

Studies of Chemical and Physical Processes with Picosecond Lasers

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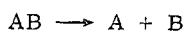
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In our efforts to understand the many competing pathways by which molecules in liquids dissipate energy by the emission of light and by nonradiative physical and chemical processes, we are inevitably led to dealing with the nature of the liquid state itself. Picosecond laser studies of the orientational and translational motions of molecules as well as the energy-exchanging processes and chemical reactions occurring in liquids are now providing new insights into both the nature of these fundamental processes and the properties of the liquid state. In this Account, I will discuss some of the work in our laboratory on ultrafast molecular processes in condensed media using picosecond lasers. In this rapidly developing field of picosecond spectroscopy a great deal of exciting work is going on, and the reader is referred to some of this excellent work in the papers and reviews indicated.¹

Photodissociation and the Cage Effect

If we were to initiate a dissociative chemical reaction in the gas phase, such as



we would find that the probability of the original fragments A and B reencountering one another before reacting with A and B fragments from other molecular dissociations in the system or reacting with other chemical species in the system is close to zero. However, if we were to carry out this experiment in a liquid, we would find that there is a significant probability for A and B to reencounter one another and thus produce the original parent molecule AB. In a liquid, the probability of recombination of the original fragments, called "geminate recombination," is greatly enhanced due to interactions with the surrounding solvent molecules which interfere with their escape. The chemistry following a dissociation event is therefore strongly dependent on the relative probability of (1) recombination of the original fragments which results in no net chemical change and (2) their escape and subsequent reaction with other species present in the system. This enhanced probability of recombination of the original fragments, first referred to by Franck and Rabinowitch in 1934 as the cage effect,² is dependent on the excess kinetic energy with which the fragments are born and the nature of the fragment-solvent interactions, e.g., the efficiency of momentum transfer.

Although there has been discussion of primary and

secondary cage effects, it is perhaps more useful to consider all recombinations of original partners as due to the cage effect. To arbitrarily separate the cage effect into primary and secondary processes is questionable since the cage is not, as originally postulated, a static structure as fragments bouncing around in a "rigid" solvent environment. As we shall demonstrate, the description of the cage effect must be of a dynamic nature dependent on the translational and rotational motions of both the fragment and solvent molecules.

Because the A and B fragments are generated by photodissociation, their distribution is not initially spatially random. Since A and B in the early time domain are more likely to be near each other, there are local concentration gradients in the solution, and one cannot use a conventional kinetic treatment to describe the dynamics of the geminate and nongeminate recombination processes. If we use a concentration-diffusion or random-flights description at least two problems come to mind. One is that the diffusion coefficient in the usual description is assumed to be independent of the separation of A and B, which may be incorrect for the processes considered here, since A and B are no more than a few molecular diameters apart in the early stages of the reaction. Second, the motions of A and B may be correlated and not describable by a random walk since the motion of one fragment influences the motion of the solvent molecules which can effect a drag on the other fragment. Furthermore, in these processes it may not be accurate to describe the solvent as a continuous and isotropic medium: motions in certain directions with certain displacement sizes may be favored.

Since the processes involved in "cage" effect reactions are in a time domain beyond the scope of conventional dynamic methods, the extensive studies of these phenomena have heretofore been investigated by indirect and time-independent methods. For example, information on the quantum yields for dissociation obtained from scavenger experiments have provided valuable insights into the nature of the "cage" processes.³ However, with these methods no

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(1) R. R. Alfano and S. L. Shapiro, *Sci. Amer.*, **228**, 43 (June 1973); P. M. Rentzepis, *Advan. Chem. Phys.*, **23**, 189 (1973); J. A. Giordmaine, *Phys. Today*, **39** (Jan 1969); J. W. Shelton and J. A. Armstrong, *IEEE J. Quantum Electron.*, **QE3**, 696 (1967); D. von der Linde, A. Laubereau, and W. Kaiser, *Phys. Rev. Lett.*, **26**, 954 (1971); R. I. Scarlet, J. F. Figueira, and H. Mahr, *Appl. Phys. Lett.*, **13**, 71 (1968); H. E. Lessing, E. Lippert, and W. Rapp, *Chem. Phys. Lett.*, **7**, 247 (1970); R. L. Carman, M. E. Mack, F. Shimizu, and N. Bloembergen, *Phys. Rev. Lett.*, **23**, 1327 (1969); N. G. Basov, P. G. Krjukov, and V. S. Letokhov, *Opt. Laser Tech.*, **2**, 126 (1970); D. J. Bradley, M. H. R. Hutchinson, H. Koester, T. Morrow, G. H. C. New, and M. S. Petty, *Proc. Roy. Soc. Ser. A*, **328**, 97 (1972).

(2) J. Franck and E. Rabinowitch, *Trans. Faraday Soc.*, **30**, 120 (1934).

(3) F. W. Lampe and R. M. Noyes, *J. Amer. Chem. Soc.*, **76**, 2140 (1954).

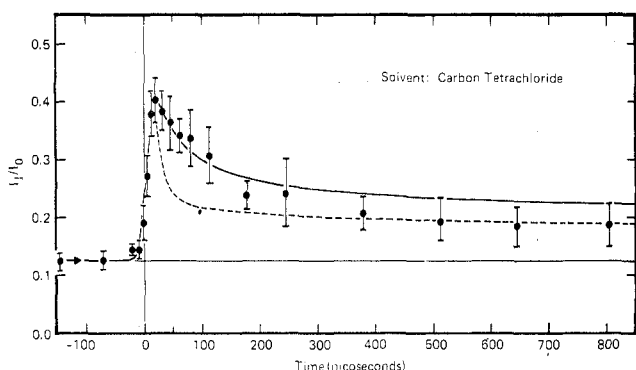


Figure 1. Probe transmission I_{\perp}/I_0 as a function of time after excitation for iodine in CCl_4 . Dashed and solid curves are the decay functions calculated from Noyes random flight model.

measurements of the dynamics of the geminate recombinations were possible, and thus we had no idea of the time scale for the geminate processes, *i.e.*, if it was of 10^{-13} sec or 10^{-11} sec or 10^{-9} sec duration. To determine the nature of "cage" effect reactions, it is necessary to obtain information on the early time motions of the fragments since this is the key to the partitioning between geminate and nongeminate recombinations.

The system selected for this study was I_2 since it is a simple molecule of great interest and a great deal is known about its spectroscopic properties and chemistry. Two different solvents, namely hexadecane and carbon tetrachloride, were used in these experiments.⁴ The system is pulsed with an intense 5300-Å picosecond light pulse (half-width ~ 5 psec). At this frequency I_2 is excited to the $^3\Pi_{0+u}(\nu' \approx 33)$ state. (A small fraction of I_2 molecules are excited to the $^1\Pi_u$ state and directly dissociate.)

The I_2 molecules in the $^3\Pi_{0+u}$ state undergo a collisionally induced predissociation leading to a pair of ground state, $^2\text{P}_{3/2}$, iodine atoms. The iodine atoms can geminately recombine or can escape and subsequently react with iodine atoms produced elsewhere in the liquid. The population of I_2 molecules is monitored with a weak 5300-Å picosecond light pulse from times prior to the strong excitation pulse up through 800 psec after the excitation pulse. The strong excitation pulse depopulates a good fraction of the ground-state I_2 molecules and thus yields an increase in the transmission of the probe pulse. As the iodine atoms recombine, the population of absorbers (iodine molecules) increases and therefore the transmission of the probe pulse decreases. In this way we can follow the recombination dynamics of the iodine atoms by monitoring the time-dependent population of I_2 molecules. The picosecond time resolution is readily obtained by spatially delaying the probe pulse with respect to the excitation pulse; a 1-mm path difference in air is equal to a 3.3-psec time delay.

In Figures 1 and 2 we see the transmission of the probe light increases to a peak value at about 20–25 psec after the strong excitation pulse in both the CCl_4 and hexadecane solvents. The transmission reaches a stable value in both solvents at about 800 psec. The residual difference in absorption between the long time values (800 psec) and the initial absorp-

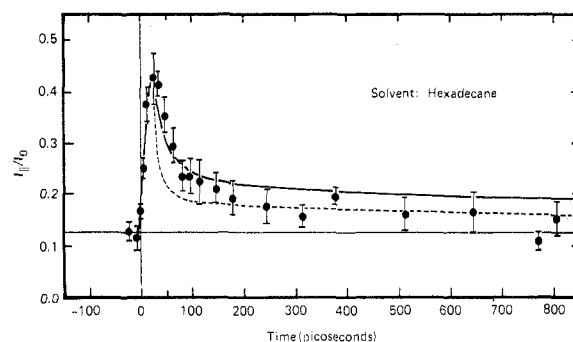


Figure 2. Probe transmission I_{\perp}/I_0 as a function of time after excitation of iodine in hexadecane. Dashed and solid curves are the decay functions calculated from Noyes random flight model.

tion ($t < 0$) is due to those iodine atoms which have escaped their original partners. The iodine atoms which have escaped will recombine at much later times ($> 10^{-8}$ sec) with iodine atoms from other dissociation events, *i.e.*, the nongeminate recombination. We thus have observed the dynamics of the geminate recombination (the cage effect) and the escape of fragments leading to the nongeminate recombination processes. The geminate recombination times (decrease by e^{-1} from peak values) are about 70 psec in hexadecane and 140 psec in carbon tetrachloride. It seems unlikely that a description of the cage effect as the collisions of the iodine atoms inside a static solvent cage would be consistent with the time scale of these geminate recombinations.

To describe the dynamics of the recombination, Noyes's treatment based on a random flight model was used.⁵ The theoretical curves, the solid and dashed lines, are shown in Figures 1 and 2. In comparing the theory to our experimental results we find that, if we adjust the theoretical curve to fit the long time behavior, where one would expect the random-walk description to be most valid, the early time behavior is too rapidly decaying. The lack of agreement between theory and our experimental results can be due to the crudeness of the theory, *e.g.*, assuming one distance between the iodine atoms on thermalization rather than a distribution of distances, or to the more fundamental issues mentioned earlier, namely the correctness of a random walk description for atoms within several Ångströms of each other. We are presently investigating this issue *via* a simulated molecular dynamic calculation of the dissociation and recombination to better theoretically describe the cage effect in liquids.

Figures 1 and 2 also provide information on the dynamics of the collision-induced predissociation process which generates the iodine atoms from the laser-excited bound $^3\Pi_{0+u}$ state. The observed peak in the probe transmission occurs at a time (20–25 psec) significantly after the decay of the excitation pulse (full width less than 8–10 psec) in both the CCl_4 and hexadecane solvents. Therefore, the continual rise in the transmission of the probe light after the excitation pulse cannot be due to the further depopulation of the ground-state iodine molecules by the excitation pulse. The rise time of the transmission can be explained by assuming that the probe light can be ab-

(4) T. J. Chuang, G. W. Hoffman, and K. B. Eisenthal, *Chem. Phys. Lett.*, **25**, 201 (1974).

(5) R. M. Noyes, *J. Chem. Phys.*, **22**, 1349 (1954); *J. Amer. Chem. Soc.*, **78**, 5486 (1956).

sorbed not only by ground-state but also by the $^3\Pi_{0+u}$ excited iodine molecules. The photodissociative recoil studies of Busch, *et al.*,⁶ on I_2 show that I_2 in the $^3\Pi_{0+u}$ state does absorb at 0.53μ . Thus, the probe pulse is monitoring the change in both the ground and excited iodine molecule populations. We therefore conclude that after the excitation pulse reduces the ground-state population the subsequently observed increase in the probe transmission is due to the decay of the excited iodine molecules into iodine atoms. We have thus obtained from this experiment what we believe to be the first direct observation of the dynamics of a collision-induced predissociation in the liquid state and find a pseudo-first-order rate constant of about 10^{11} sec^{-1} . This is about 10^5 larger than the spontaneous predissociation process observed in I_2 at low pressures in the gas phase.

Orientalional Relaxation

The excitation of isotropically distributed molecules with linearly polarized light produces a nonuniform orientational distribution in the excited- and ground-state molecular populations. This induced anisotropy in the orientational distribution of molecules decays in time (the orientational relaxation time) due to the time-varying torques the molecules experience in collision with surrounding molecules. Thus, the randomizing rotational motions of the molecules leads to a depolarization of the emitted radiation⁷ and a decay of the induced dichroism. In this study the decay of the dichroism induced with a picosecond excitation light pulse was used to obtain the orientational relaxation time of the dye Rhodamine 6G in a variety of liquids.⁸ In particular, the effects of solute-solvent hydrogen-bonding interactions on the rotational motion of the solute Rhodamine 6G was studied by measuring the orientational relaxation time in a series of hydrogen-bonding solvents.⁹

In these orientational relaxation studies we are monitoring the intensities of the transmitted probe pulses, polarized parallel and perpendicular to the excitation pulse field, at times subsequent to the excitation pulse. For the parallel component of the probe pulse we have

$$I_{\parallel}(t)/I_{\parallel}^0 = e^{-\alpha_{\parallel}(t)l} \quad (1)$$

where $\alpha_{\parallel}(t)$ is the absorption coefficient for probe light polarized in the parallel direction and l is the path length of the cell ($\sim 0.5 \text{ mm}$). We can obtain theoretical expressions for $\alpha_{\parallel}(t)$ and $\alpha_{\perp}(t)$ assuming that the rotational motion is governed by the diffusion equation or in a correlation function form which is independent of the model for rotational motion.¹⁰

The absorption coefficients are given by

$$\alpha_{\parallel}(t) \sim \int n(\Omega, t) |\hat{\mu}_{\Omega} \cdot \hat{e}_{\parallel}|^2 d\Omega \quad (2)$$

and a similar one for $\alpha_{\perp}(t)$, where $n(\Omega, t)$ is the density of unexcited molecules at the time t having their transition moments pointing in the direction Ω by $d\Omega$. In turn $n(\Omega, t)$ can be written as,

$$n(\Omega, t) = n_0 \omega(\Omega, t) \quad (3)$$

where n_0 is the density of unexcited molecules immediately after the excitation pulse and $\omega(\Omega, t)$ is the probability of a given one pointing in the direction Ω by $d\Omega$ at time t . In the diffusion picture $\omega(\Omega, t)$ obeys the equation

$$\frac{\partial \omega(\Omega, t)}{\partial t} = D \nabla^2 \omega(\Omega, t) \quad (4)$$

for the case of isotropic rotational motions where D is the rotational diffusion coefficient. We have also used the diffusion equation for anisotropic motion, i.e., ($D_x \neq D_y \neq D_z$) and the results will appear in a subsequent publication.⁸ In the experiments on Rhodamine 6G, we found that the motion was isotropic and therefore we will restrict our discussion to this case.

Substituting the solutions from eq 4 into eq 2, we find

$$\ln \frac{I_{\parallel}(t)}{I_{\parallel}^0} = C e^{-6Dt} \quad (5)$$

where C is a constant and $(6D)^{-1}$ is the orientational relaxation time τ_{OR} . If τ_{OR} is comparable to the excited-state lifetime τ of Rhodamine 6G, then we must include in our description not only the absorption at some time t of probe light by ground-state molecules which were never excited but also absorption due to ground-state molecules which were initially excited but have decayed to the ground state at some time equal to or prior to the time t . We therefore have to describe the rotational motion of the excited molecule having a τ^*_{OR} , its decay at time t' , its subsequent rotation as a ground-state molecule having a τ_{OR} up to the time t of the absorption measurement. These considerations lead to the following expression.

$$\ln \frac{I_{\parallel}(t)}{I_{\parallel}^0} = C e^{-6Dt} \left[1 - \frac{1 - e^{-t[(1/\tau) + 6(D^* - D)]}}{1 + 6(D^* - D)\tau} \right] \quad (6)$$

From our experimental results we find that we obtain the best fit assuming $D^* = D$, i.e., the orientational relaxation times for ground and excited-state molecules are equal. This assumption of $D^* = D$ to obtain the best fit with our absorption measurements was subsequently verified by us in our measurements of D^* from emission experiments. For this case of $D^* = D$ we therefore find that the decay constant in eq 6 is $(1/\tau) + 6D$. In our experiment we independently measure $(1/\tau) + 6D$ and $1/\tau$ to obtain $6D$.

In deriving expressions to relate our experimental measurements to a dipole correlation description, i.e., a description independent of any model for rotational motion, we assume for simplicity that the ground and excited state rotations are equal. As in the previous treatment, we assume that for the time scale of our measurements vibrational relaxation in the excited-state manifold is rapid and thus the probe pulse does not induce any stimulated emission. We find that for the excitation intensity and path length

(6) G. E. Busch, R. T. Mahoney, R. I. Morse, and K. R. Wilson, *J. Chem. Phys.*, **51**, 837 (1969).

(7) T. J. Chuang and K. B. Eisenthal, *J. Chem. Phys.*, **57**, 5094 (1973).

(8) K. B. Eisenthal and K. H. Drexhage, *J. Chem. Phys.*, **51**, 5720 (1969); T. J. Chuang and K. B. Eisenthal, *Chem. Phys. Lett.*, **11**, 368 (1971); T. J. Chuang and K. B. Eisenthal, to be published.

(9) R. E. D. McClung and D. Kivelsen, *J. Chem. Phys.*, **49**, 3380 (1968); N. S. Augerman and R. B. Jordan, *J. Chem. Phys.*, **54**, 837 (1971); J. Crossley, *Advan. Mol. Relaxation Processes*, **2**, 69 (1970); W. G. Rothschild, *J. Chem. Phys.*, **53**, 990 (1970); G. L. Hofacker and U. A. H. Hofacker, *Proc. 14th Colloque AMPERE (At. Mol. Etud. Radio Elec)*, **14**, 502 (1969).

(10) R. G. Gordon, *Advan. Magn. Res.*, **3**, 1 (1968); B. J. Berne and G. D. Harp, *Advan. Chem. Phys.*, **17**, 63 (1970).

of the cell used in our experiments stimulated emission arising from spontaneously decaying excited molecules is not important. Lastly, it is assumed that dephasing is sufficiently rapid that only the molecular populations of ground and excited molecules need be considered.

On excitation of the system at $t = 0$ with an intense light pulse polarized in the direction \hat{e}_i , the probability of an *unexcited* molecule (at the conclusion of the excitation pulse) having its absorption axis oriented in the direction $\hat{\mu}(0)$ is proportional to

$$1 + e^{-\alpha |\hat{e}_i \cdot \hat{\mu}(0)|^2} \quad (7)$$

where α is a constant. In the same way the probability of excitation of a molecule by a weak probe pulse polarized parallel to the excitation pulse at a time t after the excitation pulse is proportional to

$$|\hat{e}_i \cdot \hat{\mu}(t)|^2 \quad (8)$$

where $\hat{\mu}(t)$ is the unit vector giving the orientation of the molecular absorption axis at time t . Combining eq 7 and 8, we obtain the probability for absorption of probe light polarized parallel to the excitation light at time t after the excitation pulse is proportional to the ensemble average

$$\langle (1 + e^{-\alpha |\hat{e}_i \cdot \hat{\mu}(0)|^2}) |\hat{e}_i \cdot \hat{\mu}(t)|^2 \rangle \quad (9)$$

As in our earlier discussion of the case where τ_{OR} is comparable to the excited-state lifetime τ , we must include the possible absorption of light by a molecule which was initially excited but has returned to the ground state by the time t of the measurement. The probability for probe absorption at time t is now given by

$$\langle (1 + e^{-\alpha |\hat{e}_i \cdot \hat{\mu}(0)|^2}) |\hat{e}_i \cdot \hat{\mu}(t)|^2 \rangle + \left\langle \int_0^t dt' \frac{e^{-t'/\tau}}{\tau} (1 - e^{-\alpha |\hat{e}_i \cdot \hat{\mu}(0)|^2}) |\hat{e}_i \cdot \hat{\mu}(t)|^2 \right\rangle \quad (10)$$

where $1 - e^{-\alpha |\hat{e}_i \cdot \hat{\mu}(0)|^2}$ is proportional to the probability of an excited molecule having its transition moment oriented in the direction $\hat{\mu}(0)$ at $t = 0$. The analogous expression for probe light polarized perpendicular to the excitation polarization is given by

$$\frac{1}{2} \langle (1 + e^{-\alpha |\hat{e}_i \cdot \hat{\mu}(0)|^2}) |\hat{e}_i \times \hat{\mu}(t)|^2 \rangle + \frac{1}{2} \left\langle \int_0^t dt' \frac{e^{-t'/\tau}}{\tau} (1 - e^{-\alpha |\hat{e}_i \cdot \hat{\mu}(0)|^2}) |\hat{e}_i \times \hat{\mu}(t)|^2 \right\rangle \quad (11)$$

Since the system was isotropic before excitation, the absorption cross sections are independent of the polarization of the exciting pulse and we can average over \hat{e}_i . After carrying out this average and combining eq 10 and 11, we find the logarithm of the ratio of the transmitted pulses to be given by

$$\ln \frac{I_{||}(t)}{I_{\perp}(t)} \sim \langle P_2[\hat{\mu}(0) \cdot \hat{\mu}(t)] \rangle e^{-t/\tau}$$

where $P_2(\chi)$ is the Legendre polynomial of degree two and $\langle P_2[\hat{\mu}(0) \cdot \hat{\mu}(t)] \rangle$ is the dipole correlation function which contains all rotational motion information.⁸ If the rotational motion obeys the isotropic diffusion equation, then

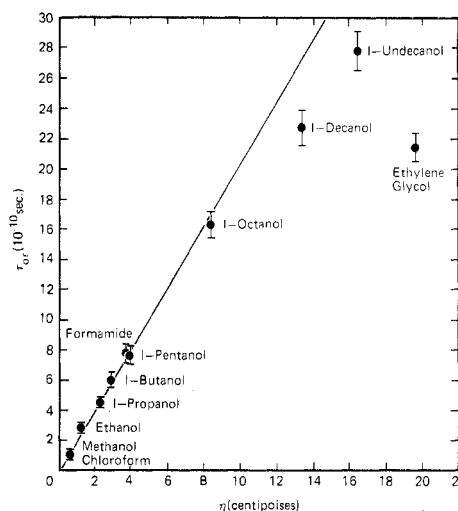


Figure 3. Orientational relaxation time vs. solution viscosity of Rhodamine 6G in various solvents.

$$\langle P_2[\hat{\mu}(0) \cdot \hat{\mu}(t)] \rangle \sim e^{-6Dt}$$

and therefore

$$\ln \frac{I_{||}(t)}{I_{\perp}(t)} \sim e^{-(6D+1/\tau)t}$$

as found earlier.

By combining these theoretical expressions with our picosecond measurements we were able to determine the effects of solute-solvent hydrogen bonding on the rotational motion of Rhodamine 6G in a wide range of solvents. As shown in Figure 3 we obtained a linear relation between the measured relaxation times and the measured solution viscosities for the series chloroform, formamide, and the alcohols from methanol through octanol. The observed linear scaling is in agreement with the Debye-Stokes-Einstein hydrodynamic model¹¹ for the case in which the hydrodynamic volume V of the rotating particle is a constant, i.e. $\tau_{OR} = \eta V/kT$, where η is the shear viscosity. This agreement with the hydrodynamic model is rather surprising since the volumes of the hydrogen-bonded complexes should vary considerably through the series from methanol, chloroform, to octanol. Furthermore one might expect that, since the strengths of hydrogen-bonding interactions of Rhodamine 6G with chloroform and methanol are different, the relaxation times would not be equal even though the viscosities are the same.¹² Similar arguments can be applied to the results obtained in the liquids formamide and 1-pentanol. To explain the apparent insensitivity of the orientational relaxation times to the volumes of the hydrogen-bonded complexes and the strengths of hydrogen-bonding interactions, we first assume that the rotational motion of the complex cannot be described as that of a rigid particle. Allowing some flexibility in the hydrogen bond,¹³ it is then assumed that rotational motion of the solute of the order of several degrees with respect to the hydrogen bond does not introduce any signifi-

(11) P. Debye, "Polar Molecules," Dover, London, 1929, p 84.

(12) L. V. Levshin and D. M. Akbarova, *J. Appl. Spectrosc. (USSR)*, **3**, 326 (1965).

(13) G. C. Pimentel and A. L. McClellan, "The Hydrogen Bond," Freeman, San Francisco, Calif., 1960, p 267; J. Donohue, *Struct. Chem. Mol. Biol.*, 443 (1968).

cant strains in the solute-solvent hydrogen bond. However, on larger rotations the resulting strains in the hydrogen bond should be reflected in the solution rotations. This effect of strain on the solute rotation is most likely minimized by the rapid forming and breaking of the hydrogen bond with the same or other surrounding solvent molecules. Thus, combining flexibility in the hydrogen bond with the dynamic process of bond forming and breaking, we see that the rotational motion of the solute will be roughly the same whether it is hydrogen bonded or not. Thus the hydrodynamic volume is unchanging through the series of liquids studied, and the linear scaling of τ_{OR} with η becomes plausible. Furthermore, if the time variation in the torques responsible for the solute rotation that the solute experiences in interacting with the surrounding solvent molecules is primarily dependent on solvent-solvent interactions (which in turn determines the solution viscosity), then the linear scaling of τ_{OR} vs. η found in the Rhodamine 6G solvent systems is not surprising. The observed deviation of τ_{OR} in the liquids 1-decanol and 1-undecanol from the linear plot is due to the breakdown of the continuum hydrodynamic model since the solvent molecules are larger than the solute molecule. The sharp deviation observed in the ethylene glycol solvent is thought to be due to the extensive solvent-solvent aggregation *via* hydrogen bonding. If the solute does not experience the full frictional effects of this aggregation, then the τ_{OR} will be faster than the measured viscosity would lead one to expect. The measured orientational relaxation time would thus deviate below the τ_{OR} vs. η line, as we find to be the case in this system.

Intermolecular Energy Transfer

Studies of the time development for the intermolecular transfer of electronic energy have heretofore been limited to the nanosecond time domain.¹⁴ Direct determination of the laws governing the dynamics of energy transfer in the previously inaccessible subnanosecond time domain has now been studied with picosecond light pulses.¹⁵

As in other studies, the system of uniformly distributed donor and acceptor molecules is perturbed by a picosecond pulse which excites some fraction of the donor molecules to their lowest excited singlet electronic state. The orientational anisotropy induced by excitation with a linearly polarized pulse can only relax, in a rigid environment, by the unimolecular decay of the excited molecules and by energy transfer since rotational motions are frozen out. In a system where the donor and acceptor molecules are of the same species, the randomization results from transfer between molecules of different orientations. On the other hand, in a mixed system the anisotropy in donor orientations can also relax by transfer between donor and acceptor molecules regardless of their mutual orientation.

The decay of the anisotropy is monitored by measuring the time-dependent change in the dichroism in the donor absorption with an attenuated picosecond probe pulse. The absorption of the probe pulse

polarized perpendicular to the excitation is initially larger than the absorption of the parallel component since the excitation pulse has preferentially depleted the population of ground-state molecules which were oriented with their absorption axis parallel to the polarization of the excitation pulse. The measured dichroism decays in time due to energy transfer and the unimolecular decay of the excited molecules. The contribution of energy transfer to the time-dependent change of the dichroism is separated from the effects of unimolecular decay by an independent measurement of the latter quantity.

Although energy transfer has been studied in both one- and two-component systems, the two-component system which consists of distinguishable donor and acceptor molecules is simpler to treat theoretically.¹⁶ This latter case is theoretically simpler to treat since the acceptor molecules, present at a higher concentration than the donor molecules, are randomly distributed with respect to the excited donor molecules. On the other hand, in the one-component system there is a nonrandom distribution of unexcited molecules (acceptors) with respect to the excited molecules (donors) due to the excitation of the system by linearly polarized light. In addition, in the one-component case several transfer steps can occur and must be included in a theoretical treatment, whereas in a mixed system, where the acceptor is at a concentration 10-100 greater than excited donors, there is only one transfer step to be considered.

The energy migration in either the one- or the two-component systems is obtained by measurements of the time dependence of the transmitted parallel and perpendicular components of the probe pulse. We obtain

$$\frac{I_{\parallel}(t)}{I_{\perp}(t)} = e^{-[\alpha_{\parallel}(t) - \alpha_{\perp}(t)]l}$$

where $\alpha_{\parallel}(t)$ and $\alpha_{\perp}(t)$ are the absorption coefficients for probe light polarized parallel and perpendicular, respectively, to the excitation pulse polarization at time t after the excitation pulse, and l is the path length of the system. The absorption coefficient for the parallel component is given by

$$\alpha_{\parallel}(t) \sim \epsilon \int n(\Omega, t) l_{\mu_{\parallel}}^2 d\Omega + \epsilon^* \int n^*(\Omega', t) l_{\mu^*_{\parallel}}^2 d\Omega'$$

where ϵ and ϵ^* indicate the strengths of the transition for ground-state and excited-state molecules, respectively, $n(\Omega, t)$ and $n^*(\Omega', t)$ are the densities of ground- and excited-state molecules at time t having their transition moments μ and μ^* oriented in the direction $\Omega \pm d\Omega$ and $\Omega' \pm d\Omega'$, respectively, and $l_{\mu_{\parallel}}^2$ and $l_{\mu^*_{\parallel}}^2$ are the squares of the projection of the transition moments on the parallel direction of the probe field. The first term gives the absorption due to ground-state donor molecules and the second term is the absorption, if any, due to excited-state molecules. Since the donor molecules were uniformly distributed prior to the excitation pulse, we obtain for the two-component case

$$n(\Omega, t) = \frac{N}{4\pi} - n^*(\Omega, 0)\bar{\omega}(t)$$

(14) R. G. Bennett, *J. Chem. Phys.*, **41**, 3037 (1964).

(15) D. Rehm and K. B. Eisenthal, *Chem. Phys. Lett.*, **9**, 387 (1971).

(16) T. J. Chuang, R. J. Cox, and K. B. Eisenthal, to be published.

N is the total density of donor molecules, $n^*(\Omega, 0)$ is the density of excited donors oriented in the direction Ω immediately after the excitation pulse at $t = 0$, and $\bar{\omega}(t)$ is the donor decay function which contains the dynamics of the energy transfer. Similarly

$$n^*(\Omega, t) = n^*(\Omega, 0)\bar{\omega}(t)$$

The absorption coefficients for the parallel and perpendicular components of the probe light are then found to be

$$\alpha_{\parallel}(t) = C_1 - C_2\bar{\omega}(t)$$

$$\alpha_{\perp}(t) = C_1 - C_4\bar{\omega}(t)$$

where C_1 and C_4 are constants.

The ratio of the transmitted parallel and perpendicular components of probe beam at the time t after excitation is

$$\frac{I_{\parallel}(t)}{I_{\perp}(t)} = \exp[(C_2 - C_4)\bar{\omega}(t)]$$

In Förster's formulation of dipole-dipole transfer, $\bar{\omega}(t)$ is given by¹⁷

$$\bar{\omega}(t) = \exp\left[-\frac{t}{\tau_0} - 0.845\pi^{1/2}N_A\left(\frac{R_0}{R_g}\right)^3\left(\frac{t}{\tau_0}\right)^{1/2}\right]$$

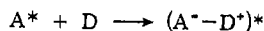
where τ_0 is the excited donor lifetime in the absence of acceptors, C_A is the acceptor concentration

$$C_A = \frac{N_A}{\frac{4}{3}\pi R_g^3}$$

and R_0 , called the critical transfer distance, is a measure of the dipole-dipole coupling strength. A comparison between theory and experiment is shown in Figure 4 for the system Rhodamine 6G (donor) at $5 \times 10^{-4} M$ and Malachite Green at $5 \times 10^{-3} M$ in glycerol. The value for R_0 obtained from this experiment is 53 Å, which is in reasonable agreement with the value calculated from the donor and acceptor spectra of 48 Å. It is thus seen from this work that the Förster treatment is a good description of singlet-singlet energy transfer up to the earliest times so far measured, i.e., about 20 psec.

Excited-State Electron-Transfer Processes

In addition to the intermolecular transfer of energy that we have just considered there is another important class of excited-state interactions that involve, rather than the transfer of energy, the transfer of charge of the type



This charge-transfer process which we are considering occurs between excited- and ground-state molecules and not between ground-state molecules. The transfer of an electron from the donor molecule D to the excited acceptor molecule A^* quenches the normal A^* fluorescence, gives rise to a new emission in low dielectric solvents, can produce ion radicals, can provide new pathways for energy degradation, and

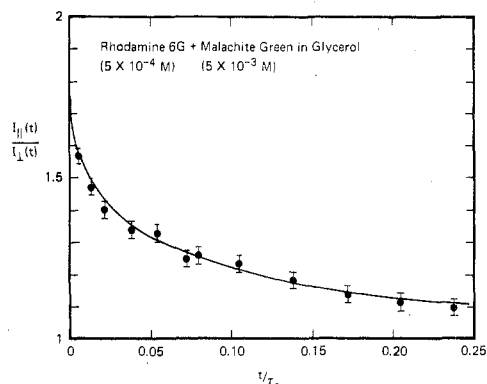


Figure 4. Probe transmission ratio I_{\parallel}/I_{\perp} as a function of time after the excitation pulse. τ_0 is the excited state donor lifetime in the absence of acceptors.

can change the chemistry of the system. The physical and chemical natures of these diverse processes have been extensively studied since the discovery of excited-state charge-transfer complexes by Leonhardt and Weller,¹⁸ but heretofore not in the subnanosecond time region which is of key importance to an understanding of these events. In addition to our interest in the charge-transfer process and the subsequent energy dissipation, the electron-transfer reaction between A^* and D provides an excellent vehicle for testing the theories of diffusion-controlled chemical reactions.

In conventional kinetic treatments it is assumed that the reactivity of a molecule does not change in any interval of time subsequent to the formation of the reactive molecule. In other words, it is assumed that the reactivity at time t is the same as it was at earlier times and will be the same at future times. This is equivalent to stating that there is an equilibrium distribution of reacting molecules at all times and thus the reaction can be described by a time-independent rate constant. However, in a highly reactive system this description is incorrect.

The time dependence of the chemical reaction can be viewed in the following way. At time $t = 0$, the molecules A^* and D are randomly distributed, but as time proceeds those distributions in which an A^* is near to a D are preferentially depleted since there is a higher probability for reaction than for those distributions in which A^* and D are far apart. This produces a spatially nonuniform distribution of molecules leading to a flux of molecules from the more concentrated to the less concentrated regions of the liquid. Since the distribution of molecules is changing with time, the rate "constant" for the reaction is also changing with time. To test theory and its limits adequately, it is necessary to determine the full time behavior of the chemical reaction. Picosecond laser studies were therefore initiated on the anthracene (acceptor) and diethylaniline (donor) system to determine the key parameters of the electron-transfer process and to test the theories of diffusion-controlled chemical reactions.¹⁹

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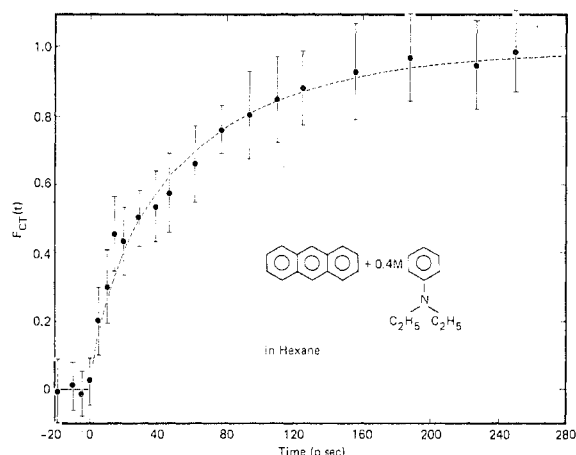
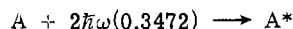


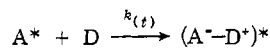
Figure 5. Charge-transfer complex formation, F_{CT} (normalized population), vs. time for anthracene plus diethylaniline in hexane. The solid line is the theoretical curve.

A single laser pulse was extracted from the train of pulses generated by a mode-locked ruby laser and was frequency doubled from the fundamental at 0.6943 μ to 0.3472 μ . The 0.3472- μ phase was then used to excite the 1L_a state of anthracene. The fundamental frequency of the laser at 0.6943 μ is resonant with a transition of the excited charge-transfer complex²⁰ (A^--D^+)*. The sequence of steps in the experiment are

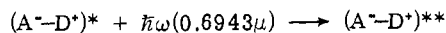
Formation of acceptor A^+



Electron transfer



Detection of (A^--D^+)* formation



To separate changes in absorption by (A^--D^+)* in time due to the (A^--D^+)* population growth on the one hand from absorption changes due to changes in the orientational distribution of (A^--D^+)*, the absorptions of probe pulses polarized in the directions both parallel and perpendicular to the excitation pulse polarization are carried out. The sum of the absorbances for the three directions is independent of any changes in the orientational distribution of (A^--D^+)* and gives the charge-transfer population at the time of the measurement.

From Figure 5 we note that our experimental results are in good agreement with the theoretical curve which includes all transient terms. This full transient term behavior, or equivalently the time changing character of the rate "constant," is thus established. There are two parameters which can now be legitimately extracted from the fitting of the theoretical

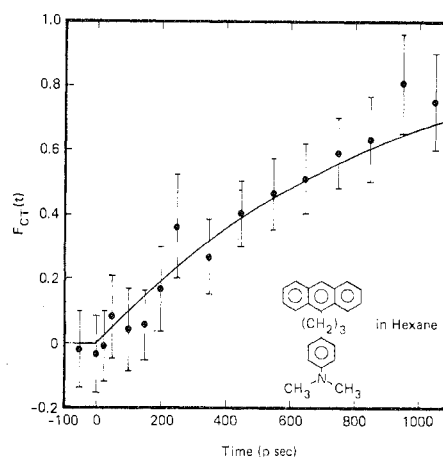


Figure 6. Charge-transfer complex formation, F_{CT} (population normalized), vs. time for anthracene-(CH_2)₃-dimethylaniline in *n*-hexane. The curve is the calculated exponential formation function.

expression to the experimental curve. One is the distance of separation between D and A^* at which electron transfer occurs, R , and the second is the rate constant, k , for the reaction between D and A^* at an equilibrium separation of R . The values obtained are $R = 8 \text{ \AA}$ and $k = 10^{11} \text{ l./(mol sec)}$. On varying the diethylaniline concentration from 0.1 to 1 *M* and maintaining a constant anthracene concentration with hexane as the solvent, good agreement with theory is obtained. In all cases the same values of R and k are obtained, namely 8 \AA and $10^{11} \text{ l./(mol sec)}$, respectively. However, in systems containing 3 *M* diethylaniline or in the neat diethylaniline liquid the formation of the excited charge-transfer complex (A^--D^+)* follows an exponential time dependence characteristic of a bimolecular process with a single time-independent rate constant of 10^{11} sec^{-1} . At these high diethylaniline concentrations it therefore appears that translational motions as contained in the diffusion treatment are not of key importance.

To determine the nature of any orientational requirements on the D to A^* electron-transfer process the dynamics of the formation of the excited-state charge complex for the model compound anthracene-(CH_2)₃-dimethylaniline in hexane was studied¹⁶ using the same methods as described earlier. In this molecule anthracene is connected to dimethylaniline by three methylene groups and the D and A separation is about 4 \AA . From our previous studies on the free anthracene plus diethylaniline system, the rate of charge-transfer complex formation should be of the order of 10^{11} sec^{-1} for distances of separation of the order of 4 \AA if there are no orientational requirements. From Figure 6 we find that the formation curve is exponential with a time constant of approximately 900 psec. We therefore conclude that, although D and A^* are within a distance at which transfer should be very rapid (10^{-11} sec), rotation of the donor and acceptor groups about the methylene bonds to some favorable orientation is necessary, and thus the orientational requirements place a severe restriction on the electron-transfer rate.

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