

Geminate recombination of I_3^- in cooled liquid and glassy ethanol

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Abstract

Geminate recombination following impulsive ultraviolet photolysis of cryogenically cooled triiodide in ethanol is followed with 100 fs time resolution. Caged fragments either recombine directly and vibrationally relax within picoseconds or produce a long-lived complex which decays in tens of picoseconds back to the I_3^- ground state. Cooling steadily enhances direct recombination at the expense of cage escape, which is essentially hindered at the lowest temperatures studied. Persistence of the slower recombination process, even in solid solutions, suggests it is due to recombination on a bound excited state of I_3^- . The identity of this long-lived intermediate, and possible mechanisms of its formation, are discussed. © 1999 Elsevier Science B.V. All rights reserved.

Impulsive ultraviolet (UV) photolysis of triiodide ($I_3^- + h\nu \rightarrow I_2^- + I$) generates vibrationally excited and phase coherent diiodide fragments in polar solvents [1,2], and in the gas phase [3], as attested by spectral oscillations which are observed in the nascent I_2^- absorption. It also impulsively excites ground state vibrational coherence in the reactant ion, seen as periodic spectral modulations in the near UV absorption band of I_3^- [1–4]. Transient absorption data in the near-infrared (NIR) and UV at extended probing delays demonstrates that a substantial portion of the excited I_3^- recombines geminately in at least two phases [5]. The first, denoted ‘fast’, direct

cage reformation leads back to relaxed I_3^- within picoseconds. The second reformation process, denoted ‘medium’, takes place via a long-lived complex of unknown origin, decaying in ~ 40 ps in a series of room temperature polar solvents, including alcohols, acetonitrile, and water.

The pronounced solvent effects observed at all stages of this reaction make it an intriguing model for studying how a condensed medium can alter chemical reactivity. Further scrutiny shows, however, that a change of solvent may also induce specific structural changes in the reactant, which can strongly influence its dissociation dynamics. I_3^- spontaneously assumes a broken symmetry in ethanol [6a,6b], evidenced by Raman activity of the antisymmetric stretch fundamental. A similar effect is not observed in acetonitrile, indicating that I_3^- is centrosymmetric in this solvent on the effective timescale

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of the Raman experiment [7,8]. The dynamic effects of this symmetry breaking are readily observed in the nascent diiodide absorption [9].

Influences of the medium on the dynamics of I_3^- photolysis are studied here using a method that avoids convolution with specific solvation effects. These experiments also clarify the mechanisms underlying the distinct stages of geminate recombination. It involves impulsive photolysis of cryogenically cooled I_3^- in ethanol solution, from room temperature, down to a disordered solid below 150 K. This Letter deals solely with the issue of geminate recombination dynamics. I_3^- vibrational dephasing at reduced temperatures will be addressed elsewhere [10]. Current results demonstrate that cooling and solidification of the solution steadily enhance direct cage recombination at the expense of dissociation. The intermediate component of recombination maintains a steady amplitude, and replenishes the ground state more slowly as T is lowered. Its persistence, even in the disordered solid, suggests that it arises from recombination on a hitherto unknown bound excited state of I_3^- .

1. Experimental

The laser system and general methods of sample preparation have been discussed elsewhere [11]. Briefly, a synchronously pumped and amplified dye laser system provided a kHz train of ~ 65 fs pulses, centered at 615 nm, containing ~ 40 mJ of energy. Pump pulses were generated by frequency doubling in KDP. Probe pulses were either derived likewise for UV/UV experiments, or by white light generation and interference filtering for visible and NIR probes. Transmission was detected by amplified photodiodes (EG&G UV-4000) and measured with a lock-in amplifier.

2×10^{-4} M I_3^- solutions prepared from KI, containing a 10% excess of the iodide salt, were stoppered in a 2 mm pathlength quartz cuvette, and thermally contacted to a closed-cycle helium cold finger under vacuum. Replenishment of the irradiated sample was achieved via 2D translation of the whole cryostat using stepper motor actuation of a precision jack and a translation stage. The sample

was continuously translated, traversing a single pump beam diameter every 100 shots. To show that this rate sufficed to overcome local heating and any long-lived chemical instabilities, we verified that room temperature data obtained with rapid sample flowing was reproduced already at half this translation rate, probing both in the NIR and at 310 nm. At lower temperatures, a twofold reduction in the translation rate was demonstrated not to influence the data or to induce an increase in the transmission of the probe at negative pump-probe delay.

Sample integrity was monitored by absorption spectroscopy during the cooling cycle, and typical results are presented in Fig. 1. The absorption spectra exhibit two major peaks centered at $\sim 34\,040$ and $27\,600\text{ cm}^{-1}$, along with a less intense band at $23\,400\text{ cm}^{-1}$. The bands narrow and become more intense during cooling. The increase in absorption is due both to an increase in the formation constant with decrease in the temperature ($K_F = 10^4$ at 300 K), and to contraction of the solution. No buildup of additional bands to the red, or broadening of the existing bands, was observed, precluding substantial concentration of higher negative complexes. No evidence of phase separation, or strong fluctuations in solution concentrations was observed during experimental runs. The cooling rate was 4 K per minute,

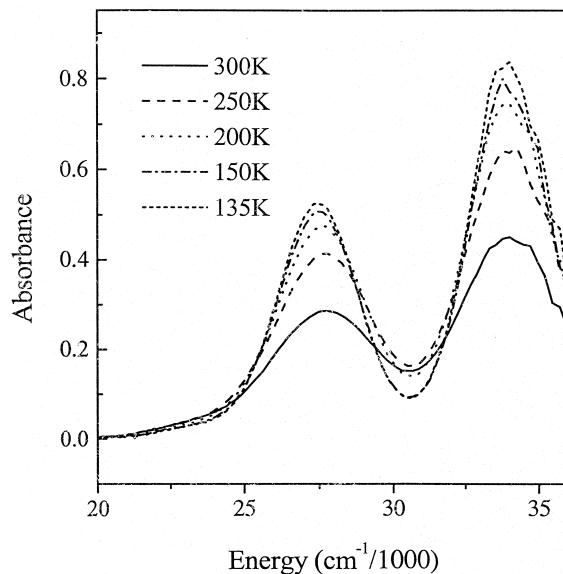


Fig. 1. Absorption spectra of I_3^- in ethanol at various temperatures, from 300 to 135 K.

and sample thawing and recooling was demonstrated not to influence results.

To test for influences of ion-pairing on the transient absorption data, samples were prepared with KI, and with $N(\text{CH}_3)_4\text{I}$. Results were found to be identical within error using both solutions. Pump-probe data were collected with solutions 3 times more concentrated, with no observable change in the time dependence of the signal. All reported data employed pump pulses of 50 nJ focussed to a spot diameter of $\sim 100 \mu\text{m}$, and the signal was verified to be linearly dependent on the pump pulse energy at this fluence.

2. Results

Magic angle UV-pump/UV-probe data at room temperature are depicted in Fig. 2. The bleach recovery is followed over a delay range of 400 ps, and the initial 8 ps of delay are expanded in the insert. The positive going signal relates negative changes in OD, indicating a net bleach in the triiodide absorption. The rapid component of decay which is complete in

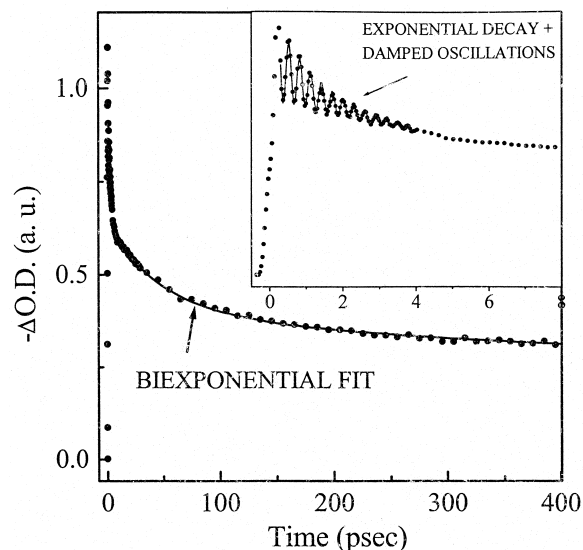


Fig. 2. Transient transmission scans of triiodide in ethanol solution with both UV pump and probe pulses. The inset depicts the first 8 ps of probe delays, exhibiting a rapid decay of the initial bleach superimposed by impulsive Raman-induced spectral modulations.

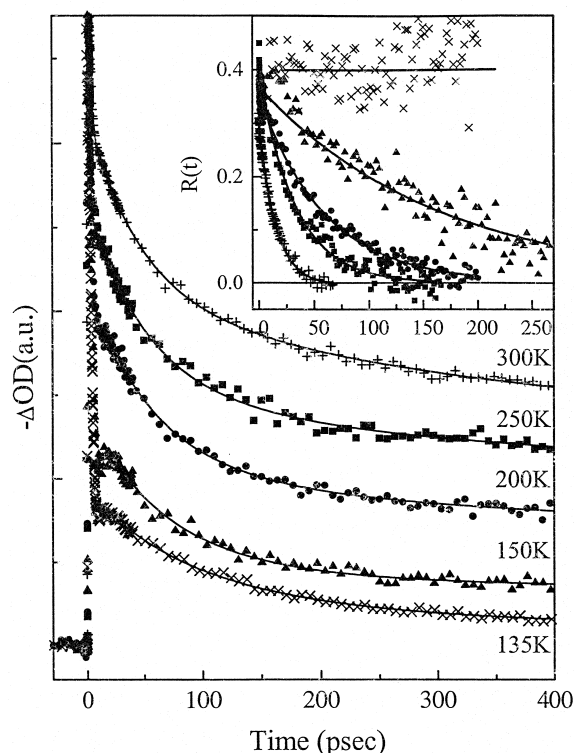


Fig. 3. Magic-angle transient transmission scans of I_3^- in cooled ethanol solutions, with both UV pump and probe pulses. Data at the various temperatures have been normalized to the same peak amplitude, and are presented along with least-squares fits according to Eq. (1). The inset presents the anisotropy of the same absorption signals at these temperatures, along with fits to an exponential decay model.

~ 6 ps, is superimposed with periodic oscillations which stem from impulsive resonant Raman excitation of the symmetric stretch in ground state I_3^- [4,12]. The decay of these modulations is a measure of vibrational dephasing, and is the focus of the sequel publication [10].

Following this 'fast' stage of UV bleach recovery, a slower decrease in transmittance commences, which takes place in two stages. The first completed in ~ 100 ps gives way to a very shallow decay component. The later portions of transmission decay beyond 10–15 ps are presented along with a fit to a biexponential functional form:

$$T(t) = A + B \exp(-t/\tau_1) + C \exp(-t/\tau_2) \quad (1)$$

In Fig. 3 normalized magic-angle UV/UV transmission scans are presented for a series of tempera-

Table 1

Time constants and amplitudes used to fit the UV/UV bleach decay, and its anisotropy $r(t)$ at various temperatures

Temp. (K)	Fast	B	C	A (escape probability)	τ_1 (ps)	$\tau_{\text{Anisotropy}}$ (ps)
300	0.36 ± 0.03	0.22 ± 0.04	0.16 ± 0.02	0.26 ± 0.01	45 ± 5	15 ± 1
250	0.46 ± 0.03	0.23 ± 0.04	0.10 ± 0.02	0.21 ± 0.01	51 ± 5	33 ± 1
200	0.56 ± 0.03	0.22 ± 0.04	0.08 ± 0.02	0.14 ± 0.01	56 ± 6	60 ± 1
150	0.72 ± 0.03	0.19 ± 0.03	0.03 ± 0.02	0.07 ± 0.01	69 ± 7	164 ± 4
135	0.81 ± 0.03	0.13 ± 0.03	0.04 ± 0.02	0.02 ± 0.02	90 ± 9	∞

tures from 300 to 135 K, along with fits using Eq. (1). The vertical scale is expanded to concentrate on later stages of bleach recovery. The data indicate that cooling leads steadily to an increase in the fast component, and in the overall absorption replenishment at 400 ps. In order to assess the rigidity of the solutions, anisotropy of the bleach was measured at

temperatures down to 135 K and is depicted in the insert to Fig. 3, along with a fit to a single exponential decay. The timescale of anisotropy decay increases monotonically with cooling, and at 135 K no change in $r(t)$ is detected throughout the first 0.4 ns. The parameters used for fitting the bleach decay and the anisotropy are summarized in Table 1.

The UV/UV experiments were complemented by transient absorption scans in the NIR. Due to the large discrepancies between pump and probe group velocities, the time resolution of these scans is reduced to ~ 0.5 ps in the 2 mm cell. They do, however, allow a viable comparison with the UV data for all but the fastest processes involved. Fig. 4 brings transient absorption scans at two NIR wavelengths at various temperatures, along with the UV bleach at the same temperature, where all three scans have been normalized to the same amplitude at the longest probe delay. They are depicted along with a fit using Eq. (1), with the same two time constants employed in fitting the data of Figs. 2 and 3.

3. Discussion

Two difficulties hamper extraction of recombination dynamics from the absorption measurements. (a) Replenishment of UV absorption requires not only repopulation of the ground state but also vibrational relaxation to take place. (b) Our interpretation invokes transient population of a long-lived intermediate, perhaps a bound excited state of triiodide, for which we have no prior knowledge concerning its UV absorption. The former is a trivial limitation, since we have strong evidence that I_2^- and I_3^- vibrations thermalize very rapidly in polar liquids [1,2,6a,6b,13–16]. The second is less easily resolved.

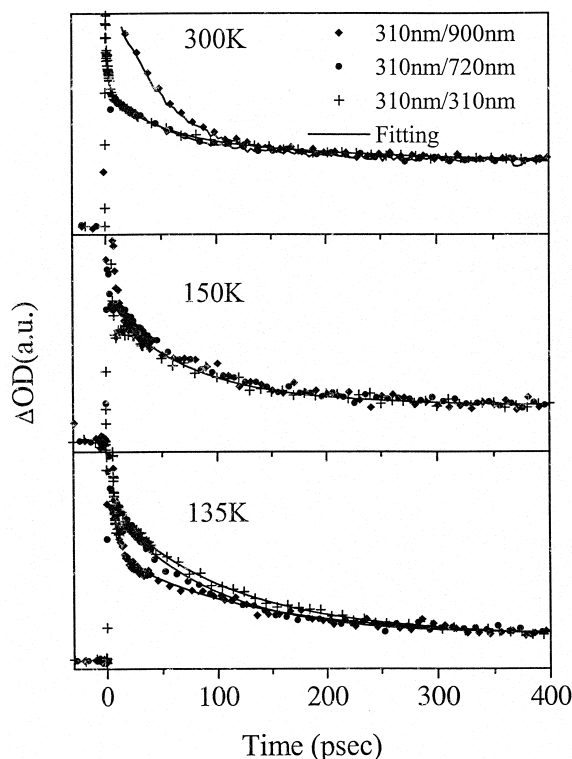
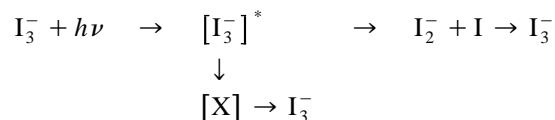


Fig. 4. Transient absorption scans at 720 and 900 nm, plotted along with transient 310 nm transmission, following 310 nm excitation of samples cooled to 300, 150 and 135 K. The signals are depicted along with least-squares fits using Eq. (1), and are normalized to a common asymptotic amplitude at 400 ps.

Qualitative trends observed in the UV and NIR scans agree with a simple scheme of reversible dissociation. Following the initial stage of photolysis and relaxation, the UV bleach and NIR absorptions decay monotonically, in similar phases. However, quantitative examination of the data shows that such a simple scheme cannot apply. I_3^- does not absorb in the visible or NIR, and I_2^- absorbs negligibly at 310 nm. Accordingly, simple reversible dissociation would produce identical kinetics for the UV bleach, and the NIR absorption decays, for delays much longer than the process of vibrational relaxation. The results in Fig. 4 serve to dispell this scheme, requiring at least one additional NIR absorbing species generated in the reaction.

The scheme we adopt was previously promoted for analysis of the room temperature data [5];



Accordingly, upon photolysis, most of the geminate recombination takes place very rapidly, most likely still within the confines of the original solvent shell. Due to the solvent caging, the excited triiodide crosses to its ground state or forms the long-lived intermediate denoted X. We cannot rule out that the X state is directly populated radiatively by the photolyzing photon. Population crossing directly to the ground state gives rise to the fast component of the absorption replenishment, with kinetics controlled by the process of vibrational relaxation [5].

The ‘medium’ replenishment component is due to an exponential reverting of the X species to the ground state of I_3^- , and gives way to a shallow residual recombination component, probably due to diffusive reformation of the triiodide from separated fragments. Since the X species absorbs in the NIR with a spectrum that is red shifted with respect to that of I_2^- above 200 K, both NIR scans, and UV bleach decays are well fit employing the *same two decay constants*, but with different amplitudes.

Making use of the UV bleach as a quantitative measure of recombination dynamics is based upon the following considerations [5]. (1) The residual absorption spectrum after the X decay, matches that of I_2^- [14,16–18]. (2) The ratio of the residual bleach

at 400 ps, to its initial value, matches the value of the quantum efficiencies for diiodide production in ethanol and acetonitrile solutions at 300 K, measured with nanosecond flash photolysis [19]. (3) The mismatch in decay kinetics between the UV bleach and NIR absorption is present only until the medium phase of recombination is complete. (4) A UV absorption of X *larger* than that of the parent ion would result in an increase of the UV bleach during the ‘medium’ phase of NIR absorption decay, contrary to observation. Even a mild UV absorption of this unidentified species at 310 nm would cause a measurable mismatch in the bleach ratio related in point (2) above.

Accordingly, the increased rigidity of the solvent shell upon cooling, which is verified by the reorientation dynamics, leads to a continuous increase of the fast component of reactant reformation, mainly at the expense of the ultimate escape probability. This trend is clearly shown by the fitting parameters summarized in Table 1. Furthermore, the cooling causes a gradual increase in the time required for the long-lived intermediate species X to relax to the I_3^- ground state. As a result, at the lower temperatures, the separation between the ‘medium’ component of bleach recovery, and the residual slow decay, is not well resolved.

Along with a reduced rate of X decay at low temperatures, the transition from fast to medium phases of bleach recovery assumes the appearance of a shoulder. This is attributed to vibrational population relaxation of the recombinant triiodide, and can best be understood in light of the absorption spectra shown in Fig. 1. At room temperature the absorbance at 310 nm is more than 70% of its peak value. Cooling to 135 K reduces this ratio to 0.5. At all temperatures, a large excess of vibrational energy reduces the 310 nm absorbance of triiodide. At the lower temperatures, along the route of thermalization, intermediate vibrational distributions actually absorb *more* than the thermalized I_3^- . This trend is observed even at room temperature when both pump and probe are at 400 nm [20].

To validate this interpretation, a one-dimensional Master equation model of I_3^- was constructed, including only the symmetric stretching mode [21]. Using a stochastic integration method [22], with initial population all in $v = 50$, vibrational relaxation

converging to thermal populations at various temperatures was simulated. The intermediate vibrational distributions served to reconstruct the changes in 310 nm absorbance and are presented in Fig. 5 for $T = 300, 150$ and 80 K. The absorption kinetics are plotted against a reduced time variable in units of $T_{1\text{vib}}$. Transition with cooling from a monotonic rise in absorption, to one which rises, peaks, and then recedes, is clearly demonstrated. Also, as shown in the insert, kinetics of the final changes in OD closely match the decay of vibrational energy, and prove to be a reliable measure of $T_{1\text{vib}}$.

While cooling obviously increases the rigidity of the solvent shell, the precise structure of the solvent in the viscous liquid and solid states is unknown. The cooling rate required for the formation of a glass in pure ethanol is much faster than that possible in our system. Also, plastic crystalline phases of pure ethanol are known [23]. Despite this we observe no changes in the sample near the solidification temperature, suggesting that the presence of the salt induces transformation to a homogeneous glassy solid. The only characteristic of our data which exhibits an abrupt change with the onset of solidification is a substantial blue shift of the X component of absorption, as demonstrated in Fig. 4.

Full understanding of the mechanism of geminate recombination requires an accurate model for triiodide electronic structure, which is not currently available¹. However, our results indicate that no substantial geometric reorganization is required for curve crossing from the excited state, to the lowest electronic surface. Had that been the case, a reduction in amplitude of the fast component, or an increase of its duration would take place upon freezing the sample, contrary to our observations.

As for the X species, the fact that its presence is not eliminated by freezing the solution indicates that it is most likely a bound excited state of I_3^- , as observed in recombination of I_2 [16], and I_2^- [25]. Accordingly, accessing this state must not require full dissociation of the reactant, and is either populated through nonadiabatic surface crossing near the Frank–Condon region, or by direct optical excitation

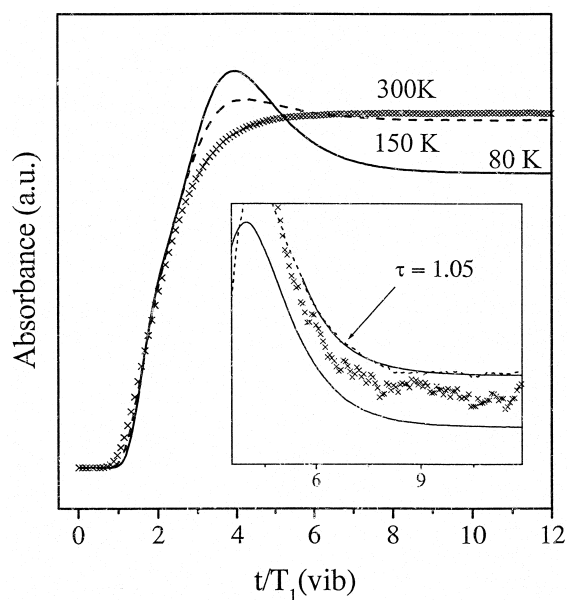


Fig. 5. Reconstructed transient 310 nm absorption of a one-dimensional model of I_3^- , during thermalization from $v = 50$ to 300, 150 and 80 K. Absorption is plotted against a reduced time unit of $T_{1\text{vib}}$. The inset depicts the final stages of variation in absorption intensity, normalized to the same sign, and depicted offset to demonstrate the similarity of these changes in units of T_1 .

at 310 nm. A recent photoelectron study of I_3^- in the gas phase has demonstrated that I_3 is a stable radical, with a symmetric stretch quantum of ~ 115 cm^{-1} [26]. Thus I_3 is also a possible candidate for the X species. However, the absence of a highly T -dependent continuous spectral *shifting* associated with solvation of an ejected electron makes this unlikely [27].

Assuming X is a bound I_3^- excited state, the intermediate recombination component reflects a delayed radiationless electronic relaxation, an interpretation which is compatible with the decrease in this rate upon cooling. Thus our earlier assertion that this rate is not temperature dependent must be due to examining too narrow a temperature range [5]. The mild temperature dependence of this process suggests a low barrier for the thermally activated relaxation of X.

Finally, the possibility that a bound excited state absorbing in the NIR is formed directly through photoexcitation of I_3^- , may require a revision of our previous analysis of the spectral modulations ob-

¹ Reliable electronic structure calculations are limited to the ground state (see, e.g., Ref. [24]).

served in the near IR, in terms of vibronic coherence in the I_2^- products alone. It may also explain a recent report of long decay components in the NIR absorption anisotropy, after following 400 nm photolysis of triiodide [28].

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