

Molecular dynamics of chemical reactions in solution: Experimental picosecond transient spectra for I₂ photodissociation

Philippe Bado, Charles Dupuy, Douglas Magde, Kent R. Wilson, and Michael M. Malley

Citation: *The Journal of Chemical Physics* **80**, 5531 (1984); doi: 10.1063/1.446664

View online: <http://dx.doi.org/10.1063/1.446664>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/jcp/80/11?ver=pdfcov>

Published by the AIP Publishing

Articles you may be interested in

[Photodissociation dynamics of I⁻ 2 in solution](#)

AIP Conf. Proc. **298**, 16 (1994); 10.1063/1.45405

[Wave packet dynamics of the Hgl₂ photodissociation reaction in solution](#)

J. Chem. Phys. **99**, 7273 (1993); 10.1063/1.465422

[Proposed experimental probes of chemical reaction molecular dynamics in solution: ICN photodissociation](#)

J. Chem. Phys. **90**, 4176 (1989); 10.1063/1.455775

[Studies of chemical reactivity in the condensed phase. I. The dynamics of iodine photodissociation and recombination on a picosecond time scale and comparison to theories for chemical reactions in solution](#)

J. Chem. Phys. **84**, 788 (1986); 10.1063/1.450578

[Dynamics of liquid state chemical reactions: Photodissociation dynamics and geminate recombination of molecular iodine in liquid solution](#)

J. Chem. Phys. **79**, 804 (1983); 10.1063/1.445830



Molecular dynamics of chemical reactions in solution: Experimental picosecond transient spectra for I₂ photodissociation

Philippe Bado, Charles Dupuy, Douglas Magde, and Kent R. Wilson
Department of Chemistry, University of California San Diego, La Jolla, California 92093

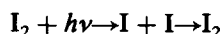
Michael M. Malley
Department of Chemistry, San Diego State University, San Diego, California 92182

(Received 14 November 1983; accepted 23 February 1984)

Picosecond transient electronic absorption spectroscopy is used to investigate the molecular dynamics of I₂ reaction in solution following dissociative excitation into the *A* state. Our aim is to provide a sufficiently detailed set of experimental observations so that theoretical treatments of the molecular dynamics of a solution reaction can be rigorously tested. We report here measurements obtained in 13 solvents, pumping at 680 nm with four probe wavelengths of 840, 690, 630, and 595 nm. The time scale of the transient electronic spectral response varies considerably among the different solvents. For a given solvent, the response in general varies strongly with probe wavelength, being slower for higher probe photon energy. This indicates that the spectral response times are not due to recombination times, but are more likely due to the time for vibrational or perhaps electronic decay of already recombined molecules. This conclusion is reinforced by the presence of transient absorption in the near infrared, where vibrationally excited molecules would be expected to absorb. The connection to vibrational decay is supported by the correlation for the different solvents between observed transient response times and the presence of solvent vibrational modes in the frequency range needed to vibrationally relax hot I₂.

I. INTRODUCTION

This experimental work and related theoretical studies¹⁻³ investigate the liquid phase dynamics of the chemical reaction sequence involving I₂ photodissociation, solvent caging, radical recombination to form a new vibrationally (and perhaps electronically) excited I₂ molecule, and the subsequent decay of its internal energy. Earlier experimental studies carried out in our laboratory¹⁻⁴ and elsewhere⁵⁻¹⁰ clearly indicate that much of the important molecular dynamics in this solution reaction occurs on the picosecond time scale. Since I₂ photodissociation and recombination is



one of the simplest possible reactions, the same diatomic being both reactant and product, it is an excellent candidate for studying solution reactions and has therefore been extensively investigated during the past decades.¹¹⁻³⁷

Figure 1 shows the gas phase potential energy curves for the iodine ground $X\text{O}_g^+(^1\Sigma)$ state and the excited $A\text{1}_u(^3\Pi)$, $B\text{O}_u^+(^3\Pi)$, $B''\text{1}_u(^1\Pi)$ states. The ground *X* state potential is taken from a semiempirical potential due to Matzen, Calder, and Hoffman³⁸ and from the experimental RKR values of Coxon.³⁹ The *A* and the *B''* dissociative states are from Tellinghuisen,^{40,41} the *B* state is from Barrow and Yee⁴² and Luc.⁴³ A more detailed description of the potential surfaces of interest is given by Bergsma and co-workers.⁴⁴

The photodissociation of I₂ in the liquid phase was investigated by Rabinowitch and Wood¹¹ in 1936, and in the same year, they did a two-dimensional simulation of caging with balls on a shaker table.¹² Several of the long time scale, steady state aspects of liquid phase iodine recombination

were investigated by Noyes and co-workers⁴⁵ in the 1950's and 1960's. Random walk and continuum diffusion models^{20,35,45} have been applied, but with only limited success, in describing the experimental results.

More recent stochastic studies have been carried out on the I₂ photodissociation reaction by Hynes, Kapral, and Torrie³¹ and by Martire and Gilbert.³⁰ A stochastic approach which brings into the model aspects of the molecular scale properties of the solvent has been developed by Adelman and co-workers.²³⁻²⁹

The first deterministic theoretical study of the molecular dynamics of reaction was by Bunker and Jacobson.¹⁹ They computed the classical trajectories for I₂ dissolved in CCl₄, with CCl₄ molecules considered as spherical, struc-

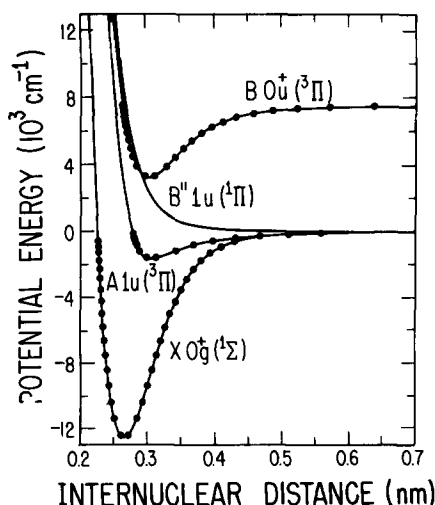


FIG. 1. Potential curves responsible for the gas phase absorption spectrum of I₂ in the visible-infrared region.

tureless particles in a specular cube. A striking finding is the relative unimportance of truly diffusive effects involving solvent intervention. They concurred with a suggestion first made by Rabinowitch¹² that once at least two solvent molecules partly intervene between the photofragments, their reunion becomes unlikely. Murrel, Stace, and Dammel^{21,22} modeled the molecular dynamics of the photodissociation of I_2 in dense inert gases and more recently, Lipkus, Buff, and Sceats⁴⁶ and Amar and Berne⁴⁷ have simulated the molecular dynamics of I_2 photodissociation in gas phase clusters.

In 1974, Chuang, Hoffman, and Eisinger⁵ published the first picosecond experimental data on this reaction in the liquid phase. With 530 nm laser pulses they photodissociated and observed I_2 in solution. They observed a transient bleaching, attributed to cage effect, of the order of 140 ps for I_2 in CCl_4 and of the order of 70 ps for I_2 in hexadecane. A delay of ~ 20 ps between excitation and the minimum in the absorption curve has been interpreted^{5,8} in terms of dissociation of the B state molecules which also absorb at 530 nm.

All of the earlier picosecond experimental studies of I_2 photodissociation in solution done by the Eisinger,^{5,6} Langhoff,^{7,9} and Rentzepis⁸ groups used the second harmonic of a Nd laser to start the reaction. Laser excitation at 530 nm, at least in the gas phase, promotes ground state $XO_g^+(^1\Sigma)$ I_2 molecules either to the $BO_u^+(^3\Pi)$ state^{41,48} (which presumably at some later time predissociates, but may absorb another photon^{49,50} in the meantime) or to the dissociative $B''1_u(^1\Pi)$ state.^{41,48} In the gas phase at 530 nm, the ratio of the absorption cross sections⁴¹ of $BO_u^+(^3\Pi)$ to $B''1_u(^1\Pi)$ is 6.6 to 1.0, so absorption to the B state might be expected to predominate.

Recently we have demonstrated that it is possible to compute from molecular dynamic calculations the contours of electronic absorption^{44,51} of I_2 in solution both at equilibrium and as a function of time following dissociation of I_2 .^{1,2} On the basis of our molecular dynamics calculations,¹⁻³ on the basis of Nesbitt and Hynes non-time dependent calculations^{31,33,34} and on the basis of Adelman and co-workers molecular time scale Langevin calculations²³⁻²⁹ it appears that the observed time scale of ~ 100 ps for the transient absorption may be due to vibrational relaxation, rather than the originally proposed time for recombination.⁵ The idea of vibrational relaxation is also implicit in the work of Troe⁵² and van den Bergh.^{53,54}

Despite these theoretical and experimental efforts, much remains to be done. Our understanding of chemical processes in liquids has fallen far behind that of similar processes in the gas phase. In fact the atomic motions which form the microscopic mechanisms for solution reactions are as yet hardly understood, even though most real-world chemical reactions occur in solution.

Our aim in this paper is thus to provide a detailed set of experimental observations against which to test theoretical models developed by us and by others, with the hope of clarifying the microscopic details of how this particularly simple solution reaction takes place. We apply a picosecond experimental technique which allows us to avoid a number of the complexities associated with earlier studies involving excitation into a combination of dissociative B'' and nondissocia-

tive B states, complexities which have up to now prevented a clear and definitive connection between experiment and theory. A key feature in our approach is the electronic excitation into the directly dissociative A state.

As has already been briefly mentioned¹⁻⁴ and will be discussed in detail elsewhere,⁵⁵ the experimental results reported here can be compared with molecular dynamics calculations of the reaction process through the intermediary of the transient spectra generated by these dynamics. Of particular interest in these comparisons are the positions as well as the appearance and decay times of new spectral features which arise during the relaxation of I_2 back to its ground state configuration. To date the comparisons of the experimental results presented here with the first molecular dynamics calculations are encouraging on both counts.

II. EXPERIMENT

The experimental system has been described before.^{4,56} Here we will summarize this description and emphasize the new improvements as shown in Fig. 2. A mode-locked argon-ion laser synchronously pumps in parallel two dye lasers producing two trains of ~ 8 ps pulses with a 4 ns pulse-to-pulse separation. Time resolved measurements are carried out using the standard pump-delayed-probe technique. The jitter between pump and probe pulses exhibits cross correlation of ~ 20 ps, thus limiting the time resolution. The delay between pump and probe is determined by an optical delay line. In order to achieve the sensitivity needed to detect the very weak⁴¹ $I_2 A$ state absorption, a multiple radio and audio frequency modulation system is used. This detection system, which is described in more detail elsewhere,⁵⁶ provides a very sensitive technique for extracting weak signals from noise. Unfortunately the sign of the transient signal is lost during signal processing since the standard output of our radio receiver is the square of the input signal. Thus we are not able to differentiate directly between induced absorption

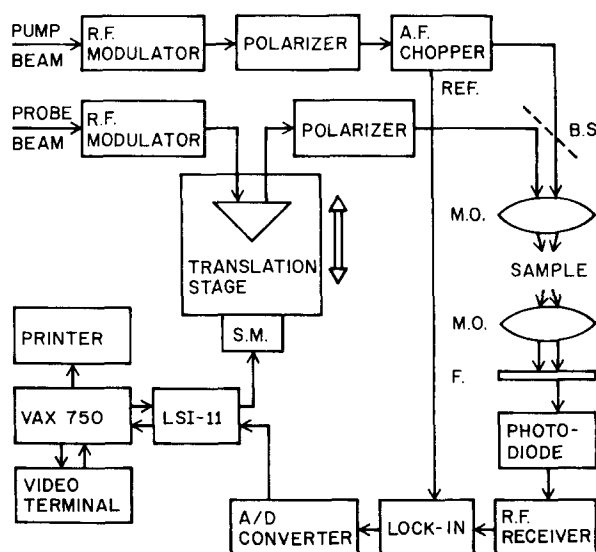


FIG. 2. Picosecond transient electronic absorption spectrometer and data collection system. (B.S. = beamsplitter; M.O. = microscope objective; A.F. = audio frequency; R.F. = radio frequency; F. = optical filter; S.M. = computer-controlled stepping motor).

and induced bleaching, except in special cases as described below.

The energy per pulse from the dye lasers is in the nJ range, and we raise the concentration of reacting species in our sample region by using a small confocal volume at the focus of a pair of microscope objectives (American Optical, infinity corrected, X6 or X10 power). The reaction solution is rapidly pumped through the confocal volume inside a small capillary with an inner diameter of ~ 1 mm. The wavelengths are checked prior to data collection with a calibrated monochromator. The sample temperature is between 295 and 305 K.

We can very crudely estimate the time for nongeminate recombination as follows, to show that it will not affect our results. We take the sample volume as roughly a cylinder with a diameter equal to the $10\text{ }\mu\text{m}$ beam focal spot and with a length equal to the $100\text{ }\mu\text{m}$ focal depth of the microscope objectives. Taking a typical value of $\sim 2 \times 10^{-2}$ molar concentration of iodine and 20 mW pump power on the sample, we calculate $\sim 10^{11}$ molecules in the sample volume and a flux of $\sim 10^8$ photons per pulse. The sample solution flows at $\sim 25\text{ ms}^{-1}$ and the laser repetition rate is 240 MHz, so there are an average of ~ 100 laser shots in each sample volume. With an absorption⁴¹ at 680 nm of $\epsilon_{680} \approx 40\text{ l mol}^{-1}\text{ cm}^{-1}$ and taking a 1.0 cage escape probability, $\sim 10^9$ iodine molecules will be dissociated in the sample volume. This represents $\sim 1\%$ change in the initial concentration.

In a 4×10^{-4} molar solution of iodine atoms, there is an average separation l between iodine atoms of $\sim 10^{-6}$ cm. Using a typical value³¹ of $3 \times 10^{-5}\text{ cm}^2\text{ s}^{-1}$ for the relative diffusion coefficient D , we obtain an estimate for the nongeminate recombination time t_{NG}

$$t_{\text{NG}} \approx l^2 D^{-1} \approx 100\text{ ns}.$$

On the time scale of our measurements, a 100 ns process will appear as a constant background.

In the experiments described here the pump and the probe beams are collinear and, in contrast to our earlier experiments,¹⁻⁴ codirectional. Both the pump and the probe power at the sample are typically on the order of 20 mW. After passing through the sample, the probe beam is diverted by a beamsplitter or a polarizer onto a photodiode (EGG, model DT-110). An optical bandpass filter is used to block any pump light still present. The delay between pump and probe is determined by an optical delay line. A stepper motor scans the delay range repeatedly while a microcomputer records data. The pump and the probe beams are cross polarized and one may expect rotational motion of the molecules to contribute to the transient spectra. However, orientational relaxation is typically fast^{5,57} and should not greatly affect our data.

Analytical reagent grade I₂, ethylene glycol, and cyclohexanol are used without further purification. Analytical reagent grade cyclohexane, hexane, nonane, dodecane, hexadecane, chloroform, bromoform, dichloromethane, dibromomethane, and diiodomethane are purified by passing through an activated aluminum oxide column. Carbon tetrachloride is of spectroscopic grade and is also purified on activated alumina. The concentration of iodine, as shown in Table I, is adjusted such that the sample absorbs between

30% and 70% of the probe light. When this is not possible due to solubility limits, then solutions saturated in iodine are used.⁵⁸ As a test we have decreased the iodine concentration in cyclohexane by a factor ~ 5 at the 690 nm probe wavelength and the observed transient spectra do not change.

III. RESULTS

By using a 680 nm pump source⁴ (dye laser with DCM dye),⁵⁹ we have excited the I₂ molecules into the A state, a dissociative transition free from the predissociation and absorption complexities possibly associated with the previous⁵⁻⁹ picosecond studies, but at a loss of a factor ~ 20 in absorption cross section.⁴¹ Also by exciting at longer wavelengths one gives less excess energy to the I radicals and the fraction of atoms escaping the solvent cage might be expected to be reduced.¹⁸ We see little baseline shift indicating escape of I atoms for the hydrocarbon solvents, while Langhoff *et al.*^{9,35} show a large baseline shift for I₂ in hexane after excitation with a 530 nm pump, which they ascribe to cage escape. We examine the recombination kinetics at a variety of probe wavelengths: 595 nm (R6G dye laser), 630 nm (DCM dye laser),⁵⁹ 690 nm (DCM dye laser), and 840 nm (LDS-820 dye laser).⁶⁰

Our experimental observations may be summarized as follows:

A. Probe photon energy dependence

For a given solvent, observation at higher probe photon energy gives longer spectral time response as shown, e.g., in Fig. 3 for cyclohexane and in Fig. 4 for chloroform. The same trend, summarized in Table II, applies for I₂ in all of the solvents studied with the possible exception of cyclohexanol and ethylene glycol, where the temporal features are nearly instrument limited and for which no significant changes are observed.

B. Solvent dependence

The 13 solvents studied can be separated into four different classes according to their chemical nature:

(i) Alcohols (ethylene glycol, cyclohexanol). The time scales of the transient spectra (FWHM) for the alcohols (~ 28 ps) are identical and nearly instrument limited (~ 20 ps) at all probe wavelengths studied, as shown in Fig. 5.

(ii) Straight chain hydrocarbons (hexane, nonane, dodecane, hexadecane). The time scales of the transient spectra for the straight chain hydrocarbons are somewhat longer than for the alcohols (~ 40 ps at 690 nm) as shown in Fig. 6

TABLE I. Iodine concentration for various probe wavelengths.

Probe wavelength	Iodine concentration mol l ⁻¹
595 nm	9×10^{-3}
630 nm	3.3×10^{-2}
690 nm	3.8×10^{-2}
840 nm ^a	$8\text{--}31 \times 10^{-2}$

^a Solutions saturated.

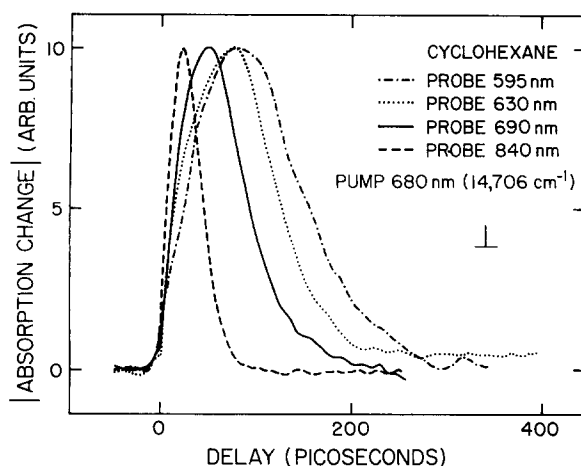


FIG. 3. Experimental transient electronic absorption spectra for I₂ photodissociation in cyclohexane at four different probe wavelengths following excitation at 680 nm. The vertical scale for this and the following figures is the absolute value of the absorption change, computed by taking the square root of the output of the quadratic detection system.

for hexane. All the straight chain hydrocarbons show the same time scale (within experimental error) at a given probe wavelength, as shown in Table II.

(iii) Cyclic hydrocarbon (cyclohexane). Cyclohexane differs from the straight chain hydrocarbons with its time scale being somewhat longer, as shown in Fig. 3 and Table II.

(iv) Halogen derivatives of methane (CCl₄, CHCl₃, CH₂Cl₂, CHBr₃, CH₂Br₂, CH₂I₂). For the halogen derivatives of methane the transient spectral time is very sensitive to substitutions. It is fastest for iodine derivatives, followed by bromine derivatives and finally by chlorine derivatives as shown in Fig. 7 and Table II. In general there is not a simple correlation between the number of substitutions and the time scale of the transient spectra.

C. Transient bleaching versus absorption

Pumping at 680 nm and probing at 690 nm, we detect a transient *absorption* for I₂ in ethylene glycol. We detect indirectly the same transient *absorption* feature for I₂ in non-

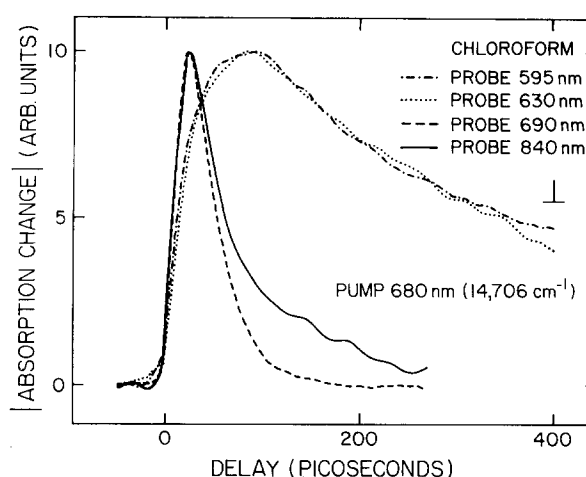


FIG. 4. Experimental transient electronic absorption spectra for I₂ photodissociation in chloroform at four different probe wavelengths.

ane while probing at 840 nm. Other investigators^{5,7,9} using 530 nm light as probe and pump have monitored a transient *bleaching* for all of the iodine solutions studied. For ethylene glycol at a probe wavelength of 690 nm and a pump wavelength of 680 nm, the transient absorption is particularly strong and we are able to detect the signal with audio modulation and phase sensitive detection alone (i.e., without radio-frequency modulation). We indirectly see the same feature of transient absorption for nonane at a probe wavelength of 840 nm by comparing the contribution of a sample of iodine and a sample dye (LDS-820) placed in series in the path of the beams and by changing the relative concentration of the two samples. This method of sign determination is awkward to use and the results are often ambiguous. Modifications recently developed by Andor, Lörincz, Sienion, Smith, and Rice⁶¹ allow the receiver to respond linearly to the input, and thereby conserve the sign.

IV. DISCUSSION

The observations presented above can be explained as follows:

TABLE II. Transient electronic absorption time for I₂ photodissociation reaction in various solvents (FWHM in ps). Data have been corrected for quadratic response of the detection system. The pump wavelength is 680 nm (14 706 cm⁻¹).

Solvents	Probe wavelength and energy			
	595 nm 16 807 cm ⁻¹	630 nm 15 873 cm ⁻¹	690 nm 14 493 cm ⁻¹	840 nm 11 905 cm ⁻¹
Ethylene glycol	29 ± 2	29 ± 2	28 ± 2	29 ± 2
Cyclohexanol	a	28 ± 2	29 ± 2	29 ± 2
Hexane	68 ± 2	70 ± 6	43 ± 2	36 ± 2
Nonane	70 ± 2	70 ± 4	42 ± 2	a
Dodecane	69 ± 2	71 ± 2	42 ± 2	a
Hexadecane	70 ± 2	69 ± 4	42 ± 2	36 ± 2
Cyclohexane	132 ± 4	114 ± 4	81 ± 2	37 ± 2
CCl ₄	270 ± 15	a	200 ± 10	a
CHCl ₃	346 ± 10	336 ± 10	55 ± 4	45 ± 2
CH ₂ Cl ₂	a	a	113 ± 5	38 ± 4
CHBr ₃	235 ± 10	a	69 ± 3	26 ± 2
CH ₂ Br ₂	85 ± 9	a	a	55 ± 7
CH ₂ I ₂	43 ± 2	42 ± 2	41 ± 2	a

* Accurate data could not be taken because of slower spectral response components perhaps due to the presence of complexes or impurities.

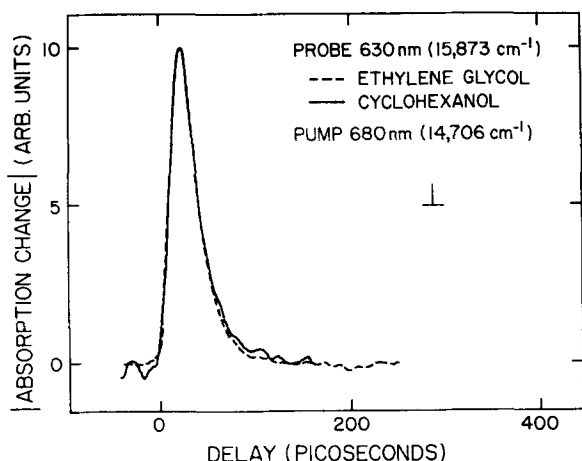


FIG. 5. Experimental transient electronic absorption spectra for I_2 photodissociation in ethylene glycol and cyclohexanol. The time scale of the transient spectra is fast in these hydrogen-bonded alcohols and essentially identical at all probe wavelengths (here shown at 630 nm).

A. Probe photon energy dependence

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 response. If the time needed for the iodine atoms to recombine is the major cause of the time scale for the electronic absorption, then the observed time delay should be approximately independent of the probe wavelength. Since, as shown in Figs. 3 and 4 and Table II, there is instead a large time scale change as a function of the probe wavelength, we can rule out recombination time as the dominant mechanism. A more likely cause is the time required for vibrational (or perhaps electronic)¹⁰ relaxation of the already recombined molecules. The experimental wavelength dependence corresponds, at least approximately, to the theoretical wavelength dependence calculated by Nesbitt and Hynes^{32,33} for CCl_4 and by Berens and Bergsma *et al.*³ for ethylene glycol, cyclohexane, and CCl_4 .

B. Solvent dependence

Calculations by Berens and Bergsma *et al.*^{1-3,55} and by Nesbitt and Hynes³²⁻³⁴ indicate that primary recombination

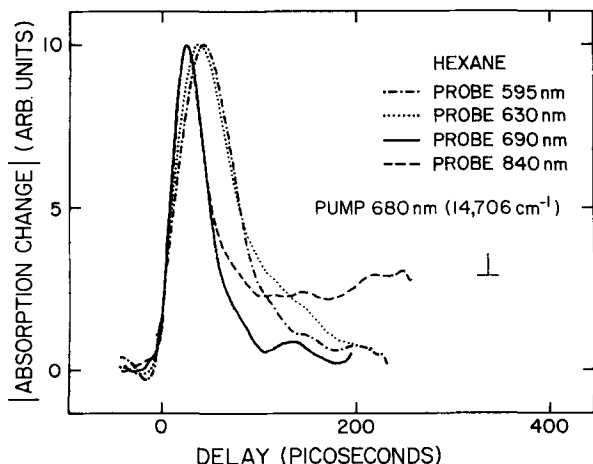


FIG. 6. Experimental transient electronic absorption spectra for I_2 photodissociation in hexane at four different probe wavelengths. The data are essentially similar for the other straight-chain hydrocarbons studied.

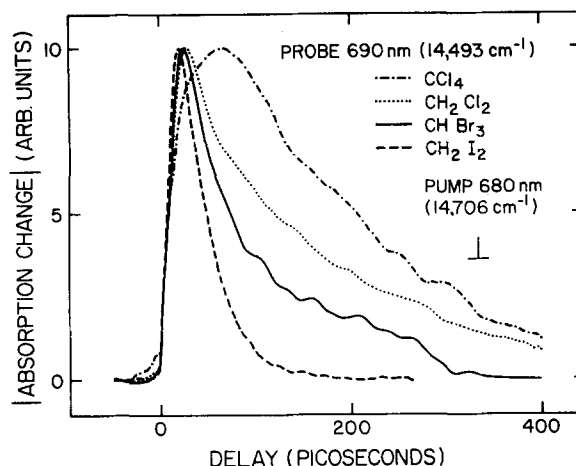


FIG. 7. Experimental transient electronic spectra for I_2 photodissociation in various halogenated methanes.

followed by vibrational energy transfer has a characteristic time in approximately the hundred picosecond range for I_2 in CCl_4 . Adelman *et al.*^{25,28,29} using their "Molecular Time-scale Generalized Langevin Equation" method find for the same system a roughly similar characteristic time.

The change in time scale with different solvents at a given probe wavelength can be correlated with the nature of the solvent as shown in molecular dynamics simulations.^{1-3,55} Hynes and Nesbitt^{33,34} have studied the different pathways by which nascent iodine can dispose of the 50–60 kT ($T = 300$ K) corresponding to its excess vibrational energy. Their calculations indicate that in liquid xenon and liquid CCl_4 vibrational to translational energy transfer is an inefficient process, at least in the lower half of the I_2 potential well. For I_2 in CCl_4 , they have studied in detail the intermolecular vibration–vibration energy transfer between the 213 cm^{-1} vibrational frequency⁶² of I_2 low in its potential well and the near resonant CCl_4 ν_2 bending mode^{63,64} at 217 cm^{-1} . Hynes and Nesbitt have calculated, with the help of a vibration–vibration energy transfer model developed by Rapp,⁶⁵ that the vibration–vibration contribution to the relaxation is negligible in the upper half of the I_2 potential well. This arises from the frequency mismatch associated with the anharmonic compression of the spacing between I_2 vibrational levels. In the bottom half of the well, the vibration–vibration contribution grows as the vibrational frequencies tune into resonance with the ν_2 mode of CCl_4 . Indeed for low vibrational levels, i.e., $v < 40$, the vibration–vibration energy transfer mechanism is by far the most efficient pathway for energy relaxation. Hynes and Nesbitt predict a spectral response at 530 nm in the order of 100 ps for I_2 in CCl_4 . This vibrational energy relaxation scenario which emphasizes resonance between the range of the vibrational frequencies of the vibrationally excited I_2 (0–213 cm^{-1}) and the range of the solvent vibrational modes may be tested with other solvents, as we have experimentally done here.

Hydrogen bonding, as in ethylene glycol and cyclohexanol, is expected to produce a broad distribution in hindered translational and rotational frequencies of the solvent,^{3,66} in the range of the vibrational frequencies of the vibrationally excited I_2 . This should yield fast relaxations, just as we observe experimentally in Fig. 5. Note, however, that the

chemistry of what actually happens in alcohols may well be more complicated.^{67,68}

The linear hydrocarbons have low frequency structural C–C–C deformation modes which tend to expand or contract the carbon chain. They also have CH₂–CH₂ torsional modes spanning the 0–153 cm^{−1} range.⁶³ The vibrational modes of large ring systems (C₁₂ and higher) do not differ significantly from those of corresponding linear systems since the same strainless low energy configuration is adopted.⁶³ However, for smaller ring systems, the presence of strain due to deviation of the valence angles from the tetrahedral value (Bayer strain) and to repulsion between neighboring nonbonded atoms (Pitzer strain) leads to some observable differences.^{63,64} For example, the low frequency modes associated with the CH₂–CH₂ torsion and the C–C–C deformation are shifted to higher frequencies by the ring structure.^{63,64} Thus one would expect a slower transient response in cyclohexane than in hexane. This is confirmed by our experiments, as shown in Table II and Figs. 3 and 6.

The correlation between fast spectral response and the presence of low (<200 cm^{−1}) solvent vibrational frequencies is also observed for the halogenated derivatives of methane, whose characteristic Raman frequencies are collected in Table III. For example, vibrational relaxation is expected to be

very fast in CH₂I₂ and CH₂Br₂, due to the presence of a strong ν_4 mode at 121 and 174 cm^{−1}, respectively, while in CH₂Cl₂ the ν_4 mode is shifted to 285 cm^{−1}, out of resonance with the vibrational range of the excited iodine molecules and the response should be noticeably slower. This is confirmed by our experimental data, as shown in Fig. 7 and Table III. Similarly, we would theoretically expect from their Raman frequencies that CHCl₃ and CCl₄ would be slow, as they are found to be experimentally. The only exception to the rule is CHBr₃ at the 595 nm probe wavelength, which is longer than we would have expected.

C. Transient bleaching versus transient absorption

According to molecular dynamics calculations^{1–3,55} one should observe at long probe wavelengths a transient *absorption* after excitation in the *A* state. This seemingly unusual feature may be explained by a simple mechanism. For example, before photodissociation the 840 nm probe beam is only very weakly absorbed ($\epsilon_{840} \approx 5 \text{ l mole}^{-1} \text{ cm}^{-1}$). After photodissociation, the iodine atoms recombine to form highly excited molecules. While these I₂ molecules are highly vibrationally excited, they spend a high fraction of their time near their classical outer turning points, where, as can be

TABLE III. Characteristic low frequency Raman modes of halogenated methanes in the liquid phase. Data are from Shimanouchi and from Dollish *et al.*

Molecule and type of mode		X = Cl	X = Br	X = I
Frequency (cm ⁻¹)				
1. CH ₂ X ₂				
CX ₂ symmetric stretch	ν_3	703	577	483
CX ₂ scissors	ν_4	285	174	121
CX ₂ antisymmetric stretch	ν_9	742	639	566
2. CHX ₃				
CX ₃ symmetric stretch	ν_2	668	539	a
CX ₃ symmetric deformation	ν_3	366	222	a
CX ₃ degenerate stretch	ν_5	761	656	a
CX ₃ degenerate deformation	ν_6	262	154	a
3. CX ₄				
CX ₄ symmetric stretch	ν_1	459	a	a
CX ₄ degenerate deformation	ν_2	217	a	a
CX ₄ degenerate	ν_3	776	a	a
CX ₄ degenerate deformation	ν_4	314	a	a

* Not liquid under standard conditions.

seen in Fig. 1, the strong transition to the *B* state lies in the near infrared and the red spectral regions. Thus the major spectral absorption strength, which is in the middle of visible region for ground vibrational state molecules, lies at much longer wavelengths for highly vibrationally excited molecules. This can be understood by simple classical⁴⁴ or wave packet⁵¹ models developed elsewhere. The net result is an enhanced transient absorption as the iodine molecules relax down through the excited vibrational states. Our experimental data, in the two special cases where we are able to determine the sign of the absorption change following photodissociation in the *A* state, reveal the theoretically predicted transient absorption.

D. Transitions among electronic states

While our experimental results correlate well with the general theoretical picture developed recently by our own group^{1-3,55} and by the Hynes³²⁻³⁴ and Adelman²³⁻²⁹ groups, there are still areas of uncertainty.

The iodine atoms are “born” on an excited electronic state. The process whereby they go from this excited state potential surface to the ground state surface is not yet well understood. A complete description of the chemical reaction would require consideration of curve-crossing probabilities and the possible fate of the atoms on any of the many electronic states that correlate with two ground state iodine atoms. Recently Flynn and co-workers have reported on the photochemical dynamics of I₂ isolated in a solid rare gas matrix.¹⁰ Following excitation into the *B* and the *B'* states, they observed emission attributed to *B*, *A*, and *A'* electronic states, depending on the host matrix. A collision-induced transition model developed by Sceats³⁷ as well as a stochastic surface hopping model by Ali and Miller³⁶ suggest that transitions among I₂ states may play a role in the recombination dynamics following photodissociation.

On the experimental side, one should note that our transient signal could also reflect the presence of complexes involving iodine molecules or atoms with solvent molecules. Many such complexes and anionic species have been reported in the literature,^{6,8,69-74} and are particularly likely to play a role for the alcohols.^{67,68} Indeed for a variety of solvent and wavelength combinations we find longer lived underlying absorption changes which may well arise from the presence of complexes (with either iodine atoms or I₂ molecules), as well as from impurities. Careful initial cleaning of the solvents substantially reduces their effect. Nevertheless for several solvents under some circumstances we see the presence of long lived (FWHM ≥ 1 ns) complexes as reflected in the gaps in the data shown in Table II. Due to the overall similarity between our experimental results and molecular dynamics simulation,^{1-4,55} there is evidence that most of what we are seeing is due to the intended reaction and not to complexes, but the case is not proven. Transient picosecond Raman measurements¹ which we hope to carry out could provide a definitive test.

V. CONCLUSIONS

For the particularly simple solution reaction initiated by I₂ photodissociation we have collected a large set of tran-

sient electronic absorption data as a function of solvent, time, and probe photon energy, in order to test theoretical solution reaction models. By using a high sensitivity dual beam synchronously pumped picosecond spectrometer and photodissociating I₂ at 680 nm directly into the *A* 1_u(³Π) state, complexities (predissociation, perhaps two photon processes) possibly associated with shorter wavelength excitation at higher pulse powers are avoided.

The experimental data are in reasonable agreement with recent molecular dynamics calculations.^{3,55} The experimental results strongly suggest that the observed characteristic electronic absorption response times are not caused by the time necessary for recombination of the atoms, and are more likely due to the time necessary for vibrational (and perhaps electronic) relaxation of the already formed molecules. The experimental measurements presented here will be compared in detail in a subsequent article⁵⁵ with molecular dynamics calculations of the reaction sequence in different solvents and of the accompanying transient spectra.

Note added in proof. Shortly following submission of the manuscript, we became aware of a picosecond laser study of I₂ dissociation in liquids recently completed by Kelley, Abul-Haj, and Jang at UCLA.⁷⁵ They studied I₂ photodissociation in several of the same solvents we have studied, but with a different experimental technique. The I₂ molecules were excited by 532 nm light into a region corresponding in the gas phase to a mixture of the *B* and *B'* states. The transient electronic absorption spectra were then recorded as a function of time following excitation using the picosecond white light continuum method. Although Kelley *et al.* reconfirm the presence of a transient absorption on the 100 ps time scale, the key results they present are: (i) the appearance of a longer-lived absorption in the 600–900 nm region whose lifetime depends on the solvent; (ii) the observed lack of spectral shift in this red absorption band. The red absorption band is interpreted as absorption emanating from a mixture of the *A* and *A'* states (and not a vibrational relaxation as we hypothesize) and the long-lived component (2.7 ns in CCl₄) is attributed to intersystem crossing from the *A* or *A'* states back down to the ground *X* state.

The discrepancies between our findings and those of Kelley *et al.* may arise from the difference in the states reached by the initial excitation or from some yet undetected systematic error in one of the two very different experimental techniques. Kelley's work involved excitation into a mixture of the *B* and *B'* states with a higher photon-to-molecule ratio which could perhaps result in multiple photon absorption effects, although he has varied the photon flux and found no change. Although our work involved the theoretically less ambiguous excitation into the *A* state, due to the high repetition rate of our laser and the higher I₂ concentration, there is always the possibility of complications from signals due to photoproducts building up during the several shots into the same sample volume. Both experimental techniques are susceptible to complications due to interference from I₂-solvent, I-solvent or I₂-I₂ complexes, and this is especially true because of the broad featureless nature of the transient electronic absorption spectra.

These two recent and extensive studies of I₂ photodisso-

ciation further attest to the interest in understanding the dynamics of chemical reactions in solution, and to the difficulties involved in clearly eliminating alternative mechanisms. Due to the ambiguities involved in electronic absorption spectroscopy, it would appear that a more selective probe, such as Raman spectroscopy,¹ might be a more appropriate way to elucidate the dynamics of these fundamental processes. We and others are currently preparing to carry out such experiments.

ACKNOWLEDGMENTS

We thank M. Hennecke for his assistance in this experiment, the National Science Foundation, Chemistry, and the Office of Naval Research, Chemistry, for the financial support which made this work possible, the Division of Research Resources of the National Institutes of Health for support of computer systems and the Swiss National Foundation for fellowship support to P. Bado.

- ¹P. Bado, P. H. Berens, and K. R. Wilson, in *Picosecond Lasers/Applications*, edited by L. S. Goldberg (Proceedings of the Society Photo-Optical Instrumental Engineers, Bellingham, Washington, 1982), Vol. 322, p. 230.
- ²P. Bado, P. H. Berens, J. P. Bergsma, S. B. Wilson, K. R. Wilson, and E. J. Heller, in *Picosecond Phenomena III*, edited by K. B. Eisenthal, R. M. Hochstrasser, W. Kaiser, and A. Laubereau (Springer, Berlin, 1982), p. 260.
- ³P. 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 *Laser Chemistry*, edited by A. Zewail (Harwood Academic, New York, 1983), Vol. 3, p. 231.
- ⁴P. Bado and K. R. Wilson, *J. Phys. Chem.* **88**, 655 (1984).
- ⁵T. J. Chuang, G. W. Hoffman, and K. B. Eisenthal, *Chem. Phys. Lett.* **25**, 201 (1974).
- ⁶C. A. Langhoff, K. Gnädig, and K. B. Eisenthal, *Chem. Phys.* **46**, 117 (1980).
- ⁷C. A. Langhoff, B. Moore, and W. Nugent, in *Picosecond Phenomena II*, edited by R. Hochstrasser, W. Kaiser, and C. V. Shank (Springer, Berlin, 1980), p. 249.
- ⁸D. F. Kelley and P. M. Rentzepis, *Chem. Phys. Lett.* **85**, 85 (1982).
- ⁹C. A. Langhoff, B. Moore, and M. DeMeuse, *J. Am. Chem. Soc.* **104**, 3576 (1982).
- ¹⁰P. B. Beeken, E. A. Hanson, and G. W. Flynn, *J. Chem. Phys.* **78**, 5892 (1983).
- ¹¹E. Rabinowitch and W. C. Wood, *Trans. Faraday Soc.* **32**, 547 (1936).
- ¹²E. Rabinowitch and W. C. Wood, *Trans. Faraday Soc.* **32**, 1381 (1936).
- ¹³R. M. Noyes, *J. Chem. Phys.* **18**, 999 (1950).
- ¹⁴F. W. Lampe and R. M. Noyes, *J. Am. Chem. Soc.* **76**, 2140 (1954).
- ¹⁵R. M. Noyes, *J. Chem. Phys.* **22**, 1349 (1954).
- ¹⁶R. M. Noyes, *Z. Elektrochemie* **64**, 153 (1960).
- ¹⁷D. Booth and R. M. Noyes, *J. Am. Chem. Soc.* **82**, 1868 (1960).
- ¹⁸L. F. Meadows and R. M. Noyes, *J. Am. Chem. Soc.* **82**, 1872 (1960).
- ¹⁹D. L. Bunker and B. S. Jacobson, *J. Am. Chem. Soc.* **94**, 1843 (1972).
- ²⁰G. T. Evans and M. Fixman, *J. Phys. Chem.* **80**, 1544 (1976).
- ²¹A. J. Stace and J. N. Murrell, *Mol. Phys.* **33**, 1 (1977).
- ²²J. N. Murrell, A. J. Stace, and R. Dammel, *J. Chem. Soc., Faraday Trans. 2* **74**, 1532 (1978).
- ²³S. A. Adelman, *Adv. Chem. Phys.* **44**, 143 (1980).
- ²⁴M. Berkowitz, C. L. Brooks III, and S. A. Adelman, *J. Chem. Phys.* **72**, 3889 (1980).
- ²⁵C. L. Brooks and S. A. Adelman, *J. Chem. Phys.* **76**, 1007 (1982).
- ²⁶S. A. Adelman and C. L. Brooks, *J. Phys. Chem.* **86**, 1511 (1982).
- ²⁷S. A. Adelman, *Adv. Chem. Phys.* **53**, 61 (1983).
- ²⁸C. L. Brooks III, M. W. Balk, and S. A. Adelman, *J. Chem. Phys.* **79**, 784 (1983).
- ²⁹M. W. Balk, C. L. Brooks III, and S. A. Adelman, *J. Chem. Phys.* **79**, 804 (1983).
- ³⁰B. Martire and G. Gilbert, *Chem. Phys.* **56**, 241 (1981).
- ³¹J. T. Hynes, R. Kapral, and G. M. Torrie, *J. Chem. Phys.* **72**, 177 (1980).
- ³²D. J. Nesbitt and J. T. Hynes, *Chem. Phys. Lett.* **82**, 252 (1981).
- ³³D. J. Nesbitt and J. T. Hynes, *J. Chem. Phys.* **76**, 6002 (1982).
- ³⁴D. J. Nesbitt and J. T. Hynes, *J. Chem. Phys.* **77**, 2130 (1982).
- ³⁵C. A. Langhoff, B. Moore, and M. DeMeuse, *J. Chem. Phys.* **78**, 1191 (1983).
- ³⁶D. P. Ali and W. H. Miller, *J. Chem. Phys.* **78**, 6640 (1983).
- ³⁷M. G. Sceats, (private communication).
- ³⁸M. K. Matzen, G. V. Calder, and D. K. Hoffman, *Spectrochim. Acta Part A* **29**, 2005 (1973).
- ³⁹J. A. Coxon, *J. Quant. Spectrosc. Radiat. Transfer* **11**, 443 (1971).
- ⁴⁰J. Tellinghuisen, *J. Mol. Spectrosc.* **86**, 393 (1981).
- ⁴¹J. Tellinghuisen, *J. Chem. Phys.* **76**, 4736 (1982).
- ⁴²R. F. Barrow and K. K. Yee, *J. Chem. Soc., Faraday Trans. 2* **69**, 684 (1973).
- ⁴³P. Luc, *J. Mol. Spectrosc.* **80**, 41 (1980).
- ⁴⁴J. P. Bergsma, P. H. Berens, K. R. Wilson, D. R. Fredkin, and E. J. Heller, *J. Phys. Chem.* **88**, 612 (1984).
- ⁴⁵R. M. Noyes, in *Progress in Reaction Kinetics*, edited by G. Porter and B. Stevens (Pergamon, Oxford, 1961), Vol. I, p. 130–160.
- ⁴⁶A. H. Lipkus, F. P. Buff, and M. G. Sceats, *J. Chem. Phys.* **79**, 4830 (1983).
- ⁴⁷F. G. Amar and B. J. Berne, Columbia University (private communication).
- ⁴⁸J. Tellinghuisen, *J. Chem. Phys.* **58**, 2821 (1973).
- ⁴⁹G. E. Busch, R. T. Mahoney, R. I. Morse, and K. R. Wilson, *J. Chem. Phys.* **51**, 837 (1969).
- ⁵⁰R. K. Sander and K. R. Wilson, *J. Chem. Phys.* **63**, 4242 (1974).
- ⁵¹J. R. Reimers, K. R. Wilson, and E. J. Heller, *J. Chem. Phys.* **79**, 4749 (1983).
- ⁵²J. Troe, in *High Pressure Chemistry*, edited by H. Kelm (Reidel, Dordrecht, 1978), p. 489–520.
- ⁵³J. M. Zellweger and H. van den Bergh, *J. Chem. Phys.* **72**, 5405 (1980).
- ⁵⁴J.-C. Dutoit, J.-M. Zellweger, and H. van den Bergh, *J. Chem. Phys.* **78**, 1825 (1983).
- ⁵⁵J. P. Bergsma and K. R. Wilson, *J. Chem. Phys.* (to be submitted).
- ⁵⁶P. Bado, S. B. Wilson, and K. R. Wilson, *Rev. Sci. Instrum.* **53**, 706 (1982).
- ⁵⁷H. E. Lessing and A. von Jena, in *Laser Handbook*, edited by M. L. Stitch (North-Holland, Amsterdam, 1979), Vol. 3, p. 753.
- ⁵⁸W. F. Linke, *Solubilities, Inorganic and Metal-Organic Compounds; A Compilation of Solubility Data from the Periodical Literature* (Van Nostrand, Princeton, N.J., 1958).
- ⁵⁹E. G. Marason, *Opt. Commun.* **37**, 56 (1981).
- ⁶⁰P. Bado, C. Dupuy, K. R. Wilson, R. Boggy, J. Bowen, and S. Westra, *Opt. Commun.* **46**, 241 (1983).
- ⁶¹L. Andor, A. Lörincz, J. Siemion, D. D. Smith, and S. A. Rice, *Rev. Sci. Instrum.* **55**, 64 (1984).
- ⁶²R. N. Zare, *J. Chem. Phys.* **40**, 1934 (1964).
- ⁶³F. R. Dollish, W. G. Fateley, and F. R. Bentley, *Characteristic Raman Frequencies of Organic Compounds* (Wiley, New York, 1974).
- ⁶⁴T. Shimanouchi, *Tables of Molecular Vibrational Frequencies. Consolidated Volume I* (Nat. Bur. Stand., U.S.G.P.O. Washington, D.C., 1972).
- ⁶⁵D. Rapp, *J. Chem. Phys.* **43**, 316 (1965).
- ⁶⁶P. H. Berens, D. H. J. Mackay, G. M. White, and K. R. Wilson, *J. Chem. Phys.* **79**, 2375 (1983).
- ⁶⁷P. Fournier de Violet, R. Bonneau, and J. Joussot-Dubien, *Chem. Phys. Lett.* **19**, 251 (1973).
- ⁶⁸P. Fournier de Violet, R. Bonneau, and J. Joussot-Dubien, *Chem. Phys. Lett.* **28**, 569 (1974).
- ⁶⁹M. Tamres and J. Yarwood, *Spectroscopy and Structure of Molecular Complexes* (Plenum, New York, 1973), Chap. 3 and references therein.
- ⁷⁰S. J. Rand and R. L. Strong, *J. Am. Chem. Soc.* **82**, 5 (1960).
- ⁷¹R. L. Strong, S. J. Rand, and J. A. Britt, *J. Am. Chem. Soc.* **82**, 5053 (1960).
- ⁷²N. K. Bridge, *J. Chem. Phys.* **32**, 945 (1960).
- ⁷³R. L. Strong, *J. Chem. Phys.* **66**, 2423 (1962).
- ⁷⁴S. L. Shostak and R. L. Strong, *Chem. Phys. Lett.* **63**, 370 (1979).
- ⁷⁵D. F. Kelley, N. Alan Abul-Haj, and Du-Jeon Jang, *J. Chem. Phys.* (in press).