Incoherent control of photodissociation pathways in I_2^- cluster ions

Andrei Sanov and W. Carl Lineberger

JILA, National Institute of Standards and Technology and University of Colorado, and Department of Chemistry and Biochemistry, University of Colorado, Boulder, CO 80309

ABSTRACT

Detailed time-resolved photodissociation and caging dynamics are reported for an $I_2^-(OCS)_{11}$ model system. The observed product channel-dependent nuclear coherence in the dissociated chromophore reflects complex dynamics of the solvent cage. The evolving pump-probe product distribution offers the possibility of incoherent control of two-photon dissociation pathways by appropriately delaying the probe laser pulse. As an example of such control, $I_2^-(OCS)_2$ is produced most effectively by a limited set of pump-probe excitations. We emphasize generality of these results that relate to caging dynamics in any cluster ions.

Keywords: negative ions, clusters, pump-probe, control, solvent dynamics, photodissociation

1. INTRODUCTION

Clusters offer a potentially well-characterized environment¹⁻⁴ for the study of chemical reactions, including solventinduced recombination, or "caging" of photofragments.⁵⁻¹⁵ Many groups have investigated caging in real time by monitoring the recovery of the dissociated chromophore's ability to absorb light,¹⁶⁻²⁶ or following the evolution of the photoelectron spectrum.²⁷⁻²⁹ We have emphasized the dynamics of dihalogen anion recombination in size-selected cluster ions.³⁰⁻³⁸ The gas-phase environment allows not only selecting the initial solvation conditions,³ but also probing the disintegrating cluster by a second photon, mass-analyzing the two-photon products to get a glimpse of the evolving cluster structure following photodissociation of the chromophore within the cluster.^{30,32,38}

These channel-resolved action spectra allow examination of the caging dynamics in unprecedented detail. The data show that coherent motion of the chromophore cannot be considered separately from dynamics of the cage, and that the evolving solvent configuration favors different types of two-photon products at various stages of evolution. While we employed $I_2^-(OCS)_{11}$ in this study, the results reflect the general dynamics of caging and will be applicable to other solvated systems, e.g., $I_2^-(CO_2)_{16}^{.39}$

One important finding in the studies of caging has been the observation of coherent motion of the chromophore persisting for several picoseconds following photodissociation.^{19,22,30,31,34} Laser-induced nuclear coherence has been extensively studied in bound-bound molecular transitions^{40,41} and successfully applied to exert coherent control of chemical reaction pathways.⁴²⁻⁴⁶ Coherent motion following excitation to a dissociative potential is fundamentally different, since the long-range forces that reverse the motion of photofragments arise entirely from interaction with surrounding solvent.^{13,19,22,30}

In I_2^- based clusters, solvent-induced coherent $I \cdots I^-$ motion is manifest as an early delay-time "bump" in transient absorption data.^{30,31,34,38} The preponderance of available evidence indicates that the maximum of this feature at about 2 ps corresponds to wave-packet localization in a Franck-Condon region on either the slightly bound first excited ${}^2\Pi_{g,3/2}$ or the ground ${}^{2}\Sigma^{+}_{u,1/2}$ electronic state potential^{47,48} of I_2^- , or both.³⁰ The assignment of the state(s) responsible for the coherence feature is extremely difficult because of the substantial solvent-induced perturbations of the I_2^- potentials at large interatomic distances.^{47,49}

The coherent feature in the transient absorption data reflects the recombination dynamics of the chromophore, providing no information about motion of the solvent itself. Section 2 is devoted to an *ab initio* investigation of the interaction of OCS with I_2^- , followed by a qualitative discussion of the structure of the $I_2^-(OCS)_n$ clusters. In Section 3, we examine dynamics of the cage by following the appearance of specific two-photon products. The changing branching ratio of these products reflects the evolving structure of the solvent cage at a given delay time. Ultimately, the evolving pump-probe product distribution offers the possibility of incoherent control of two-photon dissociation pathways by controlling the delay of the probe laser pulse.

2. STRUCTURE OF $I_2^-(OCS)_n$ CLUSTERS

Electrostatic interactions of the charged cluster core with OCS are dominated by the charge-dipole (μ (OCS) \approx 0.7 Debye)⁵⁰ interaction. This is in contrast with the $l_2^{-}(CO_2)_n$ clusters, where the markedly larger quadrupole moment of $CO_2 (\Theta(CO_2) \approx -4 \cdot \Theta(OCS))^{51.52}$ dictates the cluster structure.⁵³

We start by examining the interaction of OCS with Γ . Figure 1 shows the potential energy surface for the interaction of a rigid OCS molecule with Γ , calculated⁵⁴ using the spin-restricted Hartree-Fock method.⁵⁵⁻⁵⁷ The medium-size polarized basis set of Sadlej⁵⁸ with added polarization functions was used for iodine, while the 6-31+G(d) basis set⁵⁹ was employed for OCS. Although the calculated binding energies appear too low, the qualitative features of the potential energy surface agree well with intuitive expectations. The global potential minimum corresponds to the linear Γ ...SCO charge-dipole bound geometry with an S-I distance of 4.1 Å. A secondary minimum, separated by a small barrier, corresponds to the charge-quadrupole interaction and is analogous to the C_{2y} global potential minimum of $\Gamma(CO_2)$.^{60,61}



Figure 1. Γ ...SCO potential energy surface calculated using the spin-restricted Hartree-Fock method. OCS is frozen at its linear equilibrium geometry. The zero of energy corresponds to Γ and OCS at infinite separation. The plot is in Jacobi coordinates: *R* is the distance from Γ to the OCS center of mass; θ is the angle between the *R* vector and the SCO axis ($\theta = 180^{\circ}$ corresponds to the linear Γ ...SCO geometry).

Selective calculations on the $I_2^-(OCS)$ complex indicated that interaction of OCS with I_2^- is qualitatively similar to that in I⁻(OCS), dominated by the charge-dipole interaction. The global potential energy minimum corresponds to a T-shaped (C_{21}) I_2^- ...SCO geometry, with the OCS dipole pointing towards the waist of I_2^- . The binding energy of the linear $(I-I)^-$...SCO structure is approximately one-half that of the T-shaped structure.

Based on these results, the solvent in the smallest $I_2^-(OCS)_n$ clusters (a few solvent molecules) is predicted to be bound around the chromophore in a charge-dipole orientation, with the sulfur ends pointing towards the waist of I_2^- . As the number of solvent molecules increases, some will eventually be forced to less favorable sites near the ends of the I_2^- . Another important factor distinguishing the packing of OCS around I_2^- from that of CO₂ is the dipole-dipole repulsion of neighboring OCS molecules, oriented nearly parallel to each other due to the dominant charge-dipole interaction with the cluster core. Solvent-solvent repulsion may result in a less rigid and more spread-out cage, a more even solvent coverage of the chromophore, with a more symmetric cage configuration in the intermediate cluster size range (n = 6 - 12).

3. INCOHERENT CONTROL OF TWO-PHOTON DISSOCIATION

The ion machine⁶² consists of a cluster ion source and a tandem time-of-flight (TOF) mass spectrometer. The $I_2^-(OCS)_n$ clusters are formed by attachment of slow secondary electrons to neutral species in an electron-impact ionized free jet (80 Hz) with subsequent solvent nucleation around the negatively-charged core.³ Initial cluster ion mass selection is achieved in a Wiley-McLaren TOF mass spectrometer, while mass analysis of the ionic fragments is carried out utilizing a

second, reflectron, mass spectrometer. The femtosecond laser³³ delivers 790 nm, 120 fs pump and probe pulses with a 400 Hz repetition rate. The co-propagating pump and probe beams (250 μ J/pulse each) have parallel polarizations and are mildly focused to an ~ 3 mm diameter spot size in the interaction region.

The I_2^- ion has bond strength of ~ 1 eV,^{29,48} and exhibits a dissociative continuum absorption peaking near 790 nm, giving ~ 0.5 eV kinetic energy release to the photoproducts. One-photon dissociation of I_2^- within a cluster generally leads to both caged and uncaged ionic products.^{36,38,63} In 790 nm dissociation of I_2^- (OCS)₁₁, 80% of the one-photon fragments are caged, with the most abundant products being I_2^- (OCS)₄ and I_2^- (OCS)₅.^{38,63} Subsequent fragmentation of these caged products with a second, probe photon (at long delay allowing complete relaxation of one-photon fragments) yields ~ 75% uncaged [I_2^- (OCS)_{2,3,4}] and ~ 25% caged [I_2^- (OCS)_{0,1}] products.

The two-photon dissociation experiments at long delays are only sensitive to those one-photon trajectories that have led to the recombination of the chromophore, as only caged one-photon fragments can absorb a second 790 nm photon. However, at earlier times (less than ~ 5 ps) the distinction between one-photon trajectories ultimately leading to caged and uncaged products is ambiguous, and even clusters *en route* to uncaged fragments can conceivably absorb a probe photon.

The top curve in Fig. 2 depicts the photoabsorption recovery signal for $I_2^-(OCS)_{11}$, obtained by combining all major twophoton products. The curve exhibits a coherence maximum at about 2.5 ps. As in the earlier CO₂ studies,³⁸ the bump corresponds to the dissociated chromophore, arrested by the solvent shell, returning to the Franck-Condon region. The 2.5 ps time for the recurrence is much slower than the bound I_2^- vibrational period because it reflects the dissociating chromophore being arrested by the solvent cage and subsequently being returned to the Franck-Condon region. Accordingly, this time is better regarded as a "solvent" time, rather than a "chromophore" time. The 2.5 ps recurrence time with the OCS solvent is longer than the 1.4 ps time observed for the corresponding CO₂ cluster,³⁰ likely a result of a less rigid and less compact structure of $I_2^-(OCS)_n$ clusters.



Figure 2. Total absorption recovery signal in the photodissociation of $I_2^{-}(OCS)_{11}$ at 790 nm and its "caged" and "uncaged" components obtained by counting the respective types of two-photon products separately.



Figure 3. Delay-dependence of the uncaged/caged ratio, compared to the total absorption recovery curve reproduced from Fig. 2.

We obtain direct information about coherent motion of the solvent itself by following the absorption recovery as detected by specific two-photon products. The time evolution of these products reflects the structure of the solvent cage at a given delay time. By determining the mass of each of the two-photon ionic photoproducts, the absorption recovery curve can be decomposed into "caged" and "uncaged" components, as shown in Fig. 2. It is immediately clear that the coherence feature in the total absorption recovery arises primarily from the caged two-photon pathways.

Further understanding of the dynamics can be gained by examining the ratio of the "uncaged" and "caged" components as a function of probe delay, as shown in Fig. 3. The ratio is independent of the fraction of the initially excited ions that have recombined, and evolution of this ratio as a function of delay directly reflects changes in the solvent configuration. In the

statistical, incoherent limit, this ratio should increase monotonically to the observed long delay uncaged/caged ratio, ~ 3 . In fact, a very different behavior is observed. Rather, this ratio decreases to a minimum at about 1.8 ps and then increases to reach a maximum at ~ 8 ps. As the delay time increases, this ratio levels off at the statistical asymptote. While this behavior can be interpreted³⁸ in terms of coherent motion on the solvent, in this publication we emphasize that non-statistical dynamics in photoexcited clusters persist for ~ 10 ps.

The level of channel averaging can be further reduced by monitoring the behavior of specific caged and uncaged twophoton products. We have recently shown³⁸ that the relative amplitude of the coherence feature depends not only on the caged or uncaged nature of the final product, but also on the number of remaining solvent molecules, increasing with the product size. In the two-photon dissociation of $I_2^-(OCS)_{11}$ at 790 nm, the most pronounced effect is in the $I_2^-(OCS)_2$ channel, shown in Fig. 4. Its yield is almost unobservable at long delays (< 0.4%); however, substantial dissociation occurs in a narrow delay window coinciding with the characteristic time-scale of $I \cdots I^-$ coherent motion. We also note that the maximum of the coherence feature in $I_2^-(OCS)_2$ is shifted to about 40% shorter delay compared to the total absorption recovery (compare Figs. 2 and 4).





The number of solvent molecules lost by the cluster in the sequential two-photon process decreases if the second photon arrives at a time that favors unusually large kinetic release to a solvent molecule. The effectiveness of the energy transfer from photoexcited I_2^- to individual solvent molecules is dependent on the relative phase of the I_2^- and cage motion. The best time for large energy transfer is the same as for enhanced caging: when $I \cdots I^-$ and the solvent cage are out of phase with each other, with the cage moving inwards. Therefore, larger two-photon products are favored at the same delays as when the uncaged/caged ratio is at its minimum, just before the coherence peak in transient absorption. The production of $I_2^-(OCS)_2$ predominantly with pump-probe separations of ~ 1 to 4 ps, sharply peaking at 1.4 ps, is an extreme example of this effect.

This result demonstrates a method to control two-photon dissociation pathways by appropriately timing the two laser pulses. We emphasize the *incoherent* nature of this effect, in contrast to the coherent wave-packet methods of reaction control.^{42,44,46,64} The rapid decrease in the $I_2^{-}(OCS)_2$ yield at 4 ps reflects the solvent dynamics rather than the $I \cdots I^{-}$ coherence. Other incoherent methods of control are based on the use of interference,^{43,65} femtosecond ponderomotive forces,⁶⁶ and the feedback control.⁶⁷ The demonstrated control and the ratio measurement in Fig 3 indicate that coherence and non-statistical behavior can persist for at least ~ 8 ps in a 35 atom complex.

The maximum $I_2^-(OCS)_2$ production occurs at the time of the minimum of the uncaged/caged ratio, rather than at the time of the transient absorption coherence peak. This is a clear indication that, for the production of this "abnormally large" fragment, the optimal localization of the I···I⁻ wave-packet in the Franck-Condon region is not the most important prerequisite. The determining factor for this channel is a large (impulsive) translational energy release which is only possible at short delays, near the bottom of the uncaged/caged curve well (see Fig. 3).

In conclusion, we have shown that I_2^- dissociation and recombination dynamics within an evolving cluster are very complex, non-statistical and dependent on the composition of the monitored two-photon products. The coherence feature is most pronounced in the caged two-photon channels. Time-dependence of the two-photon uncaged/caged branching ratio reflects the dynamics of the solvent cage. Observation of a transient product channel in the dissociation of $I_2^-(OCS)_{11}$ demonstrates incoherent control of two-photon dissociation pathways by appropriately timing the two laser pulses.

Although the results presented here are for a single cluster ion, the main conclusions are general and pertain to gas-phase caging dynamics in any cluster ions. For example, similar results were obtained for $I_2^{-}(CO_2)_{16}$.³⁹

4. ACKNOWLDGEMENTS

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