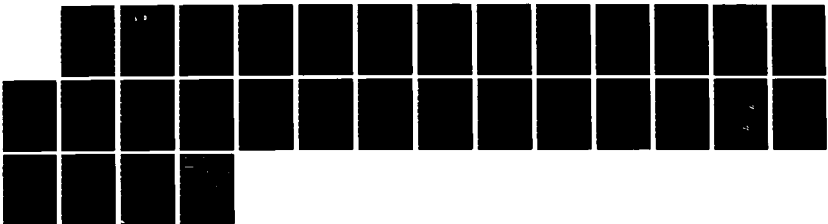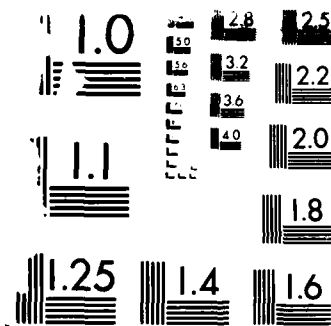AD-A175 488   CONTRIBUTION OF DIPOLAR COUPLING TO THE MECHANISM OF   1/1
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                DEPT OF CHEMISTRY AND BIOCHEMISTR..   J R MORGAN ET AL.

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MICROCOPY RESOLUTION TEST CHART

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Contribution of Dipolar Coupling to the Mechanism of the
Triplet-Triplet Energy Transfer Process at Long Distances;
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by

Jack R. Morgan, Hansjorg S. Niederwald, Chan-Lon Yang and M. A. El-Sayed
Department of Chemistry and Biochemistry
University of California
Los Angeles, California 90024

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CONTRIBUTION OF DIPOLAR COUPLING TO THE MECHANISM OF THE

TRIPLET-TRIPLET ENERGY TRANSFER PROCESS AT LONG DISTANCES;

A DOUBLE RESONANCE AND LASER LINE NARROWING STUDY

Jack R. Morgan[†], Hansjorg S. Niederwald[*], Chan-Lon Yang

and M. A. El-Sayed[‡]

Department of Chemistry and Biochemistry
University of California
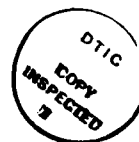Los Angeles, California 90024 U.S.A.

ABSTRACT

The results of the temporal behavior of the phosphorescence emission are analyzed when excited at different laser frequencies within the inhomogeneous linewidth of the 0,0 band of the singlet-triplet absorption of an orientationally disordered solid (1-bromo-4-chloronaphthalene) at 4.2 K. This enabled us to examine the triplet-triplet energy transfer probability as a function of the donor-acceptor distance by simply changing the laser frequency. The deviation from the expected temporal behavior for the electron exchange coupling mechanisms for triplet-triplet energy transfer in one dimension at long times or large donor acceptor distances is discussed in terms of either a contribution of dipolar coupling to the transfer mechanism or a change in the dimensionality of the

[†]Present address: Department of Chemistry, Univ. of Nevada, Reno

[*]Present address: Firma Carl Zeiss, 7082, Oberkochen/Wurtt, FRG

[‡]Mailing address: Department of Chemistry and Biochemistry, Univ. of California, Los Angeles, CA 90024 USA

system undergoing the transfer process. Results of the phospho-
rescence-microwave double resonance techniques could lend sup-
port to the possibility of a contribution of the dipolar coupl-
ing to the triplet-triplet transfer at large donor-acceptor
distances (i.e., long wavelength laser excitation).

1. INTRODUCTION

1.1. Distance Dependence of the Triplet-Triplet Energy Transfer Process

The energy transfer probability $W(R)$ occurring via an electron exchange mechanism decreases exponentially [1,2] as the distance, R, between the donor and acceptor increases, i.e.:

$$W(R) \sim e^{-cR} \quad . . . . \quad (1)$$

where c is a constant. Using this relationship, the probability, $P(t)$, that the donor remains excited after time t has been derived previously. The complex expression can be simplified (will be shown later) for situations where the transfer time is much longer than the nearest neighbor transfer time to the equation:

$$\ln P(t) \sim -\ln^D t \quad . . . . \quad (2)$$

where D is the dimensionality of the lattice on which the donors and acceptors reside. Experimentally, $P(t)$ is proportional to the donor intensity, $I_D(t)$, where $I_D(t)$ is the donor phosphorescence intensity at time t after excitation.

By spin orbit coupling, the triplet state could acquire transition dipole moment. The energy transfer process can thus in principle occur as a result of the coupling between these transition moments for the donor and the acceptor. The probability of the energy transfer for this dipolar mechanism [1,2] has the following distance dependence:

$$W(R) \sim \frac{C'}{R^6} \quad \ldots \ldots \ldots \ldots \ldots \quad (3)$$

where C' is a constant that depends on the size and orientations
of the transition dipoles and the dimensionality of the system.
The probability that the donor undergoing dipolar energy trans-
fer remains excited at time t after a short excitation pulse is
given by [3,4]:

$$\ln P(t) \sim -C\ t^{D/6} \quad \ldots \ldots \ldots \ldots \quad (4)$$

where D is the dimensionality of the system and 6 is for a di-
polar coupling. For 3-d dipolar interaction, ln P decreases
with $t^{0.5}$.

It is expected that at short distances, where the over-
lap between electronic wavefunctions is large, the exchange
coupling would be very strong and dominates the transfer mecha-
nism for triplet-triplet energy transfer where the size of the
transition moment is vanishingly small. However, due to the
exponential rapid decrease in the exchange probability with
distance, it is expected that at a certain distance, the di-
polar mechanism begins to have a nonvanishing contribution.
This would be manifested by deviation of the donor decay curve
from that predicted for the temporal behavior resulting from an
exchange coupling (equation 2). In order to carry out this
study, we should use a system for which the donor-acceptor
distance can be continuously changed while studying the donor
decay. Below we discuss such a system.

1.2. A Convenient Method for Continuously Changing the Donor-Acceptor Distance

How can we change continuously the donor-acceptor distance? The solubility of one chemical into another is usually limited. Isotope mixed crystals are a possibility. However, in these crystals one is studying donor-donor as well as donor-acceptor energy transfer simultaneously.

Lasers have both high intensity as well as sharp energy width to excite only a selected set of molecules having similar environment within a disordered pure solid, a solid with large distribution of different sites (molecules of the same chemical having different environments). These solids are characterized by a large inhomogeneous absorption linewidth. As shown in Fig. 1, excitation at ν_i with the laser makes molecules absorbing at ν_i energy donors. At low temperatures, e.g., 4.2 K, energy transport will only take place to molecules absorbing at equal or lower energy than $h\nu_i$. These molecules become the acceptors. Molecules absorbing at higher frequency than ν_i become the solvent molecules separating the donors from the acceptors. Thus by increasing the exciting laser frequency of the laser, the density of the acceptor molecules increases and the average donor-acceptor distance decreases. Thus if one studies the decay characteristics of the donor emission (those excited directly from the laser) as a function of the exciting laser frequency (i.e., the donor-acceptor distance), the

Fig. 1

distance at which the triplet-triplet energy transfer switches
its mechanism might be found.

1.3 1-bromo-4-chloronaphthalene (BCN), an Ideal System

The T_1-S_0 transition of BCN with a 0,0 band at $\sim 20,200\,\mathrm{cm}^{-1}$
has an inhomogeneous width on the order of 100 cm^{-1}. This
linewidth is about two orders of magnitude larger than the
linewidth observed for the corresponding transition in 1,4-
dichloronaphthalene (DCN) and 1,4-dibromonaphthalene (DBN),
suggesting that the width in BCN is due to the static orienta-
tional disorder in the halogen positions in the crystal [7].
Comparative studies of the crystal structures [8] and Raman
spectra [9] of the 1,4-dihalonaphthalene series show that the
one-dimensional stacking feature and intermolecular interactions
in BCN are similar to DBN for which one-dimensional exchange-
type triplet excitons have been observed [10].

2. RESULTS [13,15]

2.1. Spectral Diffusion Due to Energy Transfer

Fig. 2a demonstrates that spectral diffusion [13] of the
$T_1 \rightarrow S_0$ transition energy occurs in this orientationally dis-
ordered material. The band shape of the first vibronic band
was monitored as a function of delay time. The spectra displayed
were obtained by exciting a site on the low-energy side of the
$S_0 \rightarrow T_1$ absorption profile. The figure shows that as the
delay time increases, the resonant-type emission decreases

Fig. 2

in intensity while emission from low energy acceptors (the
traps) increases in intensity. This figure also shows the same
spectra recorded at two different sample temperatures. The
phosphorescence spectra obtained under identical conditions,
but at two different sample temperatures (the top and bottom
spectra in Fig. 2a), clearly indicate that the transfer rate
is temperature dependent and, thus, phonon assisted [14].

The results of the effect of site-selective excitation [13]
on the rate of spectral diffusion of the $T_1 - S_0$ energy is
shown in Fig. 2b. In each case the spectrum is sampled after
a 10-μs delay, using a 50-μs sampling time. In order to mini-
mize interference with stray light due to the laser, we
monitored the first vibronic band profile of the emission. It
can be seen that the observed emission profile is very much
dependent on the excitation energy. As the low-energy sites
are excited, a relatively narrow resonant emission is ob-
served, indicating a transfer rate slower than the sampling
time. On the other hand, upon the excitation of higher
energy sites, the emission profile is broadened indicating a
faster transfer time to a broader distribution of the low-
energy sites. These observations are suggestive of a trans-
fer rate which at 4.2 K is dependent on the donor site energy
(i.e., on the concentration of the acceptor's molecules).

2.2. Fit of Decay to Exchange Mechanism [15]

Fig. 3a shows the $\ln I(t)$ vs. $\ln t$ fit of the 1-d (expected from the crystal structure) exchange mechanism. An excellent fit for $\lambda = 4940$ Å (bottom decay) is observed. However as the wavelength increases, deviation at long times is seen. The fraction of the total decay that can be accounted for by the straight line exchange fit decreases as λ increases.

Fig. 3b shows the results of attempting to fit the portion that did not fit the exchange equation in Fig. 3a to the 3-d dipolar fit. Fig. 3b suggests that at long time and wavelength (long donor-acceptor distance), a 3-d mechanism could account for the data.

2.3. Possibility of Dimensionality Changes at Long Time or Low Acceptor Densities

While these results [15] might suggest a switching of the mechanism at a few percent of acceptor concentration (> 10 Å for donor-acceptor separation), the possibility of switching the dimensionality from one to greater than one could equally be an explanation for the observed deviation from the 1-d exchange equation. We need an equation for the temporal behavior of $P(t)$ for transfer on lattices having greater dimensionality than unity for the exchange mechanism. Below, we derive such an equation.

Consider the system of the acceptor randomly distributed

with the probability, C_A. Klafter and Blumen [16] extended the results obtained on a regular lattice to the self-similar structures by replacing the density of randomly distributed acceptor sites by the fractal behavior:

$$\rho = \rho_o R^{D-d} \quad \ldots\ldots\ldots\ldots\ldots \quad (5)$$

the time dependence of the donor excitation probability $P(t)$ then becomes

$$\ln P(t) \sim -\, C_A \, B \, G_D(Z) \quad \ldots\ldots\ldots \quad (6)$$

where B is the time independence constant, and G_D is defined as

$$G_D(Z) = D \int \{1 - \exp(-\, Z \exp(-Y))\} Y^{D-1} \, dY \quad \ldots \quad (7)$$

where $Z = t/\tau$ and $Y = \gamma R$. Equation 7 can be expressed as another equivalent form [3b],

$$G_D(Z) = \int \exp(-X) \, (\ln Z - \ln X)^D dX$$

where $X = \exp(Y)$.

We can expand $(\ln Z - \ln X)^D$ by the power expansion for non-integer D,

$$(\ln Z - \ln X)^D = \ln^D Z \, \{1 - D\, \frac{\ln X}{\ln Z} + \frac{D(D-1)}{2} \, (\frac{\ln X}{\ln Z})^2$$
$$+ \ldots\} \, \ldots\ldots \quad (8)$$

For non-integer D, D dimensional self-similar structure embedded in the d dimensional Euclidean space, equation 8 becomes

$$G_D(Z) = \ln^D Z \int \exp(-X) \, dX - D \ln^{D-1} Z \int \exp(-X) \ln X \, dX$$
$$+ (D(D-1)/2) \ln^{D-2} Z \int \exp(-X) \ln^2 X \, dX - \ldots \quad (9)$$

In the case of BCN, at low acceptor concentration (or long time), the time scale for which the transfer is studied in the time-resolved phosphorescence experiment (micro-millisecond) is much longer than the nearest neighbor transfer time $\tau(\sim$ picosecond). Thus (ln Z) becomes about 20. Because of the highly anisotropic property of di-halo-naphthalene, the value of γd in three dimension Euclidean space is smaller than the one dimensional case, the value of (ln X) is also quite small. Then, the higher order terms in the power expansion can be neglected, and equation 9 can now have the simple form:

$$G_D(Z) \sim \ln^D Z \quad . . . . (10)$$

which would lead to equation (2).

Fig. 4 shows the fit of the temporal behavior of the emission excited at 4943 and 4946 Å to equations (2) (exchange) and (4) (dipolar) for different dimensionalities. Both these results and others at other wavelengths [18] suggest that a fit for the exchange mechanism can be obtained for D = 2.3 for all the decay that deviated from the one dimensional behavior over the whole decay period. This is not the case for the dipolar mechanism.

2.4. Microwave Phosphorescence Double Resonance Experiments [16]

The triplet state of halogenated naphthalenes has three spin levels separated by fractions of cm^{-1}, even in the absence of magnetic field. This is the zerofield splitting which results from the anisotropic spin-spin and spin orbit

dipolar interactions [19]. Because of the molecular plane of symmetry, only two levels of the π,π^* excited triplet state of BCN are radiative (i.e., the electronic transitions from these levels to the ground state carry a transition dipole moment) and one level is dark. It is thus expected that molecules in the radiative levels will be the ones that can transfer their energy via a dipolar (as well as exchange) mechanism. The dark zerofield, on the other hand, can transfer its triplet excitation only via an exchange mechanism. It would thus be interesting to test if there is any difference between the transfer rates of molecules in the radiative and in those in the dark levels of triplet molecules having singlet-triplet energies at the lowest energy end of the absorption spectrum (i.e., separated from acceptors by large distances). We need to compare the change in the site energy distribution of molecules having triplet energy at the trap emission energies and occupying the radiative zerofield levels with those occupying the dark zerofield levels 70 ms after turning off the excitation.

The determination of the change in the site energy distribution due to energy transfer of the <u>radiative levels</u> in 70 ms is easy. We first record the steady state trap emission. Then we simply turn off the steady state excitation source and record the spectrum again 70 ms later. This is shown in Fig. 5, curve d.

Fig. 5

The study of the change in the site energy distribution of molecules in the dark levels was made by phosphorescence microwave double resonance techniques [6]. If the steady state excitation is turned off for 70 ms, the population of the radiative levels would decay mostly by radiative decay and to a smaller extent by energy transfer (as seen from the shift of curve (d) as compared to the c.w. distribution (curve a). Molecules in the dark level can only decay in 70 ms by the less probable energy transfer process (occurring at the large distances we are studying) and perhaps by spin lattice relaxation processes. If after 70 ms, a pulse of microwave of the appropriate frequency is turned on, a certain fraction of the molecules in the dark level is transferred to the radiative level and a pulse of light is observed. The intensity of this light pulse is proportional to the population of the dark level having an energy equal to that of the emitted radiation (since the zerofield splitting is very small as compared to the singlet-triplet energy separation). If this is done and the intensity of the pulse of light emitted at the different trap emission wavelength range is determined, the site energy distribution of molecules in the dark zero-field level after 70 ms from turning off the excitation can be determined.

Fig. 5 shows a comparison of the site energy distribution of molecules in the dark (b) and in the radiative (d) levels

in the 0,0 region of the trap emission spectrum after 70 ms delay as compared to the steady state emission (a). The distribution of the radiative level shifts more to lower energy than that for the dark level, suggesting a more probable energy transfer for molecules in the radiative level. This strongly suggests the presence of a dipolar contribution at these relatively long distances.

2.5. Site Dependent Spin Lattice Relaxation Rates:

Let us examine the possibility of explaining the results of Fig. 5 by invoking the possibility of the variation of the spin lattice relaxation with site energy. Under c.w. excitation, the microwave signal is found to be very weak, suggesting equal population of the dark and radiative zerofield levels at zero delay. Let us assume that energy transfer does not occur. In order to explain the red shift in the maximum of the 0,0 band after 70 ms delay, one has to conclude that the rate of the spin lattice relaxation increases as the site energy increases. If this is the case, then the distribution of molecules in the dark level should shift to the blue. This is not found to be the case. Of course, a combination of energy transfer via a three dimension exchange mechanism and site dependent spin lattice relaxation rate could account for the results in Fig. 5. The fact that the 130 ms delay (Fig. 5c) showed the same site energy distribution for the dark level as that

for 70 ms might suggest that the observed population is not determined by the spin lattice relaxation and that the exchange mechanism is probably frozen at these long distances.

3. ACKNOWLEDGMENT

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Captions for Figures

Fig. 1. The use of laser line-narrowing techniques to excite
donors in a selected environment absorbing at fre-
quency ν_1. At low temperatures, energy transfer can
only occur to the acceptor molecules absorbing at
frequency $\leqslant\nu_1$. Molecules absorbing at frequency $>\nu_1$
do not accept the excitation energy and act as the
solvent which separates the donors from the acceptors.
Thus by changing ν_1, the average distance (the
rate and mechanism of the transfer) between donors
and acceptors can be varied.

Fig. 2a. Spectral diffusion of singlet-triplet excitation
energy in an "amorphalline" solid at 4.2 K obtained
with time-resolved phosphorescence line-narrowing
techniques [11]. The system is 1-bromo-4-chloro-
naphthalene excited at 4943 Å. The top three
spectra are of the $0,0-321-cm^{-1}$ vibronic band of the
phosphorescence emission recorded at different delay
times after the laser pulsed excitation with a 50-μs
sample time. The bottom spectrum illustrates the
effect of temperature on the rate of spectral
diffusion within the inhomogeneous profile of the
0,0 absorption band and detected at the $0,0-321\ cm^{-1}$
emission band.

Fig. 2b. The dependence of the spectral diffusion rate of the singlet-triplet excitation on the donor site energy in 1-bromo-4-chloronaphthalene at 4.2 K [11]. The spectral intensity change of the $0,0-321-cm^{-1}$ band of the $T_1 \rightarrow S_0$ phosphorescence is monitored with a 10 μs delay by means of a 50-μs sampling time following pulsed laser excitation at different wavelength (i.e., different donor energies) within the inhomogeneously broadened 0,0 band of the $T_1 \leftarrow S_0$ absorption. The results show that the ratio of the line-narrowed (donor) phosphorescence to the lower energy broad emitting traps decreases as the donor (excitation) energy increases, suggesting an increase in the spectral diffusion rate.
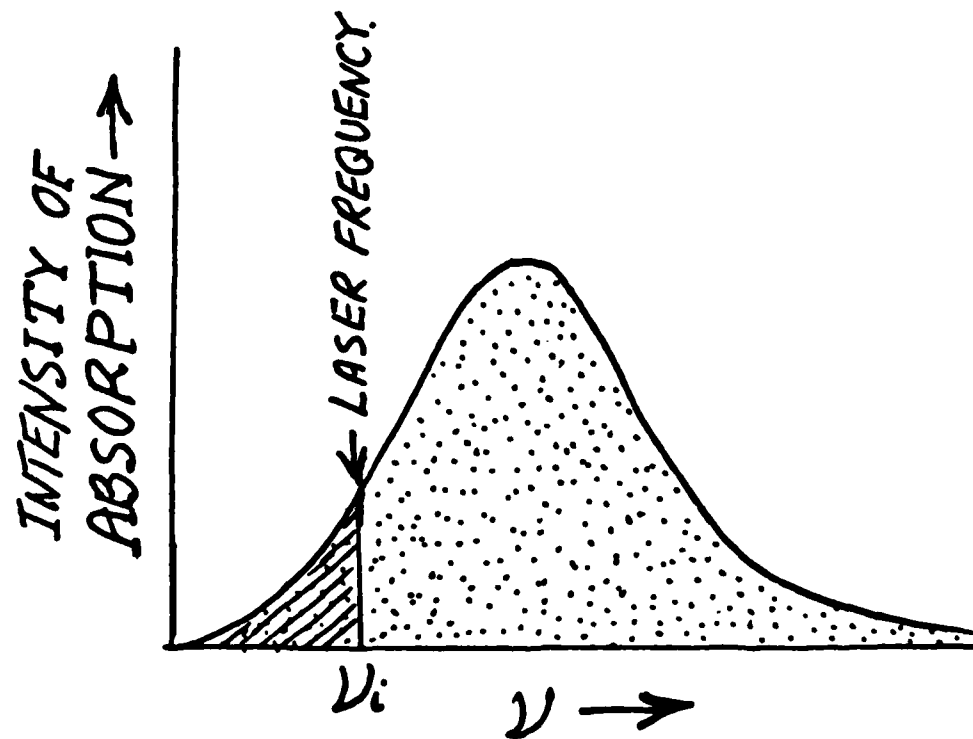
Fig. 3a. The fit of the early portion of the decay of the triplet excitation due to triplet-triplet energy transfer to an exchange mechanism for different excitation wavelengths (4947, 4943, 4942, and 4940 Å from top to bottom, respectively) within the 0,0 band of the T_1-S_0 transition in 1-bromo-4-chloro-naphthalene at 4.2 K [15]. The range of the fit increases as the excitation wavelength decreases, i.e., as the acceptor concentration increases.
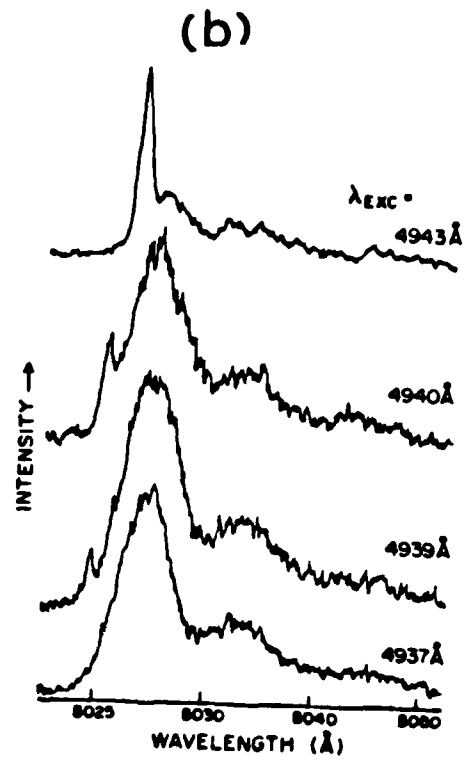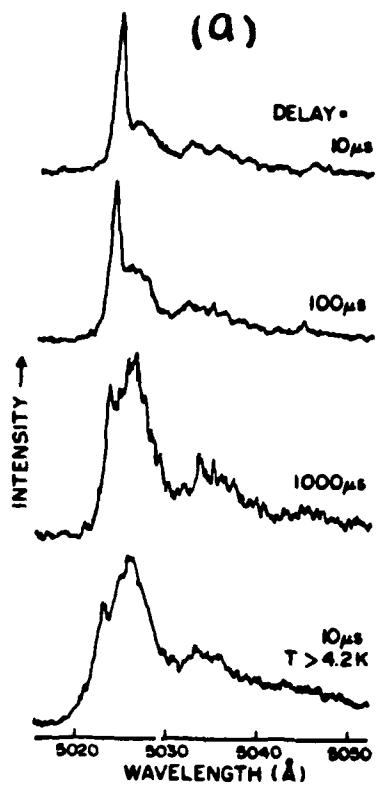
Fig. 3b.   The fit of the long time portion of the decay of the
           triplet excitation of the 0,0 band of the T_1-S_0
           transition of 1-bromo-4-chloronaphthalene at 4.2 K
           due to three-dimensional dipolar mechanism for the
           excitation wavelengths given in Fig. 3a [15].   The
           range of the fit is better at longer excitation
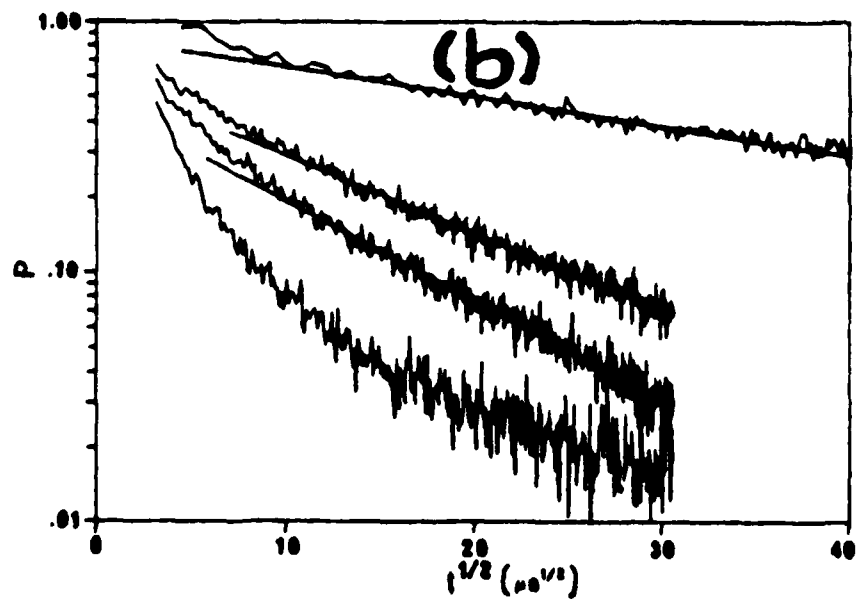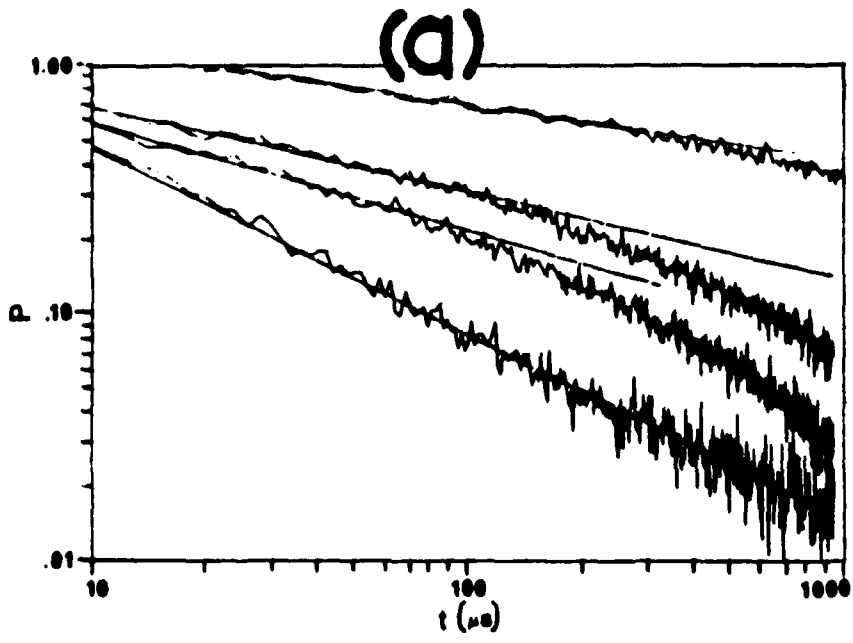   wavelengths, i.e., at low acceptor concentrations.

Fig. 4.   Testing for change in dimensionality by attempting
           to fit the decay of the 0,0-321 cm^{-1} band excited
           at 4943 and 4946 Å to exchange (left) and dipolar
           (right) equations (equations 2 and 4, respectively)
           with different dimensionalities D.   For all the
           four figures D = 2.0, 2.3, 2.5, 2.7 and 3.0 from
           top to bottom.

Fig. 5.   Inhomogeneous lineshape of the 0,0 phosphorescence
           transition at 1.8 K, taken under four different con-
           ditions [16].   Curve a shows the c.w. intensity
           distribution; curves b and c show the height of the
           leading edge of the MIDP signal at 1.05 GHz, which
           is proportional to the population of the dark level,
           after 70-ms (b) and 130-ms (c) delay time.   Curve d
           is the 0,0 band of the emission spectrum recorded
           70 ms after excitation and represents the popu-
           lation of the radiative level.   With the red shift,

curves b, c, and d also get slightly narrower and asymmetric. As parts b and d show, the distribution of the radiative level (lifetime 50 ms) at 70 ms has relaxed more to lower energies than the distribution of the dark level (lifetime 140 ms) at the same delay time.
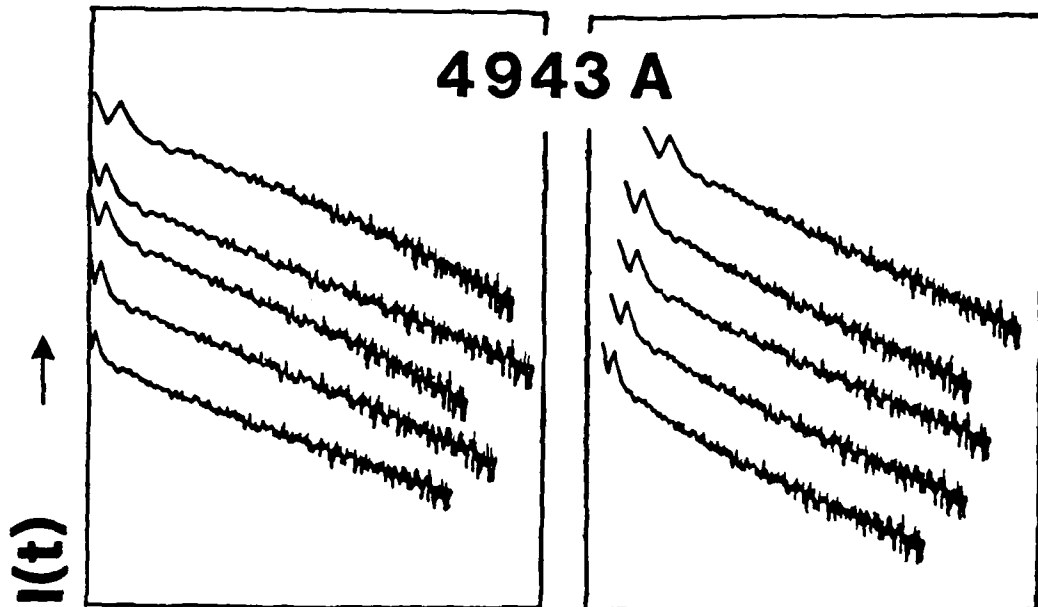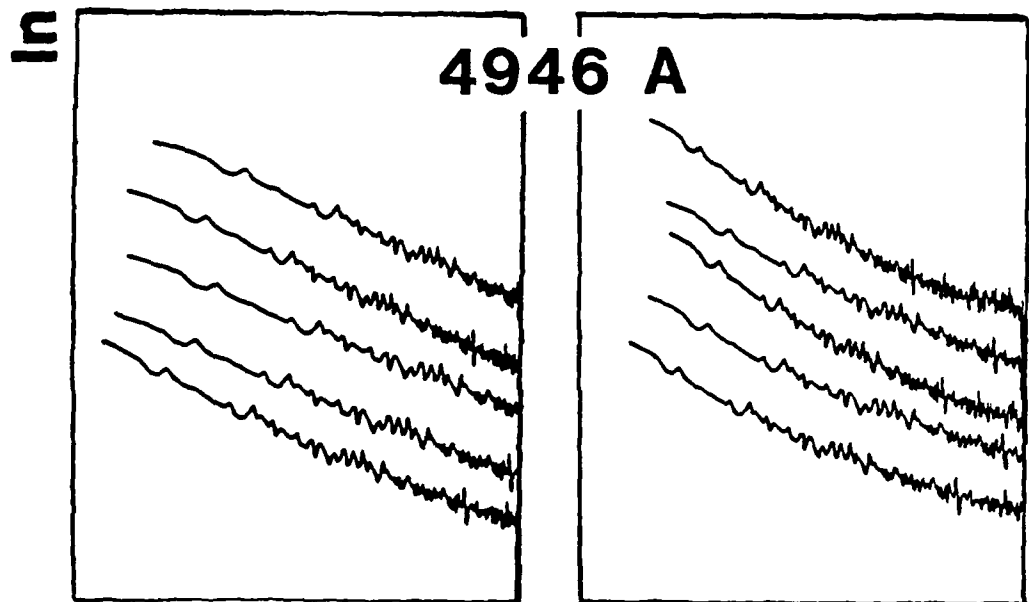
(a)

DELAY=
10μs

100μs

1000μs

10μs
T > 4.2K

INTENSITY →

5020   5030   5040   5050
WAVELENGTH (Å)

(b)

λ_EXC =
4943Å

4940Å

4939Å

4937Å

INTENSITY →

5025   5030   5040   5050
WAVELENGTH (Å)

EXCHANGE   DIPOLE

4943 A

4946 A

$\ln^D t \rightarrow$ $t^{D/6} \rightarrow$
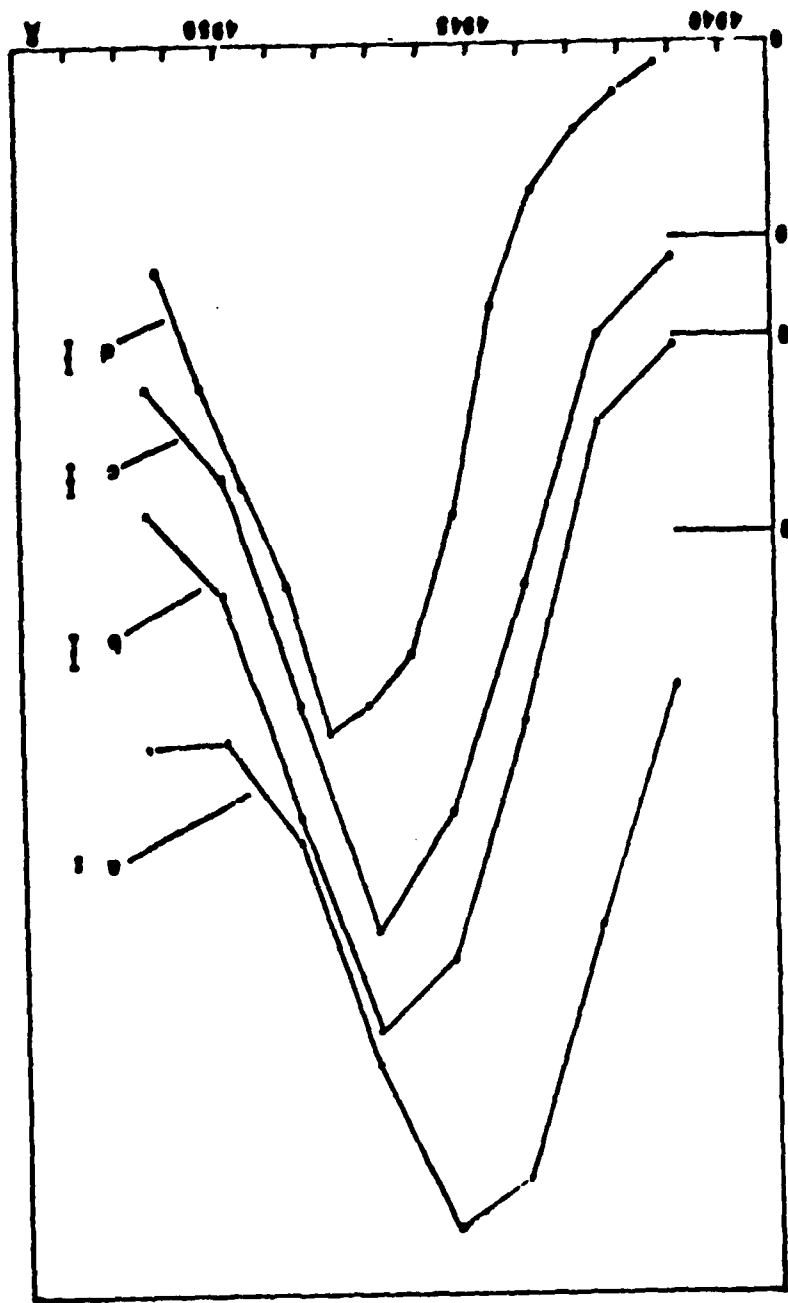
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Dr. M. A. El-Sayed
Department of Chemistry
University of California
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Dr. George E. Walrafen
Department of Chemistry
Howard University
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Dr. E. R. Bernstein
Department of Chemistry
Colorado State University
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Dr. Joe Brandelik
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Dr. G. B. Schuster
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Dr. J.B. Halpern
Department of Chemistry
Howard University
Washington, D.C. 20059

Dr. Kent R. Wilson
Chemistry Department
University of California
La Jolla, California 92093

Dr. M. S. Wrighton
Department of Chemistry
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

Dr. G. A. Crosby
Chemistry Department
Washington State University
Pullman, Washington 99164

Dr. A. Paul Schaap
Department of Chemistry
Wayne State University
Detroit, Michigan 49207

Dr. Theodore Pavlopoulos
NOSC
Code 521
San Diego, California 91232

Dr. W.E. Moerner
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Dr. A.B.P. Lever
Department of Chemistry
York University
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