higher fluorescence and the smaller Stokes shift reported for K as compared to BR [3]).

Temperature-dependent LIOAS measurements in the water-based solution (possessing a strongly temperature-dependent cubic expansion coefficient around 4 °C) yielded a temperature independent term, interpreted as the contribution of molecular movements concon. tant with the photochemical reaction, in addition to the heat evolution leading to the thermal effect (temperature-dependent) [3]. A one dimensional expansion of 100 pm/molecule for the BR to K phototransformation resulted from the measurements.

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REACTIONS DES PORPHYRINES VINYLIQUES AVEC L'OXYGENE SINGULET EN RELATION AVEC LEUR UTILISATION EN PHOTOCHIMIOTHERAPIE

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La photochimiothérapie est basée sur la rétention sélective par les tumeurs solides, de photosensibilisateurs tels que l'hématoporphyrine dérivée (Hpd) ou le Photofrin®. L'irradiation des structures biologiques marquées par ces colorants conduit à une régression des tumeurs probablement par un mécanisme impliquant l'oxygène singulet. Au cours du traitement, l'Hpd et le Photofrin® qui contiennent des porphyrines vinyliques, subissent des photo-dégradations.

Nous avons utilisé une technique de photolyse par éclair laser pour comparer les réactivités de plusieurs porphyrines vinyliques vis-à-vis de l'oxygène singulet dans différents solvants. Les porphyrines étudiées sont dérivées de la deutéroporphyrine par des substitutions en position 2 ou 4. La constante de vitesse de quenching de l'oxygène singulet, k_p est de l'ordre de 10^7 $M^{-1}s^{-1}$. Cette valeur est beaucoup plus élevée que celle déterminée en photolyse continue par d'autres groupes. Nous avons mis en évidence une augmentation de k_p avec le caractère électro-donneur des substituants directement liés au cycle porphyrine. Les valeurs de k_p mesurées pour le mélange isomérique et pour les deux isomères séparés (groupe vinylique en position 2 ou en position 4) sont identiques. Les propriétés électroniques et la viscosité des solvants aprotiques ont peu ou pas d'influence sur la vitesse de réaction. De même, la deutériation des solvants n'affecte pas k_p. Par contre, la présence de solvants protiques tels que l'eau, le méthanol, l'éthanol ou le N-méthylformamide provoque une augmentation notable de la vitesse de quenching. Ces résultats expérimentaux seront utilisés pour discuter de la nature des processus impliqués dans la photomodification des porphyrines vinyliques et de leur importance en photochimiothérapie.

REACTIONS OF VINYL PORPHYRINS WITH SINGLET OXYGEN RELEVANCE TO PHOTOCHEMOTHERAPY

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Photochemotherapy using hematoporphyrin derivative (Hpd) or Photofrin® is based on preferential labelling of neoplastic tissues by these drugs which, upon subsequent irradiation with visible light specifically induce the regression of tumors probably *via* a singlet oxygen pathway. Hpd and Photofrin® which contain vinyl porphyrins are known to undergo a photochemical change during treatment.

Laser flash photolysis has been used to examine and compare the reactivities of several vinyl porphyrins towards singlet oxygen ($^1O_2$) in various solvents. The singlet oxygen quenching constant, k_p (in the order of 10^7 $M^{-1}s^{-1}$) is found to decrease with increasing electron-withdrawing effect of substituents on the porphyrin ring. Values of k_p measured for both separated isomers and for the isomeric mixture are identical within experimental error. No direct effect of solvent electronic properties or viscosity can be discerned for aprotic solvents. Likewise, no trend in the results with $^1O_2$ lifetime in the media used, is observed. An accelerating effect of protic solvents such as water, methanol, ethanol and N-methylformamide is evidenced. We discuss the nature of the photoprocesses involved in the photomodification of vinyl porphyrins.

REACTION INTERMEDIATES OF A DIHYDROPYRIDINE DERIVATIVE OF AZT RELATED TO AIDS DEMENTIA, STUDIED BY 355nm NANOSECOND LASER FLASH PHOTOLYSIS

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The discovery that AZT is a potent inhibitor of human immunodeficiency virus (HIV) has stimulated the synthesis and biological study of a multitude of nucleoside analogues with azido substituents on the sugar rings.

In an attempt to provide a derivative which might cross the blood-brain barrier and be sequestred in the central nervous system, the dihydropyridine ester 5'-(1,4-dihydro-1-methyl-3-pyridinylcarbonyl)-3'-deoxythymidine (HPAZT) has been synthesized[1]. The delivery to the nervous system is based on dihydropyridine-pyridinium ion redox interconversion, and it is therefore of interest to characterize the intermediates involved in this transformation.

It was previously shown[2,3] that exposure of dihydronicotinamide adenine dinucleotide (NADH) in aqueous solution to 355 nm laser emission gives rise to one-electron ejection by stepwise two-photon excitation with formation of semiquinonic nicotinamide radicals.

We have now demonstrated that this photochemical reaction occurs also in the case of HPAZT in aqueous solution. The efficiency of photoionization is close to that of NADH. The HPAZT radical cation formed in this process deprotonates in approx. 10^{-7} s to give the neutral radical.

The ionization of HPAZT by two-photon excitation at 355 nm thus provides a convenient means of producing radicalar forms of this compound for study of redox reactions involving HPAZT radicals as intermediates.

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(2) B.Czochralska, L.Lindqvist, Chem.Phys.Letters 101 297 (1983)
(3) L.Lindqvist, B.Czochralska, I.Grigorov, Chem.Phys.Letters 119 494 (1985)

INTERMEDIAIRES REACTIONNELS D'UN DERIVE DE L'AZT RELATIF A LA DEMENCE
DUE AU SIDA, ETUDIES PAR PHOTOLYSE-LASER NANOSECONDE A 355 NM.

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La découverte que l'AZT est un inhibiteur puissant du virus de l'immu-
nodéficience humaine (HIV) a encouragé la synthèse et l'étude biologique
d'une multitude d'analogues nucléosidesavec des substituants azido.

Dans le but d'obtenir un dérivé susceptible de franchir la barrière
sang-cerveau et d'être piégé dans le système nerveux central, l'ester de la
dihydropyridine   5'-(1,4-dihydro-1-methyl-3-pyridinylcarbonyl)-3'-deoxythy-
midine (HPAZT) a été synthétisé[1]. L'introduction dans le système nerveux
est basée sur l'interconversion redox dihydropyridine - ion pyridinium, et
il est par conséquent intéressant de pouvoir étudier et caractériser les
intermédiaires impliqués dans cette transformation.

Il a été précedemment démontré[2,3] qu'il est possible d'obtenir
l'éjection d'un électron du dihydronicotinamide adenine dinucleotide (NADH)
en solution aqueuse, avec formation de radicaux semiquinoniques du groupe-
ment nicotinamide, à l'aide d'un rayonnement laser impulsionnel à 355 nm.

Nous avons maintenant montré que cette réaction photochimique a lieu
également dans le cas de l'HPAZT en solution aqueuse. L'efficacité de photo-
ionisation est proche de celle pour le NADH. Le radical cation de l'HPAZT
formé dans ce processus donne en $\sim 10^{-7}$s le radical neutre par déprotonation.

L'ionisation de l'HPAZT par excitation biphotonique à 355 nm donne
ainsi un moyen intéressant de produire des formes radicalaires de ce composé
pour l'étude de réactions rédox impliquant des radicaux de l'HPAZT comme
intermédiaires.

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234 135 (1988)
(2) B.Czochralska, L.Lindqvist, Chem.Phys.Letters 101 297 (1983)
(3) L.Lindqvist, B.Czochralska, I.Grigorov, Chem.Phys.Letters 119 494 (1985)

FLUORESCENCE SPECTROSCOPY AND TRYPTOPHAN CONTENT OF CHLOROPLAST COUPLING FACTOR1"CF$_1$"

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CF$_1$,is the known enzyme of photophosphorylation in chloroplasts. It couples the photo-induced electron flow to ATP synthesis via a trans-membrane gradient in electrochemical potential created by H$^+$-movement. The enzyme is one of the most complicated known enzymes (1,2). Its detailed structure, conformational transitions and molecular mechanism, although of great importance, are all poorly understood. In this context, fluorescence studies would provide valuable information(2,3). Thence, in this report, absorption spectra and fluorescence emission, excitation and polarization spectra of the protein were studied. All criteria indicated the existence of tryptophan in the protein. Depending on the method of determination there were 8 - 12 moles of tryptophan per mole of the enzyme. Tyrosine was also determined and a ratio of 8 tyrosine : 1 tryptophan was estimated in the protein. Fluorescence life time determined from simultaneous measurements of phase lag and degree of modulation at a single light-modulation frequency revealed that tryptophan exists in heterogeneous aqueous environments within the protein.

Utilization of the above properties in the study of the structure, molecular mechanism and dynamics of the enzyme will be discussed.

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HOLE BURNING STUDY OF INTACT CELLS OF PHOTOSYNTHETIC GREEN BACTERIA

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The photosynthetic pigment molecules in natural light-harvesting antennas form the lattices of a cluster type. Can this clustering of the pigment molecules be considered as one of the optimizing structural factors ensuring the high efficiency of excitation energy transfer from an antenna to a reaction center? This problem has been examined here by mathematical simulation of the light-harvesting process in model three-dimensional systems. It has been shown that only in the case of strong interactions within each molecular cluster (upon oligomerization of molecules in the cluster allowing to consider each oligomer as a single "supermolecule"), the formation of pigment clusters in a light-harvesting system increases the efficiency of such system as compared to that of a corresponding monomeric uniform isotropic system of the same volume. Therefore, the oligomerization of antenna pigments, as an efficient strategy for the light harvesting in photosynthesis, is biologically expedient[1]. The question of whether this is the case for the three-dimensional chlorosomal superantenna of green bacteria[2] has been examined with hole burning spectroscopy. The hole burning in fluorescence excitation and emission spectra of intact cells has been measured at 1.8 K. The contribution of inhomogeneous line broadening to the profiles of both spectra has been shown. The persistent hole spectra have been found to be consistent with a strongly coupled bacteriochlorophyll c chromophore system within a cluster. The results directly demonstrate that each bacteriochlorophyll c cluster in natural chlorosomal antenna of green bacteria behaves in the process of excitation energy transfer as a single supermolecule.

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PHOTODYNAMIC THERAPY AS A CHEMICAL KINETIC PROCEDURE

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Photodynamic Therapy (PDT) has emerged in the last decade as a prospective tool in clinical trials for the treatment of malignant cells. Several schools all over the world are studying and using it[1-4] in spite of the fact that kinetic parameters and adequate mechanisms are not well known.

PDT can be scientifically defined as a light (laser) activated photosensitizer effect in biological tissues. Most of literature sources assume that activation leads to singlet oxygen exerting the annihilating effect (Type II mechanism), though there are references indicating also the role of radicals (Type I mechanism).

The authors suggest that parallel to the formation of singlet oxygen as the annihilating agent, active species formed during the activation of the photosensitizer (e.g. haematoporphyrin and its derivatives) interact with active species (e.g. radicals generated by the biological entities) called Modified Type One (MTO) mechanism.

In order to support this view following experimental work has been performed:

- Laser flash photolysis studies on formation of singlet oxygen in the absence and in the presence of radicals introduced into the system
- Investigation of active species formed during the irradiation of Hp and Hpd-s
- Electron spin resonance measurements of radicals in mice before and after irradiation in the absence and in the presence of Hp and Hpd-s administered;
- Measurement of photobleaching of Hp and Hpd-s.

The present lecture summarizes results obtained in above fields.

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V- ENVIRONMENTAL PHOTOCHEMISTRY

Photolysis of Biacetyl-Oxygen Mixtures in the Temperature
Range of 233 - 333 K: Kinetics and Mechanism of the Reaction
System CH_3COO_2 - CH_3O_2 -HO_2

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Biacetyl (butane-2,3-dione) was photolyzed at atmospheric
pressure in Ar/O_2 = 80/20 mixtures between 233 and 333 K using
Philips TL03 lamps (390 - 470 nm with the maximum at 420 nm)
under steady-state flow conditions. Primary photolysis yields
CH_3CO radicals, which in O_2 subsequently generates CH_3COO_2,
CH_3O_2, and HO_2 radicals. This photolysis system thus provides
a convenient system for studying kinetics and mechanism of
mutual reactions of these peroxy radicals. The reaction
products were analyzed by the matrix-isolation FTIR
spectroscopy coupled with the molecular-beam sampling. The
reaction products were CO_2, CO, $HCHO$, CH_3COOH, O_3, CH_3COOOH,
CH_3OH, $HCOOH$, and H_2O_2.

The quantitative product data were used to determine the
rate constants and the branching ratios of the following two
important reactions over the temperature range of 233 - 333 K
by means of a computer simulation:

$$CH_3COO_2 + HO_2 \longrightarrow CH_3COOOH + O_2 \qquad (1a)$$
$$CH_3COO_2 + HO_2 \longrightarrow CH_3COOH + O_3 \qquad (1b)$$

and

$$CH_3COO_2 + CH_3O_2 \longrightarrow CH_3COO + CH_3O + O_2 \qquad (2a)$$
$$CH_3COO_2 + CH_3O_2 \longrightarrow CH_3COOH + HCHO + O_2 \qquad (2b)$$
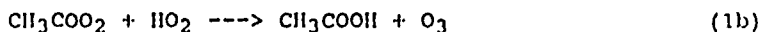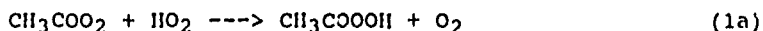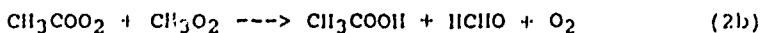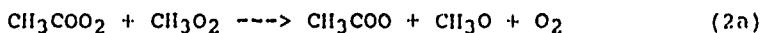
A detailed discussion on the results of the simulation will be
presented, and relevance to tropospheric chemistry will be
indicated.

LASER EXCITATION OF THE $A^3\Sigma_u^+$, $A'^3\Delta_u$ AND $c^1\Sigma_u^-$ STATES OF MOLECULAR OXYGEN

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Molecular oxygen was selectively excited to the $A^3\Sigma_u^+$ ($v'=7,8$), $A'^3\Delta_u$ ($v'=9$) and $c^1\Sigma_u^-$ ($v'=13$) states by absorption of pulsed dye-laser emission.

Time-resolved fluorescence could only be observed in the $b^1\Sigma_g^+ \rightarrow X^3\Sigma_g^-$ band at $\lambda=762$ nm.

A good signal-to-noise ratio of $\simeq 250$ could be achieved for absorption in the $A^3\Sigma_u^+ \leftarrow X^3\Sigma_g^-$ transition; smaller values were obtained for the $A'^3\Delta_u \leftarrow X^3\Sigma_g^-$ (S:N=15) and $c^1\Sigma_u^- \leftarrow X^3\Sigma_g^-$ (S:N=10) transitions.

From the temporal behaviour of the $b^1\Sigma_g^+ \rightarrow X^3\Sigma_g^-$ emission, a lower limit for the rate constant for quenching of $O_2(A^3\Sigma_u^+)$ by oxygen itself could be deduced to be $\geq 1\times 10^{-11}$ cm^{3}s^{-1} for the vibrational levels $v'=7,8$.

It was not possible to measure the corresponding rates for the $A'^3\Delta_u$ ($v'=9$) and $c^1\Sigma_u^-$ ($v'=13$) states, because of the small S:N ratios.

The data for the intensity of the $b^1\Sigma_g^+ \rightarrow X^3\Sigma_g^-$ emission as a function of the O_2/N_2 mixing ratio suggest that not all the quenching of the ungerade states leads to population of the $b^1\Sigma_g^+$ state.

A value for the yield of $b^1\Sigma_g^+$ from quenching of the $A^3\Sigma_u^+$ state by O_2 itself, α, could only be calculated relative to the yield of $b^1\Sigma_g^+$ from quenching of the $A^3\Sigma_u^+$ state by N_2, β. This ratio was fitted to the experimental data using a simple relation between the intensity of the $b^1\Sigma_g^+ \rightarrow X^3\Sigma_g^-$ emission and the O_2/N_2 mixing ratio. Assuming $\beta=1$, i.e. that $b^1\Sigma_g^+$ is the only product of quenching of the $A^3\Sigma_u^+$ state by N_2, physical sense limits the value for α into the range $0.4 \geq \alpha \geq 0.11$.

SOIL SENSITISED PHOTODEGRADATION OF BIORESMETHRIN

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A knowledge of the mode of photodegradation of agrochemicals is of importance. Studies[1,2] have shown that singlet oxygen could be implicated in the environmental breakdown of certain agrochemicals, and, furthermore, it has been suggested[3] that singlet oxygen can be formed on soil surfaces and can contribute to the photo-oxidation of organic compounds. We have used soil samples as the sensitising substrate in the separated-surface-sensitiser (s-s-s) reactor developed by Midden et al,[4] and by comparison with results obtained using known sensitisers for the formation of singlet oxygen we have been able to show that soil samples can generate singlet oxygen and that the singlet oxygen so generated causes the photo-degradation of bioresmethrin, a well known pyrethroid insecticide.

Results will be presented showing that soil samples of different pH can generate singlet oxygen, and that the photo-degradation of bioresmethrin is inhibited in the presence of the singlet oxygen quencher, β-carotene.

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PHOTODEGRADATION OF TRIBUTYLTIN (TBT) IN ENVIRONMENTAL WATER: THE ROLE OF
THE SURROUNDING ATMOSPHERIC GASES

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Tin in its inorganic form is generally accepted as being non-toxic; howe_
ver, the attachment of one or more organic groups to the tin atom, via Sn-C
bond, has a drastic effect on the biological activity[1].Organotin compounds
of the type R_nSnX_{4-n} have a considerable number of industrial applications
and are therefore able to enter the environment through a variety of routes.
In particular, the environmental impact of tributyltin (TBT) compounds in the
aquatic environment has been the subjetc of a large amount of research in the
past 10 years[1]. The degradation of an organotin compound may be defined as
the progressive removal of the organic groups attached to the tin atom,accom_
panied by a progressive lowering in biological activity.

$$R_4Sn \longrightarrow R_3SnX \longrightarrow R_2SnX_2 \longrightarrow RSnX_3 \longrightarrow SnX_4 \quad \text{(equation 1)}$$
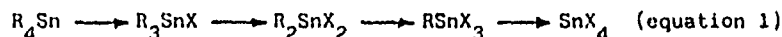
Degradation involves the breaking of a Sn-C bond, and this may occur by a
number of different processes being one of them by direct ultra-violet irra_
diation. Although the degradation of TBT has been studied in environmental
water,by direct exposure to sunlight photons[2-3], however an understanding
of the factors affecting the photolytic degradation TBT compounds require a
more detailed account. In this respect the photodegradation of TBT and rela_
ted compounds as DBT and MBT in pure water (at pH=5.5) has been studied by
us, under air pure oxygen or under pure nitrogen atmospheres. The nature of
the surrounding atmosphere (either O_2, N_2 or air) seems to play a significant
effect, which is different to each ones of the stablished rates for the pho_
todegradation of organic groups following the sequence of equation 1.

On the other hand, the presence of H_2O_2 species undergo retarded the ra_
te of the TBT photodegradation in comparison to its photolytic degradation
rate in pure aereated water.

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KINETIC STUDY OF THE REACTION OF NO_3 WITH HO_2

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The nitrate free radical NO_3 plays a significant role in nighttime atmospheric chemistry. NO_3 is produced by the reaction between NO_2 and O_3.

The reaction of NO_3 with HO_2 is of potential atmospheric interest because of their coexistence in the nighttime atmosphere. This reaction may proceed via two exothermic channels:

$$NO_3 + HO_2 \rightarrow HNO_3 + O_2$$
$$\rightarrow OH + NO_2 + O_2$$
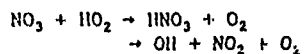
It may have an influence on both the NO_3 and HO_2 budgets and also contribute to the HNO_3 formation, which is one component of the acid deposition. It may also generate OH during nighttime[1].

Three studies of this reaction were reported recently[2-4], in only one of them[2] evidence was given for the two channels producing OH and HNO_3.

Here, we report a more direct study of the reaction of NO_3 with HO_2 at room temperature using the discharge flow laser magnetic resonance (LMR) method. Experiments were done with NO_3 added in excess over HO_2. The HO_2 radicals were formed using the reaction $H + O_2 + M$. Three methods were used to produce NO_3: a) $F + HNO_3$, b) $Cl + ClONO_2$ and c) thermal decomposition of N_2O_5.

The absolute concentrations of NO_3 in the reactor were determined by chemical titration using excess of NO: $NO + NO_3 \rightarrow 2NO_2$. The concentrations of HO_2, OH and NO_2 were measured by means of LMR.

Since OH was found to be produced in the reaction of NO_3 with HO_2, C_2F_3Cl was used to scavenge OH. The overall rate constant obtained was $k = (3.0 \pm 0.7) \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1} at 298 K and $P = (1.4 - 1.9)$ Torr which is in reasonable agreement with the previous measurements. Direct detection of HO_2 and OH radicals and the use of three different sources of NO_3 enabled us to confirm the existence of the second channel producing OH.

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UV Absorption Cross Sections of Formyl Bromide and Carbonyl Dibromide

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Formyl bromide ($CHBrO$) and carbonyl dibromide (CBr_2O) are intermediates in the atmospheric degradation of the two most important natural brominated hydrocarbons, CH_3Br and $CHBr_3$.

In the present work, UV spectra of both compounds have been recorded in a 480 l chamber from Duran glass using a diode array detector and an optical pathlength of 50.4 m. The spectra were recorded between 240 and 360 nm at a spectral resolution of 0.6 nm. Simultaneously, IR spectra were taken at a resolution of 1 cm^{-1} using a FT-IR spectrometer. Carbonyl dibromide was prepared by the reaction of CBr_4 with H_2SO_4, formyl bromide was produced in situ by photolysis of $CH_2O/Br_2/N_2$ mixtures (Niki et al., 1991). CHBrO is very unstable with respect to wall reactions, and product spectra had to be corrected for absorptions from HBr and Br_2. Absolute absorption cross sections of CHBrO were obtained by Br atom catalysed transformation of CHBrO to HBr and CO, calibrating the observed UV absorbance change by the simultaneous change of CO concentration as measured in the IR.

UV spectra of CBr_2O and CHBrO will be compared with those of CH_2O, CHClO, and CCl_2O, and the photolysis rate constants of CHBrO and CBr_2O in the troposphere will be estimated.
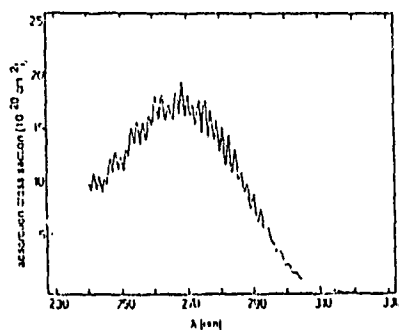
Formyl Bromide (CHBrO, preliminary)   Carbonyl Dibromide ($COBr_2$)
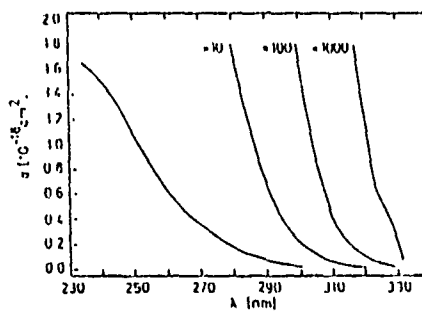
UV Absorption Spectra at 298 K in 1 bar of N_2.

PHOTOCATALYTIC DETOXIFICATION OF POLLUTED AQUIFERS:
POTENTIALS AND PROBLEMS

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Research in the area of photocatalysis has drawn the attention of many photochemists over the last ten years. The following principle is generally obeyed in all photocatalytic systems: electron/hole pairs are generated following the absorption of photons by molecules or particles (e.g. semiconductor particles in aqueous suspension). Useful chemical reactions can be driven if these charge carriers are separated and transferred to two different redox couples. Originally this concept was introduced to split water into molecular oxygen and hydrogen. Meanwhile, similar systems have been developed to achieve novel synthetic pathways as well as to mineralize toxic waste materials[1]. Advancements of the latter process will be reported here.

The destruction of toxic halogenated hydrocarbons in waste water effluents or ground water wells is a problem of growing importance in our industrial society. Since conventional methods such as chemical oxidation or microbial treatment are often not efficient for the destruction of these toxins, alternative routes for detoxification are required. It has been shown that semiconductor particles can be used as photocatalysts which are capable of inducing the complete mineralization of many of these hazardous compounds[2]. To judge the potentials of this method, it is necessary to understand the underlying reaction mechanisms. Thus the influence of light intensity, temperature and pH on the overall yield of the destruction of halogenated hydrocarbons in aqueous suspensions containing titanium dioxide powder has been studied in detail. Also, we have carried out investigations to establish the importance of the intermediacy of hydroxyl radicals in these systems. Models are presented to explain the observations made with chloroform and acetate as probe molecules and to enable predictions of the efficiency of this method for "real world" applications.

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Photooxidation of Anthracene in Aqueous Solution

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Benzenoid aromatic compounds are important man-made pollutants of natural waters. Due to their low solubilities, little is known about the efficiency and pathways of photochemical degradation. We chose anthracene 1 as a representative compound for an exploratory study. Flash photolysis of anthracene gives the radical cation 1^{+} by a biphotonic process, as has been observed also for naphthalene.[1] The radical cation 1^{+} reacts with water or hydroxide ions to give the alcohol radical 2 which then either reacts with oxygen to yield anthraquinone 4 as a major final product or (in deoxygenated solutions) dimerizes to give 5. When a continuous light source is used, biphotonic processes can be neglected. Nevertheless still the same products are found. Various lines of evidence suggest that adventitious impurities play a role in this reaction; the quantum yield for the decay of anthracene is approximately tenfold in degassed solutions ($\Phi_{254} = 0.012$) compared to aerated solutions ($\Phi_{254} = 0.001$) while the quantum yield of fluorescence is almost the same.
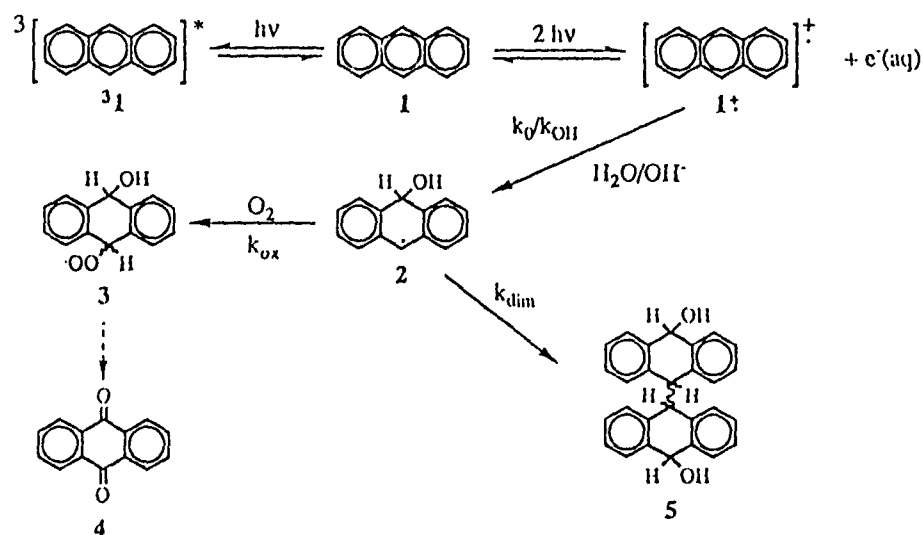
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LABORATORY STUDIES OF THE MECHANISM
OF THE OXYGEN AIRGLOW

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Laboratory studies of the oxygen airglow offer the advantage that they can cover a more controlled range of experimental conditions than atmospheric measurements. In our experiments we have studied the effect of added quenching agents on emission by $O(^1S)$, $O_2(A^3\Sigma_u^+$, $A'^3\Delta_u$, and $c^1\Sigma_u)$ associated with the recombination of oxygen atoms in an argon or nitrogen carrier. The results of these experiments cannot be explained by the Chapman mechanism, and provide evidence as to the nature of the precursor O_2^* in the Barth mechanism.

$$O + O + M \quad = \quad O_2^* + M$$
$$O_2^* + O(^3P) \quad = \quad O_2 + O(^1S)$$
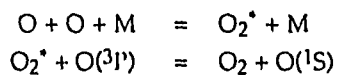
The requirement in this mechanism that an added quenching agent must quench auroral green line emission more strongly than emission by the precursor shows that $O_2(A^3\Sigma_u^+)$ in vibrational levels 0 to 6 and $O_2(c^1\Sigma_u)$ cannot be the Barth precursor. Present evidence therefore favours the $O_2(A'^3\Delta_u)$ state as the precursor. Quantitative data on these processes will be described in the paper.

THE PHOTOCATALYSED REDUCTION OF THREE OXOANIONS

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The pollutant dichromate ions were photocatalytically reduced in dil.sulphuric acid. Their concentration was determined spectrophotometically at 350 nm. Preliminary results showed the catalytic effect of the anatase pigment P25 and Ventron $SrTiO_3$. Photoplatinisation [1] of either powder enhanced their catalytic effect. The effect of platinisation on the reflectance spectra is reported. Ventron MoS_2 produced fast photoreduction, presumably augmented by reduction by H_2S, presumably released during the reaction. Prepared titania samples from $TiCl_3$ or $TiCl_4$, undoped or doped with Cr^{3+} or Cr^{3+}/Mn^{2+} and subjected to reductive heat treatment were also used, after being characterised by their reflectance spectra [2]. Results using four different lamps will be presented. The rates of reduction are slower than the reduction of permanganate solution catalysed by several semiconducting powders, when no correlation was established between their catalytic activity and their band gap. [3]

On the other hand, the rate of reduction of aqueous Na_2CO_3 was slower than either of the above reductions. Doped or heat treated samples were less active than the undoped samples. The yield of reduction products was. methanol > carbon > formaldehyde with variable small amounts of formate. [1] This sequence is tentatively explained, as well as the relative ease of reduction of the three anions.

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SPIN-TRAPPING STUDIES OF
THE PHOTOCATALYTIC DEGRADATION OF ACETIC
AND CHLOROACETIC ACIDS IN AQUEOUS
POLYCRYSTALLINE TiO$_2$ DISPERSIONS

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The photocatalytic degradation of acetic and chloroacetic acids $Cl_xCH_{3-x}COOH$ (x = 0-3) are studied by the spin trapping technique. The intermediate radicals were trapped by three spin traps, 5,5-dimethyl-1-pyrroline N-oxide (DMPO), N- tert-butyl-α phenylnitrone (PBN) and α-(1-oxo-4pyridyl)-N-tert-butylnitrone (POBN). Hyperfine splitting constants were measured for several resultant radical adducts and compared with the literature values. The acids with α-hydrogen gave high concentrations of spin adducts. The values of the splitting constants obtained and the absence of detectable radicals in the case of trichloroacetic acid are in agreement with our previous kinetic study[1]. The attack at the α-CH position with hydrogen abstraction is the major contribution to the catalyzed photochemical degradation of acetic and chloroacetic acids. The photo-Kolbe-reaction proposed by Kräutler and Bard is of secondary importance [2]. Based on the kineticc study and the spin trapping results, the decomposition of organic molecules in an irradiated aqueous TiO$_2$ dispersion is discussed.

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REACTIONS DE COMPOSES HALOGENO-CARBONYLES
D'INTERET ATMOSPHERIQUE

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Les composés halogéno-carbonylés sont des intermédiaires importants dans le processus d'oxydation atmosphérique des alcanes halogénés, largement utilisés dans l'industrie. Comme ces composés peuvent transporter des atomes d' halogène dans la stratosphère, il est nécessaire de déterminer leur durée de vie atmosphérique qui est directement liée aux constantes de vitesse de leur réaction avec les radicaux OH de la troposphère.

Les constantes de vitesse des réactions de OH avec une série d'acétaldéhydes halogéno-substitués, CX_3CHO, ont été mesurées en utilisant la technique de photolyse laser-fluorescence résonante.

Les résultats sont, à 298 K, en 10^{-12} cm^3 molécule$^{-1}s^{-1}$:

OH + CH_3CHO	17 ± 1
OH + CH_2ClCHO	3.0 ± 0.1
OH + $CHCl_2CHO$	2.4 ± 0.1
OH + CCl_3CHO	0.86 ± 0.02
OH + CF_2ClCHO	0.95 ± 0.04
OH + CF_3CHO	0.62 ± 0.02

Certaines de ces données constituent des premières déterminations absolues. Les mécanismes ainsi que les implications atmosphériques seront discutées.

REACTIONS OF CARBONYL HALIDES OF ATMOSPHERIC INTEREST

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Carbonyl halides are important intermediates in the atmospheric oxidation process of halogenated alkanes, widely used in industry. Since these compounds are potential carriers of halogen to the stratosphere, it is necessary to determine their atmospheric lifetime which is directly linked to their rate constants of reaction with tropospheric OH radicals.

The rate constants for the reactions of OH with a series of halogen substituted acetaldehydes, CX_3CHO, have been measured using the laser photolysis-resonance fluorescence technique.

The results are, at 298 K, in 10^{-12} cm^3 molecule^{-1}s^{-1} :

OH + CH_3CHO	17 ± 1
OH + CH_2ClCHO	3.0 ± 0.1
OH + $CHCl_2CHO$	2.4 ± 0.1
OH + CCl_3CHO	0.86 ± 0.02
OH + CF_2ClCHO	0.95 ± 0.04
OH + CF_3CHO	0.62 ± 0.02

Some of these data are the first absolute measurements. Mechanistic information as well as atmospheric implications will be discussed.

THE PARAMETERS AFFECTING THE REDUCTION OF AQUEOUS CARBONATE PHOTOCATALYSED BY TREATED SEMICONDUCTORS

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Heterogeneous photocatalysed reduction of aqueous Na_2CO_3 solution (1M) was achieved using phthalocyanine-coated semiconductor powders (1-3% coatings) as well as bare semiconductors. The suspensions were irradiated with 254 nm light from a low-pressure mercury lamp. The coated phthalocyanine dyes (either Fe^{2+}-Pc or Co^{2+}-Pc) were found to absorb > 80% of the 254 nm radiation and thus sensitize the semiconductor. The products of reduction were determined spectrophotometrically. The CH_3OH yields from coated-titania increased linearly with increasing irradiation time over the period (6-18 h) but the line did not pass through the origin, indicating a slowing down at times > 6 h. Both coated-titania pigments gave an optimum CH_3OH yield at 2% surface coating. At higher coatings, the Pc may be screening the surface, reducing the light reaching the semiconductor. Much higher yield of CH_3OH obtained when bare MoS_2 was used as a photocatalyst, ascribed to the characteristic behaviour of the semiconducting layer-type disulphide distinguished from that of classical semiconducting materials. It seems that there is no correlation between the position of the conduction band of the various semiconductors studied and the yield of CH_3OH, such correlation has been argued. However, a decrease in the yield of CH_3OH was observed when the band gap width of the semiconductor increased. The yields of CH_3OH photoproduced nearly increased with the percentage of light absorbed at 254 nm by the various semiconductors. Irradiation leads to the production of electrons in the conduction band of the semiconductor. It is likely that the photoproduced electrons reduce CO_3^{2-} ions initially to $HCOO^-$ and then to $HCHO$ and CH_3OH. Other parameters likely to affect the photocatalysed reduction (solid : solution, pH and $[Na_2CO_3]$) are being studied. The photocatalysed reduction of CO_2 (or CO_3^{2-}) is of particular interest in view of the undesirable accumulation of CO_2 in the atmosphere which leads to the so called "greenhouse" effect.

PHOTOCATALYTIC DEGRADATION OF SURFACTANTS FOR
ENVIRONMENTAL CONCERN IN AQUEOUS SYSTEM

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Aquatic pollution caused by harmful materials is becoming a serious problem in a grobal scale. Since a lot of these chemicals are difficult to biodegrade through bacteria, they are accumulated without decoposition in nature for long period. We have extensively reported on the photodegradation of many kinds of surfactants catalyzed by TiO_2 semiconductor[1-3]. The photocatalytic degradation will be one of the prospective methods for aquatic environmental protection.

Various kinds of surfactants were photodegraded catalytically by TiO_2 semiconductor under both UV illumination by a Hg-lamp and solar exposure outdoors. TiO_2 dispersion system, glass beads loaded with TiO_2, and a glass electrode plate (SnO_2) carrying a TiO_2 membrane were investigated. Degradation process has been monitored through aromatic cleavage (UV absorption), NMR, CO_2 evolution, intermediate formation of peroxides and aldehydes, pH changes, zeta-potential of TiO_2 particles in the dispersion and surface activity measurements. The spin-trapping ESR spectra confirm the participation of •OH radicals in the photodegradation. Surfactants can be easily degraded to mineralize to CO_2 at about 20 ∿50% yield. The poorly biodegradable aromatic moiety is a "target" for photodegradation. The TiO_2/surfactant dispersion rapidly became acidic and the zeta-potential of TiO_2 particles shift to positive under UV illumination. The photodegradation rates decrease in the order of anionic DBS > nonionic NPE > cationic BDDAC. Both TiO_2 catalyst and UV irradiation are essential for the degradation of surfactants. A possible mechanisim of photodegradation of surfactants at TiO_2/ water interface will be discussed.

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THE PHOTOCATALYZED REMOVAL OF ORGANIC CONTAMINANTS FROM WATER

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Recently, we have demonstrated that the TiO_2 photocatalyzed destruction of organic contaminants in water holds considerable promise in removing organic contaminants from water streams [1-3]. Currently, we are successfully developing a strategy to inhibit the "hole-electron" recombination process, which is a major energy wasting step. This strategy is based on adding electron acceptors to the reaction. These additives should fulfil the following conditions: (1) readily accept electrons either directly from the conduction band or from the superoxide ion, (2) rapidly dissociate into harmless products and (3) if possible produce additional hydroxyl radicals and/or other powerful oxidizing species. We have examined the effects of four additives: hydrogen peroxide, potassium peroxymonosulphate, ammonium persulphate and potassium bromate on the degradation of organic mixtures and have found the results very promising. For instance, depending on the individual additive, the degradation rates of mixtures of o-chlorophenol, 2,4-dichlorophenol, 2,6-dichlorophenol and 2,4,6-trichlorophenol (10 - 40 ppm, each) are increased by at least a factor of 10 when any of these additives are introduced into the reactor. Similar results were obtained when other organic mixtures were examined in the presence of these additives. With these results, the commercialization potential of this process into a water treatment technology becomes evident. Results of our research will be presented and critically discussed.

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Kinetics of the reactions of CX_3(X=F,Cl) with O_2
in the pressure range 0.5-8 Torr at 295 K

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The association of chlorofluoromethyl radicals CX_3(X=F,Cl) with molecular oxygen is one of the important steps in the oxidation process of chlorofluoromethanes in the stratosphere.

$$CX_3 + O_2 + M \rightarrow CX_3O_2 + M \qquad (1)$$

In this study the rate constants of reaction (1) have been determined for CF_2Cl, $CFCl_2$, and CCl_3 by using laser flashphotolysis-photoionization mass spectrometry with N_2 as the bath gas.

Figure 1 shows total pressure dependence of the rate constants k_1. The reactions are in their fall-off region, which is consistent with the results obtained for $CFCl_2$ and CCl_3 in He[1,2]. The order of k_1 is $CF_2Cl > CFCl_2 > CCl_3$. The rate constants for CCl_3 are rather small, one tenth of those for CF_2Cl. These values are compared with corresponding values found earlier for CF_3 radical[3], which are the largest among them (see Fig. 1). The correlation between rate constants within the series of reactions of O_2 with alkyl radicals and the ionization potential of the radicals is not seen in chlorofluoro-methyl radicals.

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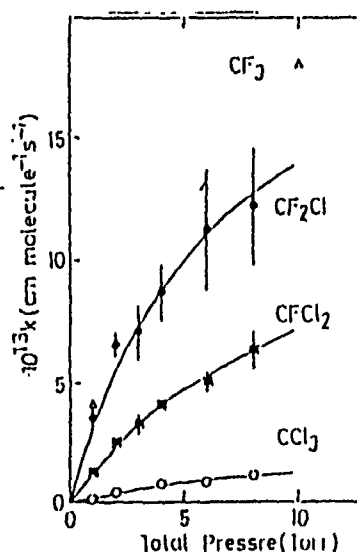
Fig. 1. Pressure dependence of k_1

VI- INSTRUMENTATION
AND
NEW TECHNIQUES
IN PHOTOCHEMISTRY

PHOTOISOMERIZATION OF STILBENE AND AZOBENZENE DERIVATIVES
IN POLYMER FILMS : INFLUENCE ON SECOND HARMONIC GENERATION.

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Stilbene and azobenzene-like molecules are well known for two completely different properties:

1. In photochemistry, there is a E-Z photoisomerization reaction, which can be followed by a thermal Z-E back-reaction in the case of azobenzene and azobenzene-like molecules.

2. In non-linear optics, when substituted by electron-donating and electron-attracting groups, the same molecules possess high non linear second-order hyperpolarisability (β coefficient). When they are arranged in a non-centrosymmetric structure (crystal or doped polymer film oriented under an electric field), this non linear property leads to the generation of the second harmonics (SHG) of a laser frequency.

The objective of our work is to connect these two properties, i.e. to measure the change in β during and after photoisomerization of the molecules by a UV beam. In order to do that, we describe an experimental set-up which allows SHG of the fundamental of a Nd-YAG laser by a polymer film and on the same time UV irradiation by either a continuous beam of UV light (xenon arc) or a UV laser flash (third harmonics of the same Nd-YAG laser). SHG is generated in polymer films doped with the active molecules (N,N-diméthyl amino nitro stilbene DANS or N -hydroxyethyl N-ethyl amino nitro azobenzene Disperse Red 1) and oriented under an applied electric field of 1 MV/cm. SHG intensity is measured and related to the second order susceptibility of the sample, which is proportionnal to N< β >, where N is the number of chromophores per unit volume and < β > is the mean second-order hyperpolarizability taking all orientations into account.

The Z forms of the above molecules are shown to have a lower β value, thus the SHG intensity is lowered after E-->Z photoisomerization. Based on this change, a pump-probe technique can be applied to monitor the fast kinetics of the reaction on a picosecond time scale: the pump signal is the third harmonics of the Nd-YAG laser (353 nm) and the probe signal is the second harmonics generated by our sample from the fundamental (1060 nm). The first transient studies will be described and discussed.

NEW ADVENT IN PHOTOCHEMISTRY: ATOMIC FORCE MICROSCOPY

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Solid state photolysis is a major part in preparative organic photochemistry. In many cases topochemical criteria apply, but there are important exceptions which require an advancement of the theory.

While crystallographic data are numerous·and polar effects are highly predictive, the problem of new solid phase formation has not been solved to a considerable extent yet. With the very recent availability of atomic force microscopy (AFM) solid state reactions may be studied by looking at the crystal surfaces during irradiation. The prospects of such studies will be discussed in terms of perspective computer drawings.

Our colour slides show, that unexpectedly there are enormous material transport phenomena on the surfaces which are usually depending on the chosen face of the crystal, in many cases. The transport may be random, or proceeding zonally across the surface. The roughness of the surface may be increased or smoothened. It will be shown, how these observations relate to the type of the abovementioned topochemical criteria and it will be essential to develop novel theories for the process of new solid phase formation. These theories must, at present, rely solely on our unprecedented observations, in the absense of any further methods of investigation.

We will deal with α- and β-trans-cinnamic acid, with selected benzylidene derivatives, styrenes, stilbenes, anthracenes as well as with unprecedented gas/solid-photoreactions.

It will become apparent, that AFM will be of similar importance for predictive purposes in organic solid state photochemistry as is X-ray analyses by now and that AFM is the tool for the attack of the problem of new-phase formations.

LASER SPECTROSCOPY AND ABLATION OF AN OPTICALLY-TRAPPED MICROCAPSULE

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We have demonstrated that laser trapping-spectroscopy-ablation technique is a potential means for manipulation, spectroscopic characterization, and microfabrication of small particles in Brownian motion[1]. The work is now extended to laser spectroscopy-ablation of an individual microcapsule.

A single melamine-resin microcapsule containing pyrene ($\sim 1 \times 10^{-2}$ M) in toluene was shown to be manipulated three-dimensionally by a focused (~ 1 µm) laser beam from a CW Nd:YAG laser (1064 nm, ~ 70 mW) under an optical microscope. Fluorescence spectroscopy of an optically-trapped microcapsule dispersed in water can be also attained by introducing an excitation laser pulse (355 nm, ~ 7 ns, 0.39 J/pulse/cm^2) into the sample solution. The pyrene excimer formation dynamics in each capsule was well explained based on Birks kinetic model while the decay and rise/decay profiles of the monomer and excimer fluorescence, respectively, were different with the capsules due to concentration distributions of pyrene between the capsules.

At the pulsed laser energy above 40 J/pulse/cm^2, laser ablation of an optically-trapped microcapsule was observed, as proved by ejection of small pyrene/toluene droplets from the capsule into the bulk water phase. The pyrene/toluene droplets ejected from the capsule upon ablation was also freely manipulated by the 1064 nm laser beam. Characteristic features of laser trapping-spectroscopy-ablation of an individual microcapsule will be discussed in detail.

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FLUORESCENCE DYNAMIC ANISOTROPY OF AN OPTICALLY-TRAPPED MICROPARTICLE

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We recently developed μm~subμm space- and ps time-resolved fluorescence spectroscopy based on a confocal laser scanning microscope and ps time-correlated single photon counting technique[1]. The system was combined with laser trapping technique to study photochemical and photophysical dynamics in individual microparticles in Brownian motion[2]. In order to study further the dynamic processes occurring in small volumes, we developed a new method for analyzing fluorescence anisotropy under a microscope.

The conventional method is not applicable to anisotropy measurements under a microscope, since the excitation laser light is not a plane wave and fluorescence from a sample is collected in a large solid angle. We therefore derived a practical theory based on a vectorial point spread function for microscope system. The system parameters, which are used for calculating precise anisotropy decays, as well as rotational relaxation time and initial anisotropy were evaluated theoretically and experimentally. The method was applied to determine the rotational relaxation time of a dye in an optically-trapped microparticle and, therefore, to estimate the local viscosity in the particle.

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OPTICAL MANIPULATION AND PHOTOCHEMICAL FIXATION OF POLYMER LATEX PARTICLES

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A single micrometer-order particle dispersed in solution is freely tweezered by a focused laser beam. Now we report a new technique of simultaneous laser trapping of plural small particles along any geometrical pattern in solution.

Figure 1 shows spatially-patterned laser trapping of polystyrene (1 μm) latex particles in water. Upon irradiation of a 1064 nm laser beam, latex particles were trapped in the high laser intensity regions of the interference pattern. When the trapping laser beam (focused ~1 μm) is repetitionary scanned along a geometrical pattern, the particles are aligned along the pattern as typically shown in Fig. 2. Depending on the repetition rate of the laser beam, furthermore, control flow of the particles (i.e., clockwise, counterclockwise, directional flow, etc) was attained. Fixation of the spatial pattern was also successful by in situ photopolymerization of the sample solution.
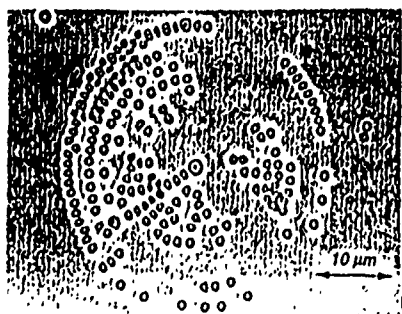
Figure 1
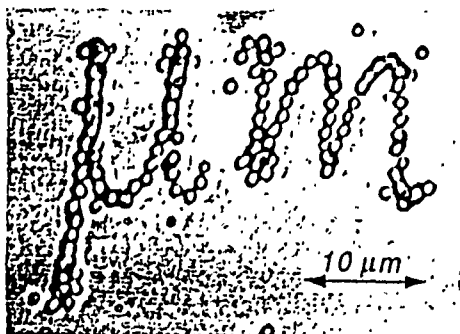
Figure 2

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VII- APPLICATIONS OF PHOTOCHEMISTRY

METAL-LOADED TiO$_2$ PHOTOCATALYZED REDUCTION OF CO$_2$ TO HYDROCARBONES

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TiO$_2$-photocatalytic reduction of CO$_2$ with water have been investigated by using a gas-circulation-type irradiation apparatus.

TiO$_2$ or M-TiO$_2$ (150 mg) dispersed in 1.5 ml water was introduced into a quartz cell. After three freeze-pump-fusion cycles, 650 Torr CO$_2$ was admitted into the cell and the solution was irradiated at >310 nm with circulation of CO$_2$ by a glass pump.

By using TiO$_2$ as photocatalyst, methane was produced as main product (Figure) with ethane, while little amounts of formic acid, formaldehyde, and methanol were detected after 5h irradiation. Pd and Rh deposition onto TiO$_2$ accelerated photo-catalyzed-methane formation, especially Pd-TiO$_2$ showed more than ten times higher activity than TiO$_2$. However deposition of Ru or Pt did not enhance methane formation. After 5h irradiation, acetic acid was detected only for Rh-TiO$_2$ and Ru-TiO$_2$ as photocatalyst but little amounts of formic acid, formaldehyde, and methanol were detected by using any M-TiO$_2$.
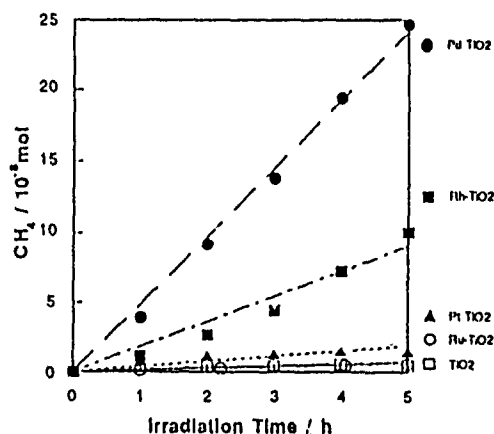
Figure   Effects of loaded metals on the formation of CH$_4$ by the TiO$_2$-photocatalyzed reduction of CO$_2$

NaOH-ETCHING ADVANTAGE OF n-Si PHOTOANODES

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Photoelectrochemical cells(PECs),composed of different epi-
taxial n-Si photoanodes coated with evaporated metal film of Ni
Pt,Ni/Pt and immersed in solution with redox couple Br_2/Br^- or
$Fe(CN)_6^{3-/4-}$ were investigated. The effect of Pt/Ni or Ni/Pt dual
film annealed at $450^\circ C$ on the surface of n/n^+-Si and p/n^+-Si is
of advantage, leading to an increase of the open-circuit photo-
voltage and of the photoanodes stability./1/ A much higher con-
version efficiency of optical to electrical energy could be
achieved if the p/n^+-Si wafer with (111) orientation is etched
in aqueous 48% HF solution for 10 min. In the case of n/n^+-Si,
the efficiency of cell composed of which, is lower, and may be
due to having different junction. The V_{oc}- value for $Pt/p/n^+$-Si
and $Pt/n/n^+$-Si photoanodes are essentially independent of the
electrolyte redox potential. An occurence of Fermi-level pin-
ning at surface implies that surface states with a high density
still exist in spite of surface modifications. In order to im-
prove the performance parameters of PECs above, attempts were
made to modify the photoanode surface by using various etching
methods more recently./2/ Some interesting results has been
found. The wafers were etched in concentrated NaOH solution,in-
stead of in 48% HF, at $95^\circ C$ for 5-10 min. The advantage of n-Si
photoanodes by hot-NaOH-etching were observed, for instance,
 - Open circuit photovoltages as functions of potential of redox
couples for various electrolytes are shown;
 - The efficiency of cell composed of n/n^+-Si is also enhanced.

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FORMATION AND PROPERTIES OF ULTRAFINE IRON PARTICLES USING A TEA CO$_2$ LASER

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We have found that γ-iron ultrafine particles are snthesized by the SF$_6$-sensitized infrared photodecomposition of Fe(CO)$_5$ with a TEA CO$_2$ laser.[1] γ-iron pepared is found to be well organized spherical ultrafine particles with a diameter $\langle$10nm (6.6 to 8.0nm, 7.6nm in average), face-centered-cubic structure, and paramagnetic at 4.2-300K.   We report formation and properties of ultrafine iron particles prepared by decomposition of Fe(CO)$_5$ by an SF$_6$-photosensitized method and a dielectric breakdown method in the absence of SF6 using a TEA CO$_2$ laser in this paper. The properties are investigated by transmission electron micrography, temperature-dependent X-ray diffraction, temperature-dependent saturation magnetization, and Mössbauer spectroscopy.

Iron particeels obtained are mixtures of γ-iron, α-iron, and iron oxides. The ratios of γ-iron:α-iron:iron oxides= 74:14:11 and 45:45:10 for the SF$_6$-photosensitized method and a dielectric breakdown method, respectively.   Therefore, the SF$_6$-photosensitized method is found to be superior with respect to synthesis of ultrafine γ-iron particles in high yield. The ratio of γ-iron to α-iron changes with changing the irradiation conditions such as pressures and laser fluences in the SF$_6$-photosensitized method. The ratio $\rangle$95% was obtained under the appropriate conditions. It should be noted that FeF$_2$ ultrafine particles ($\langle$10nm) are obtained mainly at high pressure of SF$_6$ and high laser fluence.[2]

Ball-shape γ-iron particles have 3-5nm diameters composed of 2-3nm center and 1-2nm surface layer. γ-iron begins to transfer into α-iron above 200℃, and nearly quantitatively into α-iron at 380-400℃. Saturation magnetization of γ-iron increases below 400℃, and then decreases on heating to 595 ℃.   After γ-iron becomes to be paramagnetic at around 595℃, γ-iron changes to be ferromagnetic on cooling to room temperature.

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VISIBLE LASER LIGHTS INDUCED POLYMERIZATION REACTIONS

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The efficiency of thioxanthones and ketocoumarins as photoinitiators has been checked in visible laser light induced polymerization reactions, and discussed in terms of excited state reactivity (as revealed by time resolved laser spectroscopy). These compounds undergo fast electron transfer reactions in the presence of amines and onium salts. Transient absorption spectra and rate constants of the processes involved have been determined. The combination photoinitiator - amine - onium salt appears as very promising for the design of efficient photosensitive systems.

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NEW SUPERSTABLE MOLECULES
FOR LIGHT-INDUCED ELECTRON-TRANSFER

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A new type of Ruthenium-Sensitizers[1] on the basis of coronates
was synthesized.
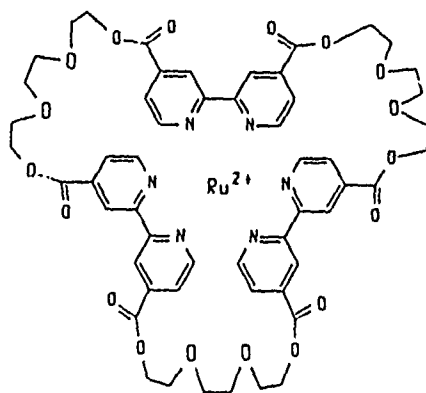
Photophysical and electrochemical properties were investigated.
The coronates show extremely high photostability[2] compared to
Ruthenium-tris(bipyridyl).

The complexes were used as sensitizers in sacrificial water
reducing systems.

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OPTICAL INFORMATION PROCESSING WITH BACTERIORHODOPSIN AND ITS
GENETICALLY MODIFIED VARIANTS

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Optical data processing is a fast expanding area, allowing
massive parallel processing on the basis of nonlinear optical and
holographic methods. Photodynamical systems play an important
part as promissing materials. It will be shown that the photocyc-
le of the biological photochrome bacteriorhodopsin (BR) can be
used advantageously for optical data processing and transient
storage. For this purpose the properties of BR are further
optimized by genetic engineering, opening a new way in material
science. Transient holographic techniques, optical phase
conjugation, dynamic optical filtering and optical pattern
recognition will be demonstrated with BR as molecular processing
system.

TIME RESOLVED REFLECTIVITY AS A PROBE OF THE DYNAMICS

OF LASER ABLATION OF ORGANIC POLYMERS

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The interaction of KrF excimer laser pulses with
polyimide, poly(ethylene terephthalate), polystyrene,
poly(methyl methacrylate), and polyethylene has been studied
by time resolved reflectivity. The width, fluence, and peak
intensity of a KrF (248 nm) laser pulse reflected from the
polymer surface was determined over a large range of incident
laser fluences, 1 - 3000 mJ/cm^2. The reflected pulse was
truncated once the incident fluence exceeded a critical value
(threshold), characteristic for each polymer. Above the
threshold the pulse decayed exponentially with time constants
ranging from 2 to 6 ns. The threshold fluences for pulse
truncation were usually somewhat lower than the ablation
thresholds measured photoacoustically. The results are
interpreted in terms of time dependent absorption and
scattering from particles emerging from the surface during
ablation. Our analysis suggests that, during ablation with
ns wide laser pulses, large particles are ejected initially
which are continuously reduced in size during the laser
pulse.

PHOTOCHEMICAL PROTON-TRANSFER LASERS

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In a photochemical laser the lasing particle is formed as a result of the photochemical adiabatic reaction. In present communication the general principles for the photochemical lasers creation have been considered. The photochemical proton-transfer lasers have been discussed in details. The criteria for acid-base system selection of active media for proton-transfer lasers have been stated.

The regularities of lasing of proton-transfer reaction products of oxy-, oxo-, amino- and azaaromatic compounds have been analyzed. The mutual negative influence of conjugated acid-base equilibrium components of azaaromatic compounds on their lasing effect has been detected. It results in the impossibility of simultaneous lasing of conjugated acid-base forms of azaaromatic compounds.

The important role of short-lived intermediates formed in photochemical electron-transfer reactions in laser active media has been shown. The active media photostability of proton-transfer lasers and the effect of medium acidity and basicity on the active solutions degradation have been considered. Some additions to active media to increase the photostability and efficiency of active media have been suggested.

The acid-base systems provided the wide tuning range have been analyzed. Some recommendations to purposeful synthesis of organic compounds for active media of photochemical proton-transfer lasers have been given. New approach for the photochemical lasers creation to get a wide tuning range has been proposed. The experimental results on the photochemical proton-transfer lasers efficiency have been given.

COMPORTEMENT PHOTOCHIMIQUE DU BOIS EXPOSE A UNE LUMIERE DU TYPE SOLAIRE : ASPECTS MOLECULAIRES

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L'étude du comportement photochimique à la lumière solaire du bois (*Abies grandis* et *Quercus robur*) nous a permis de mettre en évidence le rôle principal des lignines et des substances extractibles dans les différentes réactions induisant des modifications de couleurs de ce matériau. En s'appuyant sur les résultats obtenus sur le comportement photochimique des lignines soit directement, soit à l'aide de molécules modèles, nous avons pu montrer que, quelque soit le chromophore concerné, qu'il provienne des lignines ou des substances extractibles, les photoproduits formés ont pour origine exclusivement un radical phenoxy dont la cinétique d'apparition et la stabilité ont pu être suivies par résonance paramagnétique électronique.

Cette étude mécanistique nous permet de connaître a priori quelles sont les étapes réactionnelles qu'il faudra défavoriser pour assurer la stabilité de la couleur d'un bois exposé au rayonnement solaire.

PHOTOCHEMICAL BEHAVIOUR OF WOOD IRRADIATED WITH A SOLAR-TYPE LIGHT : MOLECULAR ASPECTS

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We have followed the photodegradation of Fir (*Abies grandis*) and of european Oaks when they are irradiated with a solar-type light. This study has shown that the main components related to the photochemical reactions leading to color changes of wood, were lignins and extractives.

Experiments carried directly on lignin or on model compounds showed that, wherever the involved chromophore came from (lignin or extractives), the photoproducts were originating exclusively from a phenoxy radical.

The kinetics of appearance and the stability of this radical have been followed by electron spin resonance.

This study about the photochemical mecanism of photodegradation of wood, allows to know which are the different steps we have to inhibit, in order to insure the stability of the color of wood exposed to solar light.

SYNTHESES DE POUDRES NANOMETRIQUES A BASE DE SILICIUM PAR REACTIONS INDUITES PAR LASER

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Des poudres nanométriques ont été préparées à partir de réactants gazeux chauffés par la radiation IR d'un laser CO_2 continu de puissance. Avec SiH_4 comme absorbant, des poudres de Si, SiC [1], Si_3N_4 et de composites Si/C/N [2] ont été formées respectivement a partir de SiH_4, de mélanges SiH_4-hydrocarbures, SiH_4 - NH_3 et SiH_4 - CH_3NH_2 - NH_3. Le mélange gazeux croise orthogonalement le faisceau laser dans un réacteur à flux croisés sans effet de parois. Les réactions se produisent en des temps très courts (1-10 ms) à haute température (jusqu'à 1800°C) et avec formation de flamme. En changeant les conditions de réactions (débits et rapport des réactants, puissance laser et enthalpies des réactions) des poudres amorphes ou cristallines à composition chimique et taille variables sont obtenues. Dans le cas de la synthèse de SiC à partir de mélanges $SiH_4 - C_2H_2$, des taux de production supérieurs à 100 g/h sont obtenues à l'échelle laboratoire avec de hauts rendements (> 95 %). Des méthodes classiques sont utilisées pour la caractérisation des poudres : spectroscopie IR, diffraction des rayons X, microscopie électronique, méthode BET (détermination des surfaces spécifiques) et analyse chimique. Mais des méthodes plus sophistiquées comme l'ESCA, l'EXAFS, ... sont mises en oeuvre actuellement.

La densification de SiC à 97 % de la densité théorique est atteinte par frittage naturel à 2050°C sous courant d'argon avec une vitesse de montée en température de 10°C/min. Les pièces densifiées présentent des propriétés thermomécaniques améliorées[3].

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SYNTHESES OF NANOSCALE SI-BASED POWDERS BY LASER DRIVEN REACTIONS

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Ultrafine powders in the nanometric range were synthesized from gaseous reactants heated with the IR radiation of a high power continuous wave CO_2 laser. With SiH_4 as absorbant reagent, Si, SiC[1], Si_3N_4 and Si/C/N composites[2] powders were formed from neat SiH_4, SiH_4-hydrocarbon mixtures, SiH_4-NH_3 mixtures and SiH_4 - CH_3 NH_2-NH_3 mixtures respectively. In a crossflow configuration cell the gaseous phase intersects orthogonally the laser beam without wall effects. Reactions occur in very short times (1-10 ms) at high temperature with flame (up to 1800°C). By changing the reaction conditions (flow rates and ratios of the reacting gases, laser power and reaction enthalpy) amorphous to crystalline powders with variable size and chemical composition are formed. In the case of SiC synthesis from SiH_4-C_2H_2 mixtures, production rate up to 100 g/h is obtained at laboratory scale with high yield (> 95 %). Conventional methods are used for the characterization : IR spectroscopy, X-ray diffraction, electronic microscopy, BET method (specific surface area determination) and chemical analysis. But more sophisticated methods like ESCA, EXAFS, ... are in progress.

Densification of SiC at 97 % of the theoretical density is reached by pressureless sintering at 2050°C under flowing argon at 10°C/min heating rate. Improved thermomechanical properties are obtained in the densified parts[3].

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DETECTION OF NO IN THE POST-DISCHARGE OF

A N2/O2 MICROWAVE PLASMA USING AN ARF LASER

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ArF Laser Induced Fluorescence (LIF) spectroscopy was applied
to the investigation of the vibrationnal temperature and
density of NO achieved in the post-discharge of a N_2-O_2
microwave plasma induced at 2450MHz in low pressure conditions
(P = 10mbar).
The light from a broad band excimer laser (193nm) excites NO
molecules in the axis of the discharge tube and the dispersed
fluorescence of NO was detected at right angle of the laser
beam as the distance d between the observation point and the
resonant cavity was varied.
The relative intensity of emission bands from $NO(D, v'=0)$ and
$NO(A, v'=3)$ provides an estimation of the relative population
$N_{v=1}/N_{v=0}$ of vibrationnaly excited ground state molecules and
then the NO vibrationnal temperature can be determined along
the post-discharge (Fig 1).
A calibration curve of the $NO(A, v'=0)$ fluorescence signal
versus known concentrations of NO in flowing mixtures $N_2/O_2/NO$
was performed to determine density of $NO(X, v''=0)$ along the
post-discharge in low temperature region :it ranges from 10^{14}
to 10^{14} molec.cm-3.

Fig 1: Post-discharge of an air plasma

	d(mm)	T(°K)
——	10	400
^-^	20	350
•-•	30	320
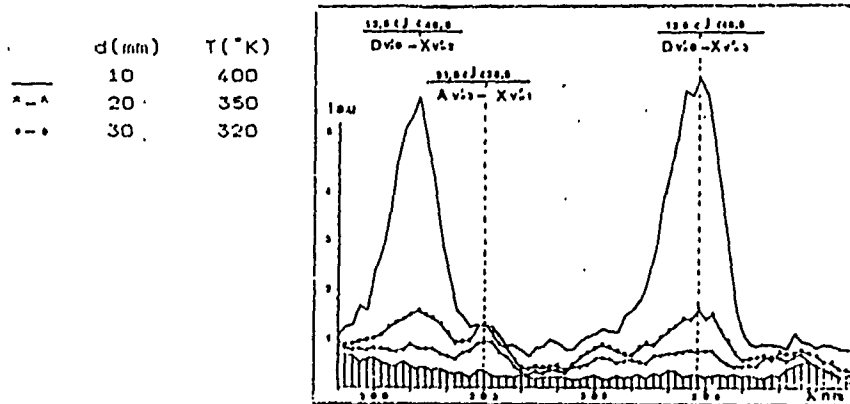
PHOTOELECTROPHYSICAL AND SPECTRAL CHARACTERISTICS OF SOLID-
STATE LIGHT ENERGY CONVERTERS BASED ON AN INORGANIC SEMICON-
DUCTOR-ELECTRICALLY CONDUCTIVE POLYMER STRUCTURE

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New solid-state converters of luminous to electrical ener-
gy based on an inorganic semiconductor-organic electrically
conductive polymer sandwich structure were suggested and con-
figured. The effect the nature of the inorganic semiconductor
and the organic polymer film had on the photo-emf and the
short-circuit current of cells was elucidated. Some insight
into the current-voltage characteristics of CdTe/polymer/Au
and Si/polymer/Au devices in the dark and under illumination
was provided and magnitude of the photo-emf and the short-
circuit current ascertained as influenced by incident light
intensity, illumination time and shelf life.

With increasing incident light intensity the photo-emf of
CdTe(polymer)Au and Si(polymer)Au cells was found to rise at
low intensities and then attain saturation as the incident
light intensity further enhanced. In contrast, the cells' pho-
tocurrent showed linear dependence on the incident light in-
tensity. The converters developed were demonstrated to be
photosensitive in the UV, visible and near IR spectral regi-
on. This made one believe that the devices proposed might
find application as photosensitive transducers for a wide
spectral range. The converters' major parameters - photo-emf,
short-circuit current, fill factor and efficiency - were de-
termined and their fabrication conditions optimized. The pho-
toconverter based on the polycrystalline cadmium telluride
and electrically conductive organic polymer has the following
specifications: photo-emf: 0.4V; short-circuit current:
2.4 mA/cm^2; fill factor: 0.5; efficiency: 3.2%; spectral pho-
tosensitivity range: 260-380 nm, extending also into the ne-
ar IR.

THE CREATION OF THE DATABASE ON PHOTOCHEMISTRY AND LUMINESCENCE

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On the base of the author's monograph[1] the database is beeing created at Weizmann Institute of Science to collect and to classify all available data on photochemistry and luminescence aromatic compounds. The compounds are classified by both spectral-luminescent (extinction coefficients, energies and lifetimes of lower excited states, quantum yields of luminescence in various solvents) and photochemical properties. The diverse variety of photochemical reactions of aromatics is considered   assuming the existence of 8 types of elementary photochemical processes: monomolecular (a)photodissociation, b)cis-trans and c)valence photoisomerization) and bimolecular (d)electron, e)proton and f)hydrogen atom transfer and g)perycyclic and h)photosubstitution reactions) Aromatic compounds are grouped roughly into 8 classes (initial aromatic hydrocarbons and their alkyl derivatives; hydrocarbons with a chain structure; amines, oxy-, nitro- carbonyl- , halogen-- and cyano-derivatives), and the possibility of occurrence of all types of elementary photoprocesses is analyzed.

The database is convenient for establishment of spectral, luminescent and photochemical properties (possibility of occurrence and efficiency) of all aromatics studied so far. Two examples for the data representation are given below.

Luminescence Parameters

Compound; Solvent; ϕ_{Fl}; τ_{Fl} ;τ_{FM} ;ϕ_T ;τ_T; E(S); E(T) ; ϕ_{Ph} ; τ_{Ph} ; References

ϕ_{Fl} and τ_{Fl} are quantum yield and life-time of fluorescence; τ_{FM} natural (calculated) life-time of fluorescence; ϕ_T and τ_T are quantum yield and life-time of triplet state; E(S) and E(T) are the energies of S_1 and T_1 states; ϕ_{Ph} and τ_{Ph} are quantum yield and life-time of phosphorescence;

Photochemical Properties

Compound;   Solvent; Reagent ; Type; Products; λ_{ex} ;ϕ; (C); References

Type (see a-h); ϕ quantum yield of product formation by concentration of reagent (if any) C at excitation λ_{ex}

The author inquires all the photochemists to take part in the data collection and to send their data to the address above

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        Compounds, CRC, Boca Raton, 1991

Progress on Sacrificial Photoinduced Hydrogen Production

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Sacrificial hydrogen production is of great interest for the storage of solar energy, if the sacrificial agent is cheap. Two different systems were studied for sacrificial hydrogen production using glucose and isopropanol as sacrificial electron donors in the presence or absence of sensitizers. When solutions containing 1,1'',1'''-trimethyl [4,2';4',4'';6',4''']quaterpyridinium trichloride (1), or 1,1'',1'''-triethyl[4,2';4',4'';6',4'''] quaterpyridinium trichloride (2), or 1,1'',1'''-tripropyl[4,2';4',4'';6',4''']quaterpyridinium trichloride (3), or 1,1'',1'''-tribenzyl[4,2';4',4'';6',4''']quaterpyridinium trichloride (4), a colloidal redox catalyst (platinum, palladium), acetate buffer, and glucose were irradiated with light (λ > 280 nm) hydrogen was detected in the gas phase. In this reaction, compounds 1 - 4 are able to combine the features of a sensitizer and an electron relay and are therefore called relay-sensitizers. The UV-VIS spectroscopy of irradiated solutions showed the formation of reduced radicals of compounds 1 - 4 (λ_{MAX} at 580 and 630 nm). Quantum yields for hydrogen production were found to be in the range of 10 % (calculated for absorbed light). In contrast, irradiation of solutions containing methyl viologen instead of compounds 1 - 4 did not lead to the formation of hydrogen even in the presence of $Ru(bipy)_3Cl_2$ or proflavine as additional sensitizer. The reaction mechanism of photoinduced hydrogen production will be discussed in detail. The electron transfer from the sacrificial electron donor (glucose or iso-propanol) to the excited relay-sensitizer (1) - (4) is postulated as a first step. Redox potentials of excited states were estimated by using zero-zero transition energies (calculated from fluorescence data) and redox potentials of ground states (measured by cyclic voltammetry); e.g. for compound 1, $E^*_{R\cdot/R\cdot}$ = 2.87 V.

Since compounds 1 - 4 have only weak absorbances in the visible light region (e.g. for 1, λ_{MAX} = 450 nm, ϵ = 12 l mol^{-1} cm^{-1}), derivatives of fluorenone (10H-6,7,8,9-tetrahydro(1)benzothieno(2,3-b)pyrrolizin-10-one(S1),8H-6-phenylthieno(2,3-b)pyrrolizin-8-one (S2), 8H-methylthieno(2,3-b)pyrrolizin-8-one (S3), 8H-6-methyl-7-phenyl-thieno(2,3-b)-pyrrolizin-8-one (S4)) were developed and shown to possess stronger absorbances in the visible region (e.g. for S1, λ_{MAX} = 458 nm, ϵ = 460 l mol^{-1} cm^{-1}). Compounds S1 - S4 were able to act as sensitizers for sacrificial hydrogen production in addition to fluorenone and benzophenone : irradiation of solutions containing S1 - S4, isopropanol (or glucose) and colloidal platinum catalyst with light (λ > 280 nm) gives small amounts of hydrogen in the gas phase. Addition of methyl viologen to such solutions increases the quantum yields. The fluorescence and absorption behaviour of compounds S1 - S4 were dependent on solvent and pH.

PHOTOCHEMICAL ENGINEERING
AND SUPERCRITICAL FLUIDS

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Photochemical and photophysical phenomena in supercritical fluids are still relatively unexplored. And yet the numerous advantages described when it is used as solvent make it attractive for studies in this field.

The use of supercritical fluids, such as liquid carbon dioxide and the development of new photoreactors adapted to high pressure, were first applied to the study of the photoisomerization of hop α acids (humulone) into iso-α acids (trans iso-humulone) [1], the compounds mainly responsible for the bitterness of beer. This research was done with the main objective to use liquid CO_2 hop extracts, with in mind the food industry requirements by avoiding use of organic solvents. Moreover, the use of CO_2 increases the photoisomerization rate, thanks to the low viscosity of liquid CO_2; this is in agreement with the observation that the photoisomerization of humulone is viscosity dependent [2].

Secondly, we have considered two other photochemical reactions involving double bond isomerizations, with the use of liquid CO_2 as solvent [3].

* The photochemical production of previtamins D, precursors of vitamins D, by B-ring opening of particular steroids (photoisomerization of a cyclohexatriene into a triene) : during this study, it was shown that ergosterol was slightly soluble in CO_2 and even if the reactivity of ergosterol is much greater in CO_2 than in ether, the mass balance of reaction products is in counterpart lower.

* The trans-cis photoisomerization of α-ionon : the photoreaction carried out in liquid CO_2 compares very well with the one done in ethanol.

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PHOTOCYCLIZATION IN SYNTHESIS OF

CATHARANTHINE AND ITS DERIVATIVES

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Vinblastine type antitumor diindole alkaloids can be
obtained starting from catharanthine $\underline{2d}$. In course of our
synthesis of catharanthine and its derivatives the various
substituted ibogane skeletons ($\underline{2a}$-$\underline{c}$) have been developed from
$\underline{1a}$-$\underline{c}$ by photochemical ring closure[1,2]. Depending on the
position of the ethyl substituent and the reaction conditions
different types of rearranged byproducts were obtained /$\underline{3}$-$\underline{8}$/
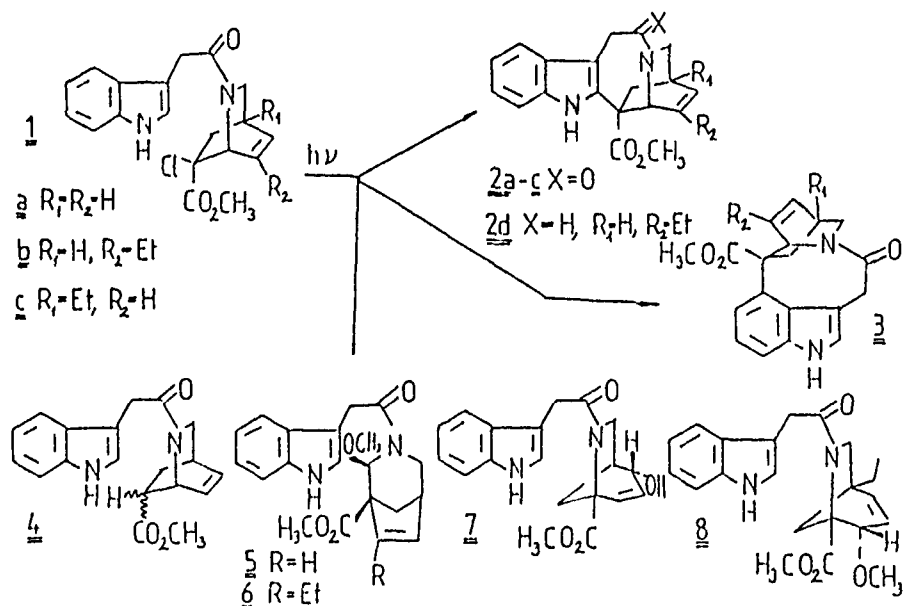
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