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Final Grant Report 1984-1987

AFOSR-84-0013

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Title: Picosecond Laser Studies of Excited State Processes

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REPORT DOCUMENTATION PAGE

1a. REPORT SECURITY CLASSIFICATION Unclassified		1b. RESTRICTIVE MARKINGS	
2a. SECURITY CLASSIFICATION AUTHORITY		3. DISTRIBUTION/AVAILABILITY OF REPORT Approved for public release; Distribution unlimited	
2b. DECLASSIFICATION/DOWNGRADING SCHEDULE			
4. PERFORMING ORGANIZATION REPORT NUMBER(S)		5. MONITORING ORGANIZATION REPORT NUMBER(S) AFOSR-TR- 88-0283	
6a. NAME OF PERFORMING ORGANIZATION Department of Chemistry Columbia University	6b. OFFICE SYMBOL <i>(if applicable)</i>	7a. NAME OF MONITORING ORGANIZATION Air Force Office of Scientific Research	
6c. ADDRESS (City, State and ZIP Code) New York, N. Y. 10027		7b. ADDRESS (City, State and ZIP Code) Bldg #410 Bolling AFB, DC 20332	
8a. NAME OF FUNDING/SPONSORING ORGANIZATION Air Force Office of Sci. Res.	8b. OFFICE SYMBOL <i>(if applicable)</i> NC	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER AFOSR-84-0013	
6c. ADDRESS (City, State and ZIP Code) Bldg. 410 Bolling AFB, DC 20332-6448		10. SOURCE OF FUNDING NOS.	
11. TITLE <i>Include Security Classification</i> Picosecond Laser Studies of Excited		PROGRAM ELEMENT NO. 61102F	PROJECT NO. 2303
12. PERSONAL AUTHOR(S) Kenneth B. Eisenthal		TASK NO. B2	WORK UNIT NO.
13a. TYPE OF REPORT scientific	13b. TIME COVERED FROM 10/1/84 to 9/30/87	14. DATE OF REPORT (Yr., Mo., Day)	
15. SUPPLEMENTARY NOTATION			
17. COSATI CODES		18. SUBJECT TERMS <i>(Continue on reverse if necessary and identify by block number)</i>	
FIELD	GROUP	SUB. GR	
19. ABSTRACT <i>Continue on reverse if necessary and identify by block number</i> The completed research was directed at fundamental investigations of ultra fast chemical reactions, the generation and decay of reactive chemical intermediates, as well as the role of the solvent and molecular motions on chemical dynamics. The construction of an amplified CPM laser enabled the opportunity to probe chemical events occurring in the femtosecond time domain. The effects of molecular geometry, solvent and solute steric effects, on the chemical dynamics was explored. An important new component of the research was the studies of chemical phenomena on surfaces as well as in bulk media. The asymmetry of forces associated with liquid surfaces was found to impose new restraints and possibilities on the generation of chemical species; thus affecting the chemical species lifetimes, motions and pathways for reaction.			
20. DISTRIBUTION/AVAILABILITY OF ABSTRACT UNCLASSIFIED/UNLIMITED <input checked="" type="checkbox"/> SAME AS RPT <input type="checkbox"/> DTIC USERS <input type="checkbox"/>		21. ABSTRACT SECURITY CLASSIFICATION Unclassified, unlimited	
22a. NAME OF RESPONSIBLE INDIVIDUAL Dr. Anthony Matuszko		22b. TELEPHONE NUMBER <i>(Include Area Code)</i> (201) 767-4963	22c. OFFICE SYMBOL NC

AFOSR-84-0013
Picosecond Laser Studies of Excited State Processes

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1. Summary

A procedure was developed for measurement of the absolute phase of the second harmonic electric field with respect to the pump radiation, and also developed a scheme for inferring the absolute orientation of molecules at an interface with respect to the directed surface normal. This new information about the sense of molecular orientation, which cannot be obtained directly from conventional linear optical spectroscopy, should help to provide insight into the basic chemical interactions at surfaces and interfaces. The principle of the method can be understood simply and was applied to aqueous phenol solutions.

The question of how the asymmetry in the forces experienced by the molecules in the interfacial region affects simple chemical equilibria was examined. Specifically, using the technique of second harmonic generation we investigated the acid-base equilibrium between p-nitrophenol (HA) and its conjugate anion (A^-). Not only do the concentrations of the various species in the interfacial region differ from their bulk values, but also the relative concentrations do not correspond to the bulk equilibrium constant. The "equilibrium constant" in the surface region was shown to be vastly different from that in the bulk.

The rates of optically induced conformational changes of nonpolar excited state 1,1'-binaphthyl in both alcohol and alkane solvents were measured by a picosecond laser technique. Excellent agreement with experiment is found for the Kramers model for the intermediate friction regime when using the solute orientational relaxation time as a measure of solvent friction.

Solute/solvent interactions were investigated in polar solvents by using dynamical photoemission methods to follow the photoisomerization of polar probe molecules in a solvent series, in polar solvent/alkane mixtures and in a single solvent as a function of temperature. Variation of the photoisomerization rate of p-N,N-dimethylaminobenzonitrile (DMABN) was attributed chiefly to static solvent polarity effects rather than to what was previously believed to be the cause, dynamic

frictional effects due to high solvent viscosities. These results were compared to data obtained for the photoisomerization of *t*-stilbene in alcohols, where it was found that the usual functional forms of solvent viscosity dependence also failed to account completely for the observed solvent dependence of the rate. Implications of all of these findings regarding the use of one-dimensional barrier crossing theories to describe photoisomerization in solution were discussed.

The selective solvation of twisted internal charge transfer by DMABN was examined. To this end a study was made of gas phase DMABN both in a supersonic jet expansion and in a thermalized vapor. It was found that 1:1 complexes are not sufficient for the local perturbation to cause charge separation. At higher temperatures in the jet, emission was found that was attributed to DMABN self-complexes. Under high pressure and temperature vapor conditions (> 30 mTorr, 60°C), red shifted fluorescence from DMABN was observed. This was attributed to the charge transfer state of DMABN in self-complexes.

An inverse deuterium isotope effect on intersystem crossing for the chemical intermediate diphenylcarbene was observed for the first time. This observation provided important insight into the nature of this radiationless transition. It was also found that by changing the structure of the carbene the energy splitting (ΔE_{ST}) can be varied from 300 cm^{-1} to greater than 3000 cm^{-1} . The ability to select the energy gap of the carbene allowed us to identify two limiting energy regimes which define the carbene intersystem dynamics. We have also investigated the photophysics of a substituted oxirane as a precursor to carbenes. A 1,3-biradical, possessing singlet state multiplicity, is found to be an intermediate to carbene formation, in the photodecomposition of the oxirane.

Lastly, a femtosecond laser, based on the colliding pulse modelocked ring dye laser (CPM) design was constructed. The output of the CPM laser was amplified to levels whereby femtosecond time resolved experiments were feasible.

2. Studies of Liquid Surfaces by Second Harmonic Generation

2.1. The Phase of Second Harmonic Light Generated at an Interface and its Relation to Absolute Molecular Orientation: In recent years the nonlinear optical process of second harmonic generation (SHG) at an interface has been shown to provide substantial amount of new information on a number of interfacial properties¹. In our continuing effort to understand the behavior of small molecules at the air-water interface we have earlier studied a monolayer of phenol on the surface of an aqueous solution and from the polarization dependence of the SHG, determined the average orientation of the principal molecular axis (passing through the phenyl-oxygen bond) with respect to the surface normal². We have now extended these studies to measure the absolute phase of the SH electric field and develop a scheme for inferring the absolute sense of the molecular orientation, namely, whether the phenyl-oxygen bond is pointing towards or away from the water.

The principle of the method can be outlined as follows. If the surface nonlinearity arises from an electric-dipole response, one can write the surface nonlinear susceptibility, $\overline{\chi}_s^{(2)}$, as a sum of the nonlinear polarizabilities $\overline{\alpha}^{(2)}$ of the molecules:

$$\overline{\chi}_s^{(2)} = N_s \overline{\alpha}^{(2)} \quad (1)$$

where N_s is the number of molecules per unit area and the angular bracket indicates an average over molecular orientations. If the nonlinear polarizability is dominated by a single component $\alpha_{\zeta\zeta\zeta}^{(2)}$ and if we assume

that the molecules are arranged isotropically with respect to azimuthal directions, the individual elements can be expressed in terms of the polar angle θ between the molecular ζ -axis and the positive surface normal,

$$(\chi_s^{(2)})_{zzz} = N_s \langle \cos^3 \theta \rangle \alpha_{\zeta\zeta\zeta}^{(2)} \quad (2a)$$

$$(\chi_s^{(2)})_{zzz} = (\chi_s^{(2)})_{zzz} = (N_s/2) \langle \cos \theta \sin^2 \theta \rangle \alpha_{\zeta\zeta\zeta}^{(2)}. \quad (2b)$$

Thus, from a comparison of the signs (or more precisely, the phases) of the elements of $\overline{\chi}_s^{(2)}$ and $\overline{\alpha}^{(2)}$ one can determine the absolute molecular orientation.

In order to determine the phase of nonlinear susceptibility, the SH light from the surface was allowed to interfere with the SH light generated in a reference crystal³. For the measurement of the absolute phase, comparison is made with a calibrated standard, a right-handed quartz crystal. The interference patterns are shown in fig. 2.1. The experimental data indicate that the trace for the phenol solution is delayed by 90° with respect to the quartz standard. From the known phase of the $\chi_{zzz}^{(2)}$ for the bulk quartz⁴ the absolute phase of $(\chi_s^{(2)})_{zzz}$ for the liquid is then found to be 180°. Theoretical calculations⁵ indicate that for phenol $\overline{\alpha}^{(2)}$ is dominated by $\alpha_{\zeta\zeta\zeta}^{(2)}$, with ζ lying along the principal molecular axis. With this definition of the molecular ζ -axis the experimental data imply that the sense of phenol molecules is such that the hydroxy group points into the bulk water.

In conclusion, we have performed the first measurement of the absolute phase of surface nonlinear susceptibility⁶. We have shown that if the nonlinear response is due to electric dipole contributions the phase data can

be related to the absolute molecular orientation. This information cannot be obtained directly from ordinary linear optical methods. Our work on the phenol-water system confirm the intuitive notion that the hydroxy end is directed towards water. A point of further interest is when surface structural information is available, one can use measurements of the type outlined here, to obtain the phases of the elements of the molecular nonlinear polarizability.

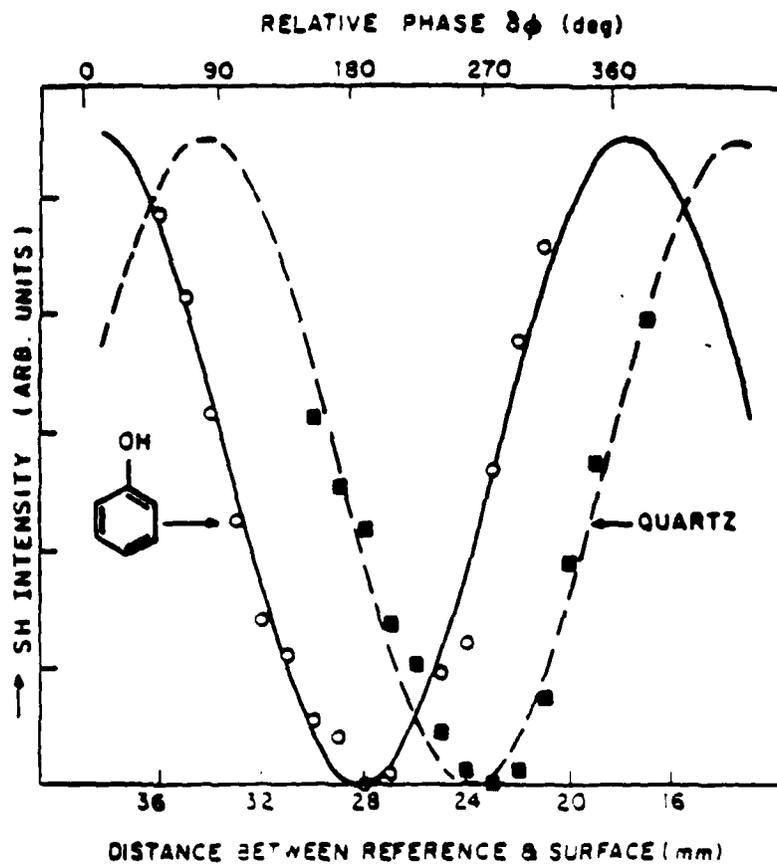
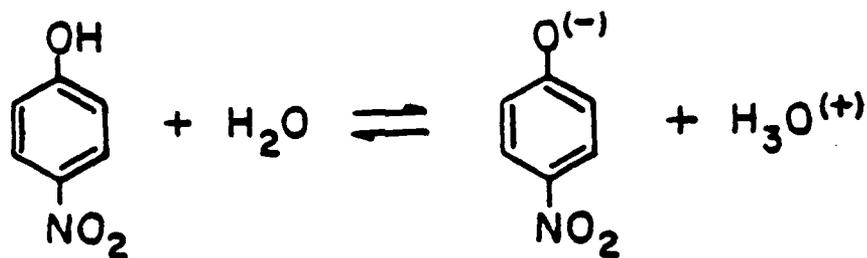


Fig. 2.1. Interference pattern of the SH fields for the surface of a 0.4 M aqueous phenol solution (open circles) and for the quartz standard (filled boxes). The points are experimental data and the curves through them represent the best fits to \cos^2 functions.

3.2. Study of Chemical Reactions by Surface Second Harmonic Generation : p-Nitrophenol at The Air-water Interface.

In our earlier work we focussed our attention on the relative² and absolute⁶ orientation of molecules at the surface of liquid solutions. We now address the question of how the asymmetry in the forces experienced by the molecules in the interfacial region affects simple chemical equilibria. Specifically, using this technique we have investigated the acid-base equilibrium between p-nitrophenol (HA) and its anion (A⁻).



As we will show, not only do the concentrations of the various species in the interfacial region differ from their bulk values, but also the relative concentrations do not correspond to the bulk equilibrium constant. The "equilibrium constant" in the surface region is vastly different from that in the bulk. The key factor is most likely the reduced polarity at the surface due to the low density of molecules on the vapor side of the surface. The effect of this is to decrease the stability of charged species, e.g. A⁻, to such an extent that the equilibrium in the interfacial region overwhelmingly favors the neutral undissociated HA molecules. It is to be noted that although the concentrations are dependent on their position, varying in a continuous, though very sharp way, from the bulk vapor to the bulk liquid, we can still define an average concentration for each of the species in this inhomogeneous

region. We then seek to compare the relative average concentrations of the species in the interfacial region, e.g. A^-/HA , with the relative concentrations given by the bulk equilibrium constant. In order to treat the position dependent concentrations (activities) in the interfacial region we would use the chemical potential since its value for a given species is the same at all positions in the system, i.e. bulk liquid, vapor and the inhomogeneous interfacial region. Discussions of this approach will be postponed to a later publication.

The observed s-polarized SH field amplitude ($E_s^{2\omega}$) as a function of bulk pH of the solution is shown in fig. 2.2. We found in earlier work⁶ that up to a monolayer the nonlinear susceptibility $\overline{\chi}_s^{(2)}$ can be written as

$$\overline{\chi}_s^{(2)} = N_s \langle \overline{\alpha}^{(2)} \rangle \quad (2)$$

where N_s is the number of molecules per unit area of the surface and $\overline{\alpha}^{(2)}$ the molecular polarizability. From this relation it follows that the second harmonic field $E_s^{2\omega}$ is linear in N_s . As the bulk pH is varied the relative amount of HA and A^- , as given by the bulk equilibrium constant for reaction (1) changes. This results in a change in N_s as the latter depends on bulk concentrations. At low pH the bulk concentration of HA has its largest value and this leads to a high surface coverage of neutral HA molecules. In accordance with this an intense signal (about 80 times that of water) was observed. In extremely alkaline media ($pH \geq 10$) the bulk HA molecules are almost totally converted into the anion and we found that the SH signal decreased to the value obtained from pure water. If there was a significant anion concentration at the surface we would readily observe it since its

SH signal should be more than 10 times that of water. The possibility of undissociated sodium phenolate formed by neutralization with NaOH, being present at the surface is also unlikely since its presence would have

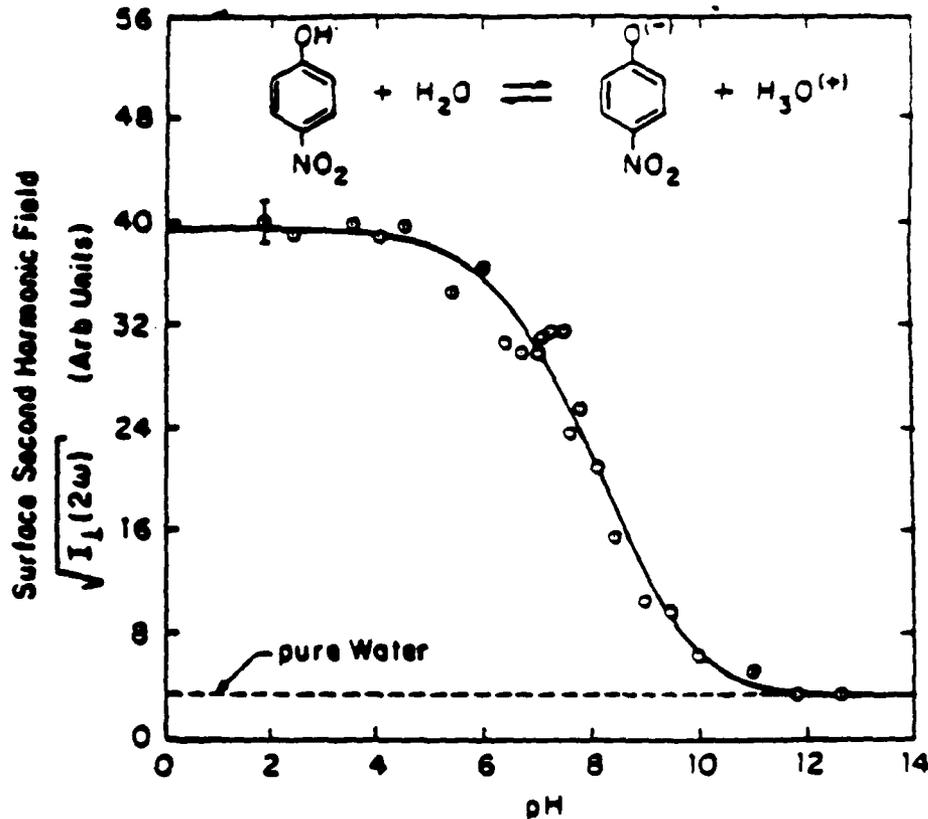


Fig. 2.2. *s*-Polarized surface second harmonic field, $E_s^{2\omega}(\sqrt{I_{\perp}(2\omega)})$ of an aqueous solution of *p*-nitrophenol as a function of pH at 22° C.

produced a second harmonic signal much above that of water. We therefore conclude that the anion once formed does not stay at the surface and thus in alkaline media the interfacial region is made up of water molecules alone. From our second harmonic measurements we estimate that the ratio of A^-

to HA is at least 50-100 times smaller in the interfacial region than in the bulk solution. The equilibrium in the interfacial region is thus clearly shifted towards the neutral molecules and differs markedly from its bulk value.

Although fig. 2.2 is similar to a neutralization curve the pH(7.9 ± 2) at which the SH signal amplitude reduces to half its maximum value is different from the pH(7.15) at which the concentration of undissociated HA in the bulk decreases to half. This is not surprising since the bulk pH controls the concentration of HA in the bulk, while the surface concentration N_s is not a simple linear function of the latter. This point will be pursued in our future work. It is furthermore of interest to note the sensitivity of surface second harmonic generation as demonstrated by these results. Under the conditions described in this work when the SH signal changes by a factor of 80 we found that the surface tension changed by less than 10%.

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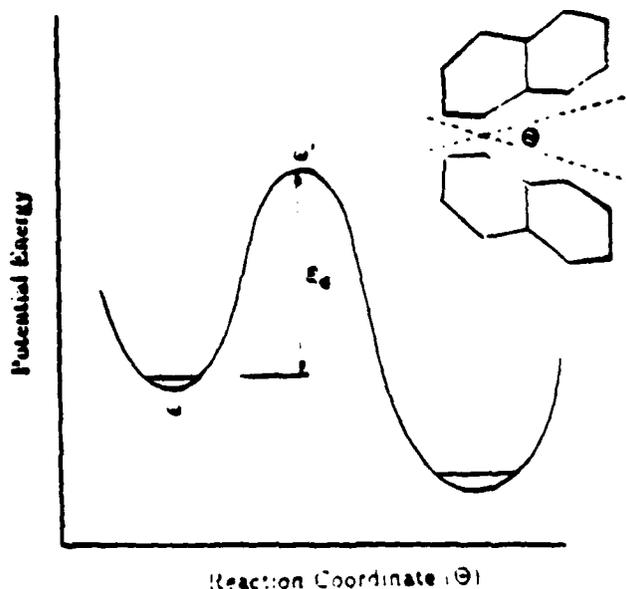
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3. Picosecond Photoisomerization in Liquids:

Dynamics of 1,1'-Binaphthyl

One of our major interests is the influence of the solvent on reactions which involve structural changes. An important reaction we have examined in this regard is the photoisomerization of 1,1'-binaphthyl, which involves only the twisting of the naphthalene moieties about a single bond⁽¹⁻⁴⁾. Since this process is one-dimensional, comparisons can be made to one-dimensional barrier crossing theories⁽⁵⁻⁷⁾, in particular to Kramers' theory⁽⁸⁾.



In our earlier work⁽⁹⁾ we have shown that the twisting time of 1,1'-binaphthyl in several linear alcohols exhibits excellent agreement with Kramers' theory (fig. 3.1). The agreement was obtained using the hydrodynamic model which relates the frictional drag coefficient to viscosity, where viscosity is a known macroscopic property of each solvent. The dynamics of 1,1'-binaphthyl in alcohols was the first observation of Kramers' behavior in the intermediate

friction regime.

A crucial issue now is to see if Kramers' behavior is observed for 1,1'-binaphthyl in other solvent series. In our current work⁽¹⁰⁾ we have measured the twisting times of 1,1'-binaphthyl in linear alkanes. The agreement of the alkane data with Kramers' theory is poor when using the hydrodynamic model. We are, however, able to get good agreement of Kramers' theory with experiment if we use the orientational relaxation times as a measure of solvent friction (fig. 3.2). In this new approach we measured the orientational relaxation rate of 1,1'-binaphthyl in each alkane. By using time correlation functions we were able to relate the orientational relaxation times to the frictional drag coefficients, as originally suggested by Velasco et al.¹¹. For completeness we measured the orientational relaxation rates for the linear alcohols. A good fit to Kramers' theory was also obtained for alcohols using the orientational relaxation times as a measure of the solvent friction.

It can be seen in the case of alcohols, (fig. 3.3), viscosity scales linearly with orientational times. Because of this linearity both viscosity and orientational relaxation times turn out to be a good measure of solvent friction. On the other hand in alkane solvents there is a clear nonlinear dependence of the rotational reorientation time on the solvent viscosity (fig. 3.4), which is especially seen at low viscosities, i.e. < 1 cP. In this case, only orientational relaxation is a good measure of friction. The problem now turns to understanding why orientational relaxation is a good measure of friction and where the discrepancy between solvent classes originates i.e. why hydrodynamics appears to break down in alkanes. Since the energy barrier for excited state isomerization is similar in both alcohols (460 cm^{-1})

KRAMERS FIT OF BINAPHTHYL ISOMERIZATION IN ALCOHOLS

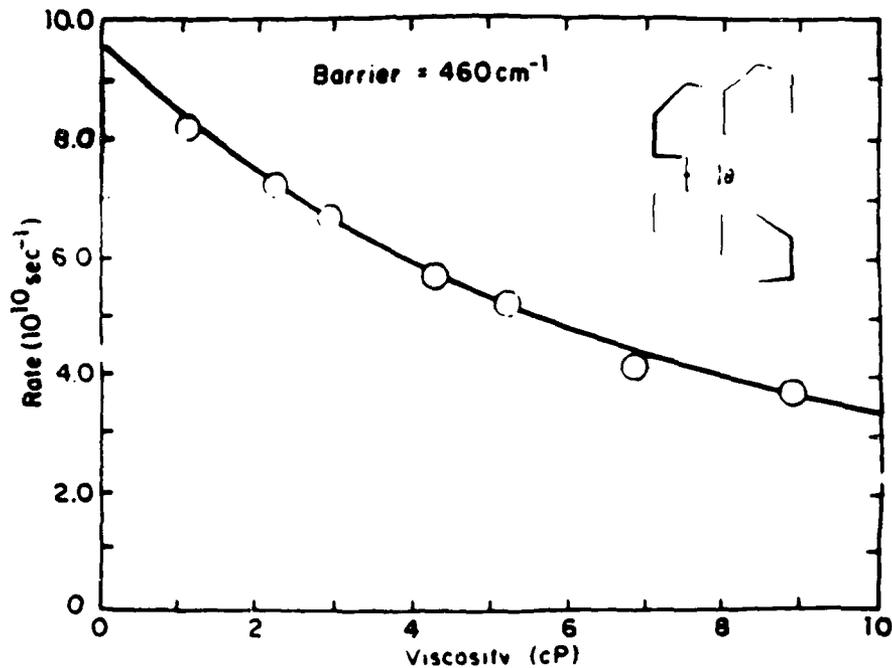


Figure 3.1. Barrier Crossing Rate of 1,1'-Binaphthyl versus Solvent Shear Viscosity in Alcohols.

KRAMERS FIT OF BINAPHTHYL ISOMERIZATION IN ALKANES

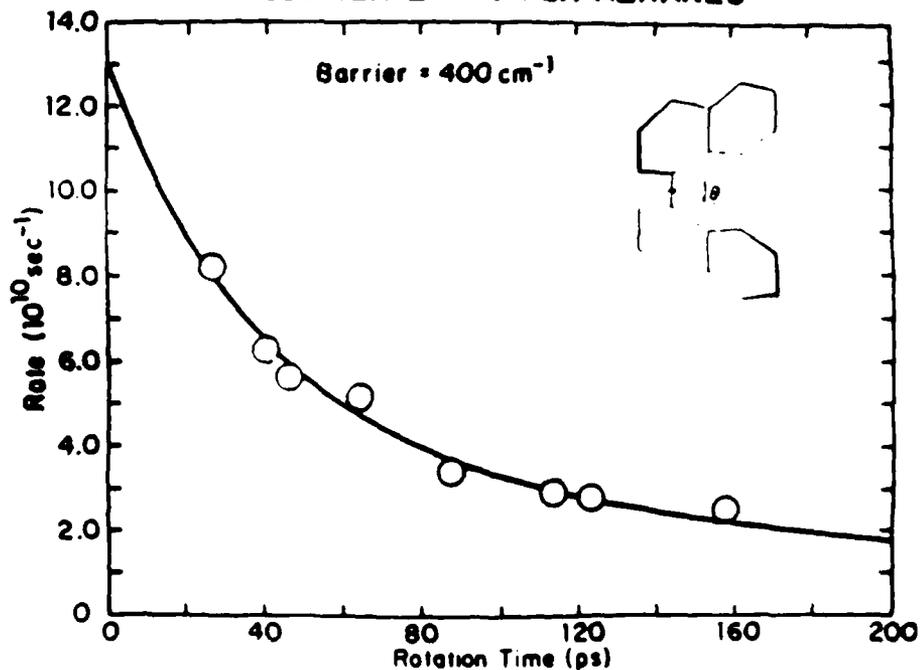


Figure 3.2. Barrier Crossing Rate of 1,1'-Binaphthyl versus Rotation Time in Alkanes.

ROTATION OF BINAPHTHYL IN ALCOHOLS

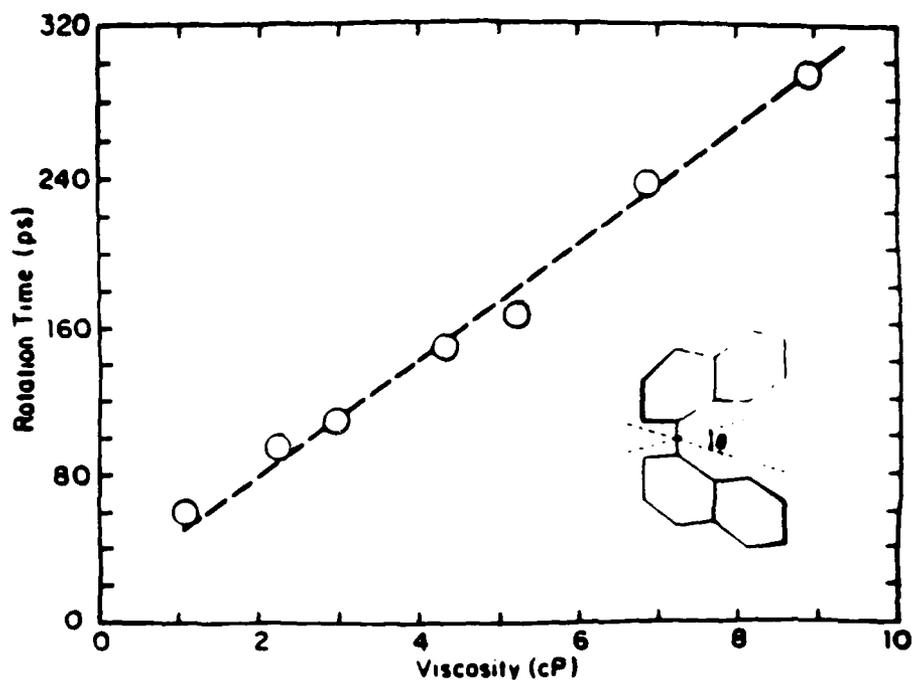


Figure 3.3. Plot of Rotation Re-orientation Time of 1,1'-Binaphthyl versus Solvent Shear Viscosity, in Alcohols.

ROTATION OF BINAPHTHYL IN ALKANES

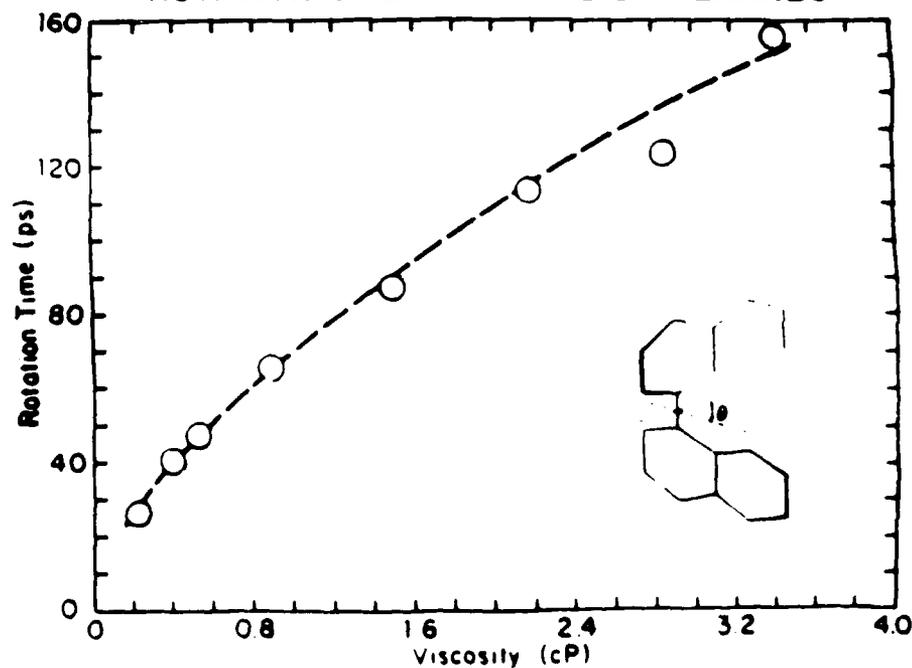


Figure 3.4. Plot of Rotation Re-orientation Time of 1,1'-Binaphthyl versus Solvent Shear Viscosity, in Alkanes.

and in alkanes (480 cm^{-1}) we expect the solute-solvent interactions for the binaphthyl molecule to be similar in both solvent systems. We note, however, that the solvent-solvent interaction in alcohol will be larger than in alkane. This arises by virtue of the fact that alcohol possesses a hydroxyl group, which permits the solvent molecules to cluster via secondary hydrogen bonding. This is just one of several possible solvent-solvent interactions that may account for the underlying differences between the two solvent classes in terms of affecting the dynamics of conformational change in 1,1'-binaphthyl. In summary, we have found that the photo-isomerization dynamics in 1,1'-binaphthyl follows Kramers' behavior in both alcohol and alkane solvent systems. It is also found that the use of orientational relaxation times as a measure of the solvent friction is crucial to the success of fitting Kramers' theory to the experimentally observed rates.

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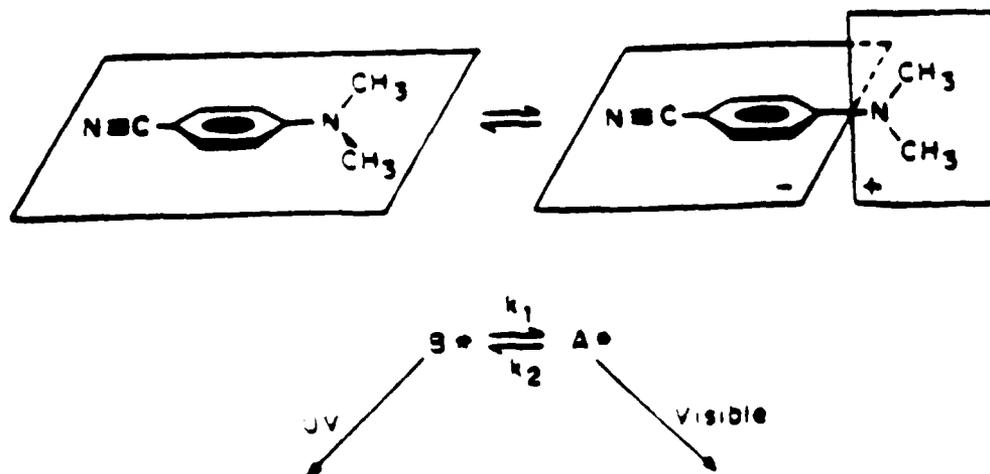
4. Polarity Dependent Barriers and the Photoisomerization Dynamics of Polar Molecules in Solution

There has been recent theoretical and experimental interest in potential energy barrier descriptions of molecular structural changes in solution¹⁻⁹. For example, the dependence of photoisomerization kinetics on solvent viscosity has been studied to test barrier crossing models¹⁻⁹. Changes in the photoisomerization rates through a solvent series or as a function of temperature have been attributed to viscosity and thermal effects; other possible effects, such as solvent dependent excited state potential surface variations, have generally not been considered⁹. In particular, strong interactions with polar solvents are expected for molecules that undergo a major charge redistribution on isomerization, whether they be polar molecules such as p-dimethylamino-benzonitrile (DMABN)⁸, or nonpolar molecules that pass through very polar intermediate structures such as t-stilbene³⁻⁶. These polar interactions can be important factors in the dynamics of isomerization, as we show in the two prototypical cases of the DMABN and t-stilbene molecules.

4.1. DMABN - Case of a Polar Molecule

DMABN is a classic example of a molecule that exhibits strong solute-solvent interactions, as demonstrated by the fact that its excited state isomerization occurs in polar solvents but not in nonpolar solvents¹⁰. A general scheme of the dynamics is given in Scheme 1¹¹. The isomerization takes place on an excited singlet potential surface and involves a 90° rotation of the dimethylamino group about the aminophenyl bond¹¹. This twisting structural change produces an increase in the excited state dipole moment from 6 D to 16 D¹². In polar solvents, a new visible emission appears due to the solvent stabilized twisted form. Due to a rapid equilibration between the planar (B^{*}) and twisted (A^{*}) structures two emissions are observed. The one in the ultraviolet is due to the planar form and the visible emission is due

to the twisted polar form. In alkanes, only the uv emission from B* is observed. Many time-resolved studies have been conducted on DMABN, yet the role of the solvent is still not clear^{8,13-17}.



Scheme I

To investigate the effects of the solvent on the photoisomerization kinetics of DMABN, we have carried out studies in a series of linear alcohols, alcohol/alkane mixtures, linear nitriles and nitrile/alkane mixtures (part of the data has been reported^{8,13}). A single pulse from the output of a Nd³⁺ glass laser was frequency quadrupled to 265 nm and used to excite DMABN. The fluorescence from the B* and A* states was time-resolved with a streak camera detection system that had a resolution of 7 ps¹⁴.

An important aspect of the solute-solvent interactions is the effect of solvent viscosity on the kinetics of a reaction. From studies in neat liquids, we find a viscosity dependence in nitriles of $\eta^{-2/3}$ and in alcohols, η^{-1} . These can be interpreted as cases of intermediate and strong solute-solvent coupling, respectively.

Of key importance in obtaining these viscosity dependences of k_1 is the assumption that only the viscosity differences among the various members of the solvent series affect the rate. The possibility that the potential surface may change in different solvents is not considered, nor are the possibilities that boundary conditions, entropy or dynamic polarity effects vary with solvent. For a polar structural transition such as in DMABN, the invariance of the potential cannot be assumed. Specifically, the changes in solvent polarity, even within a polar series, can be of sufficient magnitude to produce marked changes in the excited state barrier height. It has long been recognized that there are barrier height changes in going from a nonpolar to a polar solvent. The issue here is that these barrier effects can come into play within a solvent family, e.g. the polar alcohol series, or in one solvent at different temperatures.

To separate the effects of solvent polarity and viscosity, we have used two techniques: (i) k_1 was measured at room temperature in isoviscous mixtures of a polar solvent and an alkane, where the polarity of the mixture was controlled by the concentration of the polar solvent, and (ii) the temperature was varied for the neat solvents so that the solutions had the same viscosity but different polarity values. We find that the isomerization rate increases exponentially with increasing solvent polarity as measured by the widely used¹⁸ empirical solvent polarity parameter $E_T(30)$. It is important to emphasize that the rate dependence on $E_T(30)$ occurs when both viscosity as well as temperature remains constant.

Further support for the effects of solvent polarity on the isomerization dynamics is obtained from the second technique where the same viscosity is obtained by adjusting the temperatures of the neat liquids. The different rates measured have previously been assumed to be due to the different Boltzmann factors. This can be seen in the following Arrhenius-type expression

$$k = A f(\eta) \exp(-E_a/RT) \quad (1)$$

where E_a is the barrier height, $f(\eta)$ is the viscosity function (which is a constant for the isoviscosity experiment) and A is the pre-exponential frequency factor. We carried out these measurements in both the neat alcohols and neat nitriles, and found that the rate increases as the temperature is lowered in both solvent families. This result of a "negative" activation energy is contrary to what would be the case if only the Boltzmann factor is changing. To explain these results, we propose that the barrier height is not independent of temperature, but decreases due to a higher solvent polarity at lower temperatures. The polar twisted form of DMABN (A^*) is stabilized relative to the initially excited planar form (B^*), which thereby leads to a smaller barrier. This decrease in the barrier overcomes the usual Boltzmann effect and is responsible for the increased rate at lower temperature. When we correct for the temperature induced polarity changes, we find that the corrected rate decreases as the temperature is lowered, i. e. a normal positive activation energy is obtained.

We can explain the dynamics of TICT formation of DMABN in both alcohol and nitrile solvents by introducing a polarity dependent barrier E_a :

$$E_a = E_a - A|E_T(30) - 30| \quad (2)$$

where E_a is the activation energy in an alkane solvent having an $E_T(30)$ of 30 and A is an experimentally determined factor that determines how strongly the barrier height changes with solvent polarity. The corrected rate, κ , may be expressed as

$$\kappa = k_1 \exp(-A|E_T(30) - 30|/RT) = C \exp(-E_a/RT) \quad (3)$$

where C is the Arrhenius pre-exponential factor. It is found that $\ln \kappa$ varies linearly with $1/T$ with negative slope, and thus permits the evaluation of the intrinsic value of E_a . The values of E_a are found to be 8.0 kcal/mole in the nitriles and 14.0 kcal/mole in the alcohols. Comparing the nitriles and alcohols at a given solvent polarity, we see that the barrier E_a is apparently higher in alcohols by about 6 kcal/mole²⁰⁻²³. One explanation for this is the presence of hydrogen bonding

between the dimethylamino group of DMABN and the alcohol hydroxy group. The hydrogen bond withdraws electrons from the electron donating dimethylamino part of DMABN and thereby opposes the electron transfer to the benzonitrile part of DMABN. For the intramolecular charge transfer in DMABN to occur, the hydrogen bond must be broken. This increases the barrier for the isomerization in alcohols relative to nitriles by about 6 kcal/mole, roughly the energy of typical hydrogen bonds. Previously, by using linear free energy relations, Kupfer and Abraham also noted this fundamental difference in the solvation of the excited DMABN in protic versus aprotic solvents²⁴.

Having obtained a quantitative expression for the polarity dependence of the rate k_1 , we can now correct for the polarity differences in neat nitriles and alcohols in order to investigate the viscosity dependence of the isomerization. It is found that there is a negligible dependence of the polarity-corrected rate, κ (from (3)), on the viscosity for both nitriles and alcohols. From this result we conclude that the major role played by the solvent in the isomerization of DMABN is in stabilizing the more polar twisted form via dielectric interactions, and not in providing friction against which the dimethylamino group must twist.

4.2. *t*-Stilbene - Case of a Polar Intermediate Structure

The photoisomerization of *t*-stilbene has been studied by many groups to gain insight into how the solvent affects this simple chemical change³⁻⁶. The observed rate has been discussed in terms of (1), where $f(\eta)$ is either the Kramers function (which gives poor agreement with the observed rates)³ or more often⁶ $\eta^{-\alpha}$. This latter form can be obtained from a free volume²⁶ or frequency dependent friction model²⁷⁻²⁸. This general equation predicts that at constant viscosity, a plot of $\ln k$ versus T^{-1} should have the slope $-E_a/R$. We have tested this prediction by studying the rates of photoisomerization of stilbene in alcohols at various temperatures under constant viscosity conditions. A Nd^{3+} /YAG laser with pulses 30 ps in duration

was used to excite the t-stilbene, and the fluorescence was detected using a streak camera, as for DMABN. A polarizer oriented at 54.7° was placed in the collection optics to avoid the effects of time-dependent depolarization of fluorescence.

In fig. 4.1 it is shown that the slopes of these lines depend on viscosity, contrary to what the equation predicts. The apparent E_a 's vary from 2.6 to 1.2 kcal/mole. A similar deviation from (1) is shown by the dependence of the rate on viscosity at different fixed temperatures. We find that the value of α varies by a factor of two over a 50°K temperature range. This result conflicts with the constant α value predicted by the $\eta^{-\alpha}$ dependence of the rate equation.

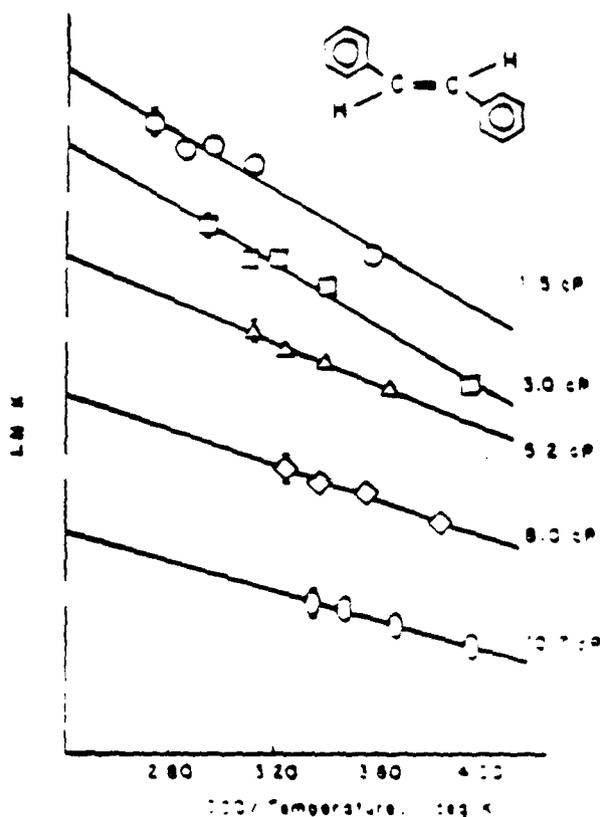


Figure 4.1: Plot of $\ln k$ versus T^{-1} for t-stilbene in isoviscous alcohols; the ordinate axis is offset for each viscosity line for viewing purposes.

Since the isomerization involves an intermediate structure that is highly polar, we ask whether polarity dependent barrier effects are important in the isomerization process. Accordingly, we carried out measurements in neat alcohols at various solvent polarities and temperatures, analogous to our DMABN study. We found that static polarity effects alone do not explain our stilbene results in alcohols. In stilbene, dynamic polarity effects could be important since extensive solvent rearrangements are required in the isomerization from the initial nonpolar form to the twisted charge separated form. This is not expected for DMABN because its transition involves an increase in dipole moment along the same axis from a polar (6 Debye) to a more polar (16 Debye) form. The solvent is already arranged about the large dipole in the initially excited DMABN, unlike the case for stilbene, where the initial solvent arrangement is that appropriate to a nonpolar solute molecule. If the solvent motions are not very rapid compared to the isomerization time, then the isomerization dynamics would depend on the dielectric relaxation properties of the solvent²⁹⁻³⁶. The energy separating the trans and intermediate form would therefore depend upon the positions of the surrounding solvent molecules, and thus be dependent on the rate of change of the solvent arrangement. Further work is underway to resolve the role of polarity and other solvent factors in the stilbene isomerization.

Conclusions

We find that the isomerization dynamics of molecules that involve a large charge redistribution, such as in DMABN, are strongly dependent on the polarity of the solvent. The solute/solvent interaction can be described in terms of a polarity dependent barrier that separates the two structural forms of the molecule. In addition to the well-recognized effects in going from a nonpolar to a polar solvent, we find that the effects of polarity change within a series of related polar liquids, e.g.

linear alcohols or nitriles, and the effects of the change in polarity with temperature are crucial to the observed kinetics. We have also found that hydrogen bonding of DMABN with alcohols impedes the isomerization relative to that of nonhydrogen bonding polar solvents such as nitriles. For t-stilbene in alcohols, we have found from measurements at various viscosities and temperatures that the isomerization cannot be described in terms of frequently applied equations that contain an $\eta^{-\alpha}$ power dependence. Although the t-stilbene isomerization passes through a very polar intermediate structure, we are not able to adequately fit the data using a static polarity correction as we did for DMABN. The possibility of a dynamic polarity effect due to a large solvent rearrangement in going from the nonpolar initially excited t-stilbene to the polar twisted intermediate stilbene structure is discussed.

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5. Stepwise Solvation of the Twisted Internal Charge Transfer State: Vapor and Jet Studies of DMABN

From previous work we showed the importance of solvent polarity on influencing the dynamics of charge separation. We found in the particular test case of DMABN that the solvent's influence on the dynamics of twisted internal charge transfer (TICT) could be explained using a static polarity effect model¹. It is pointed out that in this model the proposal of a barrier whose height changes with the polarity of the medium gives a simple explanation for the appearance of dual fluorescence in polar solvents and a single uv fluorescence in alkanes: a certain polarity is required before the TICT barrier is low enough to allow the forward TICT process to proceed within the lifetime of the initially excited state.

The recent work by Robinson et al.² and others³ attempts to deduce the number of solvent molecules that must be present in order to induce effects such as the one described above for DMABN. The idea is that a critical number of solvent molecules exists for a given charge transfer or proton transfer process. It is conceivable in the case of DMABN that a 1:1 DMABN/solvent complex could provide sufficient stabilization by charge transfer or dipolar interactions to permit the photoisomerization of DMABN to its twisted charge transfer state.⁴⁻⁷

In order to investigate some of these ideas about the role of the solvent we examined the photophysics of DMABN in a thermalized vapor and in a supersonic beam as a complement to liquid state studies. Among the central issues concerning the TICT of DMABN that were addressed were the critical

number of solvent molecules, the relative contributions of the local and long range stabilizing forces (the latter force can be important in liquids), and the details of the solute-solvent interaction, e.g. steric effects, hydrogen bonding and dipolar interactions. The high pressure vapor work sought to determine if, in a gas phase dimer or small cluster, DMABN itself could act as a stabilizing solvent molecule to a photoexcited member of the cluster. Resolution of this latter issue was important since earlier work showed that in nonpolar alkane solvents DMABN self-aggregates could be formed and were capable of undergoing the TICT process.

In collaboration with Prof. A. H. Zewail we carried out a systematic study of gas phase p-N,N-dimethylaminobenzonitrile (DMABN) both in a supersonic jet expansion and in a thermalized vapor⁸. From the jet studies, the excited and ground state vibrational spectra of the isolated molecule were resolved, and the spectroscopy of the stoichiometric complex with several polar solvent molecules was examined in the beam. It was concluded that 1:1 complexes are not sufficient to allow charge separation. This was found to be true for when water, methanol, ammonia, or acetonitrile molecules were used as the complexing partner with DMABN. In the thermalized vapor experiments, we found both uv monomer emission and the visible emission due to the charge separation made possible by the stabilization of DMABN self-complexes. Under appropriate conditions in the beam, and in the absence of solvent, we also observed visible emission that we attribute to DMABN in self-complexes.

We conclude from these studies in a thermalized vapor that self-complexes of DMABN (dimer or n-mer) can undergo twisted internal charge

transfer excite state isomerization, based on the observed visible emission characteristic of this polar state. Self-complexes were also formed in the beam, but charge transfer was not observed. Presumably, this reflects the differences in the internal temperature and/or size of the aggregates formed in the jet versus those formed in the vapor. In contrast, the beam studies reveal that the isolated molecule, and the 1:1 complex with water, methanol, acetonitrile, or ammonia does not undergo a charge transfer isomerization. These results can be understood in terms of the argument that a sufficiently polar solvent molecule or molecules are required before excited state charge transfer and structural twist can occur. Thus, one solvent molecule is not enough to stabilize the charge separated form.

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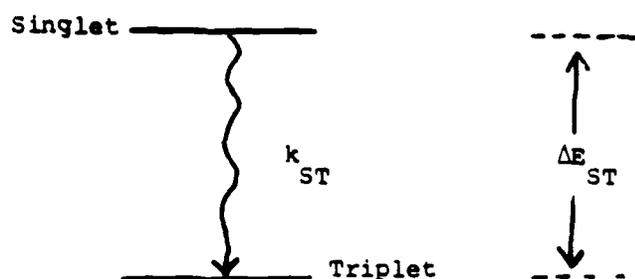
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6. Chemical Intermediates - Dynamics of Carbenes

6.1. Energy Relaxation in Diphenylcarbene - An Unusual Isotope Effect

In recent work we showed that singlet to triplet energy relaxation in aromatic carbenes is strongly dependent on the polarity of the solvent¹. We established that the energy gap between the singlet and triplet states changed with solvent polarity. It is this change of energy with solvent which is the key to the variation in the singlet to triplet relaxation. The dynamics



were unusual in that the rate of intersystem crossing increased as the energy gap, ΔE_{ST} , increased. The origin of this inverse gap effect was attributed to the fact that the gap is small ($\sim 1000 \text{ cm}^{-1}$) contrary to the usual large gap cases. As the energy gap increases the increasing number of accepting triplet vibronic states was responsible for the increasing rate. One way to

gain further insight into radiationless transitions for the small energy gap case and to further test our explanation of the variation of k_{ST} with ΔE_{ST} in carbenes is to determine the effects of deuteration on intersystem crossing. Isotope effects on radiationless transitions are well known for a number of molecules which undergo intersystem crossing. In the large gap case the main effect of deuteration on intersystem crossing from the lowest excited singlet to the excited triplet manifold is a reduction of the vibrational overlap factor thereby decreasing the rate.

For the small energy gap case of diphenylcarbene, however, we propose that it is the low density of final vibronic states that is of dominant importance. For deuterated diphenylcarbene (DPC-d₁₀) the density of triplet vibronic states near the singlet S_1 is larger than the protonated form. Thus, k_{ST} should be larger for DPC-d₁₀ than for DPC-h₁₀ if our explanation is correct. This would constitute an "inverse" isotope effect, i.e. contrary to the usual effect of deuteration on energy relaxation.

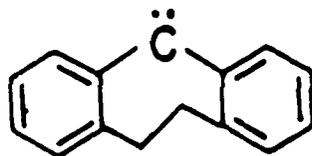
Using picosecond laser-induced fluorescence to measure k_{ST} we found an inverse isotope effect: an intersystem crossing time of 260 ps for DPC-d₁₀ versus 310 ps for DPC-h₁₀ in acetonitrile². The magnitude of the isotope effect was dependent on the solvent used. This expected dependence is caused by the variation of ΔE_{ST} with solvent, the isotope effect being largest in the solvent for which diphenylcarbene has the smallest gap. We thus conclude that intersystem crossing in diphenylcarbene can be described as a radiationless transition from the initial S_1 state to a final sparse triplet manifold. This low density of triplet vibronic states accounts for both the

dependence of intersystem crossing on solvent for which there is an inverse gap effect, and on deuteration for which there is an inverse isotope effect.

6.2. Relation Between Carbene Structure and Energy Relaxation

6.2.1 Dibenzocycloheptadienylidene (DCHD)

A key feature in the description of energy relaxation in carbenes is the structure of the carbene and how it influences the $S_1 \rightarrow T_0$ dynamics. In our previous work we found that there was indeed a pronounced effect of structure on intramolecular spin dynamics. For example, we previously reported³ for dibenzocycloheptadienylidene (DCHD) that the rate of



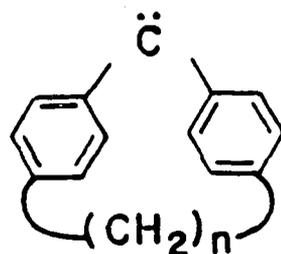
Dibenzocycloheptadienylidene (DCHD)

intersystem crossing was greater than for DPC. Furthermore, the rate was found to depend on solvent polarity, which was similar to that found for DPC. These results were related to the fact that DCHD possesses the restricting $-\text{CH}_2-$ groups, which leads to an increase in the angle between the central carbon and connected phenyl rings relative to DPC. The result of an increase in angle is to increase ΔE_{ST} . Within the small gap model for intersystem crossing, the structure-induced increase in ΔE_{ST} will lead to an increase in k_{ST} , as confirmed for the DCHD molecule. Taking advantage of the strong effect of structure on ΔE_{ST} (and thus on k_{ST}), we have now extended

the characterization of these chemically important intermediates to include carbenes that span unusually small gaps to very large gaps.

6.2.2 Paracyclophane Carbenes

For the case of DCHD it was found that an ethylenic moiety linking the two phenyl rings can increase the bond angle of the central methylene carbon atom. By employing a slightly different construction for the $-(CH_2)_n$ - bridge one can also << decrease >> the bond angle of the aromatic methylene, as exemplified by the paracyclophane carbenes. The paracyclophane carbenes are



[1,n]C Paracyclophane
Carbene

highly strained molecular intermediates, and as such, form a unique subclass of chemical intermediates⁴. These diarylcarbenes possess specific steric and electronic structures that depend on the length of the para-substituted alkane linkage. Others have found that there is a systematic decrease of the bond angle of the central methylene carbon atom (as well as an increase in the degree of phenyl-phenyl twist) in going from DPC to the [1,11]C paracyclophane. Furthermore, in collaboration with Prof. H. Staab and Prof. N. Turro we have determined⁵ that the energy splitting for [1,12]C is 650 cm^{-1} and for [1,11]C it is 330 cm^{-1} . The paracyclophanes therefore

have a very small singlet-triplet energy gap, which may be related to the fact that their geometric structures require small bond angles.

Determination⁶ of the intersystem crossing rate, k_{ST} , in a variety of solvents for [1,12]C as well as for [1,11]C paracyclophane carbene shows that there is a dramatic solvent polarity effect, being largest for the [1,11]C. It is also found that the paracyclophane carbenes manifest an exponential dependence of k_{ST} on the solvent polarity parameter $E_T(30)$, hence giving the linear relationship shown in fig. 6.1. It is pointed out that the striking

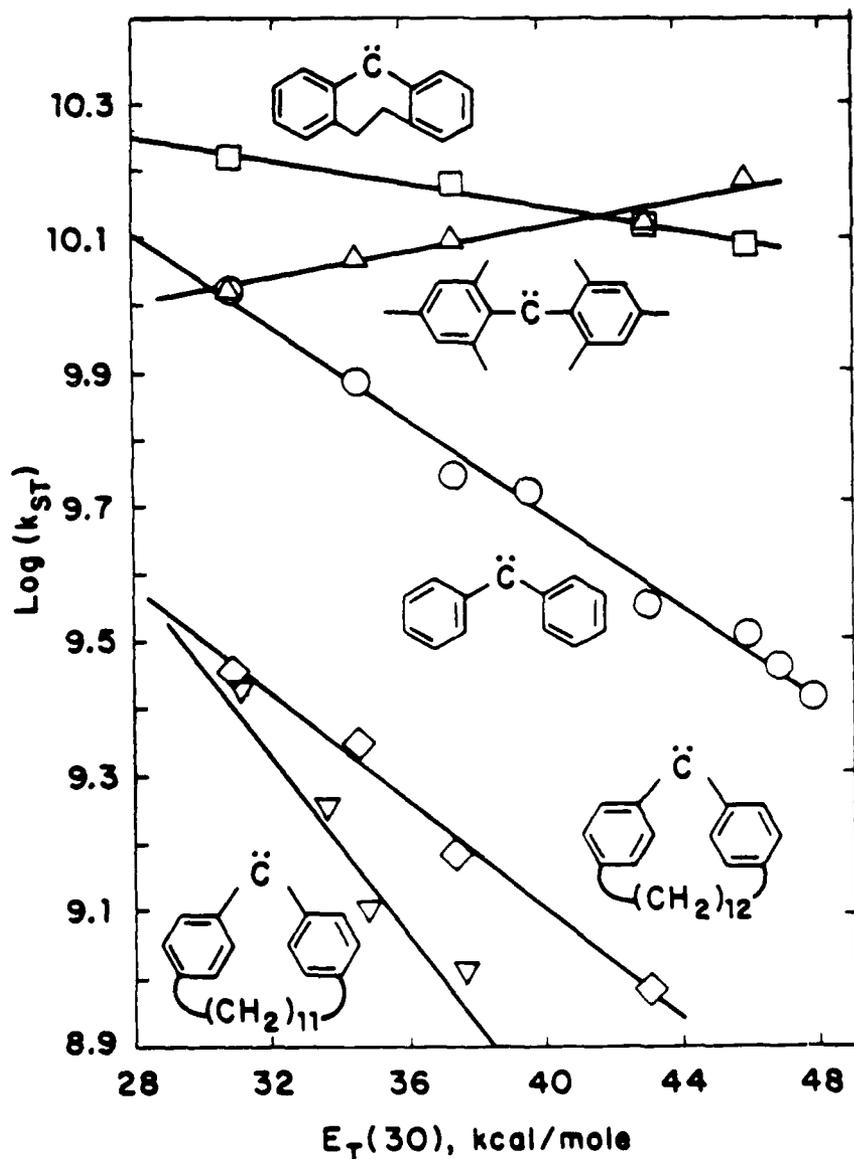
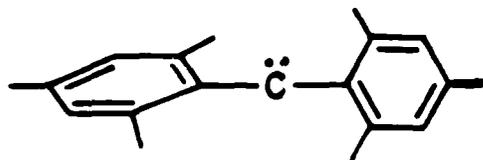


Fig. 4.1 Plot of carbene intersystem crossing rate as a function of the solvent polarity parameter $E_T(30)$

polarity dependence is the largest such effect observed for aryl carbenes, and is fully consistent with the fact that the paracyclophane carbenes possess an unusually small ΔE_{ST} .

6.2.3. Intersystem Crossing in the Large Gap Limit: Dimesitylcarbene.

To complete the picture of the dynamics of aromatic carbenes, we carried out an investigation of the dynamics of dimesitylcarbene (DMC). Due to the large steric repulsion between the two mesityl groups, DMC assumes a more



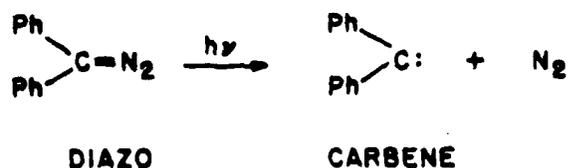
DIMESITYLCARBENE
(DMC)

linear geometry compared to either DCHD or DPC. Picosecond laser studies showed⁷ that the energy gap for DMC was sufficiently large, $>3000 \text{ cm}^{-1}$, to yield a normal energy gap rate law, i.e. the rate increases as the gap decreases. Thus, for dimesitylcarbene in the polar solvents where the gap was smaller than in the nonpolar solvents, the intersystem crossing rate was indeed larger as expected for a normal gap dependence. The interpretation of kinetics of spin relaxation in these various aromatic carbenes in terms of the measured variation of the singlet-triplet energy gap with solvent and carbene structure explains chemical reactivities of these carbenes as well. For example, dimesitylcarbene is found to have a large gap, which explains

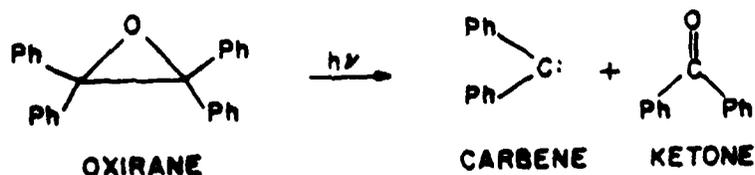
the observed variation in kinetics with solvent, and also why the reactions are predominantly from the ground triplet state.

6.3. Effects of Precursor Dissociation and Energy Decay on Pathways and Dynamics: The Case of Tetraphenylloxirane.

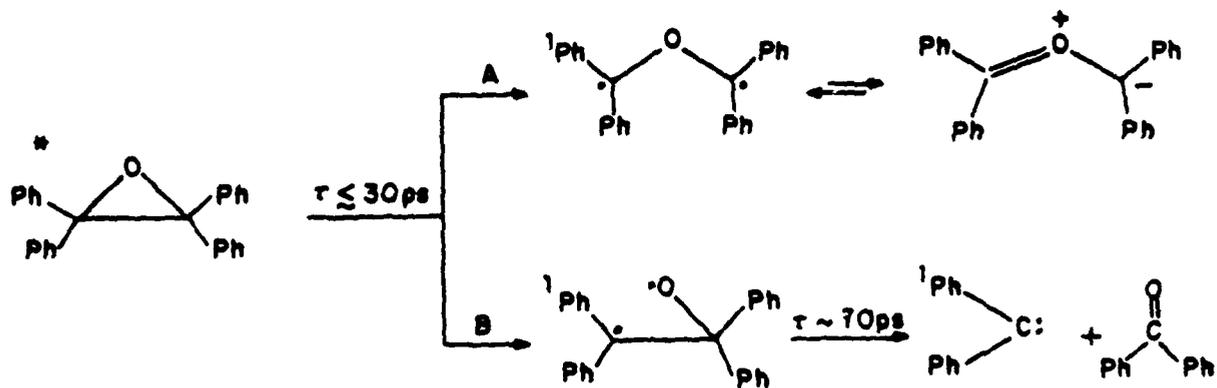
The sequence of energy relaxing steps following optical excitation of a carbene precursor are essential to unravelling the chemistry of the carbene. For example, the primary steps leading to the carbene are important in that energy decay in the excited state precursor can alter the dynamics and channels of carbene formation. In some precursors the quantum yield is wavelength dependent, indicating an extremely rapid fragmentation. A particularly important example of this effect is found for aromatic diazo compounds. In the case of diphenyldiazomethane, ultraviolet photoexcitation leads to C-N bond cleavage on the order of



less than 10 ps.⁸ Very little is known about other carbene precursors. Kinetic as well as mechanistic details for other carbene precursors remains largely unknown. With this in mind we have investigated the photophysics of tetraphenylloxirane (TPO), which like diphenyldiazomethane, undergoes photodecomposition to yield diphenylcarbene.



We find that irradiation of TPO at 266 nm produces two transients, which are observed by laser induced fluorescence at 500 nm and 580 nm, respectively⁹. The transient that emits at 580 nm grows in as a single exponential with a time constant that is < 30 ps, and persists for several nsec. The formation kinetics are found not to exhibit a significant solvent polarity dependence. We identify this species as a 1,3-biradical that is directly formed from C-C cleavage of ¹TPO. It is noteworthy that this biradical is similar to a ketyl radical, with the exception that the -H has been replaced by -C(Ph)₂. Since the chromophores are similar, we would expect that they will have similar spectral properties. The ketyl radical is known to emit strongly at 580 nm, and thus substantiates this assignment. Furthermore, the kinetics of formation (<30 ps) are also consistent with the mechanism involving direct formation from the photodecomposition of TPO (see route A in Scheme 6.1).



Scheme 6.1 Photodecomposition of Tetraphenylloxirane in fluid solution at room temperature

The formation rate of the second transient, which we assign to ^3DPC , was found to have an induction period of 70 ps before single exponential behavior was observed. The formation rate of ^3DPC was thus found to obey the kinetics of a sequential first order process involving two elementary steps. After accounting for the 70 ps induction period, it is found that the rate of formation of ^3DPC in several different solvents matches precisely the intersystem crossing rate (k_{ST}) as observed when using diphenyldiazomethane as the carbene precursor. Consistent with this kinetic evidence we postulate that ^1TPO undergoes decomposition via C-O bond rupture to produce a neutral 1,3-biradical. This 1,3-biradical persists on the order of 70 ps before it suffers annihilation via C-C cleavage to produce ^1DPC , see Scheme 6.1.

From our picosecond time resolved experiments we thus find that the photodecomposition of tetraphenylloxirane involves the competition between C-C cleavage and C-O cleavage, to produce two distinct species. Furthermore, we find that only one route is responsible for the formation of the carbene, i.e. initial C-O cleavage followed by C-C cleavage.

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7. The Femtosecond Laser System

Many fundamental processes such as energy relaxation, photodissociation and molecular motion, which we have been studying, occur on a subpicosecond timescale. In order to study these ultrafast phenomena we recently constructed an amplified femtosecond laser system. The femtosecond pulses are produced by a colliding pulse modelocked laser (CPM)¹. We have generated pulses as short as 40 femtoseconds (40×10^{-15} with pulse energies of 0.1 nJ directly from the CPM laser. These CPM pulses are then amplified to 0.5 mJ by a four stage amplifier pumped by a Q-switched Nd/YAG laser. Unfortunately, due to nonlinear chirp effects, the pulses are irreversibly broadened to 100 fs.

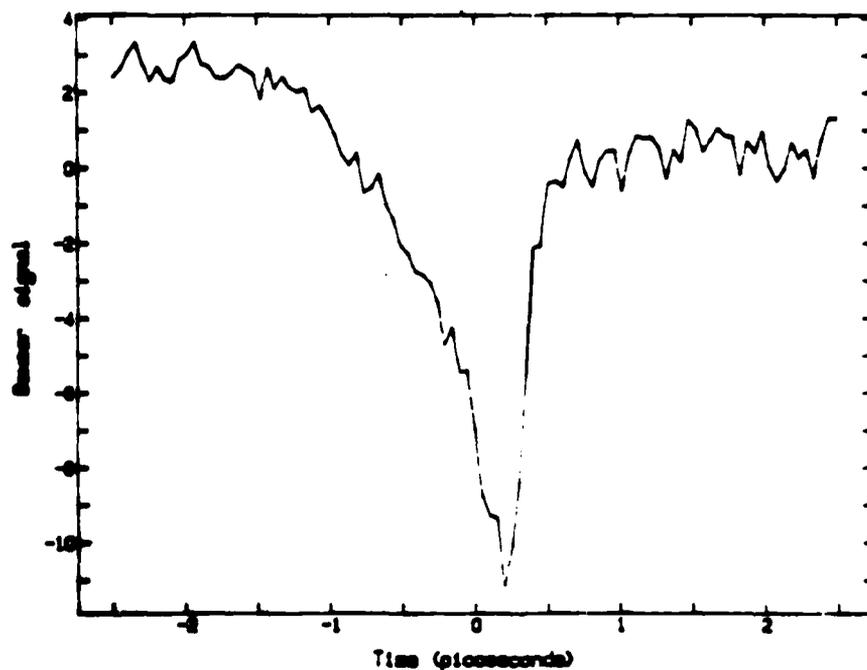


Fig. 7.1 Ground State Recovery of Malachite Green, using the Amplified CPM laser.

We have done some preliminary investigations of the ground and excited state properties of some dye molecules using ground state recovery techniques. The ground state recovery of malachite green² is shown in fig. 7.1. As demonstrated in fig. 7.1, we have succeeded in our goal of improved time resolution without sacrificing good signal to noise. By generation of a "white" light continuum as well as the uv second harmonic using femtosecond pulses that are amplified with a pump laser, we will be able to carry out transient absorption experiments in the femtosecond time domain. This will complement our present set-up that is based on a streak camera flash lamp system that allows us to routinely investigate events from picosecond to nanoseconds.

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8. Publication List for Report Period

- "Picosecond Laser Studies on the Reaction of Excited Triplet Diphenylcarbene with Alcohols," J. Phys. Chem. 87, 2283 (1983). (With E.V. Sitzmann and Y. Wang)
- "Picosecond Laser Studies on the Effects of Structure and Environment on Intersystem Crossing in Aromatic Carbenes," in Ultrafast Phenomena IV, D.H. Auston and K.B. Eisenthal, eds.; Springer-Verlag: Berlin, 1984. (With E.V. Sitzmann, J.C. Langan, and Z.Z. Ho)
- "Coherence Effects in Pump-Probe Measurements with Collinear, Copropagating Beams," Ultrafast Phenomena IV, D.H. Auston and K.B. Eisenthal, Eds.; Springer-Verlag: Berlin, 1984. (With S. Palfrey and T. Heinz)
- "Picosecond Laser Studies of the Effects of Reactants on Intramolecular Energy Relaxation of Diphenylcarbene: Reaction of Diphenylcarbene with Alcohols," Chem. Phys. Lett. 112, 111 (1984). (With E.V. Sitzmann, and J.G. Langan)
- "Coherent Coupling Effects in Pump-Probe Measurements with Collinear, Copropagating Beams," Optics Letters, 9, 359 (1984). (With T.F. Heinz and S.L. Palfrey)
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- "Divalent Carbon (Carbene) Chemistry, Time Resolved Laser Photolysis and Spectroscopy in the Investigation of Reactive Organic Intermediates," Science 225, 1439 (1984). (With R.A. Moss and N.J. Turro)
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- "The Phase of Second Harmonic Light Generated at an Interface and Its Relation to Absolute Molecular Orientation," Chem. Phys. Lett., 131, 285 (1986). (With K. Kemnitz, K. Bhattacharyya, J. M. Hicks, G. R. Pinto, and T. F. Heinz)
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- "Stepwise Solvation of the Intramolecular-Charge-Transfer Molecule p-(Dimethylamino)benzonitrile", J. Phys. Chem. 91, p. 6162 (1987) (With L. W. Peng, M. Dantus, A. H. Zewail, K. Kemnitz, J. M. Hicks)
- "Picosecond Photoisomerization in Liquids: Dynamics of 1,1'-binaphthyl". Submitted for publication. (With R. M. Bowman and D. P. Millar)
- "Effect of Solvent Polarity and Structure on Intersystem Crossing in Arylcarbenes: A Picosecond Laser Study of Dimesitylcarbene." In preparation. (With E. V. Sitzmann, J. Langan and D. Griller)
- "Picosecond Laser Studies on the Photodissociation of Tetraphenyloxirane: Effect of Carbene Precursor Dissociation and Energy Decay on Pathways and Dynamics." In Preparation. (With E. V. Sitzmann and J. Langan)

9. Names of Participating Professional Personnel

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- J. M. Hicks, Ph.D. (1986),
"Studies of Chemical Processes in Liquids Using Short Laser Pulses: 1. The Dynamics of Photoisomerization of Polar Molecules in Solution, 2. Studies of Liquid Surfaces by Second Harmonic Generation".
- J. G. Langan, Ph.D. (1986),
"Intra- and Intermolecular Effects on the Energetics and Dynamics of Arylcarbenes".

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