

Coherent Effects in Solution Photochemistry

Abstract

In this contribution we report time domain studies of photochemistry in liquids. The impulsive nature of photoexcitation using femtosecond pulses results in induction of vibrational coherence in excited, ground, and reaction product electronic states. Theoretical modeling is used in order to interpret the observed time and solvent dependencies of these motions. Coherent vibrations induced are demonstrated to be vital dynamic observables, providing profound insight into the details of solution chemical reactivity. Transient resonance impulsive stimulated scattering is introduced for the first time in order to probe reaction fragments undergoing rapid vibrational relaxation.

Introduction

The introduction of new theoretical and experimental tools^{1,2}, capable of addressing chemical reaction dynamics in the liquid phase, has generated an explosive growth of interest in this field over the last few years. The ultimate aim of this endeavor is to appreciate how, for a wide array of chemical reactions, solvation influences reactivity in the liquid phase. How a solvent arranges itself around the reactants, and how this alters the intramolecular forces³. What degree of inhomogeneity exists in the arrangement of the solvent, and what the timescale is for the structural variations of the solvent shell⁴. Which modes of motion in the solvent couple to the reaction coordinate, and how efficiently energy is dissipated from the reactants into the liquid surroundings, or the other way around⁵. To understand and be able to quantitatively reproduce the series of events which lead from the activated reactant, to thermalized products, or in the case of solvent caging, back to the relaxed reactants. In such a case we wish to quantitatively rationalize the microscopic mechanisms which determine the degree of such caging.

While these objectives are similar in nature to those of chemical dynamics in isolated molecules, methodology in the liquid phase differs markedly in one major respect. Due to the irreversible nature of the solvent induced relaxation processes which very rapidly dissipate the chemistry related motions of the reactants and products, one cannot infer the course of a chemical reaction by prob-

ing the products after the fact. Sorting out the chronology of liquid phase photo-induced reactions, and deciphering the mechanisms of solvation in each stage of molecular evolution, requires following the reacting system as chemical change is under way. In principle, this is a daunting proposition, since in many cases photoinduced chemical rearrangement may be nearly complete in no more than 50-100 fsec⁶.

In practice, the application of femtosecond laser spectroscopy, enables us to come close to realizing this. The wide spectrum and short duration of femtosecond pulses ensures simultaneous coherent population of numerous excited state vibronic levels. Disregarding broadening effects due to finite pulse durations, such 'Impulsive' photoexcitation can initiate phase coherent photochemistry in molecular ensembles, starting with uniform initial conditions defined by the equilibrium ground state configuration of the reactant, and evolving concertedly in time under the hamiltonian of the upper state. Finally, by spectroscopically probing this ensemble with a delayed ultrashort laser pulse (Pump-Probe), the evolution of induced chemical change is recorded⁷. This evolution can in certain cases give rise to nonstationary coherent superpositions of vibrations in photochemical products. If the excitation pulse is also impulsive with respect to ground state vibrations, through stimulated Raman interaction coherence can even be instilled in the ground vibronic manifold.

In the following we present a summary of recent femtosecond photochemical work on two molecular systems. Most of the following deals with photolysis of the triiodide ion in polar solvents. In a recently published paper a comprehensive study of this system was reported in which virtually all of the envisioned coherences were recorded⁸. Through a comparative solvent dependence study, and computer simulations, along with a report of preliminary results concerning a new solvated species, $(\text{Cr}(\text{C}_6\text{H}_6)(\text{CO})_3)$ we will demonstrate the vitality of these newly available dynamic variables in providing unprecedented insight into the dynamics of liquid phase chemical change.

Experimental

The laser system has been described in detail elsewhere⁸. Briefly, an anti-resonant ring synch-pumped dye laser constructed in lab is pumped by a mode locked Nd:YLF laser. The output is further amplified at a repetition rate of 1 kHz, using the frequency doubled output of a Nd:YLF regenerative cavity to pump a dye amplifier. The ultimate output consists of 55-65 fsec pulses, centered at 616 nm, containing 20-30 mJ of energy. One portion of this output is frequency doubled to produce an excitation pulse in the UV, and initiates the photolysis of triiodide ions in the solution. Probing pulses are either derived again by doubling the fundamental in order to produce a UV probe, or by generating a white continuum from which a single frequency band probe is isolated by interference filtering. This portion is continuously delayed to produce the experimental scans. A reference and probe are derived by beam splitting, and

the latter is focused onto the sample together with the excite and push pulses. The transmitted probe is spectrally filtered and detected by photodiode. Data collection was carried out by introducing a chopper wheel into the excitation beams, and differentially detecting the signal using a lock-in amplifier (SR 530). All experiments were conducted in a 200 micron flow cell, equipped with ultra-thin quartz windows, using a sample concentration of a few millimolar. Specific details concerning experimental arrangements will be reported in the relevant part of the text.

Triiodide Photodissociation

Background, and Summary of Previous Results

Triiodide is a linear negative ion, stable in many polar solvents⁸. It absorbs in two intense and broad bands centered at 295 and 350 nm, dissociating with a solvent dependent quantum yield into diiodide ions, and atomic iodine. Anywhere from 1.5, to 2.5 eV of excess photon energy is available to the fragments, depending whether the iodine atom is electronically excited or in its ground state. The diiodide also absorbs with medium intensity in two broad bands centered at 360 and 740 nm at room temperature, depending slightly on the solvent. While the former overlaps with I_3^- absorption, the later is spectrally isolated allowing selective probing of the product population. All transitions in the parent and daughter ions are parallel. Further spectrochemical data are provided in previous publications.

This system was chosen as a model triatomic photolysis reaction, since it is strongly perturbed by the solvent, and the intramolecular vibrations in both reactant and product ions are time resolvable with the described laser system. In order to record the course of this reaction in ethanol solution, two types of transient transmission scans following UV photolysis of I_3^- were undertaken. In the first, probing was conducted in the visible and near IR in order to follow the evolution in the nascent I_2^- fragments. Throughout this spectral region an instantaneous rise and rapid partial decrease of absorption within ~ 250 fsec was observed. The former was associated with absorption of I_3^- in the reactive excited state, the later with the stage of bond cleavage. Following these features a leveling off of the absorption was discerned, upon which 95 cm^{-1} oscillations decaying with a time constant of ~ 400 fsec were superimposed. Observation of a 1π phase shift in these oscillations upon varying the probe frequency from the 'blue' to the 'red' of the I_2^- band center supported our assignment of these modulations to coherent vibrations of the nascent fragment ions. Finally a subsequent gradual narrowing of the transient spectrum around the band center on a timescale of ~ 4 psec was interpreted to be the signature of vibrational product relaxation. Photoselective probing also provided a timescale of ~ 5 psec for reorientation of the newly formed I_2^- .

Two main findings resulted from transient probing in the UV. The instantana-

neous photoinduced bleach in I_3^- absorption undergoes partial replenishment in two phases. The first very rapid one takes place within 5 picoseconds. It has been assigned tentatively with primary geminate recombination, and the duration of this component is suspected to be determined by vibrational relaxation. The second phase which takes place on a 70 psec timescale is accordingly assigned as secondary geminate recombination. However at very short probe delays the bleach signal is superimposed with 111 cm^{-1} oscillations, precisely the frequency of the symmetric stretch vibration in I_3^- , starting immediately at $t=0$, and decaying with a time constant of $\sim 1.5\text{ psec}$. These modulations are the spectral signature of vibrational coherence in the ground state of the parent ion, excited through Resonance Impulsive Stimulated Raman Scattering (RISRS)⁹.

Results in Various Solvents

In order to appreciate the role played by the solvent in triiodide photochemical dynamics, similar transient transmission experiments were performed using water and a series of alcohols as solvents.

Transient transmission scans at 600 and 860 nm for short probe delays in a water solution of triiodide are depicted in Fig. 1. At first glance they look very similar to the results in ethanol, including the clear antiphased spectral modulations appearing after the initial fall off in absorption. However a comparison of transmission scans at a probing frequency near 600 nm in water, ethanol and

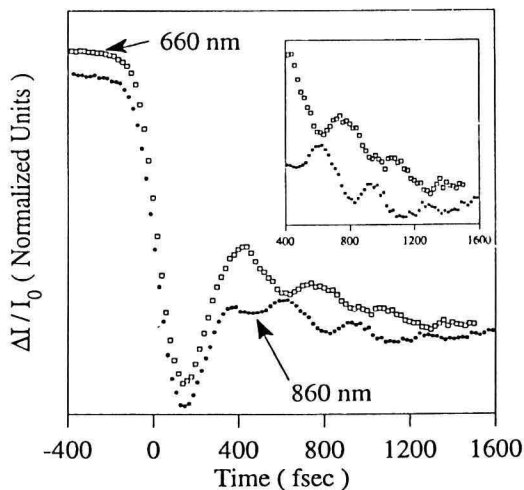


Fig. 1. Transient transmission data at early delay times for water solution at two wavelengths 600 and 880 nm. The inset depicts a portion of the data on an expanded scale.

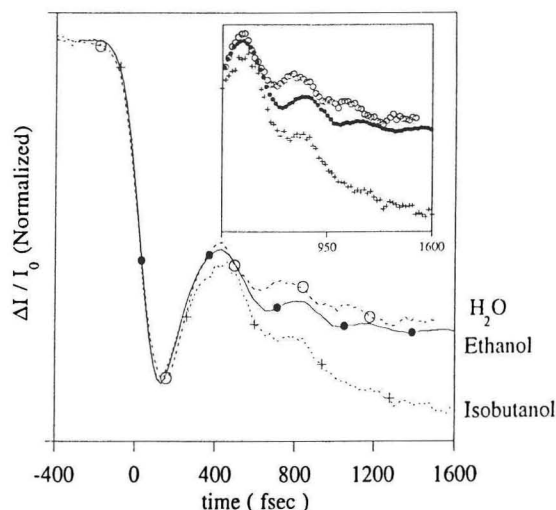


Fig. 2. Transient transmission data at short delays near 600 nm, for triiodide solutions in water, ethanol and isobutanol.

iso-butanol show substantial systematic difference, as shown in Fig. 2. The instantaneous rise and subsequent rapid fall in absorption are remarkably alike in all three solvents. In water the ensuing oscillations appear earlier and are most pronounced, are highest in frequency, and relax most slowly. In the heavier alcohol modulations appear later, and relax so rapidly that they are reduced to a single lobe. In this respect ethanol is intermediate between the two.

Marked solvent dependence is observed in the UV transients as well. In contrast to the observations in the visible, water solvent is almost twice as efficient as ethanol in dephasing RISRS induced coherence in the symmetric stretch of I_3^- as depicted in Fig. 3. Furthermore, the prominence of the primary and secondary phases of recombination are strongly solvent dependent as can be seen in Fig. 4. In solutions of heavier alcohols the rapid phase of bleach recovery is more substantial. In terms of caging, water is pathological, and behaves similarly to the heavy alcohols, exhibiting a prominent rapid phase of absorption recovery, which is extremely short in duration. This finding is in line with recent results of geminate recombination following I_2^- photodissociation¹⁰.

The strong dependence of our observations upon the solvent provides enticing riddles concerning the dynamics of this reaction. Would we not expect a light and strongly interacting solvent such as water to be most efficient in dephasing vibronic coherences, regardless if they are made up of highly excited levels in nascent diiodide ions, or near the bottom of the I_3^- potential well? If so, is it possible that the solvent molecules can interfere so effectively as to mold vastly different vibrational distributions of the emerging I_2^- ? It is reasonable that the spectral signature of bond fission is so similar in the studied solvents, and is the

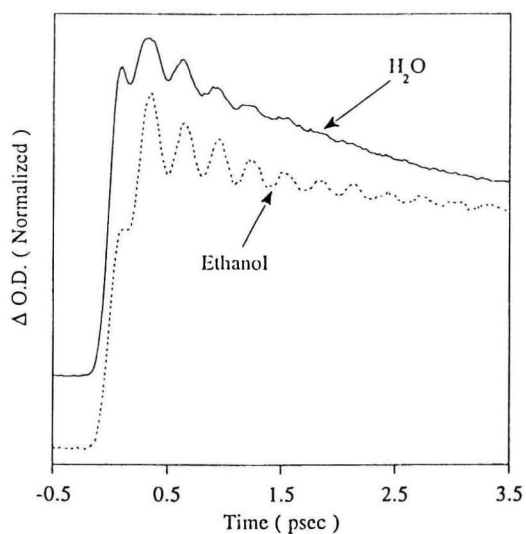


Fig. 3. Short delay transient transmission probing at 308 nm for water and ethanol solutions.

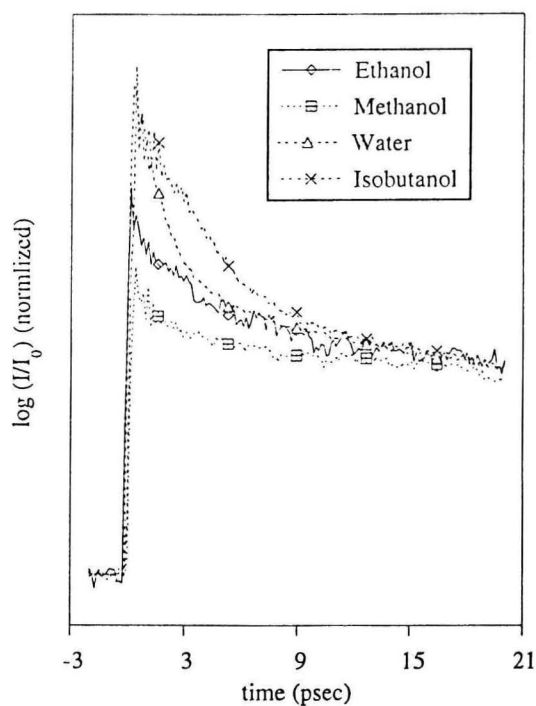


Fig. 4. Transient transmission data in the UV at long delays for triiodide solutions in a series of alcohols and in water.

timescale of ~ 200 -250 fsec for the appearance of separated fragments a realistic time span? In order to begin sorting out these and other fundamental questions concerning the case study at hand, computer simulations were conducted, and are described in the next section.

Computer Simulations

In lieu of a reliable model for the excited reactive multidimensional potential surface of I_3^- , a simple LEPS type surface was parametrized to at once fit the basic thermochemistry, and the known absorption spectrum of triiodide¹¹. This surface reduces asymptotically to a Morse potential assigned to I_2^- , and is based on the working hypothesis that absorption into the upper band in triiodide leads predominantly to iodine atoms in their spin excited state. The parameters of the reactive surface are given in Table 1. Using this model for the upper state involved in photolysis, two different simulation schemes were run.

The first involved quantum simulations of isolated ion photodissociation performed using fourier wave packet propagation methods in a collinear two dimensional calculation¹². The calculations are initiated by instantaneous promotion of the zeroth vibrational level of ground state triiodide onto the LEPS surface. The harmonic ground surface potential leads to a gaussian ground state wavefunction. Fig. 5 shows snapshots of the wavefunction at different times after the initial packet was placed on the excited surface. The initial motion is along the symmetric stretch. The striking feature is a large dispersion along the antisymmetric stretch exhibited by the wavefunction which is approximately 2 angstroms after 200 fsec. This dispersion eventually leads the wavefunction into the asymptotic channels with negligible amplitude into the three-body dissociation channel, although this channel is energetically allowed. Even before a detailed evaluation of these results begins, our conclusions concerning the assignment of the first ~ 300 fsec to the initial act of bond fission gains support. We see that the first 12,000 A.T.U. (300 fsec) go by before substantial 'filling' of the asymptotic exit channels begins.

In order to make sense of this complex wavefunction we have reduced the wavepacket in one dimension, and produced a histogram of $P(R)$, the probabil-

Table 1. Parameters for the I_3^- Potential Surfaces

ground state potential for I_3^- ;		
$r_{(\text{I-I})}^{\text{eq}} = 2.97 \text{ \AA}$	$\omega_{\text{sym.}} = 110 \text{ cm}^{-1}$	$\omega_{\text{asym.}} = 149 \text{ cm}^{-1}$
excited state potential for I_3^- ; (LEPS potential)		
$^1r^{\text{eq}} = 3.23 \text{ \AA}$	$^3r^{\text{eq}} = 2.983 \text{ \AA}$	
$^1\beta = 1.16 \text{ \AA}^{-1}$	$^3\beta = 1.00 \text{ \AA}^{-1}$	
$^1D = 1.1 \text{ eV}$	$^3D = 1.009 \text{ eV}$	

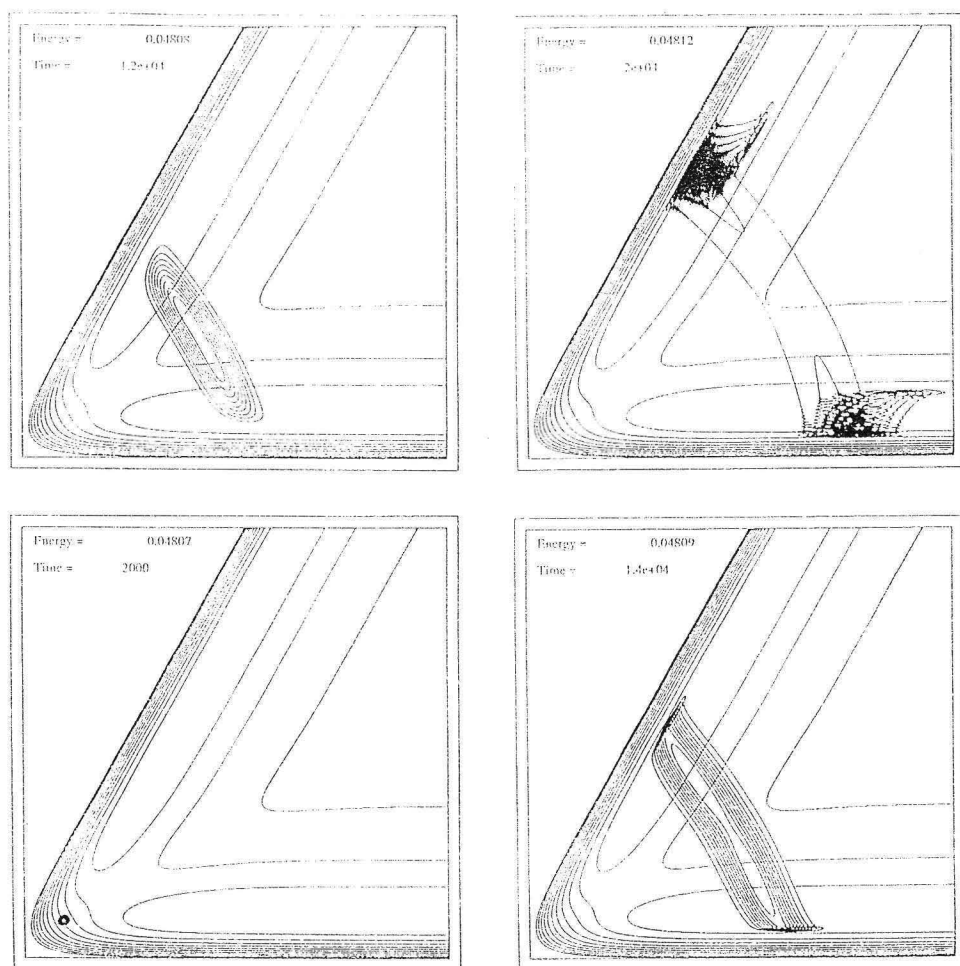


Fig. 5. A series of snapshots of the evolving wavepacket following instantaneous photoexcitation at $t=0$. The wave function is depicted as contours connecting points where $|\psi^2|$ has equal values. Along with the wavefunction we have also depicted equipotential contours of the reactive LEPS potential.

ity for fragment diiodide ions to be distanced by internuclear radius R , at various delay times. This series of histograms is shown in Fig. 6. We see that in spite of the fact that 'late comers,' or those portions of the wavefunction that enter the dissociation channel after $t=16,000$ are still entering the channel throughout the delays studied, the influx is steadily reduced. The portion of dissociating systems which entered directly at early times has already experienced an intramolecular 'collision,' and re-extended to the large radius turning point of the motion.

In order to evaluate the distribution of vibrational energies in the fragment

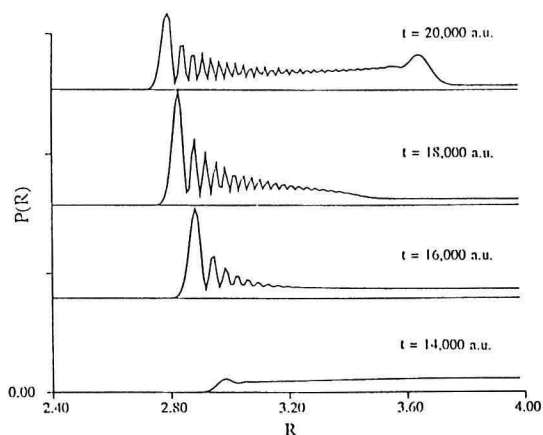


Fig. 6. An overlay of histograms depicting the probability of nascent diiodide fragments to be at a certain internuclear distance.

ions within the exit channel, the portion of the wavepacket described in Fig. 6 was resolved into eigenstates at two delays - at 14,000 and 20,000 A.T.U. These distributions are depicted in Fig. 7. We see that the population of fragment ions produced directly at early times produces a very wide distribution maximized at rather high quanta of $\sim v = 40$. The 'late comers' make a completely different contribution to the distribution which is very localized in vibronic eigenspace, with an acute maximum above $v = 42$. In either case the average portion of excess energy directed into vibration agrees very well with the prediction of 25% derived from kinematic considerations alone.

As stated above, the quantum simulations chart the course of dissociation for an isolated parent ion. While the results serve as an important reference, in order to deepen our understanding of the effects of solvation, a realistic solvent must be included in the simulation. For this purpose classical MD simulations

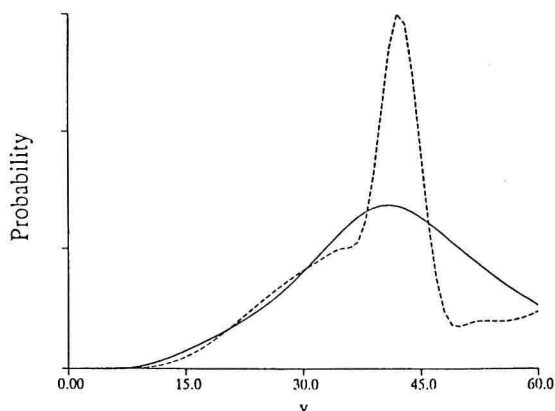


Fig. 7. A resolution into eigenstates of the portion of the wavefunction which has reached the exit channel at two delay times, 14,000 (solid line) and 20,000 (dashed line) A.T.U.

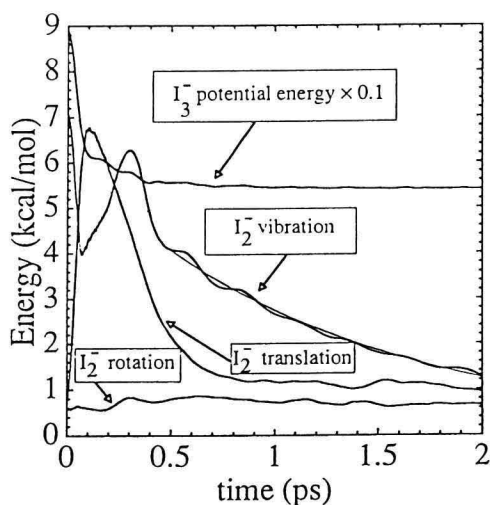


Fig. 8. The average time dependent energies of I_2^- products following photodissociation of triiodide in ethanol.

were conducted using the identical potential immersed in a model ethanol consisting of 216 solvent molecules¹³. Methyl and methylene groups were modeled as a united atom, and further details of the interparticular interactions are provided in our full report. Following instantaneous switching to the excited potential, trajectories were simulated for multiple initial configurations. The charges on the reacting ion are distributed according to a continuous charge switching function, which determines by the degree of asymmetry, which terminal iodine

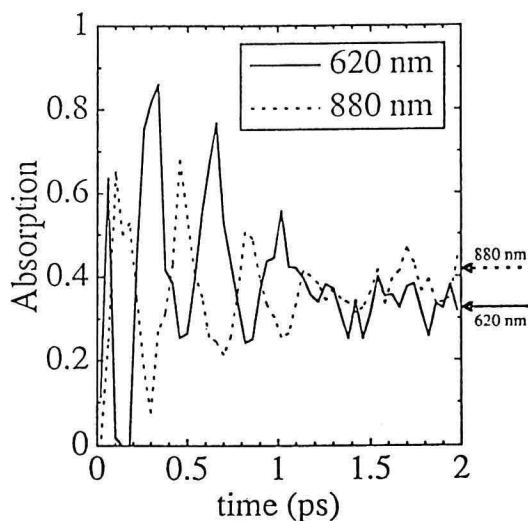


Fig. 9. MD simulated spectral intensities of I_2^- at 620 and 880 nm as a function of time.

atom is on its way to participating in an I_2^- bond. No curve crossing to the ground state, and therefore no caging effects are included at this stage.

The results of the MD calculations are depicted in Fig. 8. Very rapid solvent induced quenching of the translational and vibrational degrees of freedom in the daughter ions is manifest, the former within 250 fsec, the later on a picosecond timescale. At its peak, the distribution over the vibrational manifold reaches an average excess energy which is barely half that obtained in the isolated molecule quantum calculations. It is noteworthy that at this excess energy the vibrational frequency calculated from published vibronic constants for diiodide would be precisely that observed in the coherent oscillations following ethanol dissociation. Using a Franck Condon reflection procedure, the absorption intensity for transient probe pulses at 620 and 880 nm were calculated as a function of the delay time, and are presented in Fig. 9. The agreement with experiment is remarkable. Clear oscillations of opposed phase are observed, dephasing almost precisely on the same timescale as the experimental observable.

'TRISRS' Experiments

Before attempting integration of the above into a unified picture, we wish to relate one more experimental effort, in which impulsive Raman is for the first time employed as a transient vibrational spectroscopy in order to characterize the vibrational relaxation of nascent diiodide fragments in ethanol. Theoretical simulations of the RISRS process using wave packet propagation techniques indicate that in most situations, the coherent superposition in the ground state which is, for example, responsible for producing the spectral modulations observed in Fig. 3, involves coherent transfer of population to a limited number of levels surrounding those initially populated before the impulsive interaction with the laser pulse^{9a,14}. In view of this, as long as all the initially populated ground state levels can interact with the excitation pulse, the decay of the induced spectral modulations nearly mirrors the initial incoherent distribution of population in the ground state vibronic manifold.

Grossly speaking, through this spectroscopy one approximately records a free Raman induction decay of the vibrational distribution at the instant of the push excitation¹⁵. The duration of free induction decay defines the minimum time that a dynamic variable must be followed in order to reconstruct its power spectrum. Impulsive Raman spectroscopy is accordingly one of the most rapid methods for obtaining vibrational spectral information.

Above the overall narrowing of the product absorption band which follows the stage of coherence dephasing in the fragments, was assigned as the spectral signature of vibrational relaxation in the product ions. This stage is depicted in Fig. 10 at three probe frequencies. In order to obtain independent corroboration of this assignment, an additional method for directly probing the vibrational dynamics was deemed necessary. We have chosen to implement transient RISRS or TRISRS, with its characteristic high time resolution, in order to extract the

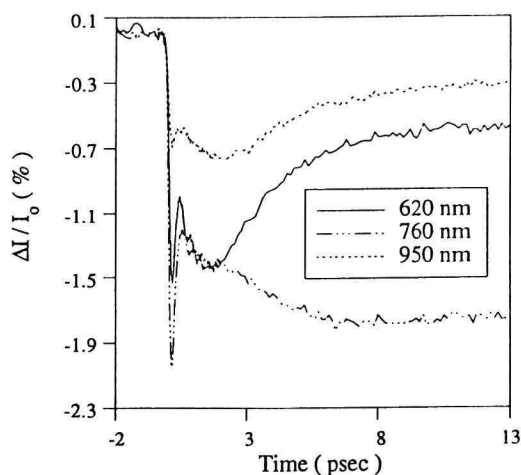


Fig. 10. Transient transmission data for triiodide in ethanol at three probe frequencies.

temporal evolution of the vibrational distribution. This involves a sequence of three ultrashort pulses. A primary photolyzing pulse in the UV initiates the triiodide dissociation. At a certain time after the photolysis which can be varied from one experiment to another, here forth denoted the push delay, a secondary intense 'push' pulse sets in motion ground state coherent vibration (in the nascent fragments!). The decay of the coherence is followed via periodic transmission modulations of a continuously delayed weak probing pulse.

TRISRS data were collected at three push delays, 2, 2.7 and 4 picoseconds after the excitation pulse. In order to clarify sequence of events, Fig. 11 depicts an overlay of two transient transmission scans probed at 840 nm, with and

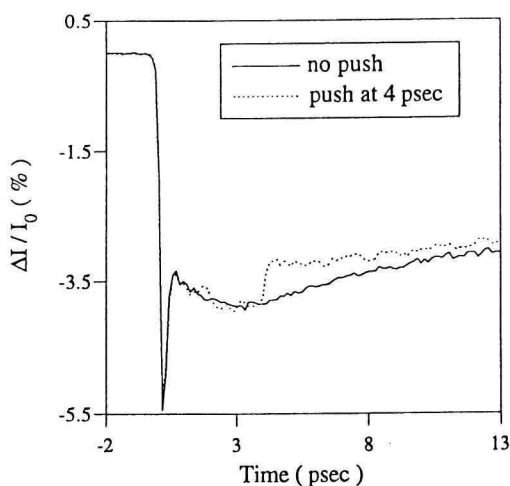


Fig. 11. Transient transmission data at 840 nm with and without the secondary TRISRS push interaction at a delay of 4 psec.

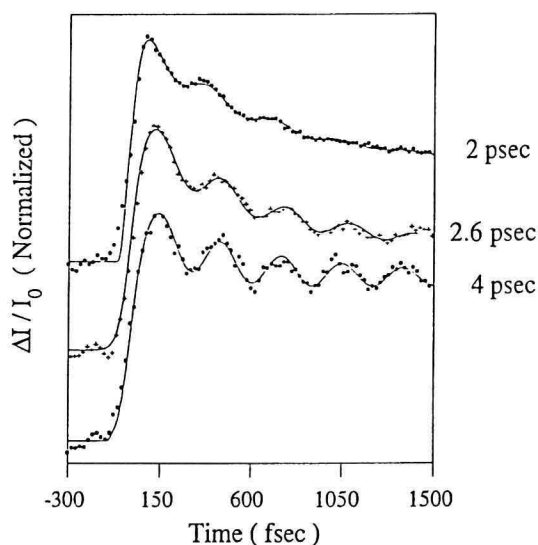


Fig. 12. TRISRS data recorded at three different push delays. Oscillations in transmission are fit to a convolved analytical response.

without the introduction of a push pulse. This second pulse introduces a substantial bleach which recovers to a certain degree but is not completely replenished at 13 picoseconds. The TRISRS bleaches at the three delays are shown in Fig. 12. The data for 2 picoseconds push delay involves probing at 680 nm, while results at later delays were obtained with an 840 nm probe pulse. The zero of time in Fig. 12 relates to the center of the pushing pulse in all three scans. At all these delays periodical oscillations of the transmission are observed. Figs generated by a nonlinear least squares method are depicted, after convolution with our instrument response, along with the data. The oscillatory feature was fit to the functional form $\sin(\omega t + \phi) \exp(e^{-t/\tau})$, and the best fit was afforded by parameters displayed in Table 2.

The first push delay immediately supersedes the decay of spectral oscillations due to bond fission, and the fragment distribution must be broad, involving highly excited vibrational levels. It may however have undergone substantial cooling since its inception about 200 fsec after the UV excitation. The mean vibrational quantum level of the coherent vibrations are experimentally and theoretically determined to be at $n \approx 20$ ^{13,8}. Using the documented vibrational

Table 2

PUSH DELAY (psec)	ω (cm ⁻¹)	τ (psec)	ϕ (radians)
2.0	102 +/ - 4	0.5 +/ - 0.2	0.2 +/ - 0.4
2.67	105 +/ - 3	0.9 +/ - 0.2	-1.2 +/ - 0.4
4.0	112 +/ - 2	1.2 +/ - 0.3	-2.0 +/ - 0.4

constants of I_2^{-16} , the coherence frequency of $102\text{--}103\text{ cm}^{-1}$ indicates that the earliest TRISRS induced superposition is made up of levels centered around $n \approx 13$. The ultrafast rate of coherence dephasing ($\sim 500\text{ fsec}$) at this push delay cannot be due to anharmonicity alone, and must involve substantial homogeneous contributions such as pure dephasing and population relaxation. Inhomogeneity of the solvent following the violent act of bond fission may also contribute to rapid vibrational dephasing.

As the push delay is increased, the population of fragment ions has relaxed further, leading to a reduction of both the first and second moments of the vibrational distribution. Accordingly, the frequency and the timescale of RISRS coherence dephasing should increase. The frequency will increase due to the larger level spacings closer to the bottom of the potential well. The dephasing is prolonged because of a reduction in the rate of pure dephasing at low v levels¹⁷, and a reduced contribution of anharmonicity which is proportional to $\omega_e \chi_e$ times the second moment of the distribution. These trends are in fact observed. Within 4 psec of push delay, the modulations have already reached the asymptotic vibrational frequency, within our experimental error. The accumulating evidence from this experiment, along with the previous transient transmission data, show clearly that the highly vibrationally excited population of diiodide ions does in fact lose most of its excess vibrational energy within a few picoseconds. This finding agrees with a growing body of work on vibrational relaxation of molecular ions in polar solvents^{18,10}.

Discussion

Solvation plays a major role in the reaction studied, as attested to both by simulations and experiments. In the simulation of isolated triiodide dissociation the excess vibrational energy deposited in the diiodide fragment is much higher than is expected by any of the criteria we have previously discussed, such as the frequency of the spontaneous coherence, or the breadth of the absorption spectrum in nascent diiodide. This is not surprising since we have not included the influence of the solvent. It is however tempting to speculate how the seemingly distinct two populations, the 'early and latecomers' should fare upon encounter with the solvation layer. The MD simulations demonstrate that by far the most rapidly dephased and dissipated motion in solution will be fragment translation¹⁹. The population which decides early on which pair of iodine nuclei will be diiodide, will from that point on vibrationally evolve relatively independently of the solvent. These early-comers will therefore behave similarly if not identically in gas phase and solution with respect to vibrational coherence.

The late comers in contrast continue to evolve along the symmetric stretch coordinate as if all intramolecular motion were translation. This should lead to an all and all crash of the system into the solvent shell, leading to extensive energy transfer and dephasing of this portion of the wavefunction, which in our isolated ion model forays deep into the region of three atom separation, before settling into a two body dissociation. For this reason we believe that upon solva-

tion any coherence in vibration must be due predominantly to the early formed diiodide ions, and the more delayed dissociation should produce relatively cold and dephased fragments.

The MD simulations definitively show that the solvent can absorb large amounts of excess energy from the reaction in very short times, and mold the coherent portion of the vibrational distribution into a sufficiently compact packet in order to reproduce the observed oscillations. A more polar and rapidly responding solvents will at once accept larger amounts of excess vibration during the early stages of bond fission, and stabilize the breaking of symmetry along this initial track, thereby assisting the decision of 'who will become the molecular fragment.' This may well explain why water leads to such high frequency and slowly dephasing fragment coherences, indicating a lower excess energy content and a narrower distribution of vibrational energies in the products. This notion is further supported by the TRISRS results which vividly demonstrate the profound dependence of the dephasing rate on the excess vibrational energy content.

That the very initial stages of photolysis may be relatively insensitive to solvation, and resemble that in the isolated species, is not surprising. The question is when the presence of the solvent will begin to have impact on the spectroscopy, one which will be answerable only when good images of the higher excited states triiodide to which absorption takes place at short delay times are available. Our simulations do, as stated, support our estimates for the appearance of free fragments.

Finally the issue of caging needs further consideration. Our simulations can not guide us on this issue. The importance of mass in the alcohol series in inducing direct recombination portrays a ballistic image of this process. However the case of water demonstrates that this need not always be the case, and that when sufficiently strong interactions between solvent molecules prevail, the strongly knit solvent shell can take a beating even though the individual solvent particles are lightweight. Only further solvent studies will determine if in fact water is singularly unique in this respect.

Preliminary results on $\text{Cr}(\text{C}_6\text{H}_6)(\text{CO})_3$

Up to this point our discussion has involved impulsively induced periodically evolving vibrational coherences in the photo reactant ground state, and in photochemical product states as well.

In the following case we believe that during the first few hundred femtoseconds following photoexcitation of $\text{Cr}(\text{C}_6\text{H}_6)(\text{CO})_3$ in ethylene glycol solution, oscillations due to vibrational coherence in a metastable reactive state are detected.

The primary photochemical event of this complex has been studied, and shown to consist exclusively of carbonyl loss followed mainly by ligand replacement or recombination²⁰. The strong band into which we pump at 308 nm, is

assigned as a metal to benzene charge transfer transition. We have conducted a series of transient transmission measurements in analogy with those reported for the triiodide system.

Throughout the visible and near infrared portion of the spectrum an instantaneous rise of absorption is observed, followed by an absorption decay to a nonzero value with a time constant of 1 psec. At very early times a faint oscillatory feature is observed. A representative scan probing at 740 nm is depicted in Fig. 13, along with a best fit. The fitting procedure indicates that the rapidly damped oscillation is best represented as a $160 \pm 15 \text{ cm}^{-1}$ vibration, decaying extremely rapidly, with a 120 fsec time constant. In order to test whether we are directly observing a photochemical product or, at least initially, the reactive excited state, simultaneously optical Kerr effect scans were run in a 150 micron thick quartz flat. The rise in absorption is displayed along with the relevant Kerr scan in Fig. 14. To within our experimental error, the zero of time or maximum in pump and probe overlap, is symmetrically situated with respect to the rise. Simulations show that only a dissociation process which induces an exponential rise in the spectrum, with $\tau \sim 10 \text{ fsec}$, would elude detection in our measurement.

Therefore we tentatively assign the observed absorption and oscillations to the initially excited state, and the 1 psec decay to the act of carbonyl loss. This interpretation is contrary to findings in earlier work on metal hexacarbonyls where the carbonyl ligand was found to dissociate directly²¹. If our assignment is correct, the process of bond fission may require electronic relaxation to low lying ligand field excited states eluded to in the literature²⁰. Determining the precise shift in equilibrium structure which gives rise to the observed oscillations will require more work. Bending motions of the benzene-metal-CO system fall

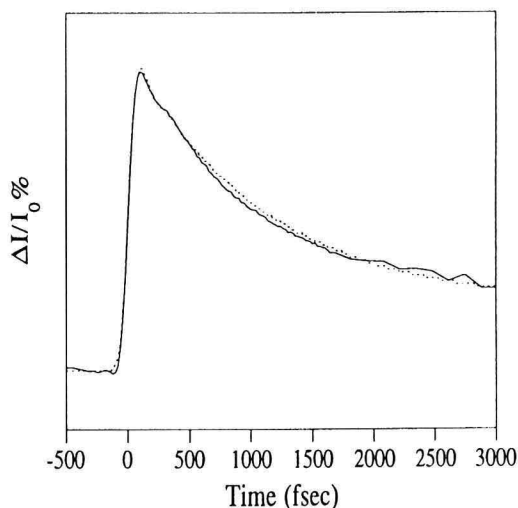


Fig. 13. Transient transmission data of $\text{Cr}(\text{C}_6\text{H}_6)(\text{CO})_3$ at 740 nm, along with best fit.

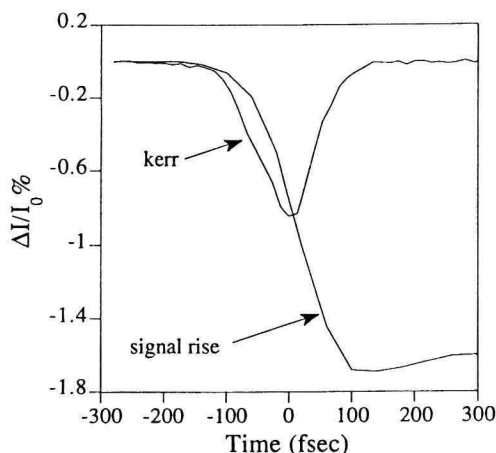


Fig. 14. Rise of the transmission data depicted in the previous figure, along with optical Kerr data.

within this frequency range in the ground state²². For this coordinate to be preferentially active would require a Jahn-Teller type symmetry breaking in the excited states. Work is ongoing to increase our appreciation of these points.

Conclusion

In this report we have described the application of impulsive photoexcitation on the femtosecond time scale in order to study detailed chemical dynamics of small molecular species in solution. We have demonstrated how monitoring of coherent nuclear motions so induced in ground, excited, and product electronic states, provides new insight into the microscopic mechanisms of solution photochemistry, and allows us to comprehensively characterize the course of photochemical evolution. In particular we have demonstrated the experimental feasibility of the TRISRS scheme, and applied it to measure the vibrational dynamics of rapidly relaxing diiodide ions.

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