

FIG. 2. (a) Rotation rate vs temperature diagram. Symbols indicate states with wave bounded away from the edge (■), wavelength-doubled states (●), and states with various mixtures of bounded and extended waves (▲); open and closed symbols indicate different runs. (b) The intensity variation around the annulus at a radius 77% across the gap from the inner edge of the gel for the wavelength-doubled state at  $T = 15$  °C; all waves are present at this radius. (c) The intensity variation for the same state as in (a) but at a larger radius (93% across the gap), reached only by every other wave. (d) Plot of the intensity around the annulus at a radius 93% across the gap, recorded every 2 min for an 8 h period. White lines indicate the leading edge of the extended waves, and breaks in these lines imply a transfer of an extension from one wave to an adjacent one. ( $T = 21$  °C.)

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## Time-resolved measurements of the photodissociation and recombination dynamics of $I_2^-$ in mass selected cluster ions

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Small molecular complexes have been used as a means of preparing reactants in well defined orientations to elucidate the dynamics of simple chemical reactions.<sup>1,2</sup> Larger clusters similarly have been employed to examine the effects of solvation on the energetics of chemical reactions.<sup>3,4</sup> The experiments described here are designed to explore the effects of solvation on the dynamics of chemical reactions. In this letter we present the results of picosecond time-resolved pump-probe measurements of the photodissociation and recombination dynamics of  $I_2^-$  interacting with a specific number of  $CO_2$  molecules in mass selected  $I_2^- (CO_2)_n$  clusters.

$I_2^- (CO_2)_n$  clusters are generated and mass analyzed in a pulsed-valve tandem time-of-flight (TOF) mass spectrometer.<sup>5</sup> Typically  $< 10^3$  ions of a given mass are generated on each valve pulse. Mass selected ions are intersected by laser pulses at the focus of the primary TOF mass analyzer. Following laser interaction, a reflectron type secondary TOF is employed to mass analyze the ionic photoproducts. Pump and probe laser pulses are obtained by beamsplitting the 720

nm pulse-amplified output of a synchronously-pumped, cavity-dumped dye laser into two pulses. Each 2 ps pulse has an energy of  $\approx 500$   $\mu$ J and the same polarization.

Approximate gas phase potential energy curves for  $I_2^-$  are shown in Fig. 1.<sup>6</sup> The visible absorption spectra of the  $I_2^- (CO_2)_n$  clusters are similar<sup>7</sup> to the absorption spectrum of  $I_2^-$ ;  $I^- (CO_2)_n$  and  $(CO_2)_n^-$  clusters are transparent at 720 nm. Absorption of one 720 nm photon by  $I_2^- (CO_2)_{16}$  excites  $I_2^-$  to the  $2^1\Pi_{g,1/2}$  repulsive state and yields  $I_2^- (CO_2)_{8,9,10,11}$  as ionic photoproducts, i.e. recombination occurs with unit quantum yield.<sup>7</sup> Absorption of *both* a 720 nm pump photon and a 720 nm probe photon yields lower mass ionic photoproducts:  $I_2^- (CO_2)_{2,3,4}$  and  $I^- (CO_2)_{5,6,7}$ . For  $I_2^- (CO_2)_9$  the ionic photoproducts due to absorption of one 720 nm photon are  $I_2^- (CO_2)_{1,2,3,4}$  and  $I^- (CO_2)_{4,5,6,7}$  (recombination occurs with  $\approx 50\%$  quantum yield<sup>7</sup> for this precursor); the ionic photoproducts due to absorption of two 720 nm photons are  $I^- (CO_2)_{0,1,2}$ .

We obtain the transient bleaching signal by measuring the number of ionic photoproducts resulting from the ab-

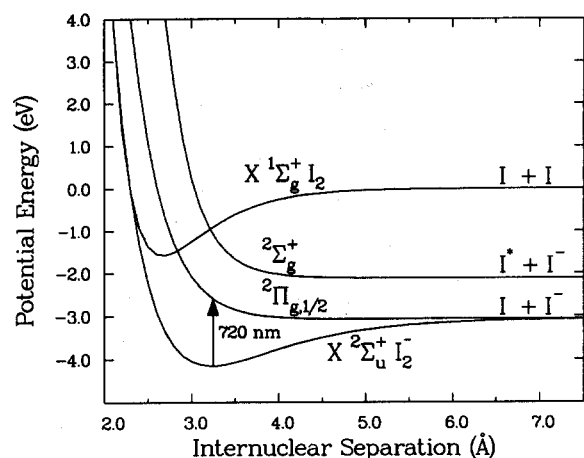


FIG. 1. Relevant gas phase potential energy curves for  $I_2^-$  (Ref. 6). The  $^2\Sigma_u^+ \rightarrow ^2\Pi_{g,1/2}$  transition peaks near 720 nm and results in photodissociation of  $I_2^-$ .

sorption of two photons by a mass selected precursor as a function of the time delay between the pump and probe pulses. The signal is equivalent to the quantity measured by Chuang *et al.*<sup>8</sup> in their classic experiments on the photodissociation and recombination of  $I_2$  in liquids. The absorption recovery data for  $I_2^-(CO_2)_{16}$  and  $I_2^-(CO_2)_9$  are shown in Fig. 2. Each data point in Fig. 2 represents 1000 laser shots. Typical signal count rates were  $< 2$  per 10 shots. The data are adequately represented by a single exponential risetime,  $30 \pm 10$  ps for  $I_2^-(CO_2)_9$  and  $10 \pm 5$  ps for  $I_2^-(CO_2)_{16}$ , convoluted with the instrument response function.

Absorption recovery data taken with pump and probe pulses polarized perpendicularly<sup>7</sup> indicate that the timescale for rotational reorientation<sup>9</sup> is longer than the timescale for absorption recovery. Another possible complication is the resonance of the probe pulse with the  $^2\Sigma_u^+ \rightarrow ^2\Sigma_g^+$  transition at an internuclear separation of  $\approx 4$  Å. The ionic photoproducts resulting from this transition have masses which are

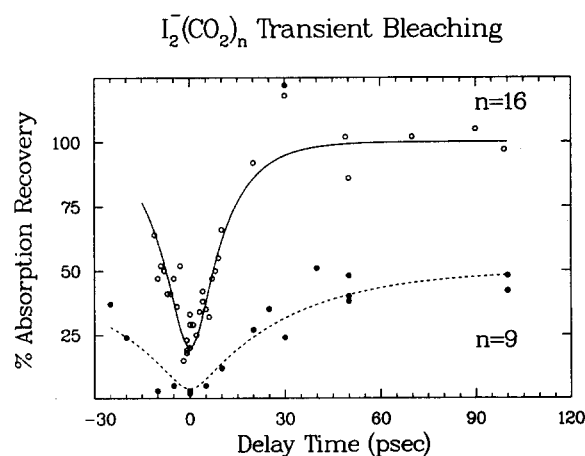


FIG. 2. Absorption recovery data for  $I_2^-(CO_2)_{16}$  (open circles) and  $I_2^-(CO_2)_9$  (filled circles) as a function of time delay between 720 nm pump and probe pulses. Since the pump and probe pulses are equivalent, the data are symmetric about 0 ps delay. The asymptotic values have been scaled to the quantum yield for recombination as determined in a separate experiment.<sup>7</sup> Also shown are single exponential recoveries: 30 ps for  $I_2^-(CO_2)_9$  (dashed line) and 10 ps for  $I_2^-(CO_2)_{16}$  (solid line), convoluted with the instrument response function (gaussian,  $\sigma = 3$  ps, due to counterpropagating pump and probe pulses).

different<sup>7</sup> from those monitored in this experiment. Thus the observed absorption recovery is due to the reappearance of vibrationally relaxed  $X^2\Sigma_u^+ I_2^-$  now solvated by fewer  $CO_2$  molecules.

The processes relevant to the absorption recovery include some of those operative in the dynamics of photodissociation and recombination of neutral  $I_2$  in the condensed phase, viz. geminate recombination and vibrational relaxation.<sup>10-13</sup> For neutral  $I_2$  in molecular liquids, geminate recombination occurs in  $< 2$  ps,<sup>14</sup> with vibrational relaxation in the ground electronic state taking 50–150 ps.<sup>15,16</sup> The faster absorption recovery reported here suggests an increased rate of vibrational relaxation. This increase is possibly due to the irreversible energy flow which accompanies the ejection of  $CO_2$  molecules, a process which has no condensed phase analog. The generally faster rates of vibrational energy transfer in ion-neutral vs neutral-neutral collisions<sup>17</sup> may also contribute. Molecular dynamics (MD) simulations of the photodissociation and recombination dynamics of  $Br_2^-$  in  $Br_2^-(CO_2)_n$  clusters<sup>18</sup> give timescales similar to those we observe, but do not indicate the dominant mechanism for vibrational relaxation. The MD simulations<sup>18</sup> evidence a slower absorption recovery in smaller clusters, in consonance with our measurements, due to decreases in the rates of both geminate recombination and vibrational relaxation. Further experiments are currently underway to elucidate the relative contributions of these processes to the recombination dynamics. We conclude by noting that the results presented indicate the feasibility of real time measurements of reactive dynamics in clusters and suggest that such measurements may provide qualitatively new information on chemical reaction dynamics in a microsolvant environment.

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