# Experimental Picosecond Transient Spectra for I<sub>2</sub> Photodissociation in Liquids

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After dissociative excitation into the A state the molecular dynamics of the I2 reaction in solution are followed by picosecond transient electronic absorption spectroscopy. The time scale of the transient spectra varies considerably among different solvents. For the same reaction process, observation at higher photon energy gives longer transient spectral times. The results appear consistent with a model in which the major determinant of the observed time scale is due to vibrational (or possibly electronic) decay after recombination and inconsistent with a model in which the time scale is dominated by recombination time.

## Introduction

This Letter experimentally investigates the liquid-phase dynamics of the chemical reaction sequence involving I2 photodissociation, solvent caging, and radical recombination to form a new highly vibrationally (and perhaps electronically)<sup>1</sup> excited  $I_2$ molecule and the subsequent decay of its internal energy.

The photodissociation of  $I_2$  has been frequently studied in the liquid phase, as it is one of the simplest chemical reactions, the same diatomic being both reactant and product. Earlier experimental work<sup>2-9</sup> clearly indicates that much of the important molecular dynamics in this solution reaction occurs on the tens to hundreds of picosecond time scale. Two very different mechanisms have been proposed to account for the experimentally observed time scale for the transient absorption. The first<sup>2,8</sup> is that the time scale mainly represents the recombination time for the I atoms to re-form  $I_2$  molecules. The second, proposed more recently by us, 5,6,9 and by Nesbitt and Hynes, 10,11 with related ideas also expressed by Troe<sup>12</sup> and by van den Bergh,<sup>13</sup> is that recombination is relatively quick and that the time scale is dominated by the time for vibrational decay of the newly formed  $I_2$ . In this Letter we experimentally test these alternative hypotheses for photodissociation initiated through the A electronic state.

#### Experiment

The theoretical interpretation of most previous picosecond experiments<sup>2-4,7,8</sup> has been made difficult by the possible role of predissociation (or second photon absorption) by the B state which is presumably reached by initial pumping with green light. Therefore, we use a red 680-nm source (dye laser with DCM dye)<sup>14</sup> to excite the I<sub>2</sub> molecules into the A state, a dissociative transition free from the predissociation complexity associated with

(1) P. B. Beeken, E. A. Hanson, and G. W. Flynn, J. Chem. Phys., 78, 5892 (1983).

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

(3) C. A. Langhoff, K. Gnädig, and K. B. Eisenthal, Chem. Phys., 46, 117 (1980).

(4) C. A. Langhoff, B. Moore, and W. Nugent, in "Picosecond Phenomena", Vol. II, R. Hochstrasser, W. Kaiser, and C. V. Shank, Ed., Springer-Verlag, Berlin, 1980, p 249.

(5) P. Bado, P. H. Berens, J. P. Bergsma, S. B. Wilson, K. R. Wilson, and E. J. Heller in "Picosecond Phenomena", Vol. III, K. B. Eisenthal, R. M. Hochstrasser, W. Kaiser, and A. Laubereau, Ed., Springer-Verlag, Berlin, 1982, p 260.

(6) P. Bado, P. H. Berens, and K. R. Wilson, in "Picosecond Lasers/ Applications", Vol. 322, L. S. Goldberg, Ed., Proceedings of the Society of Photo-Optical Instrument Engineers, bellingham, WA, 1982, p 230.

(7) C. A. Langhoff, B. Moore, and M. DeMeuse, J. Am. Chem. Soc., 104,

(1) C. A. Languett, P. M. Rentzepis, Chem. Phys. Lett., 85, 85 (1982).
(8) D. F. Kelley and P. M. Rentzepis, Chem. Phys. Lett., 65, 85 (1982). (9) P. Bado, P. H. Berens, J. P. Bergsma, M. H. Coladonato, C. G. Dupuy, P. M. Edelsten, J. D. Kahn, K. R. Wilson, and D. R. Fredkin in "Proceedings of the International Conference on Photochemistry and Photobiology", A. Zewail, Ed., Harwood Academic, New York, in press.

 (10) D. J. Nesbitt and J. T. Hynes, Chem. Phys. Lett., 82, 252 (1981).
 (11) D. J. Nesbitt and J. T. Hynes, J. Chem. Phys., 77, 2130 (1982). (12) J. Troe in "High Pressure Chemistry", H. Kelm, Ed., Reidel, Am-

sterdam, 1978, p 489-520.

(13) J. M. Zellweger and H. van den Bergh, J. Chem. Phys., 72, 5405 (1980)

(14) E. G. Marason, Opt. Commun., 37, 56 (1981).

TABLE I: Concentration of Iodine in Saturated Solution for Various Solvents at 25 °C

 solvent	conen, mol L <sup>-1</sup>
 ethylene glycol	~0.28
cyclohexanol	~0.14
cyclohexane	~0.11
CCl <sub>4</sub>	~0.11

TABLE II: Transient Electronic Absorption Time for I<sub>2</sub> Photodissociation Reaction in Various Solvents (Fwhm in ps)<sup>a</sup>

	probe wavelength, nm		
solvents	630	650	710
ethylene glycol	27 ± 3	27 ± 3	27 ± 3
cyclohexanol	29 ± 3	29 ± 3	29 ± 3
cyclohexane	$110 \pm 10$	$95 \pm 10$	$65 \pm 10$
CCl4	b	$240 \pm 20$	$180 \pm 20$

<sup>a</sup> Data have been corrected for quadratic response of the detection system. <sup>b</sup> No useful data obtained.

the previous picosecond experimental studies,<sup>2-4,7,8</sup> but at a cost of a reduction of a factor  $\sim 20$  in absorption cross section.<sup>15</sup> A schematic diagram of the experimental system is shown in Figure 1. An argon-ion laser (Spectra Physics, Model 171) synchronously pumps in parallel two dye lasers (Spectra Physics, Model 375), each producing a train of  $\sim$ 8-ps fwhm pulses, separated by  $\sim 4$  ns. The jitter between pump and probe pulses limits the time resolution of our measurements to  $\sim 20$  ps.

In order to achieve the sensitivity needed to detect the very weak<sup>15</sup>  $I_2$  A state absorption, a multiple radio- and audio-frequency modulation system is used.<sup>16</sup> By processing the signal information initially in the radio-frequency regime much of the intrinsic laser noise is avoided. The pump and the probe beams are modulated at two different radio frequencies (4.45 and 11.2 MHz, respectively) and the signal is observed at the difference frequency with an AM radio receiver. In addition the pump beam is audiomodulated at 400 Hz and the signal is synchronously detected at that frequency. This detection system, which is described in more detail elsewhere,<sup>16</sup> provides a very sensitive technique for extracting weak signals from noise. In addition, this technique strongly discriminates against pump and probe beams, as well as against electrical pick-up from their modulating electronics. Even further rejection against the pump beam is achieved by placing an optical bandpass filter in front of the photodiode. It should be noticed that the sign of the transient signal is lost during signal processing in the receiver; therefore, we are presently not able to differentiate between induced absorption and induced bleaching.

Since the energy per pulse is in the nJ range, in order to achieve sufficient excitation our sample region is a small confocal volume at the focus of microscope objectives (American Optical, infinity corrected, power 6X) in both the pump and the probe beams which

<sup>(15)</sup> J. Tellinghuisen, J. Chem. Phys., 76, 4736 (1982).
(16) P. Bado, S. B. Wilson, and K. R. Wilson, Rev. Sci. Instrum., 53, 706 (1982).



Figure 1. Picosecond transient electronic absorption spectrometer. M. Indicates a megaHertz electro-optical modulator, CH is a mechanical chopper,  $\tau$  is the optical delay, S is the sample, and D the photodiode detector. The probe beam is polarized perpendicularly with respect to the pump beam.

are collinear but traveling in opposite directions to avoid nonlinear mixing of the probe and pump carrier frequencies in the photodiode. The reaction solution is rapidly pumped through the confocal volume inside a small capillary. The pump and probe power at the sample is typically on the order of 20 mW. The inner diameter of the capillary is  $\sim 1 \text{ mm}$  (this slightly restricts our time resolution due to the counterpropagating geometry) and the sample temperature is between 296 and 304 K.

Reagent grade I2, ethylene glycol, cyclohexane, and cyclohexanol are used without further purification. Carbon tetrachloride is of spectroscopic grade. The solutions are saturated in iodine as shown in Table I, except for measurement at 630 nm where the concentration is cut by half for the ethylene glycol solution to improve the signal-to-noise ratio. The wavelengths are checked prior to data collection with a calibrated monochromator. After passing through the sample, the probe beam is diverted by a beamsplitter or a polarizer onto a photodiode (EGG, Model DT-110).

Since cross-polarized light is used to pump and probe the sample, one may expect rotational motion of the molecules to contribut to the transient spectra. This orientational relaxation is expected to be fast<sup>2,17</sup> and should not significantly affect our data.

## **Results and Discussion**

The transient absorption spectra for iodine in ethylene glycol, cyclohexane, cyclohexanol, and carbon tetrachloride as a function of time for three different probe wavelengths are shown in Figure 2. The pump wavelength is fixed at 680 nm, while the probe wavelength is at 630, 650, or 710 nm. The results are summarized in Table II. Note that we could obtain no useful data for CCl<sub>4</sub> at 630 nm, possibly due to the effect of complexes or impurities. The raw data are corrected by taking the square root of the signal, to account for the quadratic response of the receiver.

The following general observations can be made:

(1) For a given solvent, observation at a higher photon energy gives longer spectral time scales, at least for cyclohexane and CCl<sub>4</sub>. Changing the I<sub>2</sub> concentration by a factor of five in cyclohexane does not significantly change the transient spectral response curve. The time scale of the transient spectra for cyclohexanol and ethylene glycol at  $\sim$  27-ps fwhm is identical and nearly instrument limited ( $\sim 20$  ps) at all probe wavelengths.

(2) For a given probe wavelength, the time scale of the transient spectra is fast in ethylene glycol and cyclohexanol, intermediate in cyclohexane, and slow in CCl<sub>4</sub>.

Both sets of observations can be theoretically rationalized as follows:

(1) The dependence of the observed time scale of the transient electronic spectra on the probe wavelength may be used to test the alternative mechanisms proposed as the explanations for the observed transient spectral time scale. If the time for the I atoms to recombine were the major cause of the delay for the electronic absorption, then observation at any probe wavelength should show this time delay caused by recombination. Since, as shown in Figure 2, there is a large time scale change with probe wavelength for

(17) H. E. Lessing and A von Jena in "Laser Handbook", Vol. 3, M. L. Stitch, Ed., North-Holland, Amsterdam, 1979, pp 753-846.

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Figure 2. Experimental transient electronic absorption spectra for I<sub>2</sub> photodissociation in ethylene glycol, cyclohexane, and chloroform at three different probe wavelengths (630, 650, and 710 nm). Pump wavelength is 680 nm. Note that the timescale of the observed absorption change increases with probe photon energy. Cyclohexanol has the same transient spectra as ethylene glycol; for clarity it is not shown here.

CCl<sub>4</sub> and cyclohexane (the instrumental time resolution would mask any change for ethylene glycol and cyclohexanol), we can rule out recombination time as the dominant mechanism, at least for the reactions initiated through the A state as tested here.

(2) The change in time scale with different solvents at a given probe wavelength can be correlated with the nature of the solvent<sup>5,6,9,18</sup> as shown in a molecular dynamics simulation.<sup>19-22</sup> Hydrogen bonding, as in ethylene glycol and cyclohexanol, is expected to produce a broad distribution in hindered translational and rotational frequencies of the solvent, in the range of the vibrational frequencies of the vibrationally excited  $I_2$ , quickly relaxing them as we observe. In contrast, molecular dynamics calculations<sup>9,18</sup> show that the distribution of frequencies in liquid  $CCl_4$  has a low overlap with the range of relaxing  $I_2$  frequencies, and therefore one would expect, as observed, a longer time scale for the electronic transient spectra of I<sub>2</sub> photodissociation in CCl<sub>4</sub> if vibrational relaxation were the dominant mechanism in terms of time scale.<sup>5,6,9-11,23-26</sup>

With the advent of new infrared dyes,<sup>27</sup> we are presently probing at longer wavelengths. Our preliminary results<sup>28</sup> confirm the good

- (18) J. P. Bergsma and K. R. Wilson, J. Chem. Phys., to be submitted. (19) D. L. Bunker and B. S. Jacobson, J. Am. Chem. Soc., 94, 1843 (1972)
- (20) A. J. Stace and J. N. Murrell, Mol. Phys., 33, 1 (1977).
- (21) J. N. Murrell, A. J. Stace, and R. Dammel, J. Chem. Soc., Faraday, Trans. 2, 74, 1532 (1978)
- (22) A. H. Lipkus, F. P. Buff, and M. G. Sceats, J. Chem. Phys., in press.
  (23) C. L. Brooks and S. A. Adelman, J. Chem. Phys., 76, 1007 (1982).
  (24) C. L. Brooks III, M. W. Balk, and S. A. Adelman, J. Chem. Phys.,
- **79**, 784 (1983
- (25) M. W. Balk, C. L. Brooks III, and S. A. Adelman, J. Chem. Phys., 79. 804 (1983).
- (26) S. A. Adelman, *Adv. Chem. Phys.*, **53**, 61 (1983).
   (27) P. Bado, C. Dupuy, K. R. Wilson, R. Boggy, J. Bowen, and S. Westra, Opt. Commun., 46, 241 (1983).

correlation between experimental and theoretical spectra.

Three important caveats should be kept in mind. The first is that our transient signals could also reflect the presence of iodine atoms or molecules complexed with solvent molecules.<sup>3,8,29-36</sup> In particular, at the high iodine concentrations used in this work, there may be a considerable dimer population<sup>36,37</sup>  $(I_2 + I_2 \rightarrow I_4)$ . It is also known that ground-state I<sub>2</sub> molecules form complexes with hydroxylic solvents such as ethylene glycol and cyclohexanol and that iodine atoms generated by photolysis of  $I_2$  form transient complexes with the solvent molecules. It should be noted that in most cases these complexes are long lived (fwhm  $\geq 100 \text{ ns}$ )<sup>35</sup> and, due to the very high repetition rate of our laser source, should be recorded as nearly time-independent signals, as for example in CCl<sub>4</sub> at 630 nm where we observe slower signal components which make accurate measurement of fast decays difficult or impossible. Due to the overall similarity between our experimental results and molecular dynamics simulation, 5,6,9,18,38 there is evidence

(28) P. Bado, C. Dupuy, D. Magde, K. R. Wilson, and M. M. Malley, J. Chem. Phys., to be submitted.

- (29) S. J. Rand and R. L. Strong, J. Am. Chem. Soc., 82, 5 (1960).
   (30) R. L. Strong, S. J. Rand, and J. A. Britt, J. Am. Chem. Soc., 82, 5053 (1960).
  - (31) N. K. Bridge, J. Chem. Phys., 32, 945 (1960).
- (31) R. L. Strong, J. Chem. Phys., 65, 2423 (1962).
   (33) S. L. Shostak and R. L. Strong, Chem. Phys. Lett., 63, 370 (1979).
- (34) J.-C. Dutoit, J.-M. Zellweger, and H. van den Bergh, J. Chem. Phys., 78, 1825 (1983).
- (35) P. Fornier de Violet, R. Bonneau, and J. Joussot-Dubien, Chem. Phys. Lett., 19, 251 (1973).
- (36) P. Fornier de Violet, R. Bonneau, and J. Joussot-Dubien, Chem. Phys. Lett., 28, 569 (1974).
- (37) M. Tamres, W. K. Duerksen, and J. M. Goodenow, J. Phys. Chem., 72, 966 (1968).

that most of what we are seeing is due to the intended reaction and not to complexes, but the case is not proven. The second caveat is that the pathway from initial A state to final X state involves at least one interelectronic state transition whose details are unknown, and may involve other intermediate states as well.<sup>1</sup> The third caveat is that there might be differences in mechanism, for example involving predissociation, when  $\mathrm{I}_2$  is dissociated in the B state region.<sup>2-4,7,</sup>

#### Conclusion

Transient electronic spectra for the I<sub>2</sub> photodissociation reaction initiated through the directly dissociative A state have been measured as a function of the nature of the solvent and of probe photon energy. The results indicate that, at least for the case of direct excitation into the A state, the previous interpretation of the characteristic time scale as being due to the time for recombination does not apply. A more likely cause is the time required for vibrational (and perhaps electronic) decay of the already recombined molecules.

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**Registry No.** I<sub>2</sub>, 7553-56-2; CCl<sub>4</sub>, 56-23-5; ethylene glycol, 107-21-1; cyclohexanol, 108-93-0; cyclohexane, 110-82-7.

# Energy Disposal in Hydrogen Atom Abstraction Reactions: Energy in the Radical Fragment by Laser-Induced Fluorescence

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Vibrational distributions of the SD, SH, and CH<sub>3</sub>O radical product fragments from the F, Cl, H +  $D_2S$  (H<sub>2</sub>S) and F + CH<sub>3</sub>OH reactions have been measured in a flowing afterglow by laser-induced fluorescence. The results  $(N_1/N_0 = 0.15, N_0 = 0.15)$ 0.08, and 0.28 for SD from F, Cl, and H + D<sub>2</sub>S, respectively, and  $N_2/N_1/N_0 \ge 0.04/0.23/1.0$  for CH<sub>3</sub>O( $\nu_3^{(\prime)}$ ) from F + CH<sub>3</sub>OH) correspond to  $\langle f_V(SD) \rangle = 0.02, 0.03, 0.07$  and  $\langle f_V(CH_3O) \rangle \approx 0.02$ , respectively. These data, combined with the results from the infrared chemiluminescence measurements, directly show that little energy is released to the internal energy of the radical fragment in H atom abstraction reactions proceeding by direct pathways over repulsive potential surfaces.

#### Introduction

The initial product energy distributions contribute toward an understanding of chemical reactions at the microscopic level. Considerable progress has been made in characterizing the energy disposal to HF and HCl in F and Cl atom reactions with diatomic and polyatomic hydrides<sup>1-6</sup> by using the infrared chemilumines-

(4) (a) Beadle, P.; Dunn, M. R.; Jonathan, N. B. H.; Liddy, J. P.; Naylor, J. C.; Okuda, S. J Chem. Soc., Faraday Trans. 2 1978, 74, 2158, 2170. (b) Jonathan, N. B. H.; Sellers, P. V.; Stace, A. J. Mol. Phys. 1981, 43, 215. cence technique to observe HF(v) and HCl(v). Reactions with diatomic hydrides give HF and HCl molecules with about 70% of the total energy,  $^{1-4,6}\langle f_V \rangle \simeq 0.60$  and  $\langle f_R \rangle \simeq 0.10$ . The energy disposal to HF does not change significantly for F reacting with small polyatomic hydrides,<sup>1,24-6,8</sup> e.g.,  $(f_V(HF))$  for F + CH<sub>4</sub>, CH<sub>3</sub>Cl, PH<sub>3</sub>, and GeH<sub>4</sub> are 0.64, 0.62, 0.54, and 0.58, respectively. The rotational energy released to HF and HCl is somewhat lower for polyatomic cases<sup>1,4,7</sup> than for diatomic hydrides.<sup>3,6</sup> The remaining energy must be partitioned to the relative translational energy for the diatomic hydrides, since there is no significant

<sup>(38)</sup> P. H. Berens, J. P. Bergsma, and K. R. Wilson in "Time Resolved Vibrational Spectroscopy", G. Atkinson, Ed., Academic Press, New York, 1983, p 59.

 <sup>(1) (</sup>a) Holmes, B. E.; Setser, D. W. In "Physical Chemistry of Fast Reactions"; Smith, I. W. M., Ed.; Plenum: New York, 1980; Vol. 2. (b) Bogan, D. J.; Setser, D. W. J. Chem. Phys. 1976, 64, 586.
 (2) (a) Manocha, A. S.; Setser, D. W.; Wickramaaratchi, M. A. Chem.

Phys. 1983, 76, 129. (b) Wickramaaratchi, M. A.; Setser, D. W. J. Phys. Chem. 1983, 87, 64.

 <sup>(3) (</sup>a) Maylotte, D. H.; Polanyi, J. C.; Woodall, K. B. J. Chem. Phys. 1972, 57, 1547. (b) Nazar, M. A.; Polanyi, J. C. Chem. Phys. 1981, 55, 299.

<sup>(5) (</sup>a) Dill, B.; Heydtmann, H. Chem. Phys. 1978, 35, 161. (b) Ibid. 1980, 54, 9.

<sup>(6)</sup> Tamagake, K.; Setser, D. W.; Sung, J. P. J. Chem. Phys. 1980, 73, 2203.

<sup>(7)</sup> Bogan, D. J.; Setser, D. W.; Sung, J. P. J. Phys. Chem. 1977, 80, 888. (8) This statement is based on the results reported in ref 2 and 6, rather than the findings of ref 3b, for F + substituted methane reactions.