

Direct femtosecond measurements of single collision dominated geminate recombination times of small molecules in liquids

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We report the femtosecond transient absorption spectra of the CH_2I photoproduct of the methylene iodide (CH_2I_2) photodissociation. The results indicate a disappearance of this photofragment on a ≈ 350 fs time scale in several different solvents. The implication is that in these simple liquids, methylene iodide is undergoing geminate recombination. Recombination yields, but not rates are shown to be solvent dependent. Comparison to the photodissociation dynamics of other small molecules suggests that the kinetics of geminate recombination are dominated by a single collision with the surrounding solvent cage in a large class of molecules and that the process may be universal.

One of the unique aspects of liquid-phase chemical reactivity is the ability for reacting species to become trapped in a "cage" of solvent molecules. Compared to a gas-phase photodissociation reaction, this ability of the solvent to confine the photofragments leads to a reduction in the dissociation yield due to the back reaction of the photoproducts which are trapped in the solvent cage. The time scale of this process, known as geminate recombination, has been a central problem in liquid-phase reaction dynamics [1]. Secondary geminate recombination, the diffusive recombination of original partners that have left the solvent cage, has been well documented in many molecular systems [2,3]. This secondary geminate recombinative process takes place on a time scale of tens of picoseconds or greater, much longer than solvent caging times which last for less than a few picoseconds [1-3]. Indeed, of the many theories proposed to describe this process, most rely on some type of stochastic or diffusive motion for the recombining fragments [1-4]. Primary geminate recombination, the non-diffusive recombination of fragments still subject to solvent caging, however, has not been as well characterized.

The prototypical system for studying radical geminate recombination has been the photodissociation

of I_2 [1]. Since the 1934 suggestion of the possibility of geminate recombination in this system [5], many experimentalists have worked to measure the rate of this process. Early picosecond bleach experiments [6] indicated a ≈ 100 ps recombination time, suggesting that geminate recombination is diffusion controlled. Subsequent experiments [7], however, have indicated that recombination is essentially complete in ≤ 1 ps, and that longer ground state bleach recovery times were due to slow vibrational cooling of the newly recombined fragments. This result, the blue-shift of the transient absorption spectrum with vibrational cooling, is in agreement with molecular dynamics simulations [8,9]. The molecular dynamics simulations of the I_2 photodissociation in liquid Xe of Brown et al. [9,10] indicate that most of the geminate recombination occurs quickly after photoexcitation. The recoiling I atoms usually lost enough energy on their initial collisions with the solvent cage to recombine on a very short time scale. Those atoms that escaped the solvent cage could eventually undergo recombination with their original (geminate) or with other (non-geminate) partners, but on a much longer time scale; the rate of this secondary recombination becomes essentially controlled by diffusion. For those atoms that did di-

rectly recombine to form molecular iodine, vibrationally hot I_2 appeared just a few hundred femtoseconds after the photofragmentation [10].

These results suggest that for systems without strong Coulombic forces or orientational restrictions between the fragments, most of the geminate recombination is controlled non-stochastically. In one limit, this means that essentially a single collision of the photofragments with the solvent cage could dominate the recombination process, and that the role of subsequent diffusive recombination is secondary. This assumption of a single cage collision allows a crude estimate for the time scale of this primary, non-diffusive geminate recombination. Direct photodissociation of small molecules has been shown in the gas phase [11] to take place in 50–200 fs^{#1}. Resonance Raman data indicate that the early dissociative dynamics of small molecules which are similar to methylene iodide are essentially unchanged between the solution and the gas phases [12]. The time scale for a single collision with a solvent molecule in a typical room temperature liquid is about 100–150 fs. If the photofragments then need an additional 100–150 fs to collide and recombine on their ground electronic state, this gives an estimate for a total primary geminate recombination time of 250–500 fs; the dynamical features should be largely independent of the details of the photodissociating molecule and the solvent [13]. With the use of femtosecond spectroscopy, it should be possible to observe this process by monitoring the appearance of a photofragment ≈ 100 fs after photoexcitation, and the subsequent disappearance of the fragment 250–500 fs later due to this single-collision geminate recombinative process. To our knowledge, however, there has been no direct observation of the primary geminate recombination of neutral fragments produced after the photodissociation of a small polyatomic molecule.

In this Letter, we report the use of transient absorption spectroscopy to directly follow the production and disappearance of CH_2I radical fragments produced after the photodissociation of methylene iodide (CH_2I_2) with femtosecond time resolution.

^{#1} Assuming direct excitation to a dissociative state, the time scale for photofragmentation will vary depending on the slope of the repulsive potential, the partitioning of the excess energy among the various fragment degrees of freedom as well as the mass of the fragments.

The results provide the first direct observation of primary geminate recombination, and solvent-dependent experiments indicate that geminate recombination occurs on a similar time scale in a variety of liquid environments. By comparing the results to similar studies on different chemical systems, we speculate that the geminate recombination process has a "universal" behavior that transcends the specific details of the photodissociating species or the solvent involved in the reaction, and that it is associated with only the initial collisions of the photofragments with the surrounding solvent cage.

The experimental apparatus used to perform the femtosecond transient absorption measurements has been described previously [14]. Briefly, the output of a cavity-dumped colliding-pulse-mode-locked ring laser amplified by a copper-vapor laser was doubled and used to photodissociate CH_2I_2 at 310 nm, while the 620 nm laser fundamental was used to measure the population dynamics of the CH_2I photofragment. The instrument function, determined by cross-correlation of the UV and visible femtosecond pulses as the transient absorption rise of diphenylbutadiene, was fit to a 120 fs Gaussian. Data collection was performed in a dual-beam geometry, with signal and reference pulses normalized on every laser shot at the 8 kHz repetition rate of the laser. In the transient absorption traces presented below, there were typically 25000 laser shots averaged at each stage position (time delay).

Samples were 1–10 mM of CH_2I_2 in CCl_4 , $CHCl_3$ or CH_2Cl_2 . Both the sample molecule, obtained from Aldrich, and the spectral grade solvents, obtained from Burdick and Jackson were used as received. The samples were flowed in a jet through a 300 μm nozzle (Spectra-Physics). This prevented the formation of photoproducts on cell walls, and also ensured that a fresh sample was being probed every laser shot. UV-visible absorption spectroscopy indicated degradation of the samples after ≈ 1 h exposure to the femtosecond UV pump pulses (e.g., a visible absorption band appeared, indicating the formation of I_2 photoproduct from diffusive non-geminate recombination). Samples were replaced frequently; no changes in absorption dynamics were observed between fresh solutions and those that had been exposed to the laser for an hour.

CH_2I_2 has an absorption band which extends from

280–350 nm [15], with a cross section of $\approx 850 \text{ \AA} \text{ mol}^{-1} \text{ cm}^{-1}$ at the 310 nm wavelength of the excitation pulse. The photofragmentation of CH_2I_2 in the gas phase has been extensively studied [16–20]. Wavelength-dependent quantum yields for I/I^* product channels [16], resonance Raman spectra [17], photofragment angular distributions [18] and IR emission from the vibrationally hot CH_2I fragment [19] have been measured for this photoreaction. The photofragment angular distribution is highly anisotropic, indicating the dissociation is direct, and rapid with respect to the CH_2I_2 rotational period [18]. Resonance Raman data also indicate a rapid dissociation [17]; a wavepacket model of the resonance emission spectrum [20] has shown that dissociation must take place in $\leq 80 \text{ fs}$ to correctly explain the observed overtone intensities. All of the available data suggests that the dissociation of methylene iodide is *direct* and takes place on a sub-100 femtosecond time scale. Matrix isolation work [21] indicates that the vibrationally cool CH_2I radical fragment has an electronic absorption maximum centered near 620 nm, providing a convenient wavelength for monitoring the presence of the CH_2I species.

Transient absorption results for the photodissociation of CH_2I_2 in CCl_4 are shown in fig. 1a. The data were taken by exciting the sample with the 310 nm pump pulse, and monitoring the change in absorbance of the sample at 620 nm. The results are fit to a combination of simple exponentials convoluted with a 120 fs Gaussian representing the instrument function. The results fit nicely to a fast 350 fs exponential decay superimposed on a slower, 10 ps exponential rise. By extrapolating the slow rise back to $t=0$, the amplitude ratio of the exponential decay to the initial absorption rise is determined to be 0.38.

The data of fig. 1a can be interpreted in the following manner. The rapid absorption rise at 620 nm measures the presence of the CH_2I radical fragment, indicating that the *direct* dissociation is essentially complete within the 120 fs instrument response, in agreement^{#2} with the gas-phase photofragment angular distribution and resonance Raman data. The slow, 10 ps rise time can be assigned to vibrational relaxation; as the vibrationally hot CH_2I fragments cool, their electronic absorption spectra shift better into resonance with the 620 nm probe light^{#3}. This

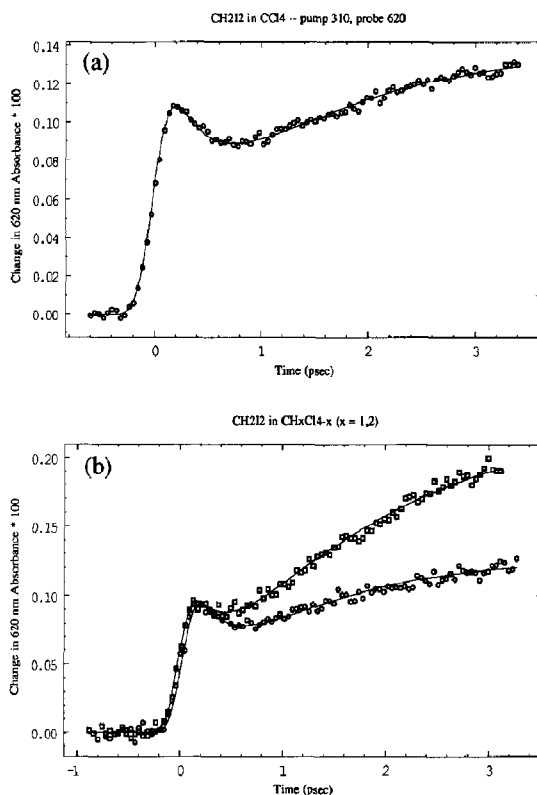


Fig. 1. 620 nm transient absorption spectra of CH_2I_2 excited at 310 nm in different solutions. Symbols are data points, solid lines are fits to the data consisting of an instrument limited rise with a fast exponential decay followed by a slower exponential rise. (a) For CCl_4 solutions, the amplitude ratio of the fast decay to the initial rise is 0.38. (b) For CHCl_3 (\square) and CH_2Cl_2 (\circ) solutions, the amplitude ratios of the fast decay to the initial rise are 0.33 and 0.24, respectively. These scans have been scaled to have the same absorbance after the initial rise for better comparison. The slow exponential rise times follow the trend $\text{CCl}_4 > \text{CHCl}_3 > \text{CH}_2\text{Cl}_2$.

^{#2} An alternative interpretation, in which the initial absorption rise is due to electronically excited CH_2I_2 which dissociates into $\text{CH}_2\text{I} + \text{I}$ in 350 fs, is not consistent with the resonance Raman and anisotropy data which indicate direct ($\leq 100 \text{ fs}$) dissociation of CH_2I_2 . This interpretation is also not consistent with the solvent dependence; it is unlikely that the pre-dissociation lifetime would remain constant in solvents of such widely differing polarity as CCl_4 and CH_2Cl_2 .

^{#3} As with many small molecules, vibrationally hot CH_2I absorbs to the red vibrationally cool CH_2I [22]. Since the cool species has its absorption maximum near 620 nm, the Franck-Condon overlap with the 620 nm probe pulse increases as the hot species cools and its absorption blue-shifts.

10 ps cooling time is typical for small molecules in room temperature molecular liquids [23]. The 350 fs decay after the initial absorption rise corresponds to a disappearance of the hot CH_2I radicals ^{#4}. Since the gas-phase photodissociation quantum yield is unity [16,18], the disappearance of CH_2I must be due to geminate recombination of CH_2I and I to reform the parent CH_2I_2 molecule. Comparison to the molecular dynamics simulations of the I_2 photodissociation reaction supports this assignment as observation of the primary geminate recombination [13] ^{#5}. (CH_2I absorption loss due to secondary geminate recombination, the diffusive recombination of fragments which have escaped the solvent cage, cannot be easily detected under the vibrational cooling absorption rise.)

If the primary geminate recombination interpretation holds for the CH_2I_2 dissociation, then it should be possible to vary the amount of recombination by changing the solvent cage without significantly altering the recombination rate. This idea was tested by studying the dissociation dynamics of CH_2I_2 in CHCl_3 and CH_2Cl_2 solutions, as shown in fig. 1b. If the molecules comprising the cage are lighter and more easily brushed aside by the recoiling I atom, then a lower recombination yield would be expected since there should be a higher percentage of I atoms escaping the cage. Those atoms that do recombine, however, should still do so on the same, single cage collision time scale of 350 fs. The results of fig. 1b support the idea of single-collision dominated primary geminate recombination. The amplitude of the 350 fs decay component is smaller in the lighter solvents, which implies that the recombination yield decreases as the solvent is hydrogenated from CCl_4 to CH_2Cl_2 . The recombination rate, however, remains at 350 fs in all the solvents, as expected for the single-collision dominated recombination mecha-

nism. In addition, the vibrational cooling times decrease as the solvent is varied from CCl_4 to CH_2Cl_2 , a trend also observed in the vibrational relaxation of I_2 [1].

It would be interesting to compare the relative recombination amplitudes of CH_2I_2 in the various solvents to dissociation quantum yields. Unfortunately, there have been no solution-phase quantum yield measurements for CH_2I_2 dissociation reported to our knowledge. Even with known quantum yields, direct comparison with the amplitudes of fig. 1 may be complicated by the fact that the dissociation quantum yields might also include some of the secondary, diffusive geminate recombination. Another test of this primary, non-stochastic geminate recombination idea would be to directly monitor the formation of the newly recombined parent molecule on this same 350 fs time scale. However, this is experimentally difficult. Ground state bleach experiments are complicated by the fact that the recombined molecules are vibrationally hot, and the bleach will not recover until after the subsequent vibrational cooling. It may be possible to detect the formation of the vibrationally hot recombined parent (which would likely occur in the near UV for CH_2I_2 , a difficult wavelength range to study with present femtosecond laser technology), as long as one of the photofragment species does not also absorb in the same wavelength range.

In lieu of these technical difficulties, the best way to test this idea is by example. Since the rate of collision dominated recombination should be very similar for all photodissociation reactions, the same type of results should be obtained for many different molecules. This makes it interesting to compare the dynamics of photodissociating methylene iodide (fig. 1) with those of photodissociating $\text{Cr}(\text{CO})_6$ [26]. (See especially fig. 2 of ref. [26].) The transient absorption traces for the two molecules are remarkably similar. Joly and Nelson [26], however, interpret their data for chromium hexacarbonyl as follows: the fast initial absorption rise is due to electronically excited $\text{Cr}(\text{CO})_6^*$; this absorption then decays in ≈ 350 fs as $[\text{Cr}(\text{CO})_6]^*$ dissociates into $\text{Cr}(\text{CO})_5 + \text{CO}$. The subsequent absorption increases/decreases (depending on probe wavelength) are assigned to solvation and vibrational relaxation of the $\text{Cr}(\text{CO})_5$ photofragment; geminate recombination is not con-

^{#4} Recent work by Banin et al. [24] has shown transient absorption oscillations due to vibrational coherence of the photofragments produced after photodissociation of I_2^+ . This explanation is not likely to apply to CH_2I_2 since a 350 fs recurrence would correspond to a vibrational frequency which is several times lower than the known vibrational modes of CH_2I .

^{#5} Direct comparison of CH_2I_2 photodissociation dynamics to those of I_2 is difficult since I_2 is predissociative with an excited state lifetime of ≥ 200 fs [25]. The simulations of refs. [9,10], however, used a directly dissociative model for the iodine photodissociation.

sidered. This alternative interpretation of predissociation does not seem likely to hold for the CH_2I_2 data of fig. 1 based on the resonance Raman [20] and gas-phase anisotropy [18] data which suggest that the *direct* dissociation of methylene iodide occurs in much less than 350 fs.

The data of Joly and Nelson, in fact, could be interpreted in a manner consistent with the observation of geminate recombination of $\text{Cr}(\text{CO})_5$ and CO. Many studies [27] #6 have indicated that the quantum yield for $\text{Cr}(\text{CO})_6$ dissociation in solution is ≈ 0.7 ; the ≈ 0.3 recombinative yield should have a marked presence on the femtosecond transient absorption spectra, and could explain the observed 350 fs absorption decay. In addition, the striking similarity of transient absorption traces of the $\text{M}(\text{CO})_6$ family ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$) suggests that either the curve crossing is very rapid, or that the dissociation is direct [28]; predissociation times are expected to be different for the different metal atom centers. The dissociation, if direct, should take place quite rapidly as the light CO fragment carries a significant portion of the kinetic energy and should quickly separate from its $\text{Cr}(\text{CO})_5$ partner. This makes the geminate recombination interpretation of the fast decay in the $\text{M}(\text{CO})_6$ data plausible; the dissociation could be rapid, leading to instrument limited rises, and all three species show identical decay times, as would be expected for single-collision primary geminate recombination.

Other photodissociation studies have also provided data which are consistent with this idea of fast primary geminate recombination. Femtosecond extensions of picosecond transient absorption studies on $\text{Mn}_2(\text{CO})_{10}$ in solutions [29], shown in fig. 2a, also show a fast 300 fs decay consistent with the interpretation of primary geminate recombination. Work on photochromic spiropyrans [30], in which the photoexcitation cleaves a ring system leaving the reactive fragments tethered together, shows a ≈ 200 fs absorption decay as seen in fig. 2b. Transient resonance Raman studies on similar spiro molecules have suggested that photodissociation of these species is direct [31], strongly supporting the interpretation of this ≈ 200 fs decay as primary geminate re-

#6 Note that the quantum yield is solvent dependent, but is ≈ 0.7 in alkane and simple alcohol solvents.

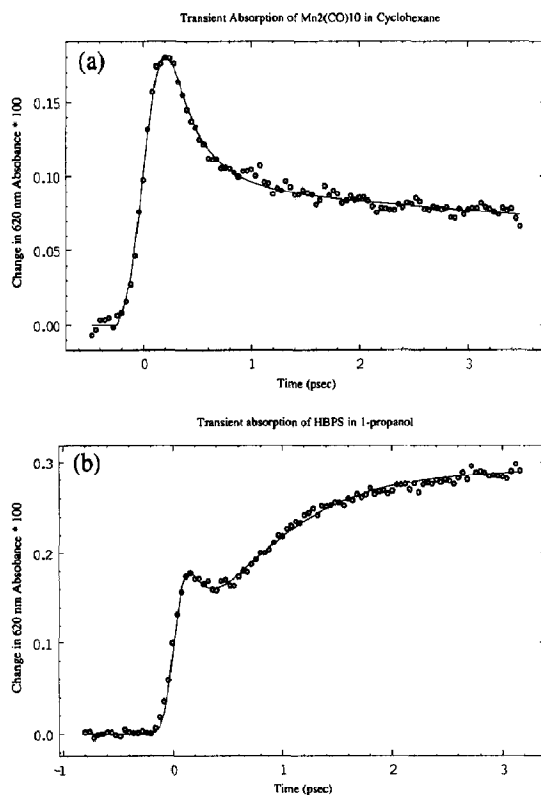


Fig. 2. 620 nm transient absorption spectra of different small molecules in solutions. Circles are data points, lines are simple exponential fits to the data. (a) $\text{Mn}_2(\text{CO})_{10}$ shows an instrument limited absorption rise followed by a 300 fs decay and a slower ≈ 10 ps decay which has been assigned to vibrational cooling (see ref. [28]). (b) The photochromic spiropyran molecule HBPS (ref. [29]) has an instrument limited absorption rise with a 225 fs decay followed by a ≈ 2 ps absorption rise due to vibrational cooling.

combination of the tethered fragment [29]. For this example, tethering by the ring system as well as solvent caging help to confine the reacting fragments (as suggested by Scott and Doubleday [2]), leading to the slightly higher primary geminate recombination rate. In all these systems, the decay of the photoproducts on a few hundred femtosecond time scale supports the picture of primary geminate recombination dominated by the initial collisions of the fragments with the surrounding solvent cage.

In summary, femtosecond transient absorption spectroscopy has been used to monitor the population of the photofragments produced after the photodissociation of CH_2I_2 . All the spectra show tran-

sient absorption traces which indicate the disappearance of the CH_2I photofragment on a 350 fs time scale. This result is consistent with the idea of two distinct components of geminate recombination. The primary, non-stochastic component is dominated by a single collision of the photofragments with the surrounding solvent cage, leading to recombination on the 300–500 fs time scale. This recombination rate depends primarily on the kinetic energy of the fragments and the density of the surrounding solvent molecules, and hence, is largely independent of the molecular details of the system under investigation. Those fragments that escape the solvent cage can then undergo secondary, or diffusive geminate recombination, but on much longer time scales. The similarity of the CH_2I_2 data to the results obtained on metal carbonyls and other chemical systems suggests that these dual kinetics may be a universal feature of geminate recombination of neutral fragments produced after the photodissociation of small molecules in normal, non-reactive room temperature molecular liquids.

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