Rapid Solvent-Induced Recombination and Slow Energy Relaxation in a Simple Chemical Reaction: Picosecond Studies of Iodine Photodissociation in CCl_4

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The time scale for solvent "caging" in the classic I_2 photodissociation reaction appears to be ≤ 15 ps, on the basis of examination of new picosecond absorption spectra. The previously observed slow recovery (> 100 ps) of molecular absorption is shown to be due to both ground-state vibrational relaxation and excited-state trapping in the recombined molecule. In addition, newly observed absorptions in the 350–400-nm region provide direct information on solvent-induced predissociation and excited-state vibrational relaxation.

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A central problem in liquid-phase chemical dynamics is determination of the time scale of reaction for species trapped together in a solvent "cage." The iodine photodissociation reaction has been the primary model system for studying cage recombination,[1] yet the cage recombination time for this system is still in controversy. Some experiments have indicated an ~100-ps recombination time,[2,3] in disagreement with other experiments,[4] and in contrast with theoretical predictions[5] of 1–10-ps recombination times. This Letter reports results which strongly suggest that cage recombination occurs in ≤ 15 ps. The results also demonstrate that both solvent-induced vibrational relaxation and excited electronic-state relaxation are important in the understanding of this reaction.

The basic processes in iodine photodissociation which are needed to explain these results can be outlined with reference to the potential-energy diagram (Fig. 1). The reaction is initiated by a transition from the ground (X) state to a vibrationally excited level of the bound B state. The solvent induces both vibrational relaxation within the B state, as well as crossing to several repulsive states (only one shown). After initial separation, the two atoms may escape through the solvent to dissociate permanently, or they may recombine on either the A, A', or X potential. Those recombining on the X potential must dissipate their excess vibrational energy to the solvent before they return to the initial state. Those recombining on the A or A' potentials must undergo a solvent-induced crossing to the X potential before they can vibrationally relax to the initial state.

Chuang, Hoffman, and Eisenthal[2] first probed the loss of absorption near the peak of the ground-state molecular absorption (530 nm) upon photodissociation. The bleach of the ground-state absorption showed a recovery time of ~140 ps in CCl_4, which was associated with atomic recombination. Nesbitt and Hynes,[6] however, presented a contrasting interpretation. The Franck-Condon principle predicts that the maximum absorption for a molecule in a given vibrational state will occur at an energy corresponding to a vertical transition from the classical turning points. For the $X \rightarrow B$ transition, this implies that the absorption from a vibrationally relaxing X-state population will initially be in the near ir and will move to shorter wavelengths as the population relaxes (Fig. 1). Thus, only recombining X-state molecules in the lowest vibrational levels should absorb at 530 nm. Nesbitt and Hynes,[6] followed by Bado *et al.*[4] and Brooks, Balk, and

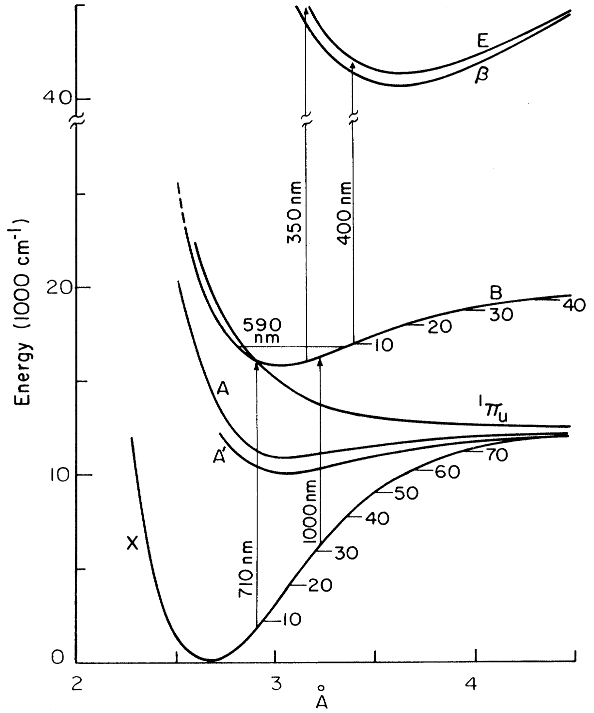

FIG. 1. Relevant electronic states of I_2. Several states similar to the $^1\Pi_u$ which may participate in predissociation are not shown. The initial B-state level excited at 590 nm is marked. Several transitions illustrating the shift in the Franck-Condon maximum with vibrational relaxation are also marked.

Adelman,[7] produced theoretical results which proposed that the ground-state vibrational relaxation was slow enough to account for the 530-nm bleach recovery time in solvents such as CCl_4.

Bado *et al.*[4] also made experimental measurements in chlorinated solvents of transient (40–350 ps) absorptions between 600 and 860 nm, which shifted to shorter wavelengths with time. On the basis of the time-dependent shift of the absorption spectrum, they concluded that the red absorptions and the bleach recovery are due to vibrationally relaxing ground-state molecules and that cage recombination is faster than the absorption recovery at 530 nm. However, Kelley, Abul-Haj, and Jang[3] have made absorption measurements from 575 to 800 nm which show a slowly decaying (~2700 ps) absorption with a time-independent spectrum. Kelley concludes that the long-wavelength absorption arises from molecules trapped in excited A and A' electronic states, that vibrational relaxation is rapid, and that the ~140-ps bleach recovery is indeed due to cage dynamics. This Letter reports results which should help to resolve these conflicting interpretations.

The absorption dynamics for I_2 photodissociation in CCl_4 from the near uv (350 nm) to the near ir (1000 nm) have been measured with improved time resolution and signal-to-noise ratio over previous experiments. 5-millimolar solutions of I_2 in CCl_4 were photodissociated by 590-nm pulses from a 10-Hz, amplified, synchronously pumped dye laser. Probe pulses at 350, 370, 400, 500, 635, 710, 760, 860, and 1000 nm were selected from a continuum by bandpass filters. Absorption changes were typically 1%–5% in the visible and 20%–39% in the ultraviolet. The experimental time resolution was 1–2 ps. Experiments in other simple solvents show similar results and will be discussed in detail in a forthcoming publication.[8]

The induced absorptions from 635–1000 nm have a slowly decaying component with a 2700-ps time constant, independent of wavelength. This is consistent with Kelley's observations and his assignment as an absorption from molecules trapped in (A,A') states.[3] However, an additional short-time component has a clearly wavelength-dependent decay rate. This is the first resolution of two decay components in the red absorption. Figure 2 shows the decay of the short-time component to the level of the (A,A')-state absorption, which appears as a long-time offset on each curve in the figure. The short-time component rises and decays quickly at 1000 nm, and becomes progressively slower at shorter wavelengths, as shown by the arrows marking the peak absorption at each wavelength in Fig. 2. This behavior is predicted for vibrationally relaxing molecules in the X state. The short-time component is thus assigned to absorption from slowly relaxing, vibrationally excited X-state molecules. The analysis of the two components in the red absorption thus indicates that upon initial recombination molecules are formed both in the (A,A') states and in the upper vibrational levels of the X state, and that slower energy relaxation follows.

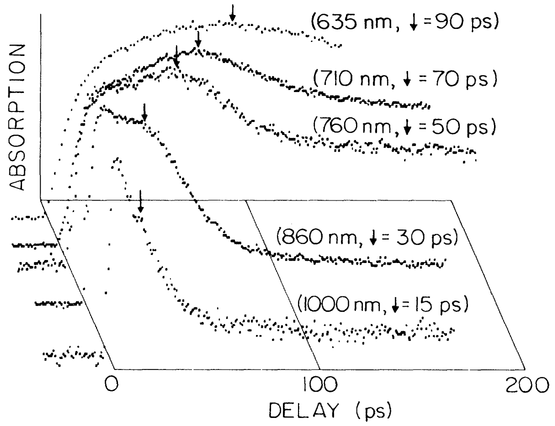

FIG. 2. Induced absorptions at long wavelengths following I_2 photodissociation (maximum absorptions set equal). Arrows mark the estimated peak of the vibrational component of absorption.

Although most of the wavelength-dependent absorption can be attributed to vibrationally excited molecules, it appears that there is an additional transient absorption for 10–15 ps following excitation. This initial transient is weak at 635 nm, appears as an initial shoulder at 710 nm and 760 nm, and is large enough at 860 nm to cause the absorption to be nearly double peaked. It seems likely that this initial peak is due to absorption from an as yet unassigned state which decays in 10–15 ps, possibly the initially populated B state.[9] At each wavelength in Fig. 2, the arrow marks the position which appears to be the peak of the vibrational component of the absorption, as distinct from this initial transient. At 1000 nm, the absorption kinetics appear relatively smooth because the vibrational absorption is too fast to be completely resolved from the initial absorption transient. There is, however, a slight but reproducible shoulder (arrow in Fig. 2) which may result from the vibrational absorption component. Thus care must be exercised in measuring a precise time for the vibrational relaxation from the 1000-nm absorption curve.

On the basis of the Franck-Condon arguments previously given, and knowledge of the molecular potential surfaces, the 1000-nm absorption is primarily from molecules with $v \sim 32$ (about halfway down the X-state potential well) and the 635-nm absorption from molecules near $v \sim 4$. It appears that relaxation proceeds rapidly through the upper part of the potential, but slows significantly near the bottom of the well. Langevin treatments of vibrational relaxation do not account for this slowing of the relaxation.[7] Molecular-dynamics calculations of I_2 in Xe have predicted that a vibration-to-translation transfer mechanism alone would take ~350 ps for complete vibrational relaxation of I_2.[4] Two analytical theories have predicted even longer (> 500 ps) vibration-to-translation transfer times.[6,7] By inclusion of strong, resonant, vibration-to-vibration transfer to the solvent, however, the observed time scale can be accounted for.[6] Experiments in vibrationless rare gases[10] should clarify the relative contributions of vibration-to-vibration and vibration-to-translation transfer in I_2 vibrational relaxation.

Newly observed absorptions in the 350–400-nm region (Fig. 3) provide further insight into the dissociation-recombination dynamics. Prominent from 350 to 370 nm is an absorption with the same decay time as the slow component of the red absorption. This is also assigned to absorption from the (A,A') states. However, the most interesting absorption feature in the 350–400-nm region is a fast decay seen from 350 to 400 nm. Figure 3 shows the decay of this transient to the level of the (A,A') absorption, which again appears as a long-time offset on each curve. The absorption at 400 nm rises within the expected experimental time resolution. On this basis, the fast absorption is assigned to absorption from the initially populated B state.[9] The upper molecular states for the absorption transition which are at the correct energy and have the corrrect symmetry are the very similar E and β states[11] (Fig. 1).

The B-state absorption (Fig. 3) rises and falls more slowly at 350 nm than at 400 nm, indicating a blue shift in the absorption spectrum with time. The simple Franck-Condon arguments used above predict a blue shift in absorption as the B state vibrationally relaxes. Therefore, the wavelength-dependent kinetics are probably due to vibrational relaxation within the B state. Based on the decay of the B-state absorption, the predissociation time constant can be put in the range 10–15 ps, with some uncertainty due to the blue shift of the absorption with time.

An upper bound on the time scale of cage recombination can be inferred from these data. If the cage recombination time were longer than the predissociation time, there would be a dip in the uv absorption after the predissociation but before trapping to the (A,A') states was complete. Since the B-state absorption decays smoothly into the (A,A') absorption, cage recombination must occur in ≤ 15 ps. Although it appears that the majority of geminate recombination occurs on a rapid time scale, it is possible that a small fraction of the atoms, after separating to a significant distance, undergo geminate recombination through a longer, difffusional process.

Finally, the bleach dynamics, first measured ten years ago, can be reanalyzed. Figure 4 shows the bleach at 500 nm, which has four temporal components: (i) an initial transmission jump[12] at $t=0$; (ii) a slower (~15-ps time constant) rise to a maximum; (iii) an initial recovery which is nearly complete in ~200 ps; and (iv) a slower 2700-ps time constant recovery. Chuang, Hoffman, and Eisenthal[2] first noted that the bleach maximum is delayed, and hypothesized that the B state continues to absorb until it has predissociated. Figure 4 confirms this, showing for the first time a separation of the initial transmission change on excitation to the B state (i) from the further increase in transmission as the B state predissociates and vibrationally relaxes (ii). Component (iv) is assigned to relaxation out of the (A,A') states, on the basis of the match with the red absorption decay time, and in agreement with a previous assignment.[3] Component (iii) represents the time scale which has previously been attributed to cage recombination[2,3] or to vibrational relaxation.[4] The results discussed above demonstrate that recombination occurs in ≤ 15 ps, while the time scale of vibrational relaxation is more appropriate: The red absorption from $v \sim 4$ is decay-

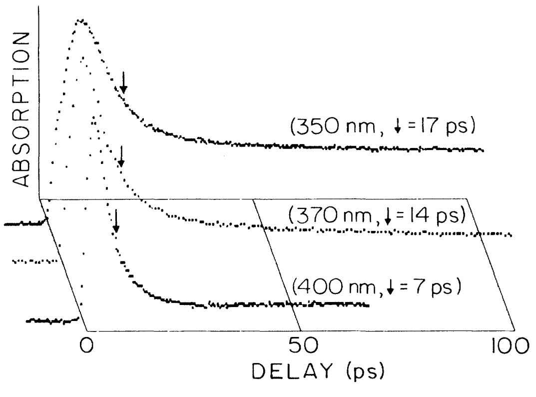

FIG. 3. Induced absorptions in the uv following I_2 photodissociation (maximum absorptions set equal). Arrows mark the point where the initial transient has decayed to e^{-1} (37%) of the peak.

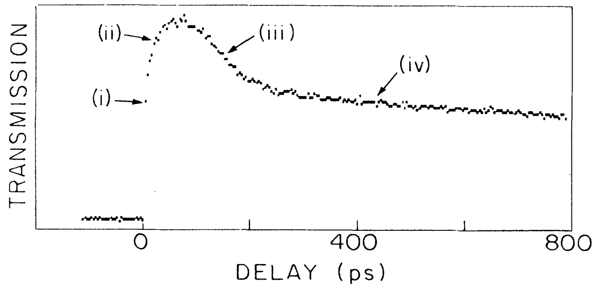

FIG. 4. Increased transmission at 500 nm following I_2 photodissociation.

ing at 100–150 ps. Thus, component (iii) is due to vibrational relaxation of those molecules which initially recombined on the X-state potential.

In conclusion, after excitation of iodine in CCl_4, solvent-induced predissociation occurs with a 10–15-ps time constant. The initial partitioning to either separated atoms, recombined (A,A') electronic-state molecules, or vibrationally excited X-state molecules appears to occur with a time constant of $\leqslant 15$ ps. These results support previous theoretical predictions[4,6,7] that fast recombination is followed by slow energy relaxation. They demonstrate that *both* slow electronic relaxation $(A,A' \rightarrow X)$ and slow vibrational relaxation on the X-state potential are important, clarifying previous experimental interpretations.[3,4]

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[1] Cage recombination is meant to be the recombination of atoms to form a molecular species as a result of solvent dynamics. It is not meant to include subsequent internal relaxation of the molecule.

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[9] Assignments to absorptions from the B state can be confirmed by repeating these experiments with use of excitation to the A state (Ref. 4).

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