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CHAPTER 10
Time-Resolved Dynamics in Large Cluster Ions

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Introduction

In recent years a number of groups have focused on studying the spectroscopy and dynamics of large molecular cluster ions. A principal motivation for this work is the desire to develop a microscopic picture of reaction and solvation dynamics in the condensed phase. The general strategy has been to prepare an ionic chromophore clustered with a solvent of specific size and composition, and then explore the photophysics. This approach affords the opportunity to study the stepwise effect of increasing solvation on electronic structure and reactivity. This methodology has been successfully used by several groups in recent years to study a variety of species. The complexity of the experimental data have almost always led to multi-faceted investigations, integrating experiment, ab initio structure calculations, and molecular dynamics simulations. For example, there have been theoretical and experimental studies of hydrated electron clusters, \((\text{H}_2\text{O})_n^+\), comparing\(^{1,2}\) the electronic states to those of the bulk hydrated electron. In addition, Lisy and coworkers have utilized vibrational absorption of \(\text{Cs}^+(\text{MeOH})_n\) clusters as a probe for solvent shell structure.\(^{4}\) Further, several groups have studied excited state proton transfer (ESPT) in small clusters and generally find a strong solvent size dependence, where a small number of molecules are required to observe a photoinduced proton transfer to the solvent, forming an ion-pair complex.\(^{5-10}\)

Our approach has been to study photoinduced intracluster chemical reactivity, focusing on caging of the photodissociated anion in \(\text{I}_2^+ (\text{CO}_2)_n\) and \(\text{ICl}^- (\text{CO}_2)_n\) clusters. In these experiments, a dissociative transition is photexcited in the ionic chromophore, and subsequent measurements probe the effectiveness of the solvent cage to induce recombination. The quantum yield for recombination is measured as a function of cluster size, which begins to develop a microscopic picture of the solvent in this process. For \(\text{I}_2^+\) in \(\text{CO}_2\) solvent, unit quantum yield for recombination was observed for \(n=16\), suggesting that 16 \(\text{CO}_2\) molecules are required to form the first solvent shell around the chromophore.\(^{11}\) Subsequently, time resolved pump-probe experiments were employed to follow the transient \(\text{I}_2^+\) absorption bleach created by the photodissociation.\(^{12-17}\) This experiment revealed coherent \(\text{I}_2^+\) motion lasting approximately 3 ps, arising from the action of the solvent shell. In these experiments, we compare our results to analogous experiments in solution. For example, Barbara and coworkers have recently studied \(\text{I}_2^+\) caging in a variety

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of solvents and observed coherent motion remarkably similar to our cluster results. The aggregate of all these experiments argues persuasively that mass-selected cluster ions are useful tools in modelling reactivity in solution and often allow a more detailed picture of the role of the solvent in reactive processes.

While the excess charge on the ion is essential for preparing and isolating a species of a given size, it also introduces an array of interesting new phenomena. For example, the electrostatic interactions between the solvent and the charged I⁺ solute are much stronger than for solvated I; and these enhanced forces will greatly affect reactivity. Consider photoexcitation of I⁺ (CO₂)₆ clusters, where the charge is initially symmetrically distributed between the two iodine atoms. Photoexcitation to a dissociative state that forms an I⁺ I⁻ based product is a dissociative electron transfer process, where the solvent is expected to exert considerable forces on the dissociation. There will be a dynamic competition between the electrostatic attraction to reform the I⁻ bond, and the solvent, which will try to localize the charge onto one of the atoms. Photodissociation in ICl⁻ (CO₂)₆ clusters with a partially completed solvation shell is considerably more complex and interesting because of the initial asymmetric charge distribution between the I and Cl atoms. Due to its smaller size and larger electron affinity, the Cl end of the diatomic anion will be preferentially solvated, leaving the I end almost bare for clusters of four or fewer CO₂ solvents. Following photoexcitation nominally correlating to an I⁻ dissociation asymptote, we have observed Cl⁻ products. Such products must result from charge transfer from I to Cl within the disintegrating complex. This charge switching process most likely also occurs in I⁻ (CO₂)₆ clusters, but since we rely on the detection of mass analyzed photoproducts, such a process cannot be confirmed. In this article, we highlight recent results on I⁻ (CO₂)₆ and ICl⁻ (CO₂)₆ clusters, utilizing nanosecond photofragmentation to determine the effect of solvation on the respective geometric and electronic structures and draw comparisons between these two clusters species. In addition, we present results on pump-probe photofragmentation of I⁻ (CO₂)₁₄ to follow the solvent-induced recombination in real time and describe forthcoming experiments on ICl⁻ (CO₂)₆ clusters.

Experimental Setup

A detailed description of the tandem time of flight mass spectrometer and the ultrafast laser system has been given previously and so the apparatus will only be described briefly here. Cluster ions are produced by electron impact ionization of a free jet expansion. Clustering occurs via nucleation of CO₂ molecules around an I⁺ core ion during the several hundred microseconds that the ions drift in the expansion; after 20 cm of drift, a pulsed electric field injects the clusters ions into a Wiley-McLaren time of flight mass spectrometer. Mass-selected ions are photoexcited by either a 6 nanosecond or 200 femtosecond laser pulse and the resulting ionic photofragments are analyzed in a second time of flight region.

The ultrafast laser system consists of a mode-locked synchronously pumped dye laser, which after pulse compression and further amplification yields 200 femtosecond pulses with 1 mJ pulse energy. The 720 nm pulse was split in two equal intensity components (pump and probe) and the pump pulse travelled a fixed distance, while the probe pulse travelled a variable distance to create the optical delay for the pump-probe transient bleaching measurements.
Results and Discussion

A) Cluster Structure

Before proceeding to a discussion of the dynamics of the caging process, it is illustrative to provide a qualitative picture of the geometric structure of the I$_2$ (CO$_2$)$_n$ clusters. We have calculated minimum energy structures for $n=8,16$, shown in Figure 1. These structures were calculated by a Monte Carlo simulation where the potential included the I$_2$ internuclear potential, the I$_2$-CO$_2$ interactions, and the CO$_2$-CO$_2$ interactions. Of particular interest is the packing of CO$_2$ molecules around the I$_2$ core. For the $n=16$ cluster, the solvent molecules are evenly distributed and this size represents the closing of the first solvent shell. However, for the I$_2$ (CO$_2$)$_n$, the CO$_2$ molecules preferentially solvate one end of the I$_2$. While this asymmetric packing can arise solely from the fact that the CO$_2$-CO$_2$ bond strength is comparable to the I-CO$_2$ bond strength, the asymmetry itself produces an electric field which polarizes the charge distribution on the I atoms, enhancing the solvation energy of the cluster. Similarly, Monte Carlo simulations of ICl$^-$ (CO$_2$)$_n$ ions (n≤5) show unequivocally a preferential packing of the CO$_2$ molecules around the smaller Cl atom, further polarizing this initially asymmetric charge distribution. In this case, four or five CO$_2$ molecules are required to completely enclose the Cl end of the ion.

B) Potential Energy Surfaces of I$_2$ and ICl$^-$

The gas phase potential energy surfaces for I$_2$ and ICl$^-$ are shown in Figure 2. The semi-empirical I$_2$surfaces were developed by Chen and Wentworth using dissociative electron attachment data. The ground state is parameterized by $r_e=3.23$ Å and $\omega_e=113$ cm$^{-1}$; all the excited states are dissociative. The ab initio ICl$^-$ potential surfaces, produced by all-electron MRCl calculations using a moderate size basis (-DZP), a Davidson correction for size consistency and an empirical spin-orbit correction, are characterized by an $\Omega=1/2$ ground state with $r_e=2.91$ Å and $\omega_e=185$ cm$^{-1}$, and dissociative excited states. Further, CCSD(T) calculations yielded very similar results. All calculations were performed with the MOLPRO ab-initio program. Inspection of these curves illustrates the increased complexity of ICl$^-$ photodissociation relative to I$_2$, as evidenced by the increased number of dissociation asymptotes.

These potential energy curves only provide qualitative information concerning the electronic.
structure of I₂ and ICl'. The excited Ω=1/2 states give rise to three absorption bands in the visible spectrum: The two lower energies states dissociate to I, while the highest energy state dissociates to Cl. The calculated absorption strengths for the Ω=1/2 transitions are plotted in Figure 3 on the same intensity scale with the experimental data. In our experiments, we have verified the qualitative nature of these potentials and demonstrated that only I is seen as a dissociation product following 600-700 nm photoabsorption. A very weak Cl⁻ product is first observed near 500 nm, but only becomes a significant channel at much shorter wavelengths. Detailed measurements of the 700 nm Ω=1/2 photoabsorption are shown in the next section to establish the validity of the calculated bare ion absorption spectra. In the presence of solvent, care must be taken in extrapolating these surfaces to large internuclear separation where the important dynamics occur.

C) ICl' Absorption and Bond Strengths

As shown in Figure 3, we have measured the photodissociation cross sections for the ICl' + hν → I⁻ + Cl transition in isolated ICl'. The I' photofragment intensity was normalized to the parent ion signal and to the laser intensity to provide relative cross sections. An absolute photodissociation cross section was measured at 644 nm via parent ion depletion and the entire spectrum was then scaled. The spectrum is ~90 nm wide and peaks at ~690 nm with an absorption coefficient of 2.5 × 10⁻¹⁸ cm². These results for this band are in good agreement with the theoretical spectrum. The absorption spectrum of ICl' with CO₂ solvent molecules will be measured to study the effect of solvation on the electronic structure of the chromophore.

The bond strength of ICl' was obtained by analyzing the neutral Cl atom recoil velocity following photodissociation. The observed doublet splitting in the Cl atom arrival time distribution is simply related to the kinetic energy release of Cl⁻ I during photodissociation; from this splitting the bond strength of ICl' is found to be 1.1 ± 0.15 eV. To our knowledge, this is the only spectroscopic measurement of the ICl'
bond strength; it is in good agreement with the value of 0.95 ± 0.1 eV derived from a charge transfer threshold study.22 Similarly, we found the bond strength of I\textsuperscript{2} to be ~1.2 eV.

![Graph showing absorption cross section vs wavelength](image)

**FIGURE 3**

Theoretical and Experimental Absorption Spectrum of ICl\textsuperscript{−}

**D) Caging Fractions**

The caging efficiency and timescales for recombination of I\textsuperscript{2} in solution are known to be strongly dependent upon the solvent.\textsuperscript{23} Here we compare the caging probabilities for I\textsuperscript{2} and ICl\textsuperscript{−} in CO\textsubscript{2} solvent. In these experiments, a transition is excited from the ground state to a dissociative state as shown in the potential surfaces in Figure 2. The excitation wavelengths were chosen to give similar kinetic energy release for both ions. In these measurements, the products of photoexcitation are monitored and we observe a mixture of caged and uncaged, e.g. I\textsuperscript{−} (CO\textsubscript{2})\textsubscript{n−}, and I\textsuperscript{−} (CO\textsubscript{2})\textsubscript{n+}, photofragments. Measurement of this branching ratio as a function of cluster size provides a microscopic view of the efficiency of the solvent in inducing recombination.

The caging fractions as a function of cluster size for I\textsuperscript{2} and ICl\textsuperscript{−} in CO\textsubscript{2} solvent are shown in Figure 4. The caging fraction for I\textsuperscript{2} increases monotonically (almost linearly) with the number of solvent molecules and becomes unity at n=16, providing further support for this number of solvent molecules closing the first solvent shell. At comparable kinetic energy release, the caging dynamics for ICl\textsuperscript{−} are qualitatively different, as evidenced by significant caging at smaller cluster size. This difference results largely from the difference in geometric structure: For I\textsuperscript{2}, the charge is symmetrically distributed and the first few solvent molecules pack around the center of mass, while for ICl\textsuperscript{−} the first CO\textsubscript{2} molecules pack around the smaller and more electronegative Cl atom. This latter arrangement produces a fairly strong electric field component along the bond axis; such a field will distort the electronic structure of the
diatomic ion in a fashion that favors caging. The dissociation kinematics also favor ICl' caging for small clusters: Upon dissociation the light Cl fragment takes most of the released kinetic energy. It is surrounded by a solvent whose components have roughly the same mass as Cl, and this is an efficient energy transfer partner. This asymmetric structure is not present for I$_2$ clusters, and the mass match is missing; both these effects will reduce the I$_2$ caging efficiency relative to ICl' for small cluster size. Unit caging efficiency for ICl' is not observed because as will be shown an internal charge transfer occurs resulting in Cl' based products.

E) ICl' (CO$_2$)$_n$ Photofragmentation

Photofragmentation of ICl' (CO$_2$)$_n$ clusters was studied at 644 nm to investigate the role of the solvent on the dynamics of the photodissociation process. At this wavelength photodissociation of bare ICl' produces only an I' ionic product. When there is partial solvation of the ICl' ion, one might still expect primarily I' photoproducts, as the I end of the diatomic anion has no CO$_2$ solvents attached to it for n≤4. However, other photoproducts are observed in this size range. There are three different product channels observed:

ICl' (CO$_2$)$_n$ + hν \[\rightarrow\] I' (CO$_2$)$_j$ + mCO$_2$ + Cl
\[\rightarrow\] ICl' (CO$_2$)$_k$ + kCO$_2$
\[\rightarrow\] Cl' (CO$_2$)$_p$ + pCO$_2$ + I

The first corresponds to the expected I' release and is dominant for the smallest clusters. The other two channels reflect recombination or electron transfer to the Cl' moiety within the disintegrating complex. These last "reaction product" channels become dominant as the cluster size increases, as shown
in Figure 5. It is clear that in both product channels the role of the solvent is extremely important. When the charge (which was localized on the Cl end) transfers to the I' moiety, the solvent moves toward the newly formed ion. Since the larger I' ion will be less solvated than would Cl', and the electron binding energy is less for I', there will be a time late in the solvent reorganization process when it is thermoneutral for the electron to transfer back to the Cl atom. Depending on the I-Cl distance at this time, there may be a significant probability for this curve crossing to occur. The experimental data show that this crossing probability is near 25% for ICl· (CO₂)₄. The driving force for this process derives from the differential solvation energy of Cl' and I' at large internuclear separation. This charge transfer may also occur for I₂ based clusters but is not observable in our experiment for the symmetric chromophore.

![Graph showing yield vs number of CO₂ solvent molecules]

**FIGURE 5**

Photofragmentation Products of ICl· (CO₂)₄ Clusters

**Recrmination Dynamics**

Having mapped out caging fractions in I₂ (CO₂)₄ clusters at 720 nm, we probe the time dependence of the recombination dynamics. The one color pump-probe photofragmentation experiment can be described as follows: Following dissociative photoexcitation of the I₂ at 720 nm, the two I atoms move to large internuclear separation and the cluster will then be transparent to further 720 nm excitation. Upon solvent induced recombination, the cluster can absorb a delayed probe pulse of 720 nm. Each absorption results in the evaporation of several solvent molecules and the intensity of mass-analyzed photofragments resulting from absorption of two photons are monitored as a function of pump-probe delay. This absorption recovery for I₂ (CO₂)₄ is shown in Figure 6. Inspection of these data show several interesting features. The absorption recovery is effectively complete by ~10 picoseconds, a timescale which is very rapid compared to neutral I₂ in solution (30-1000 ps). In addition, there is a "bump" or recurrence in the absorption recovery at 2 picoseconds. Recombination on the ground state surface cannot account for a nonmonotonic absorption recovery and we turn to the I₂ potential energy curves shown in Figure 2 for a clue as to the origin of this feature. Inspection of these curves in conjunction with polarization dependencies of the absorption recovery suggests this feature arises from coherent motion on the first two excited state surfaces. Since there are no bound excited states, this coherent motion arises solely from the collective action of the solvent.

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A major goal of this research is to compare the cluster ion results to those in the condensed phase. Barbara and coworkers have recently studied the caging of $I_2^+$ in various solvents and find results remarkably similar to our work on $I_2^-$ (CO$_2$)$_n$. They observe absorption recovery times of several picoseconds, just slightly more rapid than for the cluster case. It is particularly striking that for several solvents, they also observe a recurrence at approximately 2 picoseconds. It is very tempting to assert that this feature arises from the same physics in both the solution and cluster environment. In any event, the experiments compel the conclusion that the caging dynamics of $I_2^+$ are governed primarily by the action of the first solvent shell.

Conclusions and Future Directions

We have presented an overview of our recent work on caging of the anion in $I_2^-$ (CO$_2$)$_n$ and ICl$^-$ (CO$_2$)$_n$ clusters and have begun to develop a microscopic picture of the role of the solvent in this seemingly elementary process. These experiments certainly raise as many questions as they answer and point to the necessity of a variety of future time resolved experiments. A particularly interesting experiment will probe the charge transfer processes in the photodissociation of ICl$^-$ (CO$_2$)$_n$, using a photoelectron probe pulse to gauge the solvent response to the new charge distribution created upon photodissociation. This time-resolved photoelectron spectroscopy will enable the extension of these ideas to more complex intracluster photochemistry.

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