PICOSECOND STUDIES OF THE CAGE EFFECT AND
COLLISION INDUCED PREDISSOCIATION OF IODINE IN LIQUIDS

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In this work we report the first time dependent study of the role of the cage effect in the geminate recombination of iodine atoms produced by photodissociation of I_2. We have also directly observed the rate of the collision induced predissociation of the excited iodine molecule, $I_2 (B^3 \Pi_{0^+u})$.

1. Introduction

On photoexcitation of I_2 in the liquid state the excited molecule either undergoes a direct dissociation or a collision induced predissociation leading to a pair of iodine atoms. This is then followed by a recombination of the original iodine atoms or at a much later time by the recombination of iodine atoms originating from the dissociation 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.

This enhanced recombination was first referred to by Frank and Rabinowitch as the "cage" effect in 1934 [1]. They considered the possibility of recombination of the fragments trapped in the solvent "cage" and called this process a primary recombination. Zimmerman and Noyes [2] subsequently considered the possibility of secondary recombination in which the initial separation of the particles was about equal to or greater than the molecular diameter as opposed to the primary one in which the pair never became separated as much.

For clarity, the term geminate recombination proposed by Hamill[†] will be used for all recombinations

[†] Cited by Noyes [3].

of original partners and non-geminate recombination for recombinations of particles from different "cages". While the process of non-geminate recombination has been extensively studied and established to be diffusion-controlled [4], the dynamics of geminate recombination had not been investigated due to the ultrafast nature of this process.

In view of the importance of the "cage" effect in chemical reactions and the importance of understanding the fundamental interactions in liquids, we have applied the picosecond laser technique [5, 6][#] to study the processes of collision induced predissociation and the recombination of iodine atoms following the dissociative steps. In this first paper, we will present the experimental results and discuss various aspects of the problem.

2. Experimental

The experimental arrangement is shown in fig. 1. An Nd^{3+}-glass laser is mode-locked by Eastman Kodak #9740 dye and capable of generating a train of 1.06μ light pulses with pulse separation of 8 nsec. A single pulse is selected from the train of pulses by an electro-optical shutter activated by the breakdown of a spark gap. The shutter consists of a pair of crossed

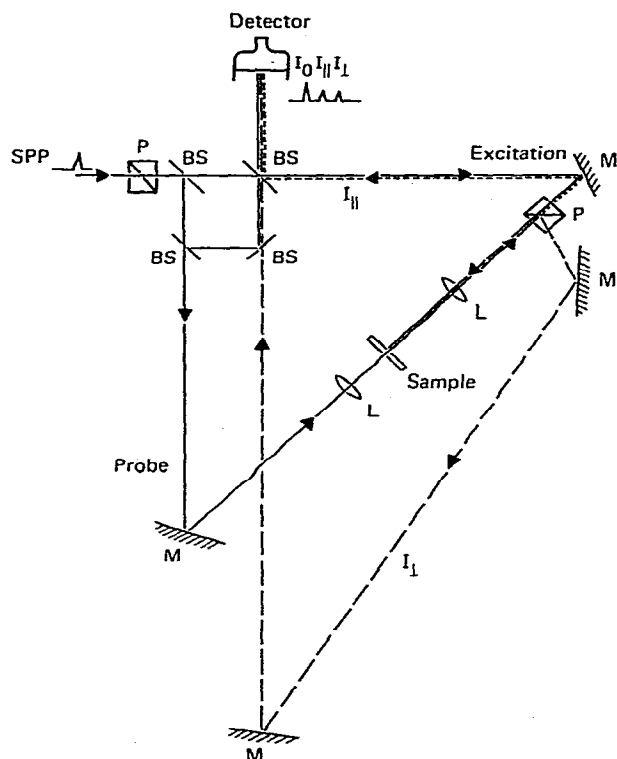[#] For a general review of picosecond methods, see ref. [7].

Fig.1. Experimental arrangement for monitoring $I_{\parallel}$ and $I_{\perp}$ transmissions at 5300 A following photoexcitation of iodine solutions. SPP — single picosecond light pulse at 5300 A from the laser oscillator, single pulse selector, laser amplifier systems and second harmonic crystal; P — polarizer; BS — beam splitter; M — mirror; L — lens.

polarizers and a 10 cm nitrobenzene Kerr cell. The single pulse is amplified by three flash lamp pumped Nd-glass rods (diameter 1.25 cm, length 15 cm). The light pulse so produced has a width of about 5 psec determined by two-photon excited fluorescence methods [8] and the energy is about 50—100 mJ. This light pulse is then frequency doubled to 0.53μ by a properly phase-cut KDP crystal. A major fraction ($> 90\%$) of this second harmonic pulse is used to excite iodine samples of 1mm thickness. Meanwhile, a minor fraction of the pulse is split off the main beam and optically delayed with respect to the exciting pulse to probe the absorbance of the sample.

The amount of absorbance at different times after the exciting pulse is obtained by varying this optical delay. Since linearly polarized light is used and

only one of the three sample axes is excited, anisotropic distribution of the transition dipole moment is created. Therefore, rotational motion of the molecule may contribute to the changes of absorbance. To account for this effect, we use a polarizer in the probe beam and measure the parallel ($I_{\parallel}$) and perpendicular ($I_{\perp}$) transmission with respect to the polarization of the exciting pulse simultaneously [6]. The light intensities are measured with an ITT photodiode and Tektronix 519 oscilloscope. The experimental result at each delay time is an average of five laser shots.

Spectrophotometric grade carbon tetrachloride (Matheson, Coleman and Bell) and hexadecane (Aldrich) used as solvents are purified by passing through an aluminum oxide column. Iodine crystals obtained from MC&B are used without further purification. The concentration of the solution is fixed at $1.0 \times 10^{-2}M$. All experiments are carried out at room temperature.

3. Results and discussion

When excited at 5300 Å, I_2 ($X\,^1\Sigma_g^+$) can be either promoted into the bound state $B(^3\Pi_{0^+u})$ or the direct dissociative state $1U(^1\Pi)$. The relative oscillator strength for these two transitions is $5.18:1.0$ [9]. The experimental results shown in figs.2 and 3 indicate a peak in the transmission of the 5300 Å probe light at about 20 psec after the excitation pulse in both CCl_4 and hexadecane solvents. This observed peak occurs at a time significantly after the decay of the excitation pulse. Thus, the continued rise in the transmission of the probe light after the excitation pulse cannot be due to the further depopulation of the ground state iodine molecule by the excitation pulse. The rise time of the transmission can be explained by assuming that the probe light can be absorbed not only by ground state but also by excited iodine molecules. Thus, the probe pulse is monitoring the change in both the ground state and excited iodine molecular populations. Indeed the photodissociative recoil studies of I_2 by Busch et al. [10] demonstrate that the bound B state can also absorb at 5300 Å. The possible transition is $B \rightarrow\ ^1\Sigma_g^+(2422)$ [11]. We therefore conclude that after the excitation pulse reduces the ground state concentration the further observed increase in the probe transmission results from the decay of the excited iodine molecules into iodine atoms. We have thus obtained from this experiment
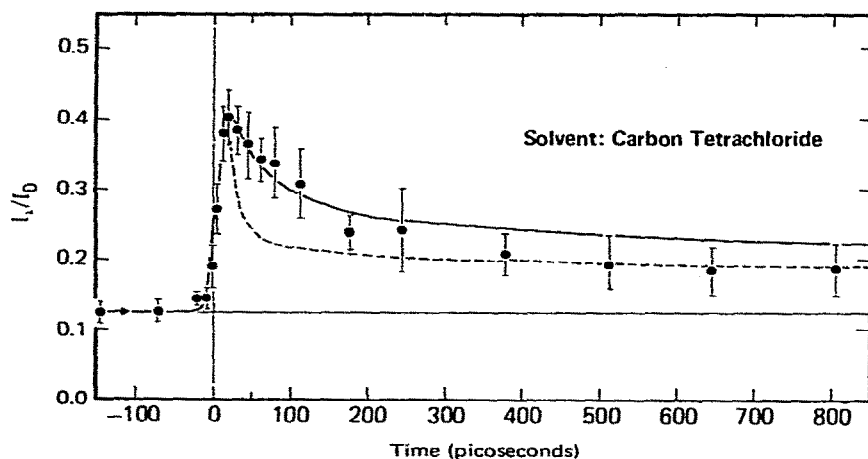
Fig.2. Probe transmission $I_\perp/I_0$ as a function of time after excitation for iodine in CCl_4. Dashed and solid curves are the decay functions calculated from Noyes random flight model.
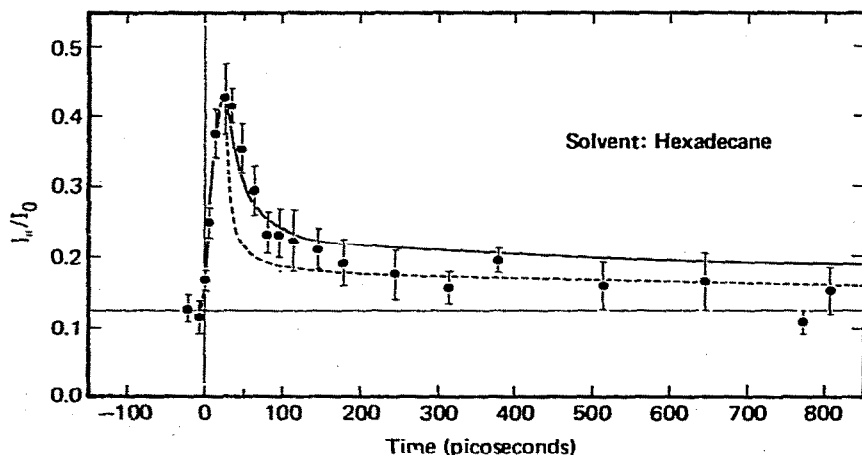

Fig.3. Analogous results to those of fig.2, with hexadecane as solvent.

what we believe to be the first direct observation of the dynamics of a collision induced predissociation and find a rate constant of about 10^{11} sec^{-1}.

The parallel $(I_\parallel)$ and perpendicular $(I_\perp)$ intensity components of the transmitted probe light are found to differ slightly in the early time domain for I_2 in hexadecane. This difference is attributed to the anisotropy induced by the linearly polarized excitation pulse in the orientational distribution of the excited and remaining ground state iodine molecules. The data is not adequate to go beyond stating that the orientational relaxation time of iodine is somewhat faster than the rise time of the probe transmission. In carbon tetrachloride the orientational relaxation of iodine is rapid and therefore no differences are observed between $I_\parallel$ and $I_\perp$. In either case any orientational anisotropy is accounted for in our data analysis.

In both CCl_4 and hexadecane the absorption of the probe light, figs. 2 and 3, has reached a stable value by 800 psec. The residual change in absorption is attributed to the iodine atoms which have escaped their initial partners. The magnitude of these residual absorp-

tions indicate that approximately 25% and 5% of the iodine atoms escape in CCl_4 and hexadecane, respectively. These quantum yields are estimated from the ratios of the concentrations of iodine atoms at the long time region ($\approx$800 psec) to the concentrations of the peaks of the transmission curves. Flash photolysis [12] and scavenger studies [13] of the quantum yield of photodissociation of I_2 in CCl_4 yield values of 19% (excited by light, $\lambda > 5000$ Å) and 14% (excited by light at 4350 Å), respectively. Measurements [13] of the quantum yield of photodissociation in the solvent hexachlorobutadiene-1,3, which has similar viscosity as hexadecane, yielded a value of 8%. The theoretical hydrodynamic continuum treatment [14] by Noyes of atom recombination gives values for the quantum yield of photodissociation of I_2 in CCl_4 and hexadecane, on excitation by 5300 Å light, of 21% and 6%, respectively.

The somewhat larger values for the quantum yields for photodissociation in CCl_4 estimated from our experiments can be due to a recombination of about 20% of the iodine atoms in the first 20 psec or possibly to the effects of consecutive two photon excitation in which excited I atoms ($^2P_{1/2}$) are produced. These excited atoms can have a greater chance for escape from the original partners and thus contribute to higher quantum yield because of the time required for spin relaxation [15] and also because of the energy released in this process. Based on the concentration of iodine molecules and the diffusion coefficient of iodine atoms we can estimate that non-geminate recombination will take at least 10^{-8} sec and therefore is not significant in the time region of this study. The observed decay curves shown in figs.2 and 3 are therefore attributed to the geminate recombination of iodine atoms and the times for this process are determined to be 70 psec in hexadecane and 140 psec in carbon tetrachloride. We have therefore observed directly in time the effect of the "cage" on the geminate and non-geminate recombination processes.

Since the Noyes model for the calculation of the quantum yields for photodissociation of iodine agrees reasonably well with our results as well as previous experimental data [14], one asks whether this approach based on the probability of encounter in a random walk is also suitable for a description of our time dependent measurements. The probability of recombination for a random flight model has the form

$ae^{-b/t}/t^{3/2}$ [16], where a and b are constants related to the encounter diameter, average displacement of a diffusive step, and the frequency of displacements.

From the Noyes theory one can calculate the decay function corresponding to molecular pair recombination for comparison with the experimentally observed curves shown in figs.2 and 3. In comparing the theory to our experimental results, if we adjust the theoretical curve to fit the long time behaviour, where one would expect the random walk description to be most valid, then we find that the early times behaviour is too rapidly decaying. The "best" fit for the entire time region, shown in figs.2 and 3, leads to a value for escape which is somewhat high in the long time region. The values for this latter case for the jump size and frequency of jumps are found to be 0.5–1.0 Å and $(1-5) \times 10^{12}$ sec^{-1} for CCl_4 and 0.1 Å and $(2-20) \times 10^{12}$ sec^{-1} for hexadecane. Considering the crudeness of the theory, as for example, in assuming that the distance between the iodine atoms on thermalization is given by one distance rather than a distribution of distances, the agreement between the Noyes model and experiment is not unreasonable.

We are presently carrying out a computer simulated molecular dynamic calculation of the dissociation and recombination to more adequately describe the cage effect in liquids. The effect of the formation of weak transient complexes between the I atoms and the solvent molecules [17, 18] on the geminate recombination rates is also considered in this calculation.

Acknowledgement

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