I_2^- photofragmentation/recombination dynamics in size-selected $I_2^-(CO_2)_n$ cluster ions: Observation of coherent I···I$^-$ vibrational motion

John M. Papanikolas, Vasil Vorsa, María E. Nadal, Paul J. Campagnola, James R. Gord,[a] and W. C. Lineberger

Department of Chemistry and Biochemistry and Joint Institute for Laboratory Astrophysics, University of Colorado and National Institute of Standards and Technology, Boulder, Colorado 80309-0440

Molecular clusters offer a unique environment in which the size of a solvent cage surrounding a chromophore can potentially be controlled, allowing one to study the effects of increasing solvation on reaction dynamics.[1-6] If charged species are employed, size selection of the initial cluster is easily accomplished with standard mass spectrometric techniques.[1,2] Studies of the 720 nm $I_2^-(CO_2)_n$ photofragmentation and the subsequent recombination of I_2^- showed[6] no caging for $n \leqslant 5$, increasing steadily from $n=6$ to complete caging at $n=16$, where the first solvent shell is complete. Preliminary picosecond pump–probe experiments on $I_2^-(CO_2)_n$ demonstrated[7] that the absorption recovery following I_2^- photodissociation depended upon cluster size. The recovery time, ~ 10 ps for $n=16$ and ~ 30 ps for $n=9$, was attributed to the time required for the recombination and subsequent vibrational relaxation of the photodissociated I_2^-. The time resolution was only 6 ps, and scatter in the data allowed only a single-exponential fit to the data.[7] The experiments reported here represent substantial improvements in both aspects, and exhibit a clear recurrence at ~ 2 ps in the photodissociated $I_2^-(CO_2)_{16}$ absorption recovery.

Coherent vibrational motion extending over many periods has been observed in *isolated* diatomic molecules such as I_2 (Refs. 8 and 9) and Na_2.[10] Here the nuclear dephasing is due predominantly to anharmonicity in the potential surface, and thus the nuclear phase coherence can persist for many vibrational periods. However in a liquid environment, collisions with solvent molecules dominate vibrational dephasing, greatly reducing the time over which coherent nuclear motion can be maintained. For example, Ruhman and co-workers[11] have observed a few oscillations in the transient absorption of I_2^- produced by the photodissociation of I_3^- in ethanol. The authors attribute these oscillations, which last for ≈ 1 ps, to coherent I_2^- vibrational motion in a low vibrational energy level. Scherer *et al.*[12] report multiple I_2 vibrational recurrences lasting a few picoseconds in *n*-hexane solvent. All of these studies represent nuclear coherences taking place on a single potential energy surface. One possible example of a recurrence following dissociation is the report by Nelson and co-workers[13] of what may be coherent Mn–Mn vibrations following excitation of $Mn_2(CO)_{10}$ in ethanol. Otherwise, we believe our results represent the first observation of coherent nuclear motion following photodissociation and subsequent recombination.

One possible reason for the successful observation of

long-lasting coherence in this cluster ion lies in the strong ion–solvent bond[14] (~ 150 meV/CO_2) and the low internal temperature (~ 40 K). These two conditions produce a much more restricted set of initial geometries than is the case in the liquid studies, and would appear to allow the initial nuclear motion coherence to survive for 2–3 ps in spite of the ensemble averaging inherent in the observations. Another important feature is the strong CO_2–CO_2 bonding interaction, giving the first solvent shell some of the character of a soft "net." In any event, the motion rapidly loses coherence as the cluster disintegrates.

A thorough understanding of the photophysics of $I_2^-(CO_2)_n$ clusters is hampered by the fact there is little quantitative information concerning the low lying states of I_2^- and correspondingly less information on $I_2^-(CO_2)_n$. Figure 1 depicts semiempirical potentials[15] for the ground and low-lying dissociative states of I_2^-. In the present experiments we excite the $A'^2\Pi_{g,1/2} \leftarrow X^2\Sigma_u^+$ transition at 720 nm (1.72 eV), producing I and I$^-$ with a total kinetic energy release of ≈ 0.5 eV. The inappropriateness of the Hunds case (a) coupling notation is illustrated by the fact that we find this transition moment to be oriented essentially *parallel* to the bond axis,[16] whereas in case (a) it should be exactly perpendicular. This result illustrates the strong spin–orbit mixing of the $A'^2\Pi_{g,1/2}$ state with an excited $^2\Sigma_{g,1/2}^+$ state, and provides a clue to the surface on which the recurrence probably occurs.

The absorption of a photon by the I_2^- chromophore results in an internally excited cluster, which then cools by CO_2 evaporation. Photoabsorption is detected by the appearance of ionic products at lower mass. Since the cluster ion source and tandem time-of-flight mass spectrometer required to detect the photoabsorption have been previously described,[2,5,6] only a brief summary will be given here. I_2^- ions are created in a pulsed supersonic expansion ($\sim 1\%$ I_2 in CO_2) by a continuous, 1 keV electron beam, allowed to drift 20 cm in the expansion, during which time they react and aggregate CO_2 molecules. A high voltage pulse then extracts the ions into a tandem time-of-flight mass spectrometer, where they interact with a pulsed laser at the spatial focus of the first stage. Adjustment of the time delay between the extraction pulse and laser pulse provides mass-selective photoexcitation. The resulting ionic photofragments are mass analyzed in a second time-of-flight stage, a single field reflectron, which they enter approximately 10 μs after laser interaction.

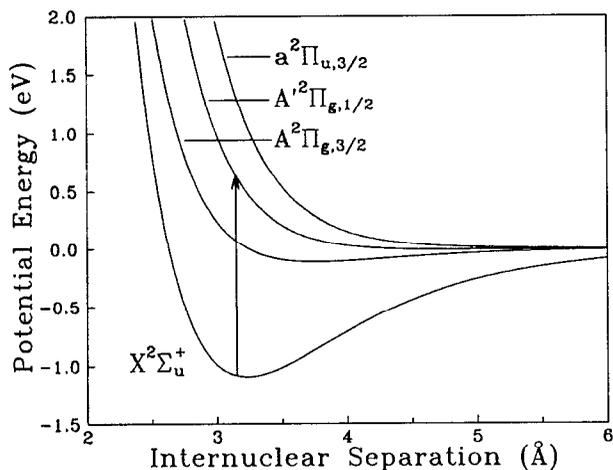The picosecond laser used in these experiments pro-

FIG. 1. Semiempirical potential energy curves for I_2^- derived by Chen and Wentworth (Ref. 15). Only the ground and three lowest excited states of I_2^- are shown. The vertical arrow indicates the 720 nm, $A'^2\Pi_{g,1/2} \leftarrow X^2\Sigma_u^+$, transition excited in these studies.

FIG. 2. $I_2^-(CO_2)_n$ ($n = 12$–17) absorption recovery data obtained with 720 nm pump and probe pulses with parallel polarization. The number below each cluster size represents the fraction of caged products following absorption of a single photon.[6] The curve above the $n = 17$ data is the laser pulse autocorrelation function.

duces 30 Hz, 720 nm pulses with a near transform limited ~ 1.2 ps width. Any amplified spontaneous emission (ASE) in the laser pulse gives rise to extensive noise; ASE has been limited to $< 0.5\%$ of the total pulse energy by use of apertures and saturable absorbers. The pump and probe pulses are created by splitting the 1 mJ laser pulse into two identical components; adjustment of the time delay is accomplished by varying the optical path length for one of the pulses. A half-wave plate placed in one beam permits adjustment of the polarization angle between pump and probe pulses. The frequency width of the nonamplified pulse is typically 17 cm^{-1} and the autocorrelation FWHM is 1.5 ps, corresponding to about 1.2 times the width expected for a transform-limited pulse. The noncollinear autocorrelation function (FWHM ≈ 1.25 ps) of the amplified pulse is shown at the top of Fig. 2.

The manner in which this apparatus is used in a pump–probe experiment is as follows. The size-selected $I_2^-(CO_2)_n$ ion absorbs a 720 nm photon from a picosecond pump pulse, dissociating the I_2^- inside the cluster. While the I_2^- is dissociated, the cluster ion is transparent to 720 nm radiation. Only when a reformed I_2^- chromophore has reached a region of the potential curves with an appreciable 720 nm absorption cross section can the excited cluster ion absorb a second photon from a picosecond probe pulse of the same color. The most obvious region where such a transition can take place corresponds to vibrationally relaxed I_2^-. Absorption of two 720 nm photons by a single cluster results in the evaporation of 12–13 CO_2 molecules, forming two-photon ionic photoproducts at masses that are easily resolved from the one-photon ionic photofragments. The transient bleach created by the pump pulse is monitored by measuring the total number of two-photon ionic photofragments[17] as a function of pump–probe delay. Even at high peak powers, multiphoton processes leading to I_2^- electron detachment are not important, due to the absence of appropriate intermediate states in I_2^-. The fact that this two-photon signal is detected against "zero back-
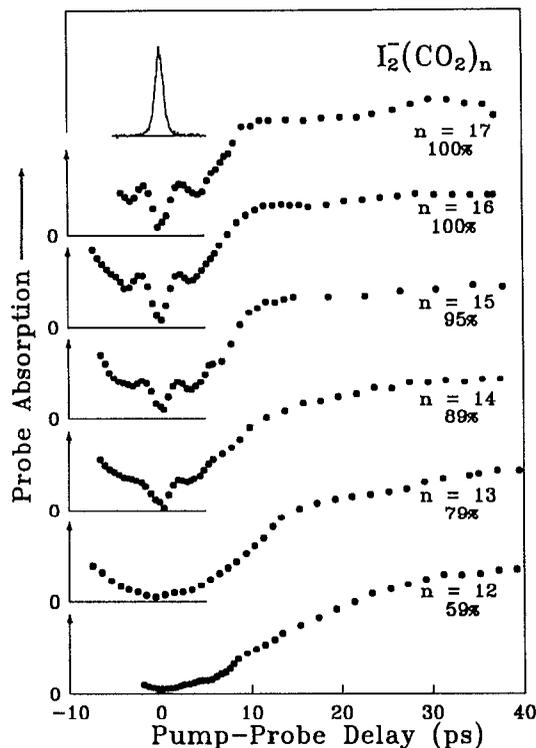
ground" is essential to the success of this experiment, making it possible to perform experiments on mass-selected samples which contain only 10^3 to 10^4 cluster ions. At each delay time, the signal was averaged over $\approx 15\,000$ laser pulses.

The absorption recovery curves for $I_2^-(CO_2)_n$ ($n = 12$–17) are shown in Fig. 2. Since the pump and probe pulses are identical, these curves should be symmetric about zero delay. The data presented in Fig. 2 were obtained with pump and probe pulses polarized parallel to each other, and thus reflect the orientational decay of the excited I_2^- ensemble, as well as the actual I_2^- recombination and vibrational relaxation dynamics. The overall recovery times are consistent with those previously[7] obtained; however, the greatly reduced scatter and improved time resolution make it apparent that there are multiple time scales involved in the absorption recovery.

The most intriguing result is the observation of a local absorption maximum, occurring at ≈ 2 ps in the larger clusters. Since this feature is so unusual, many different tests were undertaken to ensure that it was not an experimental artifact. Very careful measurements of the laser pulse autocorrelation width show that the feature occurs at a time close to the instrument response time, but it is not a result of the laser pulse shape. The fact that the pump and probe pulses have the same energy content places further constraints on possible "coherence spike" artifacts in the absorption recovery. Convolution of a monotonic ($|1-e^{-\alpha|t|}|$) absorption recovery with a variety of (as-

sumed) multiple peaked laser pulse shapes fails to reproduce simultaneously both the 2 ps maximum and the small absorption signal at zero delay. This feature has been present over many different setups, including very preliminary measurements with < 300 fs time resolution. The observed width of the maximum may be influenced by the time resolution of the apparatus. It is still present (but less pronounced) with perpendicular pump and probe pulse polarization, indicating that the feature is not *solely* due to orientational decay of the excited I_2^- ensemble. The question remains as to the physical origin of this maximum.

While vibrationally relaxed I_2^- would obviously be able to absorb a second 720 nm photon, it cannot account for the *decrease* in absorption following the maximum. The decrease must be attributed to *passage* of the photoexcited I_2^- cluster ion *through* a region of the I_2^- potential surface where a second 720 nm photon can be absorbed. Our studies of the time dependence of the product mass spectra indicate that at $t \approx 2$ ps, 2–3 CO_2 molecules have effectively departed the cluster, leaving it at this time at a total energy near the I_2^- dissociation limit. The observed absorption recovery is in actuality an average of the I_2^- nuclear motion over all the photoexcited cluster ions in the ensemble, and thus the observation of a recurrence indicates that *coherent* I_2^- nuclear motion is maintained for at least 3 ps following I_2^- photoexcitation. Up to this point, the arguments do not depend upon a detailed knowledge of the interaction potentials. The degree of uncertainty in the actual potentials makes the following plausible interpretation more speculative.

Inspection of the qualitative I_2^- potential curves yields two possible regions where 720 nm photoabsorption could produce the 2 ps absorption maximum. The first is at the inner turning point of the ground state surface at an energy near the I_2^- dissociation limit, with a possible transition to the $A\ {}^2\Pi_{g,3/2}$ state. The second region is on the $A\ {}^2\Pi_{g,3/2}$ state potential at an internuclear separation of ~ 3 Å, where a transition to the $a\ {}^2\Pi_{u,3/2}$ state appears energetically possible. Polarization data for $I_2^- (CO_2)_{16}$ taken between 0.5 and 4 ps delay show the *same* electronic transition moment orientation for both the pump and probe absorption. This observation is consistent *only* with the second possibility above.

Based upon this interpretation and the transient mass spectral data, the I_2^- recombination dynamics can be described as follows. About 1 ps after photoexcitation, the excited I_2^- has transferred ~ 0.5 eV energy to the surrounding CO_2 solvent, and the dissociating $I \cdots I^-$ motion is arrested by the solvent cage, leaving a substantial fraction of the I_2^- in the $A\ {}^2\Pi_{g,3/2}$ state at a large separation, perhaps 5–6 Å. At ≈ 2 ps, these I_2^- ions reach the inner turning point of the $A\ {}^2\Pi_{g,3/2}$ potential, and an increase in the probe absorption is observed. The subsequent decrease in the absorption recovery at ≈ 3 ps corresponds to the departure of the electronically excited I_2^- from this region. The majority of the remaining events must take place on the ground state surface. The rapid recovery, but not the recurrence, has very recently been observed[18] for I_2^- in 300 K alcohols.

Figure 2 shows that as the cluster size decreases from 16 to 14, the recurrence gradually disappears, becoming only a shoulder in $I_2^- (CO_2)_{14}$, and is absent for 12 and 13. The absorption recoveries for $n = 8$, 9, and 12 are indistinguishable and slower than for any of the larger clusters. One possible explanation of this behavior is suggested by the minimum energy structures[19] and molecular dynamics simulations[20] by Amar and Perera. These calculations suggest that in the smaller clusters ($n = 8$–12) the photodissociated I_2^- is able to undergo large-amplitude motion before recombination. As I and I^- separate, a CO_2 molecule can fit between them, forming a "solvent-separated" pair. The driving force for this rearrangement is the strong electrostatic attraction between I^- and the positive partial charge on a nearby carbon atom. The formation of a "solvent-separated" pair would delay I_2^- recombination and of course destroy the coherent $I \cdots I^-$ vibrational motion. Much more work will be required before this solvent-separated pair picture can be confirmed.

a) Present address: Systems Research Laboratories, Wright Laboratory, Power and Propulsion Directorate, Dayton, Ohio 45440-3696.

[1] A. W. Castleman, Jr., in *Clusters of Atoms and Molecules*, edited by H. Haberland (Springer-Verlag, New York, 1992) (in press).

[2] M. A. Johnson and W. C. Lineberger, in *Techniques for the Study of Ion Molecule Reactions*, edited by J. M. Farrar and W. Saunders, Jr. (Wiley, New York, 1988), pp. 591–635.

[3] T. Droz, R. Knochenmuss, and S. Leutwyler, J. Chem. Phys. **93**, 4520 (1990).

[4] J. J. Breen, L. W. Peng, D. W. Willberg, A. Heikal, P. Cong, and A. H. Zewail, J. Chem. Phys. **92**, 805 (1990); J. Steadman and J. A. Syage, *ibid.* **92**, 4630 (1990).

[5] M. L. Alexander, N. E. Levinger, M. A. Johnson, D. Ray, and W. C. Lineberger, J. Chem. Phys. **88**, 6200 (1988).

[6] J. M. Papanikolas, J. R. Gord, N. E. Levinger, D. Ray, V. Vorsa, and W. C. Lineberger, J. Phys. Chem. **95**, 8028 (1991).

[7] D. Ray, N. E. Levinger, J. M. Papanikolas, and W. C. Lineberger, J. Chem. Phys. **91**, 6533 (1989).

[8] R. M. Bowman, M. Dantus, and A. H. Zewail, Chem. Phys. Lett. **161**, 297 (1989).

[9] N. F. Scherer, R. J. Carlson, A. Matro, M. Du, A. J. Ruggiero, V. Romero-Rochin, J. A. Cina, G. R. Fleming, and S. A. Rice, J. Chem. Phys. **95**, 1487 (1991).

[10] T. Baumert, V. Engel, C. Röttgermann, W. T. Strunz, and G. Gerber, Chem. Phys. Lett. **191**, 639 (1992).

[11] U. Banin, A. Waldman, and S. Ruhman, J. Chem. Phys. **96**, 2418 (1992).

[12] N. F. Scherer, L. D. Ziegler, and G. R. Fleming, J. Chem. Phys. **96**, 5544 (1992).

[13] A. G. Joly, S. Ruhman, B. Kohler, and K. A. Nelson, *Ultrafast Phenomena VI*, edited by T. Yakajima, K. Yoshihara, C. B. Harris, and S. Shionoya, Springer Series in Chemical Physics (Springer-Verlag, Berlin, 1988), Vol. 48, pp. 506–510.

[14] M. L. Alexander, M. A. Johnson, N. E. Levinger, and W. C. Lineberger, Phys. Rev. Lett. **57**, 976 (1986); M. L. Alexander, M. A. Johnson, and W. C. Lineberger, J. Chem. Phys. **82**, 5288 (1985).

[15] E. C. M. Chen and W. E. Wentworth, J. Phys. Chem. **89**, 4099 (1985).

[16] Photodissociation of I_2^- with 720 nm light polarized parallel to the ion beam results in two distinct I atom arrival times at a detector located approximately 30 cm downstream of the laser interaction region. The observed doublet, whose splitting reflects the I and I^- kinetic energy

release, indicates that the photofragments are primarily oriented *parallel* to the polarization vector of the laser. The doublet splitting qualitatively confirms the ~ 1.25 eV I_2^- bond dissociation energy (to be published).

[17] The ionic fragments differ for different parent ions, but are concentrated in three or fewer mass peaks. We measure the sum over the four most intense products, normalized by the parent ion intensity and the square of the laser flux.

[18] A. E. Johnson, N. E. Levinger, and P. F. Barbara, J. Phys. Chem. (submitted).

[19] F. G. Amar and L. Perera, Z. Phys. D **20**, 173 (1991).

[20] L. Perera and F. G. Amar, J. Chem. Phys. **90**, 7354 (1989).