Picosecond Laser Studies of Ultrafast Processes in Chemistry

Ying Wang and K. B. Eisenthal

Columbia University, New York, NY 10027

A molecule absorbs photons by interaction with a light field. The absorbed energy can then be dissipated by either the reemission of light or by competing nonradiative processes. Some of the relaxation processes (e.g., internal conversion and energy transfer) do not change the chemical nature of the molecular system, while others (e.g., electron transfer and bond cleavage) can induce permanent chemical transformations. An understanding of the various pathways by which molecules dissipate their energy is of foremost importance in the study of molecular photophysics, photochemistry, and photobiology. Many of these relaxation processes occur on a subnanosecond time scale. It is thus necessary to monitor the time evolution of the system in this time domain.

In the past several years, we and others have applied the techniques of picosecond laser spectroscopy to study various molecular energy relaxation phenomena in liquids, obtaining new insights into the nature of these processes and the properties of the liquid state (1). In our laboratory these studies include: (a) orientational relaxation of molecules in liquids (2, 3), (b) molecular energy transfer (4), (c) inter- and intramolecular charge transfer interactions (5-10), (d) photoionization and electron solvation (11), (e) intramolecular proton transfer reactions (12, 13), (f) photodissociation (14, 15), and (g) cage effects in liquids (16). In this paper we will discuss excited state charge transfer interactions and cage effects in liquids to exemplify the power of picosecond laser spectroscopy in the study of rapid molecular phenomena.

Experimental Techniques

We use a picosecond laser pulse to excite the molecules of interest and monitor the subsequent time evolution of the system by the emission, absorption, and Raman scattering characteristic of the transient species. These techniques are discussed in the following sections.

I. Picosecond Time-Resolved Emission and Absorption Spectroscopy

Generation and Tuning of a Picosecond Laser Pulse

A Nd³⁺-glass laser is set up for the emission and absorption studies. Two different cavity configurations have been used to generate the picosecond pulses as shown in Figure 1a and 1b. In the "normal" passive mode-locking configuration (Fig. 1a) a train of picosecond pulses separated by the round trip time of the cavity (~8 ns) is generated from the output mirror of the laser cavity. A single pulse is then extracted from the pulse selector, which consists of a Pockels cell and two crossed polarizers. The first polarizer is oriented such that its polarization axis is parallel to that of the laser beam, while the second polarizer with a perpendicular polarization axis rejects the pulses in the train onto a pin photodiode. As the intensity of successive pulses grows, one pulse finally reaches the threshold to trigger the Pockels cell driver, and a high voltage pulse is then applied to the Pockels cell. This rotates the polarization of the next pulse to reach the Pockels cell by 90° and

thus enables it to pass through the second polarizer. A typical rejected pulse train with a single pulse extracted from it is shown in Figure 2a.

In the passive mode-locking/cavity dump configuration (Fig. 1b), the Pockels cell and polarizer are situated inside the cavity. The mode-locked pulse oscillates inside the laser cavity as in the earlier configuration until the Pockels cell is triggered by the pulse leaking through the output mirror. This rotates the polarization of the oscillating pulse and effectively

a) PASSIVE MODE-LOCKING



b) PASSIVE MODE-LOCKING / CAVITY DUMP



Figure 1. *a*, A passively mode-locked laser oscillator and single pulse selector. *b*, A passively mode-locked and cavity dumped laser oscillator. M = mirrors (front mirror has 80% reflectivity, rear mirror has 100% reflectivity), A = apertures; SA = saturable absorber; P = polarizers; PC = Pockels cells, PD = photodiode, W = dye cell window.



Figure 2. *a*, A picosecond laser pulse train emitted from a passively mode-locked oscillator and rejected by the second polarizer. The missing 10th pulse was selected by the pulse selector. *b*, A truncated pulse train from a cavity dumped oscillator. The 12th pulse, which is not in the picture, was dumped out of the oscillator.

switches it out through the crossed polarizer and thus stops the mode-locking. In Figure 2b a rejected pulse train from a cavity-dumped oscillator is shown. Both cavity configurations generate pulses of about 4–8 ps duration at 1054 nm. The cavity-dumped oscillator offers higher power and more reliable Pockels cell operation but care has to be taken to insure that no spurious reflections from various optical elements get into the beam path. A single pulse from the laser cavity usually has an energy of a few tenths of a millijoule (mJ). It is then amplified to a maximum of ~30 mJ by passing successively through three Nd³⁺-glass amplifiers.

Since the fundamental frequency of the laser pulse is fixed at 1054 nm, various nonlinear optical techniques are used to tune the laser frequency. These techniques are now briefly described below. Appropriate references are given for readers interested in the details.

(1) Harmonic generation (17) is an efficient method to convert low frequency light to higher frequencies. By using an appropriate nonlinear crystal such as KD_2PO_4 (KD*P), the 1054-nm beam can be frequency doubled to 530 nm, and the 530 nm pulse may be doubled again to 264 nm by an $NH_4H_2PO_4$ (ADP) crystal. By mixing the 1054-nm and 530-nm beams in a KD*P crystal, a 351-nm pulse can also be generated.

(2) The high frequency photons can be broken down into lower frequency photons by *parametric generation processes* (18, 19). The 264-nm beam is used to generate visible light tunable from 450 nm to 650 nm by passing it through two AD*P crystals (18). Lithium niobate crystals can be used to generate tunable IR pulses (1.2–4 μ m) by pumping with the fundamental 1054-nm pulse (19).

(3) Stimualted Raman emission is another technique often used to tune the laser frequency (20). By focusing a laser pulse at frequency ω_0 into a Raman active medium having its highest Raman cross section at ω_R , a Stokes shifted beam of frequency ω_s , where $\omega_s = \omega_0 - \omega_R$, is then generated. To tune the laser to different frequencies, different materials have to be used.

(4) The most versatile way to tune the frequency is to use a pi-cosecond dye laser. We will discuss the details of such a laser in section II.

Equipped with a high-power, tunable, picosecond pulse, we can now excite the molecule at various wavelengths and probe its time evolution by emission and absorption spectroscopy. Some of the techniques currently used in our laboratory will be discussed in the following.

Picosecond Emission Spectroscopy with Streak Camera

To monitor the emission from a molecule following the picosecond pulse excitation, a most convenient and direct technique is streak camera detection. A streak camera is simply a photon detector with ultrahigh time resolution. It mainly consists of a photocathode, a high voltage ramp, and a phosphor screen. By collecting and focusing the emission from the sample cell onto the photocathode, photoelectrons are produced. These photoelectrons are then focused and accelerated through the high voltage ramp region. Electrons passing through the high voltage region at different times are deflected to different parts of the phosphor screen, forming a streak image. This streak image is further amplified by an image intensifier and digitized by an optical multichannel analyzer for subsequent data analysis. In other words, the signal having an intensity versus time profile is transformed by the streak camera into an intensity versus distance display. With this technique, time resolution of ~ 2 ps can be achieved. An example of a fluorescence signal measured by the streak camera is shown in Figure 14. The pulse preceding the fluorescence signal is used both as a signal averaging marker and a pulsewidth monitor.

Picosecond Absorption Spectroscopy with Streak Camera

This streak camera can also be used in time-resolved transient absorption studies. To do this, a probe light source synchronized with the excitation laser pulse is needed. In our laboratory we have used two different techniques to achieve this purpose. The most convenient method is to use the fluorescence emission from an excited molecule pumped by part of the laser beam. It suffers the drawback that in order to probe different wavelength regions, different molecules and different laser pump frequencies (thus different experimental set-ups) may have to be used. A better method is to use a flashlamp with an output spectrum continuous from the UV to the visible. In this case the probe wavelength can be selected simply with monochromator or narrow band filters. Since no commercial lamp is available with a fast risetime which can be readily synchronized with the laser, we have built such a lamp based on the principles of laser-triggered spark gap. The lamp consists of two electrodes in a chamber which is usually pressurized to about 140 psi of nitrogen gas. Before use, a high voltage is applied across the electrodes and is adjusted to just below the self-breakdown threshold. Part of the 1054-nm laser beam is then split from the main beam and focused into the space between the electrodes through the entrance window. This creates a plasma which emits a light pulse having about a 10-ns risetime and a 150-ns full width at half-maximum.

Figure 3a shows the set-up for the transient absorption studies. The probe pulse and the excitation pulse overlap in the sample cell while the pre-pulse passes through a different portion of the sample cell. After the cell, both probe pulse and pre-pulse are imaged onto the camera and any residual excitation light is blocked. The probe pulse from the lamp gives a constant background, I_o , on the streak camera. Upon the arrival of the excitation pulse, which creates the absorbing transient species, the probe intensity I_o is attenuated by an amount $I_a(t)$. The time-dependent attenuation $I_a(t)$ reflects the time evolution of the transient species and is related to the molecular population through Beer's law. We have used this technique to study the electron solvation phenomenon in reference (11).

Picosecond Absorption Spectroscopy with a Pump-and-Probe Technique

Although the streak camera provides the most direct way to monitor transient absorption, its prohibitive cost shifts interest to other less expensive but indirect techniques. One of the most commonly used methods is pump-and-probe de-





tection. As shown in Figure 3b, the pump pulse creates a transient species and a weak probe pulse follows the pump pulse and monitors the time evolution of the transient. By changing the relative time separation between the pump and probe pulses with an optical delay line, the attenuation of the probe pulse intensity as a function of the time separation directly gives the time-dependent absorption profile. An example of the data obtained by this technique is shown in Figure 7.

Picosecond Absorption Spectroscopy by Laser-Induced Fluorescence

If the transient fluoresces after the absorption of light, its absorption-time profile can be indirectly measured by means of laser-induced fluorescence. The experimental set-up is similar to the pump-and-probe technique and is shown in Figure 3c. Rather than monitoring the intensity attenuation of the probe pulse, the fluorescence signal induced by the probe pulse, which is directly proportional to the population of the absorbing transient species, is collected. Scanning the relative delay between the pump and probe pulses therefore gives the time-dependent absorption profile. An example of this technique can be found in reference (15).

II. Picosecond Time-Resolved Raman Spectroscopy

Monitoring the molecular relaxation phenomena by electronic absorption and fluorescence spectroscopy suffers from the limitation that the molecule must have electronic transitions in the UV-visible region. In addition, electronic absorption and fluorescence spectra in liquids are usually broad and do not provide information on the molecular structure. These limitations can be removed, in principle, by studying Raman spectra. In the following we will discuss the laser system and technique we use to obtain time-resolved Raman spectra.



Figure 4. An argon ion synchronously pumped dual dye lasers and the CW autocorrelator for pulse width measurement. PMT = photomultiplier; KDP = KH₂PO₄ crystal.

Argon Ion Synchronously Pumped Dual Dye Lasers

To study time-resolved Raman spectroscopy, we use argon ion synchronously pumped dual dye lasers. The experimental set-up is shown in Figure 4. An argon ion laser is actively mode-locked by an acoustic-optic mode locker. Pulses of ~100 ps at 514.2 nm are generated at a repetition rate of 82 Mhz. They are split and used to pump two Rhodamine-6G dye lasers. The dye lasers' outputs are synchronized with the argon ion laser at 82 MHz. An average pulse width of ~5 ps, tunable from 570 nm to 630 nm for Rhodamine-6G, is usually obtained. Different dyes can be used to extend the tuning range. For a more detailed discussion of synchronously pumped dye lasers, readers are referred to reference (21).

The technique used to measure the width of these dye laser pulses generated at a rate of 82 Mhz is cw autocorrelation, as shown in Figure 4 (51). The dye laser beam is first split into two independent beams. One of the beams passes through a variable optical delay consisting of a retroreflecting prism riding on the cone of an audio speaker driven by a 10 Hz sine wave. The two beams are then recombined and focused into a thin KDP crystal. When both pulses overlap in time at the focus spot, a second harmonic UV pulse is generated. The intensity of the UV pulse depends on the extent of overlap. No UV light can be produced if the two pulses do not overlap in time. By measuring the UV intensity as a function of the relative separation of the two dye laser pulses, information on the pulse width can be extracted. In Figure 5a we show such an autocorrelation function from one dye laser. Pulse width of ~ 5 ps is typical. The cross correlation function between two dye lasers is shown in Figure 5b. Generally the cross correlation width is broader due to the time jitter between the two dye lasers.

Picosecond Raman Gain Spectroscopy

To obtain picosecond time-resolved Raman spectra, we use a stimulated Raman gain technique (22, 23). In this method, two time coincident picosecond pulses with frequencies ω_0 and ω_s are focused into the medium under study. When the difference frequency $(\omega_0 - \omega_s)$ equals the frequency ω_R of a Raman active mode, gain is observed at the stokes frequency ω_s . The loss in the beam at ω_0 can also be monitored and is usually called inverse Raman spectroscopy. Assuming one of the beams is predominant in magnitude (i.e. $I_0 \gg I_s$) and the overall gain is small, then the gain (ΔI_s) or loss (ΔI_0) can be written as (23)

$$\Delta I_{\rm s} = -\Delta I_{\rm o} = G l I_{\rm s} I_{\rm o} \tag{1}$$

where *l* is the pathlength of the gain medium and *G* is the gain constant, which contains molecular information and the vibrational spectrum. When the difference frequency $\omega_{\rm o} - \omega_{\rm s}$ equals a Raman active vibrational frequency, $\omega_{\rm R}$, then the gain $\Delta I_{\rm s}$ is at a maximum. By scanning one of the laser frequencies, say $\omega_{\rm o}$, the gain at $\omega_{\rm s}$ as a function of $(\omega_{\rm o} - \omega_{\rm s})$ would therefore yield the Raman spectrum.

To obtain the time-resolved Raman spectrum three pulses have to be used, one to create the transient species and the other pair to probe the Raman gain. The pair of probe pulses are first tuned to resonance with one of the Raman active modes (ω_R) of the transient species; the relative time delay between the excitation pulse and the probe pair is then scanned at fixed ω_R . The gain at ω_s as a function of the delay thus gives the time evolution of the vibrational population at ω_R . The experimental set-up is shown in Figure 6. Phase sensitive detection is used to enhance the sensitivity. The excitation and the ω_o beam are chopped at 11 MHz by an electro-optical modulator. The gain of the ω_s beam is then detected by a photodiode and signal averaged through a lock-in amplifier driven at 11 MHz. Detection sensitivity of one part in 10⁸ has been achieved with this technique (24).







Figure 6. Experimental set-up for time-resolved Raman gain measurement. L = focusing lens; s = sample; PD = photodiode; A/D = analog to digital converter.

Applications of Picosecond Laser Spectroscopy

We will now consider the applications of these techniques to two problems studied in our laboratory: excited state charge transfer interactions and the cage effects in liquids. For discussions of other topics, interested readers are referred to references (25-27).

Excited State Charge-Transfer Interactions

Photo-induced charge separation is one of the most important primary processes in photochemistry and photobiology. An excited molecule can dissipate its energy through charge transfer (CT) interaction with other ground state molecules, leading to the formation of an exciplex or an ionpair. It can also redistribute the charges intramolecularly to form a large molecular dipole. We have studied the CT interaction in two prototype systems: (1) anthracene and dial-kylaniline, and (2) p-cyanodimethylaniline. In the former system, either an exciplex or an ion-pair can be formed upon photoexcitation, while in the latter system a true intramolecular dipole.

Dynamics of Exciplex Formation between Anthracene and Dialkylaniline

A photoexcited molecule can relax its energy through the CT interaction with the surrounding ground state molecules. This can be experimentally observed by the quenching of excited state fluorescence and either the appearance of a new, red-shifted exciplex emission or the formation of ion radicals depending on the environment. Since the first discovery of perylene-dimethylaniline exciplex by Leonhardt and Weller (28), numerous studies have been made on the subject (29). Three key questions concerning the nature of the excited CT interactions are particularly interesting, namely the reaction distance required for interaction, the effect of geometrical factors, and the role of the solvent. Different experiments were designed to answer these questions and these will be discussed separately.

Interaction Distance and Reaction Rate. A photoexcited anthracene molecule (A*) interacts with a ground state diethylaniline molecule (D) to form an exciplex,

$$\mathbf{A}^* + \mathbf{D} \to (\mathbf{A}^{-\delta}\mathbf{D}^{+\delta})^* \tag{2}$$

Information concerning the interaction distance and the reaction rate can be revealed by the formation dynamics of the exciplex. For an intermolecular exciplex, the formation rate is controlled by the relative translational diffusion motion of the electron donor and acceptor molecules. The rate for a diffusion-controlled reaction has been given as (30)

$$\phi = \frac{4\pi RD'c}{1 + 4\pi RD'/k} \left[1 + \frac{k}{4\pi RD'} \exp(x^2) \operatorname{erfc}(x) \right]$$
(3)

where

$$x = (1 + k/4\pi RD')\sqrt{D't/R}$$
(4)

In these equations, R is the average radius of the interaction sphere, D' is the sum of the translational diffusion constants of the two molecules, c is the concentration of DEA, and k is the elementary rate constant such that

$$\phi = kc_{\rm p} \tag{5}$$

where c_p is the concentration of DEA at an intermolecular distance equal to R. The transient terms in eqn. (4) and the general time dependence of the chemical reaction can be viewed in the following way. At t = 0, the molecules A^{*} and D are randomly distributed, but as time proceeds those distributions in which A^{*} is near to a D are preferentially depleted since they have a higher probability for reaction than those distributions in which A^{*} and D are far apart. This produces a spatially non-uniform 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. In conventional kinetic treatments the reaction rate is usually assumed to be time independent, which is adequate for describing the long time behavior but not acceptable on the short time scale.

To extract values of R and k based on the diffusion theory (eqn. (3), we excited the anthracene molecule at 347 nm and monitored the exciplex formation by its characteristic absorption at 694 nm (6). An example of the time-dependent exciplex absorption is shown in Figure 7. Our experimental results are in good agreement with the theoretical curve calculated from eqn. (4) using R = 8 Å and $k = 10^{11}$ mole-sec, respectively. The full transient behavior of this diffusioncontrolled reaction is thus established and the key parameters, R and k, in the excited charge transfer process are extracted.

Geometric Requirements. An important issue concerning the excited CT interaction is the role of the relative orientation between the donor and acceptor molecules. We approach this problem by connecting the anthracene and dimethylaniline (DMA) molecules with three methylene groups (I) to restrict their relative orientations while still maintaining their close proximity, maximum separation between them being less than 4 Å (7, 8).



Upon excitation, this model molecule should form an intramolecular exciplex as rapidly as the free anthracene and DMA system, as described earlier, if there are no significant orientational requirements for CT interaction. On the other hand, if the time course for exciplex formation is different for the two cases, then molecular motions to achieve a favorable geometry must be involved and can be directly followed by monitoring the formation of the intramolecular exciplex.

The absorption and fluorescence spectra of the model molecule is the same as that of the free molecules, indicating that there is no significant ground state interaction between the two moieties. A 351-nm ps laser pulse was used to excite the anthracene moiety in the model compound (8). The decay of the anthracene fluorescence and the rise of the exciplex fluorescence were then monitored by a streak camera. In Figures 8 and 9 we show the decays of anthracene fluorescence monitored at 410 nm and the rises of exciplex fluorescence monitored at 520 nm in four nonpolar solvents (isopentane, hexane, decane, and tetradecane). The fluorescence curve for exciplex formation consists of a very rapid initial rise (within the laser pulse width), which is due to the tail of the overlapping anthracene emission, followed by a much slower rise. By subtracting the contribution of the anthracene emission, a true exciplex formation curve can be obtained. Several conclusions can be drawn from these data.

(1) In all the solvents studied, the formation of the intramolecular exciplex is slow (on the nanosecond time scale) and strongly dependent on the solvent viscosity. As the viscosity increases, the formation rate decreases. If there were no geometric requirements for exciplex formation, then we know from the earlier results on the intermolecular exciplex that a rise time of ~10 ps should be obtained. The much slower formation rate and the strong dependence on solvent viscosity which we find in the intramolecular case indicate that rotational motions are required to bring the two moieties into a favorable conformation to form the exciplex. The time dependence of this motion thus provides direct information about the end-to-end relaxation dynamics of this short chain molecule.



Figure 7. The formation curve of exciplex absorption monitored at 694 nm in hexane solution.



Figure 8. The fluorescence decay curves of anthracene moiety in isopentane (C₅), hexane (C₆), decane (C₁₀), and tetradecane (C₁₄). The points are experimental, the solid curves are theoretical.



Figure 9. The fluorescence rise curves of intramolecular exciplex in various nonpolar solvents.

(2) All the decay and formation curves can be fit with exponentials. The anthracene decay times and the exciplex formation times are found to be the same within experimental uncertainty in all the solvents studied. This indicates that there is no long-lived nonfluorescent intermediate state present before the formation of the fluorescent exciplex. The Effect of Solvent Polarity. The CT interactions, though determined by the intrinsic properties of the donor and acceptor pair, are greatly modified by environmental effects. Due to the charge separation associated with the CT interaction the solvent polarity can play an important role. To examine the interplay between geometric and solvent dielectric effects, we have studied A-(CH₂)₃-D in the strongly polar (e = 37) solvent acetonitrile (9).

The anthracene moiety was excited at 351 nm and the weak exciplex emission monitored in the 500–600 nm region. In marked contrast to the results in nonpolar solvents, where the exciplex is formed in a few nanoseconds and lives for more than one hundred nanoseconds, we have found in acetonitrile that it is formed in a time shorter than we can resolve (<2 ps) and decays in 580 \pm 30 ps, as shown in Figure 10. Although the exciplex is formed "instantaneously," we find that the excited anthracene moiety, which is monitored at 411 nm, has a lifetime of 7 \pm 1 ps, Figure 11. Since the CT rise is faster than the anthracene decay we conclude that these observed emissions correspond to independent processes.

The very fast CT rise suggests that only those molecules in a favorable ground state conformation at the time of excitation lead to the exciplex. For those molecules in unfavorable extended conformations a new nonradiative decay channel is responsible for the observed 7 ps lifetime of the excited anthracene moiety. We believe this new ultrafast decay channel is direct e^{-} transfer to form a nonfluorescent ion-pair which is strongly stabilized by the polar solvent. The internal rotational motions necessary for the formation of the exciplex are too slow to compete in this case. This is confirmed by the direct observation of ion-pair formation (≤ 10 ps) observed by its characteristic absorption at 530 nm, as shown in Figure 12. The fraction of the molecules with favorable ground state conformations can be estimated to be smaller than a few percent from the relative fluorescence intensity measured on the streak camera. The following scheme summarizes our results in acetonitrile



Dynamics of Intramolecular CT Interactions in P-(Dimethylamino)benzonitrile

In this section we shall focus on the intramolecular charge redistribution process which causes the well-known anomalous dual fluorescences of p-(dimethylamino)benzonitrile (DMABN).



In nonpolar solvents, excitation into the S_2 state of the DMABN molecule results in a single fluorescence band centered around 340 nm. However, in polar solvents a new,



Figure 10. The fluorescence decay curve of intramolecular exciplex in acetonitrile.



Figure 11. The fluorescence decay curve of anthracene moiety in acetonitrile.



Figure 12. The time-dependent absorption curve of ion-pair in acetonitrile.

Stokes-shifted fluorescence appears, which is associated with a very large dipole moment of ~16 Debye (43). A number of mechanisms have been proposed to explain the origin of this new emission band (31-45). These include the solvent-induced level reversal of the two lowest lying excited singlet states, S_2 and S_1 , by Lippert et al. (31), the excimer formation by McGlynn et al. (32-34), the excited state proton transfer by Kosower et al. (35, 36), the complex formation with solvent by Chandross et al. (37), and the twisted internal charge transfer by Grabowski et al. (38-43). The results accumulated over the past several years indicate that both bond twisting (between the amino group and the benzene ring) and solvation play important roles in causing the charge redistribution (43-45). We, therefore, have a situation where the CT interaction is controlled by the molecular conformations around a single bond. As the molecule rotates around the bond, it emits light at different frequencies, each corresponding to different conformations. By monitoring the time-evolution of the emission we can directly observe the dynamics of single bond rotation in the liquid state. This is illustrated graphically in Figure 13.

We excite the DMABN molecule to its S_2 state with a single 264-nm picosecond laser pulse (10). The "normal" short wavelength fluorescence and the CT fluorescence were then monitored at 350 nm and 480 nm, respectively. The short wavelength fluorescence decay can be clearly resolved into two exponential components. The fast component decays with a lifetime of 19 ± 3 ps, which is equal to the rise time of the CT fluorescence. The slow component has a lifetime of 2.3 ± 0.2 ns, which is the same as the decay of the CT emission. These results are shown in Figures 14 and 15.

These results provide definitive evidence that equilibrium is rapidly established between the states responsible for the short wavelength emission and the CT emission. This equilibrium can be described by

$$\begin{array}{cccc}
\mathbf{S}^* & \stackrel{k_1}{\longleftrightarrow} & \mathbf{CT}^* \\
\stackrel{k_s}{\swarrow} & & & & & \\
\end{array} (8)$$

where S* represents the state responsible for the short wavelength emission, k_s and $k_{\rm CT}$ represent all the other radiative and nonradiative decay rates for S* and CT*, respectively. In Figures 12 and 13 the solid curves are the theoretical calculations based on eqn. (8). We obtained $k_1 = 20$ ps, $k_1/k_2 \ge 30$, and $k_s + k_{\rm CT} = 2.3$ ns (10). The forward reaction rate, 20 ps, is interpreted as the time required for the molecule and solvent to relax conformationally to the twisted charge transfer geometry.

Photodissociation of Iodine and Cage Effects in Liquids

On photoexcitation of I_2 in the liquid state the excited molecule undergoes a direct dissociation or a collision-induced predissociation, leading to a pair of iodine atoms. This is followed by a recombination of the original iodine atoms (termed geminate recombination) or at a much later time by the recombination of iodine atoms originating from the dissociations of different iodine molecules. Unlike the gas phase, in which the probability of original partner recombination is close to zero, the recombination of original fragments in the liquid phase is greatly enhanced by interactions with the solvent molecules which interfere with the escape of the fragments (see Fig. 16). This enhanced recombination was first referred to by Frank and Rabinowitch as the "cage" effect (46).

Since the chemistry following a dissociation event in liquids is strongly dependent on the cage effect, its importance has attracted extensive studies (16, 47-50). The first experimental attempt to monitor directly the time characteristics of ultrafast cage effects in liquids was carried out on I2 at room temperature (16). A picosecond laser pulse at 530 nm was used to excite I₂ to the bound state ${}^{3}\Pi_{o+u}$ (a small fraction of the I₂ molecules were excited to the ${}^{1}\Pi_{\mu}$ state and directly dissociated). The excited I₂ then undergoes collisionally induced predissociation leading to a pair of ground state $p_{3/2}$ 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 530-nm picosecond light pulse from times prior to the strong excitation pulse up through 800 ps after the excitation pulse. The strong excitation pulse depopulates a good fraction of the ground state I₂ molecules and thus causes an increase in the transmission of the probe pulse.





Figure 13. Potential energy diagram for the twisting motion along the C-N bond.



Figure 14. The fluorescence decay of S_1 state monitored at 350 nm and the formation of CT state monitored at 480 nm in propanol solution. Time scale is 0.95 ps/channel.



Figure 15. The fluorescence decay of S_1 state monitored at 350 nm and the formation of CT state monitored at 480 nm in propanol solution. Time scale is 19 ps/channel.

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.

We have studied the photodissociation of I₂ in two solvents, hexadecane and carbon tetrachloride. The result in hexadecane is shown in Figure 17. The transmission of the probe light first rises to a maximum and then drops rapidly to a stable value at about 800 ps after excitation. This occurs for CCl₄ also. The residual difference in absorption between the long time values (800 ps) and the initial absorption (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 nsec) 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 nongeminate recombination processes. The geminate recombination times are about 70 ps in hexadecane and 140 ps in carbon tetrachloride. The escape probabilities of iodine atoms are about 25% in carbon tetrachloride and 5% in hexadecane.

Literature Cited

- (1) Eisenthal, K. B., Acc. Chem. Res., 8, 118 (1975).
- Eisenthal, K. B., and Drexhage, K. H., J. Chem. Phys., 51, 5720 (1969).
 Chuang, T. J., and Eisenthal, K. B., Chem. Phys. Lett., 11, 368 (1971).
- (4) Rehm, D., and Eisenthal, K. B., Chem. Phys. Lett., 9, 387, (1971).
- Chuang, T. J., and Eisenthal, K. B., J. Chem. Phys., 59, 2140 (1973).
 Chuang, T. J., and Eisenthal, K. B., J. Chem. Phys., 62, 2213 (1975).
- (7) Chuang, T. J., Cox, R. J., and Eisenthal, K. B., J. Amer. Chem. Soc., 96, 6828 (1974).
- (8) Wang, Ying, Crawford, M. K., and Eisenthal, K. B., J. Phys. Chem., 84, 2696 (1980).
- (9) Crawford, M. K., Wang, Y., and K. B. Eisenthal, Chem. Phys. Lett., 79, 529 (1981).
 (10) Wang, Y., McAuliffe, M., Novak, F., Eisenthal, K. B., J. Phys. Chem., in press, 1981.
- (11) Wang, Y., Crawford, M. K., McAuliffe, M. J., and Eisenthal, K. B., Chem. Phys. Lett., 74, 160 (1980).
- (12) Hou, S. Y., Heterington, W. M., Korenowski, G. M., and Eisenthal, K. B., Chem. Phys. Lett., 68, 282 (1979)
- (13) Hetherington III, W. M., Micheels R. H., and Eisenthal, K. B., Chem. Phys. Lett., 66, 230 (1979)
- (14) Dupuy, C., Korenowski, G. M., McAuliffe, M., Hetherington III, W. M., Eisenthal, K. B., Chem. Phys. Lett., 77, 272 (1981).
- (15) Eisenthal, K. B., Turro, N. J., Aikawa, M., Butcher, Jr., J. A., Dupuy, C., Hefferon, G., Hetherington, W., Korenowski, G. M., McAuliffe, M. J., J. Amer. Chem. Soc., 102, 6563 (1980).
- (16) Chuang, T. J., Hoffman, G. W., and Eisenthal, K. B., Chem. Phys. Lett., 25, 201 (1974).
- (17) Terhune, R. W., and Maker, P. D., in "Lasers", 2, (Editor: Levine, A. K.) Marcel Dekker, Inc., New York, 1968.
- Byer, R. L., in "Treatise in Quantum Electronics", 1, Part B, (*Editors*: Rabin, H., and Tang, C. L.) Academic Press, New York, 1975, pp. 587–702.
 Smith, R. G., in "Laser Handbook", (*Editors*: Arecchi, F. T. and Schultz-Dobois, E. O.) North Holland, Amsterdam, 1972, p. 837.
- (20) Maier, M., "Applications of Stimulated Raman Scattering," App. Phys., 11, 209-231, 1976
- (21) Sundström, V., and Gillbro, T., App. Phys., 24, 233 (1981).
 (22) Owyoung, A., IEEE J. Quantum Electro., QE-14, 192 (1978).

- (23) Nestor, J. R., App. Spec., 35, 81 (1981).
 (24) Heritage, J. P., Bergman, J. G., Pinczuk, A., and Worlock, J. M., Chem. Phys. Lett., 67, 229 (1979)
- (25) "Ultrashot Light Pulses," (Editor: Shapiro, S. L.) "Topics in Applied Physics," 18, Springer-Verlag, 1977.
- "Picosecond Phenomena," (Editors: Shank, C. V., Ippen, E. P., and Shapiro, S. L.) (26)Springer Series in Chemical Physics, Vol. 4, Springer-Verlag, 1978. "Picosecond Phenomena II," (*Editors:* Hochstrasser, R. M., Kaiser, W., and Shank,
- (27)C. V. Springer Series in Chemical Physics, 14, Springer-Verlag, 1980. (28) Leonhardt, H., and Weller, A., Ber. Bungsenges., Phys. Chem., 67, 791 (1963).
- (29) Mataga, N., and Ottolenghi, M., in "Molecular Association," Vol. 2, (Editor: Forster, R.) Academic Press, 1979, p. 1.
 (30) Noyes, R. M., *Prog. Reac. Kin.*, 1, 128 (1961).
 (31) Lippert, E., Lüder, W., and Boos, H., *in* "Advan. Mol. Spectrosc.," (*Editor*: Mangini,
- A.), Pergamon Press, Oxford, 1962, p. 443.



Figure 16. Photodissociation of iodine molecule in, a gas phase, and, b, liquid phase.



Figure 17. The recovery of ground state iodine molecules in hexadecane solution monitored after a 5300 Å picosecond laser pulse excitation.

- (32) Khalil, O. S., Hofeldt, R. H., and McGlynn, S. P., Chem. Phys. Lett., 19, 479 (1972).
- (33) Khalil, O. S., Hofeldt, R. H., and McGlynn, S. P., J. Luminescence, 6, 229 (1973).
 (34) Khalil, O. S., Meeks, J. L., and McGlynn, S. P., Chem. Phys. Lett., 39, 457 (1976).

- (35) Dodius, H., and Kosower, E. M., Chem. Phys. Lett., 34, 253 (1975).
 (36) Kosower, E. M., and Dodiuk, H., J. Amer. Chem. Soc., 98, 924 (1976).
 (37) Chandross, E. A., in "The Exciplex," (Editor: Gordon, M., and Ware, W. R.) Academic Press, 1975, p. 187.
- (38) Rotkiewicz, K., Greelmann, K. H., and Grabowski, Z. R., Chem. Phys. Lett., 19, 315 (1973).
- (39) Rotkiewicz, K., and Rubaszenska, W., Chem. Phys. Lett., 70, 444 (1980). (40) Rotkiewicz, K., Grabowski, Z. R., Krowczynski, A., and Kühnle, W., J. Luminescence,
- 12/13, 877 (1976). (41) Lipinski, J., Chojnacki, H., Grabowski, Z. R., and Rotkiewicz, K., Chem. Phys. Lett.,
- 58, 379 (1978) (42) Kirkov-Kaminska, E., Rotkiewicz, K., and Grabowska, A., Chem. Phys. Lett., 58, 379
- (1978).(43) Grabowski, Z. R., Rotkiewicz, K., Siemiarczuk, A., Cowley, D. J., and Baumann, W.,
- Nouveau J. De.Chimie, 3, 443 (1979). (44) Rettig, W., Wermuth, G., and Lippert, E., Ber. Bunsenges. Phys. Chem., 83, 692 (1979).
- (45) Rettig, W., and Bonačic-Koutecký, V., Chem. Phys. Lett., 62, 115 (1979).
- (46) Frank, J., and Rabinowitch, E., Trans. Faraday. Soc., 30, 120 (1934).
 (47) Langhoff, L. A., Gnadig, K., and Eisenthal, K. B., Chem. Phys. Lett., 46, 117 (1980).
- (48) Evans, G. T., and Fixman, M., J. Phys. Chem., 80, 14 (1976).
- (49) Hynes, J. T., Kapral, R., and Torrie, G. M., 72, 177 (1980).
 (50) Martire, B., and Gilbert, R. G., Chem. Phys., 56, 241 (1981)
- (51) Sala, K. L., Kenny-Wallace, G. A., and Hall, G. E., IEEE. J. Quantum. Electro., QE-16, 990 (1980).