

## Chapter 1

### Understanding Photodissociation of Molecular Cluster Ions

The fable of the blind men and the elephant [1] teaches us that to reveal the true nature of something mysterious and new we must be careful not to draw our conclusions from any one fragment of information, but rather incorporate a wide range of observations. I have been fortunate to be involved in a course of research at a time when a critical mass of information has become available and it is possible to see how it can all fit together to reveal new insights. The challenge has been in reconciling seemingly contradictory data, filtering out misinformation and irrelevant details, and stripping away false assumptions. What results is a clearer view of the relatively simple pieces that create a complex but understandable whole.

Understanding the effects of solvation on simple chemical reactions is a central goal of chemical dynamics. Recent advances in modeling the photodissociation and recombination of dihalide anions in clusters have enabled us to make predictions of novel dynamics which can be, and in many cases have been, verified experimentally. Furthermore, the strong solute-solvent interactions which result from the charged nature of these systems open up reaction pathways that are not well described by traditional conceptualizations of the dynamics. Results of several recent experiments have the potential to teach us much more about the dynamics on excited electronic states, if we can learn to tease out the information from the experimental signals. This highlights the continued need for analysis of molecular dynamics calculations which reaches beyond

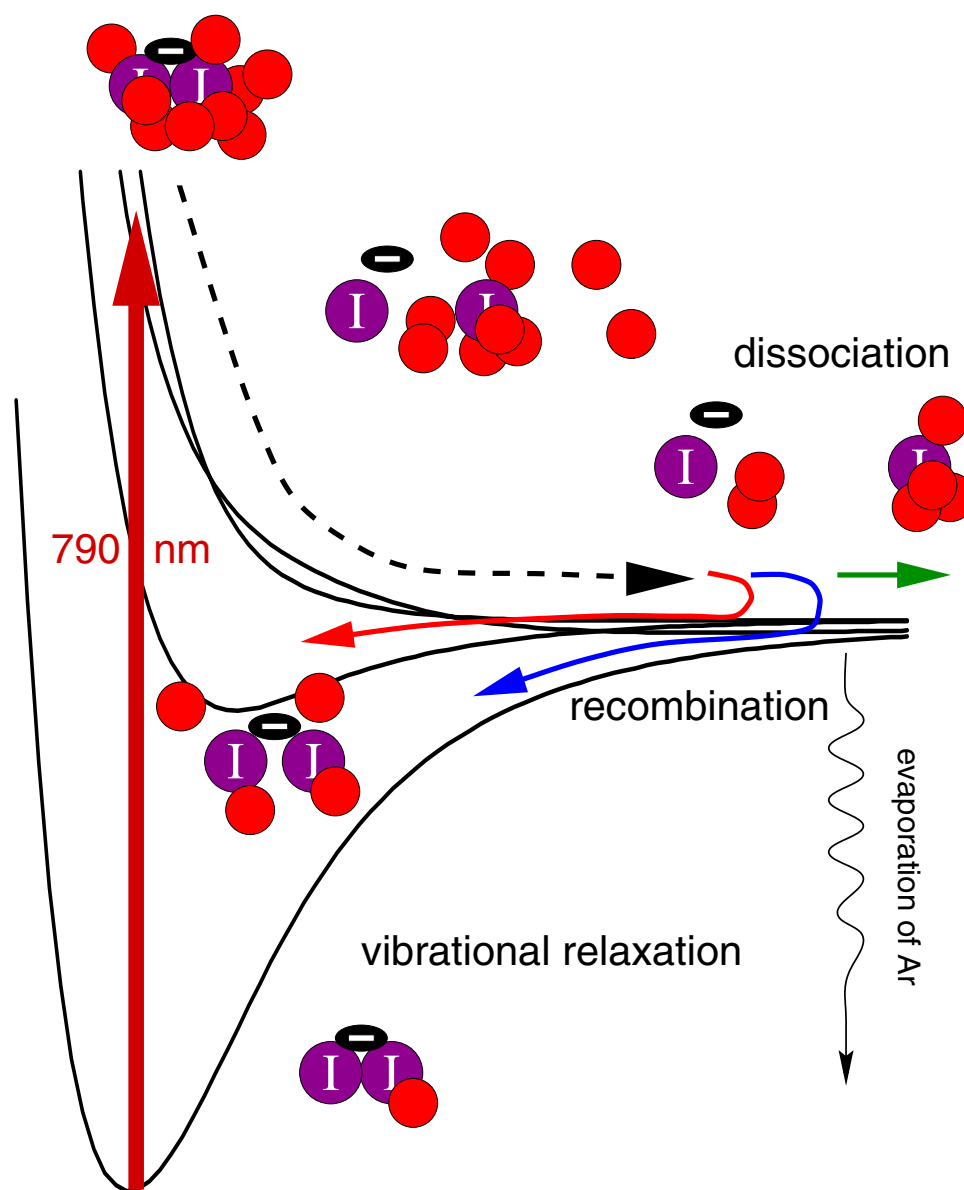


Figure 1.1: Photodissociation and recombination of solvated  $I_2^-$ .

comparing final product distributions and seeks to uncover the mechanisms through which the products form. The goal of this thesis is to explore the simulated dynamics and develop techniques to bring simulations to bear on experimental results.

An important lesson featured here is that the reaction dynamics of solvated molecular ions cannot be understood solely in terms of the potential curves of the isolated solute. Nevertheless, these curves provide a starting point for discussion. Figure 1.1

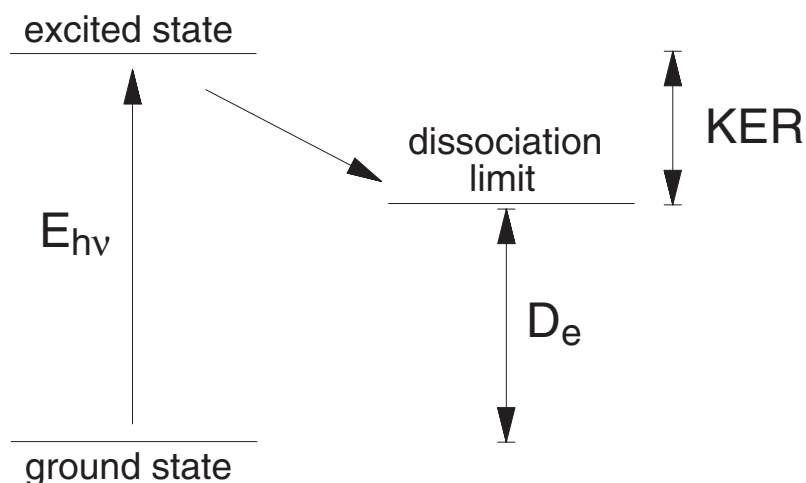


Figure 1.2: Energy disposal following solute excitation.

illustrates the photodissociation dynamics of  $\text{I}_2^-$  solvated by a small atomic cluster. The potential curves shown are the four lowest electronic states of the isolated solute. The thick arrow represents photoexcitation of  $\text{I}_2^-$  to a repulsive electronic state. As  $\text{I}_2^-$  breaks apart, the excess charge localizes onto one iodine atom and the fragments interact with the cluster atoms. In small and weakly bound clusters, the solute dissociates completely. When the interaction with the solvent is strong, dissociation is halted and the fragments recombine on either of the two lowest electronic states. Evaporation of solvent atoms from the cluster removes excess energy, allowing the solute to vibrationally relax.

What is missing from this picture is information about **how** the solvent exerts its influence on the photodissociation reaction. A conventional way to depict the solvent cage is to sketch in a repulsive wall from which the solute recoils at large bondlengths. This illustrates the role of “kinematic caging”, which does play an important part in inducing recombination, but utterly fails to describe the Coulombic interactions between the solute and solvent, referred to as “electrostatic caging”, which play a crucial role in the dissociation of solvated ions.

The interplay between the solute charge distribution and the solvent environment

is exemplified by the photodissociation of  $\text{I}_2^- \text{Ar}_n$  clusters. In the photofragmentation experiments of Vorsa et al.,  $\text{I}_2^- \text{Ar}_n$  clusters were excited at 790 nm and the products were mass analyzed [2]. For intermediate cluster sizes ( $n \approx 13$ ), a bimodal distribution was observed among the dissociative products,  $\text{I}^- \text{Ar}_k$ . One product channel remained peaked around  $k = 1$  regardless of the initial cluster size, while the other channel reflected a loss of roughly 7 argon atoms ( $k = n - 7$ ). The heavier products are consistent with the standard interpretation of the photodissociation process as illustrated above, which assumes that the amount of energy available for solvent evaporation is given by the photon energy minus the solute bondstrength, as shown in Fig. 1.2. The implicit assumption about the dynamics of the process is that the  $\text{I}_2^-$  bond breaks, leaving  $\text{I}^-$  solvated by a hot cluster which evaporates argon atoms as it cools. Given this view of the reaction, it is difficult to account for the low mass products, and a satisfactory explanation did not surface until simulations revealed that a second mechanism is at work, in which  $\text{I}^-$  is ejected, leaving behind a neutral cluster [3]. At the source of this surprising behavior, which has been experimentally verified, is a phenomenon called anomalous charge flow, which will be discussed in detail beginning in Chapter 2. The point to be made here is that the interpretation presented in Fig. 1.1 leads us to believe there is a single dissociative asymptote for  $\text{I}_2^-$ , whereas in an asymmetric solvent environment, which shifts the relative energies of each electronic state, this is no longer true. The unanticipated dynamics resulting from the strong coupling between the solute and solvent are explored in this thesis. The implications of these results for the analysis of recent experimental findings are also considered.

## 1.1 Background

The term “caging” was first coined by Franck and Rabinovitch in the 1930’s to describe the trapping and recombination of dissociating fragments induced by a solvent bath [4]. Further studies by Noyes and coworkers focused on determining how

excitation wavelength and solvent viscosity affect caging efficiency [5–8]. The first time-resolved experiments on  $I_2$  photodissociation revealed that the overall process required from 50-200 ps up to nanoseconds, depending on the solvent [9]. Modeling of the process by Nesbitt and Hynes determined that the timescale was a measure of the slow vibrational relaxation, not electronic relaxation which was expected to be much faster [10]. This was followed by a second wave of  $I_2$  experiments with better time resolution [11–17].

In the mid 1980's, Lineberger and coworkers began investigating the photodissociation of dihalide ions embedded in mass-selected molecular clusters. Levinger and Alexander developed experimental methods to produce and detect  $X_2^-(CO_2)_n$  clusters ( $X = I, Br$ ) [18, 19]. Their mass selected photofragmentation experiments studied caging efficiency as a function of initial cluster size ( $n$ ) and found that long range electrostatic forces present in these charged systems greatly enhance caging relative to neutral  $I_2$  in solution.

Building on these results, Papanikolas et al. used a combination of experiments and modeling to elucidate the dynamics of the recombination process [20]. In their pump-probe experiments, a 720 nm pulse excites  $I_2^-$  to the  $A'$  electronic state, initiating photodissociation. A second 720 nm pulse monitors the progress of the reaction at various delay times. Immediately following the initial pulse, the absorption is bleached, the probe photon is not absorbed. At longer delay times, as  $I_2^-$  is caged by the solvent and recombines, its ability to absorb at 720 nm is restored. The absorption recovery profile, therefore, contains information about the timescales for electronic and vibrational relaxation. In addition to the overall recovery of the absorption signal, a transient feature at a time delay of 2 ps was observed for the larger clusters [21, 22]. Barbara and coworkers probed  $I_2^-$  photodissociation in liquid solution with direct absorption measurements and also found evidence of enhanced absorption within a few picoseconds of excitation and a similar overall timescale for recombination [23, 24]. These two sets

of experiments generated considerable interest in the photodissociation of molecular cluster ions and yielded several plausible explanations to account for the experimental observations. The most popular theory was that the transient absorption peak was evidence of coherent motion of  $I_2^-$  at the inner turning point of the  $A$  state; however, this was never conclusively demonstrated.

The first, and for several years the only, theoretical treatment of this problem was carried out by Amar and Perera. Their simulations of the photodissociation of  $Br_2^-(CO_2)_n$  clusters were the first to include, in even a crude way, the dynamics on the excited electronic state [25]. Recognizing the importance of incorporating the ionic nature of the system into the dynamics, they modeled charge mobility by assigning a partial charge to each bromine atom and allowing these charges to vary as a function of the solute bondlength, such that as the molecule dissociates, the charge becomes localized on one atom. That is,  $Br_2^-$  dissociates to form  $Br^-$  and  $Br$ . The atom which receives the charge was chosen at random. In the presence of a solvent cluster, this leads to two scenarios: one in which the charge localizes on the solvated atom (Case A) and another in which the charge and solvent are separated (Case B). Although Case A is the result one would conventionally assume, they investigated both possibilities and found that the subsequent dynamics differed greatly in the two cases. For example, the second, counterintuitive, charge localization scheme produced caging from clusters with only one end of the solute 'capped' by a solvent molecule at an axial position, while caging with the normal charge localization scheme required capping at both ends of the solute. The dynamics clearly showed that in both cases, the kinetic energy of the dissociating bromine atoms was effectively quenched by collisions with solvent molecules at the cap sites. Additionally, in Case B, the uncapped, but charged, bromine atom was unable to escape the attractive electrostatic force of the solvent cluster, thus producing caging from half a solvent shell, consistent with the experimental results of Alexander et al. Amar and Perera gave no rationale for this anomalous charge localization, and some

researchers in the field initially dismissed it as an artifact of the simulation procedure; however, Maslen et al. subsequently demonstrated that it is correct [26]. Although the evolution of a more sophisticated treatment of the excited state dynamics required several years and contributions from multiple researchers, the localization of charge on the less solvated atom leading to electrostatic caging, first suggested by Amar and Perera, is now generally accepted as a fundamental characteristic of the photodissociation dynamics.

Until recently, subsequent simulations focused on characterizing the relaxation dynamics following recombination on the ground electronic state. The  $I_2^-(CO_2)_n$  cluster dynamics developed by Papanikolas et al. improved on the treatment of the solute electronic structure implemented by Amar and Perera by incorporating the polarization of  $I_2^-$  by the solvent [27]. This was accomplished by extending the charge switching function to depend on the strength of the electric field produced by the solvent environment [26]. They found that the delocalization of charge that accompanies recombination forces the solvent to reorganize and therefore efficiently transfers energy from the solute bond into the cluster. This is in agreement with bulk liquid simulations by Hynes, Benjamin and coworkers which conclude that charge flow on the ground electronic state accelerates the rate of vibrational relaxation [28–30].

## 1.2 Recent Advances

Several additional systems have been studied by the Lineberger group including  $I_2^-$  in a variety of solvent clusters and at multiple wavelengths and  $ICl^-$  in  $CO_2$  clusters.  $I_2^-Ar_n$  clusters were the first of these systems to be explored jointly with experiments and theory on roughly equal footing. In late 1996, Batista and Coker [31], and Faeder et al. [3] independently used nonadiabatic surface hopping methods [32] to simulate the excited state photodissociation and recombination process explicitly. Batista and Coker employed a semiempirical Diatomics-in-Ionic-Systems Hamiltonian, while we

have developed a model Hamiltonian based on **ab initio** electronic structure calculations and the distributed multipole analysis of Stone and coworkers [33]. Both simulations reproduce the experimental product distributions reported by Vorsa et al., which revealed a bimodal distribution of recombined products [2]. Several possible explanations for this had been proposed, but both simulations found that recombination on the first excited state and the ground state of  $I_2^-$  was the cause. In addition, our simulations revealed the mechanism for  $I^-$  escape, which leads to a bimodal distribution of dissociative products, as mentioned earlier.

These theoretical results have since been verified by time resolved techniques. Femtosecond photoelectron spectroscopy (FPES) techniques developed by Neumark and coworkers provide a complement to the absorption recovery techniques of the Lineberger group by monitoring the cluster energetics through the photodissociation process and providing information about the changing solvation dynamics [34–37]. In these experiments,  $I_2^-$  is excited at 780 nm and after a variable delay time a second, high-energy pulse detaches the electron. By measuring the excess kinetic energy of the electron, one can determine the energy of the cluster which in turn is a function of the instantaneous cluster configuration. Comparison of experimental and simulated spectra verify anomalous charge flow on the dissociative excited states and recombination on the first excited state [38, 39]. Furthermore, overall timescales agree well throughout the dynamics (complete relaxation requires  $>200$  ps). This is in agreement with earlier results of Lineberger and coworkers [40].

As for the photodissociation of  $I_2^-(CO_2)_n$  clusters, the results presented here, considered along with the work of our experimental collaborators in the Lineberger [21, 22, 40–43] and Neumark [39] groups and in the Coker group [44], show we have a solid understanding of this system. The bulk of this thesis is devoted to exploring the dynamics of this system.

Hovering around the fuzzy line between what we do and don't understand are the

dynamics of  $\text{ICl}^-(\text{CO}_2)_n$  clusters. Experiments by Nadal et al. hint at the complexity of solvent perturbation of the solute electronic states [45, 46]. The photofragmentation products, which include  $\text{I}^-$ ,  $\text{Cl}^-$ , and  $\text{ICl}^-$  based clusters, show a complicated dependence on the initial cluster size, again emphasizing that the isolated solute potential curves are inadequate for deducing which dissociative asymptotes are accessible. Current research in the Parson and Lineberger groups is aimed at uncovering the mechanisms at work in this system [47, 48].

Finally, there are the experimental results about which theory has thus far had little to say. These include the two-photon photofragmentation experiments [22, 49] and two-color pump-probe experiments [41, 50] on solvated  $\text{I}_2^-$  clusters of Lineberger and coworkers and the solution phase experiments of the Barbara group which investigate the photodissociation dynamics of  $\text{I}_2^-$  in a range of solvent baths using multiple probe wavelengths [23, 24]. Each class of experiments provides a wealth of information about the photodissociation process, including details about the break up of the solvent cage (clusters), and lifetimes of the excited electronic states. To date, there has been insufficient knowledge of the spectroscopy of the excited solute-solvent system to extract this information, with confidence, from the experimental signals. This is an ideal opportunity for exploiting the advantages of molecular dynamics simulations and collaborations are underway to make progress on this front.

### 1.3 Thesis Overview

Chapter 2 gives an overview of the model developed by the Parson group that was used to calculate the results presented in this thesis, and describes methods to analyze the simulation trajectories. Chapter 3 describes the dynamics following 790 nm excitation of  $\text{I}_2^-(\text{CO}_2)_n$ . Chapter 4 provides evidence for fast spin-orbit relaxation in  $\text{I}_2^-(\text{CO}_2)_n$  following UV excitation. Simulation of the absorption recovery is presented in Chapter 5. Chapter 6 compares the dynamics of  $\text{I}_2^-(\text{CO}_2)_n$  and  $\text{I}_2^- \text{Ar}_n$ . Finally, Chap-

ter 7 describes work in progress developing a potential model for  $I_2^-(OCS)_n$  clusters.

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