

An Ultrafast Glimpse of Cluster Solvation Effects on Reaction Dynamics

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Contents

1. Introduction	4039
2. Cluster Types and Production	4040
3. Experimental Methods Using Laser Spectroscopy	4041
4. Ionization Processes in Clusters	4042
A. The Formation of Protonated Ammonia Clusters: A Paradigm	4042
B. The Phenomenon of Coulomb Explosion	4042
a. Quantifying Coulomb Explosion	4043
b. Direct Evidence for the Role of Clusters in the Coulomb Explosion Process	4045
c. Consideration of Models of Coulomb Explosion	4046
d. Ionization Dynamics and Coulomb Explosion: Chemical Applications	4048
5. Cluster Solvation Effect on Reaction Dynamics	4048
A. Excited-State Proton Transfer	4049
B. Electron-Transfer Reactions	4051
C. Caging Dynamics	4053
6. Outlook	4054
7. Acknowledgment	4055
8. References	4055



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Cluster science has undergone an explosive growth in activity during the past few years, prompted both

1. Introduction

Determining the influence that solvation has on the dynamics of chemical reactions^{1–8} is one of the scientifically challenging problems in the field of chemical physics. There is particular interest in contrasting differences in the behavior and reactivity of ions as well as neutral species in the gaseous compared to the condensed phase, and studies of clusters at selectively increased degrees of aggregation offer the opportunity to explore the changes due to solvation. In this context, studies of selected chromophores excited within clusters, or cluster ions produced via selected ionization, and of the “ensuing solvation” that takes place within a cluster shed light on the understanding of excitation processes in the bulk condensed state.^{9–25} In terms of basic knowledge, the results of studies of the interaction of ions and molecules provide information on the forces involved and gas-phase studies of interactions within a cluster can contribute to knowledge about the structure and bonding of complexes having analogies to those existing in solutions.

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by the large number of basic problems to which studies of clusters may provide new insight as well as the vast array of applied areas to which clusters relate. Elucidating from a molecular point of view the differences and similarities in the properties and reactivity of matter in the gaseous compared to the condensed state has been an overriding theme of many of the investigations, with both experimental and theoretical attention being directed to studies of structure, thermochemical properties, reactivity, and dynamics.

In addition to their application in elucidating the molecular details of condensed matter, studies of clusters also serve to reveal the microscopic aspects of nucleation phenomena, including the formation of highly dispersed media having a large surface-to-volume ratio, e.g., aerocolloids, ultrafine particles, and nanoscale materials. Investigation of thermochemical properties as well as the kinetics of association reactions has been particularly important in the subject of phase transitions, where progress has been impeded by lack of fundamental data for comparison with molecular theories. Related both to studies of condensed phases as well as surfaces are investigations involving the scattering of high-energy neutrals and ionic particles from surfaces, where clusters (usually in ionic form) are often the observed reaction products. Determining factors that influence their size, stability, and mechanisms of formation provide a basis for explaining the results of such experiments.

Ionization accompanied by subsequent mass-spectrometric detection has usually been the most widely used technique to quantify the size-dependent properties of large clusters. However, the ionization step ultimately involves a relaxation about the newly formed charge, with concomitant evaporative dissociation and sometimes other chemical reactions taking place. In addition to providing details on the energetics of interactions, studies of cluster ions yield information on basic mechanisms of ion reactions within the cluster (termed an intracuster reaction, sometimes distinguished as an ion–molecule half-reaction). The entire course of a chemical reaction following either a photophysical or ionizing event depends on the mechanisms of energy transfer and dissipation away from the primary site of absorption. Neighboring solvent or solute molecules can influence this by collisional deactivation (removal of energy), through effects in which dissociating molecules are kept in relatively close proximity for comparatively long periods of time due to the presence of the solvent and in other ways where the solvent influences the energetics of the reaction coordinate. Through the use of supersonic molecular beams, it is now possible to produce and tailor the composition of virtually any system of interest. Utilizing these methods, coupled with laser spectroscopy, one can selectively solvate a given chromophore (site of photon absorption/site of ionization) and investigate changes between the gas and condensed phase by selectively shifting the degree of solvent aggregation, i.e., the number and location of solvent molecules attached to or bound about the site of absorption of the electromagnetic radiation.

This review deals largely with work involving neutral van der Waals/hydrogen-bonded clusters. It attempts to show the readers some of the recent developments in the field and the breadth of the scientific questions which are being addressed through investigations of the kinetics and dynamics of reactions mediated through the presence of bound solvent molecules. In addition to the prospects of investigating new fundamental phenomena through their study, extensive work on clusters has been motivated by the promise of providing insights into the possibility of using clusters as building blocks for assembling new nanoscale materials. To bring these prospects to fruition entails detailed investigations of their unique physical and chemical behavior. The processes of interest occur on very short time scales and require special techniques for direct observation. Herein we consider the important subject of the reaction dynamics of clusters, also with particular consideration to a unique phenomenon termed “Coulomb explosion” which we have found can be enhanced in the case of irradiating clusters with femtosecond light pulses of moderately high fluence.

2. Cluster Types and Production

One of the exciting aspects of cluster research stems from the fact that these small aggregates have properties that often differ significantly from those of the bulk and typically display behavior that is not fully characterized as being due to a solid, liquid, or gas. Indeed, clusters are often referred to as a new state of matter. Because of their small size, a large fraction of their constituents lie on their surface and they frequently give rise to quantum effects that involve the energy levels imposed by size-dependent constraints. The field has developed along several lines including extensive efforts devoted to carbon clusters, metal and semiconductor systems, rare-gas and related van der Waals systems, as well as those composed of hydrogen-bonded molecules.⁷ The latter are of primary value in elucidating the important process of proton transfer that pervades so many fields.

Molecular clusters constitute an aggregated state of matter in which the individual constituents are held together by forces that are relatively weak compared to those responsible for the chemical bonding of the constituent molecules. Hence, by necessity, neutral clusters are usually formed by utilizing supersonic expansion techniques, which facilitate cooling and concomitant association steps leading to their growth. Supersonic expansion techniques including both continuous sources as well as pulsed jets are commonly used to produce beams of neutral clusters. In both cases, cooling of the beam is accomplished through the conversion of the random thermal energy of a high-pressure source gas into a directed beam velocity.²⁶ The latent heat of condensation released during the clustering process leads to internal vibrational and rotational heating of the aggregate, and clusters often do not attain internal temperatures as low as unclustered species. However, cooling collisions with an inert gas serve to reduce the internal temperature of the cluster and enable

clusters to be produced that have sufficiently long lifetimes to be interrogated in an experiment. The production of clusters of mixed composition enhances the range of systems that can be investigated, and coexpansion and pick-up source techniques have been widely developed which now enable species of virtually any composition to be prepared for investigation.

Supersonic expansion, now a comparatively mature technique, has benefited from advances provided by pulsing techniques. This not only has the advantage of requiring less extensive differential large-system pumping capacity, but has served to reduce concomitant experimental problems which may arise from unwanted collision-induced dissociation in the region where the clustered species are probed either spectroscopically and/or mass spectrometrically.

Electrospray techniques have been successfully utilized in some cases to produce ionic clusters containing more than one charge on a solvated metal cation.²⁷ This is a comparatively new development and promises to enable investigation of species that could not be heretofore explored in terms of microsolvation effects. Related thermal vaporization methods have been employed to produce clusters of neutral species from liquids.²⁸ Cluster ions also have been produced by fast atom and ion bombardment on surfaces. Particularly interesting are the developments of Michl and co-workers²⁹ in which clusters are formed by sputtering rare-gas matrixes in which various atoms and/or molecules have been trapped. The sputtering of ice surfaces has also been a promising technique to produce protonated water clusters, enabling determination of various properties.

There have been a number of modeling studies to account for the nature of cluster distributions that develop. In some cases this has been accomplished through estimates of the rate constants of the individual association reaction steps which are generally difficult to measure. The development of scaling laws has been a particularly valuable contribution to this problem, enabling a reasonable selection of the appropriate experimental conditions to produce clusters of the desired size range for study.³⁰ The resulting neutral clusters have been successfully probed using a variety of techniques, where noninvasive spectroscopic probing sometimes has provided valuable insight into the developing cluster structures.^{31–38}

In the case of metal and semiconductor clusters, the technique of laser vaporization has been especially valuable as a method for cluster production. However, condensation sources^{39–41} have been found to be very valuable methods in the case of more volatile systems, especially in forming large alkali metal clusters.

3. Experimental Methods Using Laser Spectroscopy

Not surprisingly, as in many other areas of physical chemistry, advances in experimental techniques have paved the way for new investigations into the dynamics and reactivity of molecular clusters. Through the use of lasers, studies of cluster photodepletion and photodissociation are being undertaken.^{42–48}

Concomitant investigations of cluster unimolecular and collision-induced dissociation are further contributing to an understanding of dynamical processes involved in energy transfer and reactivity.^{49–53} Additionally, *ab initio* calculations are contributing significantly to an understanding of the structure and bonding of both strongly and weakly bound clusters.

The study of neutral cluster spectroscopy and dynamics has depended in large measure on inferences reached from investigations of cluster metastability in products of dissociation. Cluster ion-dip spectroscopy, with size selection obtained through mass detection, has allowed for a comparison study of cluster size-dependent structures and spectroscopic transitions in the ground electronic state.^{54,55} Rotational coherence spectroscopy, through monitoring the quantum interference of different rotational levels in time domain, has provided useful information on cluster structure.^{56–58}

With recent advances in generating laser pulses of subpicosecond duration, a fascinating new field, femtochemistry, was born, which was pioneered by the Zewail group,⁵⁹ and many breakthroughs in this emerging field have already been witnessed over the past decade.⁶⁰ As we know, nuclear motion is the fundamental motion that characterizes chemical bonding and determines reaction dynamics at the molecular level. Time scales for nuclear motion are typically subpicoseconds for vibration and subnanoseconds for rotation. Now with the time resolution and coherence provided by femtosecond laser pulses, real-time observation of chemical reactions as they proceed along the reaction path from reactants, via transition state, toward products is made possible by employing femtosecond pump–probe techniques. In the case of neutral molecules, fluorescence spectroscopic methods have been invaluable in monitoring the course of events following their optical excitation.⁶¹ However, the vast majority of the spectroscopically related cluster work is accomplished using clusters formed via supersonic expansion and detected using time-of-flight mass spectrometry techniques (TOFMS).⁶² Improvements in fast timing electronic circuitry and the incorporation of reflection electric fields (reflectron)⁶³ have enabled high mass resolution to be attained, on the one hand, or with an alternate mode of operation direct information on kinetic energy release following metastable cluster dissociation.

In cases where clusters are subjected to intense laser fields, a detailed study of the ensuing ionization processes reveals the role of clusters in facilitating the tunneling and barrier suppression phenomena which are responsible for the generation of high charge states of ions that often arise. The Coulomb explosion phenomenon enables intermediates to be arrested at various stages of transformation in selected classes of fast reactions. In conjunction with optical responses from femtosecond laser pump–probe experiments, we have developed a method whereby the Coulomb explosion process enables the dynamical events of competitive reactive processes to be elucidated.

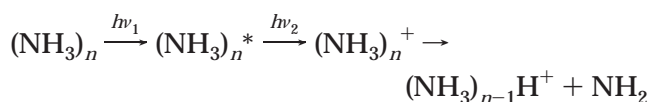
4. Ionization Processes in Clusters

A. The Formation of Protonated Ammonia Clusters: A Paradigm

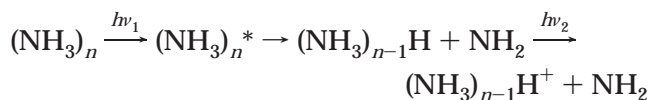
The use of femtosecond pump-probe techniques enables the identification of the detailed mechanisms of reactions at the molecular level and also to follow the course of a reaction in real time. The study of ammonia clusters has provided an example of what can be accomplished using these methods.

The ionization of ammonia clusters (i.e., multiphoton ionization,^{53,64} single photon ionization,^{65–67} electron impact ionization,⁶⁸ etc.) mainly leads to formation of protonated clusters. For some years there had been a debate about the mechanism of formation of protonated clusters under resonance-enhanced multiphoton ionization conditions, especially regarding the possible alternative sequences of absorption, dissociation, and ionization. Two alternative mechanisms^{69–75} have been proposed: one proceeds through an absorption-dissociation-ionization mechanism (ADI) and the other via an absorption-ionization-dissociation process (AID).

For the AID mechanism, intracluster ion-molecule reactions of ammonia clusters occur following photoionization



An alternative mechanism referred to as ADI considers that the neutral clusters are first excited via photoabsorption processes. Subsequent intracluster neutral-neutral reactions lead to formation of hydrogenated clusters, $(\text{NH}_3)_n\text{H}$, and ionization of the radical species results in the observed protonated cluster ions as depicted in the following



The fact that protonated clusters are observed to be formed under electron impact ionization as well as under single-photon ionization conditions provides evidence that the AID mechanism must be operative at least to some extent. The ADI mechanism was initially proposed on the basis of theoretical calculations by Kassab and co-workers⁷⁶ and supported by experimental finding that hydrogenated ammonia clusters do have lifetimes of at least a few microseconds following neutralization of the protonated cluster ions as shown by Gellene and Porter.⁷⁷ Nanosecond pump-probe experiments carried out by Misaizu et al.^{69,70} show that the lifetime of the intermediate to the formation of $(\text{NH}_3)_n\text{H}^+$ ($n > 1$) is at least 500 times longer than that to the formation of NH_4^+ and $(\text{NH}_3)_2^+$. However, due to the broad nanosecond laser pulses employed in the experiments, the issue of ionization and formation mechanisms of protonated ammonia cluster ions has not been resolved until a recent series of femtosecond

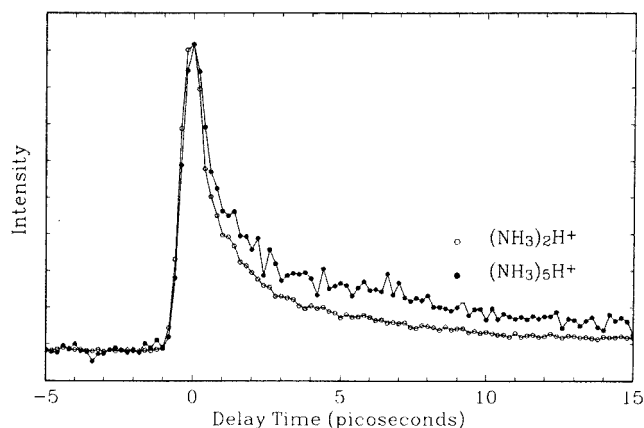


Figure 1. Pump-probe spectrum of $(\text{NH}_3)_n\text{H}^+$ ($n = 2,5$) excited to the \tilde{A} ($v = 2$) state with pump pulses at 208 nm and probe pulses at 312 nm.

pump-probe experiments by Castleman and co-workers^{71–75} and in what follows.

Pump-probe studies on the Rydberg \tilde{C}' state of $(\text{NH}_3)_n$ clusters revealed that the optical transients for all ions, i.e., protonated and unprotonated, at least for $n < 5$, are identical. This suggests that the intermediate state leading to the formation of both the unprotonated and protonated clusters is the same. The failure to observe any ionization attributable to that of NH_4 incorporated in the cluster via the predissociation of NH_3 to NH_2 and H , and subsequent reaction of H with NH_3 , eliminates the ADI path as the major mechanism for photoionization of ammonia clusters via the \tilde{C}' state.

Pump-probe experiments on the ionization of the $(\text{NH}_3)_n$ clusters via Rydberg \tilde{A} state show different mechanism from that via the \tilde{C}' state. Results indicate that the neutral clusters excited to the \tilde{A} state can undergo intracluster reactions commencing with predissociation of the excited ammonia moiety, which leads to the formation of $(\text{NH}_3)_{n-2}\cdot\text{NH}_4$. Subsequently, ionization of either $(\text{NH}_3)_n^*$ or $(\text{NH}_3)_{n-2}\cdot\text{NH}_4$ leads to formation of protonated cluster ions. The formation of long-lived $(\text{NH}_3)_{n-2}\cdot\text{NH}_4$ ⁷⁷ is in accordance with the findings of nonzero ion intensity values at long pump-probe delays observed in the data (see Figure 1). There is an overall dependence observed for the decaying signal intensity on the vibrational levels, which indicates the influence of the energetics on the predissociation and reaction forming NH_4 , while the trend in the long-time tail reflects effects due to solvation and retainment of NH_4 . It is evident that the \tilde{A} state competes between both the AID and ADI mechanisms. The AID, which is the dominant process, is seen when the pump and probe pulses are overlapped ($t = 0$), while the ADI occurs when the probe photon is absorbed at long time delays.

B. The Phenomenon of Coulomb Explosion

Most attention paid to the dynamics of clusters and cluster ions has involved ionization to a singly charged state, such as the example of the formation of protonated ammonia clusters mentioned in the preceding section. However, another class of reactions has been observed when clusters become multiply

charged, which can result in fission and Coulomb explosion processes.^{78–85} Ionization involving multiple electron loss is not new, having been first observed in various systems ionized via electron impact techniques. In most of these experiments, clusters containing one, two, or three charge centers were produced but only being observable in systems which remained metastable. The metastability arose only in systems of sufficient size that the charge centers could separate by a large enough distance to reduce the Coulomb repulsion to a magnitude that did not exceed the cohesive binding energy of the cluster. Early examples include clusters composed of CO₂,⁷⁸ various metal atoms such as those of the alkali metals,⁷⁹ hydrogen-bonded systems such as water and ammonia clusters,^{80–82} and rare-gas clusters.^{83,84} Below a critical cluster size, fission leads to the loss of the multiple charges from a cluster and hence to the production of a singly charged species. Metastable evaporation of the solvating molecules can take the stable cluster to degrees of aggregation below critical size and subsequently lead to fission.

In practice, Coulomb explosion results when multiply charged clusters are suddenly generated in systems smaller than the critical size required for metastability. However, in general it has been difficult to investigate the process due to its fleeting nature. Recent observations^{73,86–94} have shed considerable light on our understanding of this phenomenon, with new findings coming from investigations of the interaction of intense laser field with atoms,^{86–89} molecules,⁹⁰ and clusters.^{91–94} Specifically, during the course of experiments to study reaction dynamics within clusters, Castleman and co-workers observed an unexpected phenomenon in which femtosecond laser pulses instantaneously created clusters with a high charge state at surprisingly low fluxes of light, enabling a new and detailed look at the actual Coulomb explosion process. We first observed this with clusters of ammonia;⁹¹ results we reported were at just about the same time as work on high charge states of xenon reported by Rhodes and co-workers.⁹⁴ With the use of high-flux femtosecond laser pulses, the very short burst of light leads to the delivery of many photons to the cluster that can almost instantaneously lead to the loss of many electrons. These initially ionized free electrons can further ionize the inner-shell electrons of the atomic constituents of the cluster via intracluster inelastic electron–atom collisions. The resulting ions with core-electron vacancies can then decay by X-ray emission, as observed by Rhodes et. al. when rare-gas clusters⁹⁴ are irradiated by subpicosecond lasers with powers of $\geq 2 \times 10^{16}$ W/cm². See Figure 2. During the photon absorption and subsequent ionization processes, there is little time for nuclear motion, the highly charged atomic ions of the cluster are formed in very close proximity, and the system thereafter rapidly explodes due to the Coulomb repulsion from like charges, releasing atomic ions with high kinetic energies,⁹¹ see Figure 3. As discussed below, the exact mechanisms leading to the phenomenon are a subject of intense current interest among theoreticians as well as experimentalists.

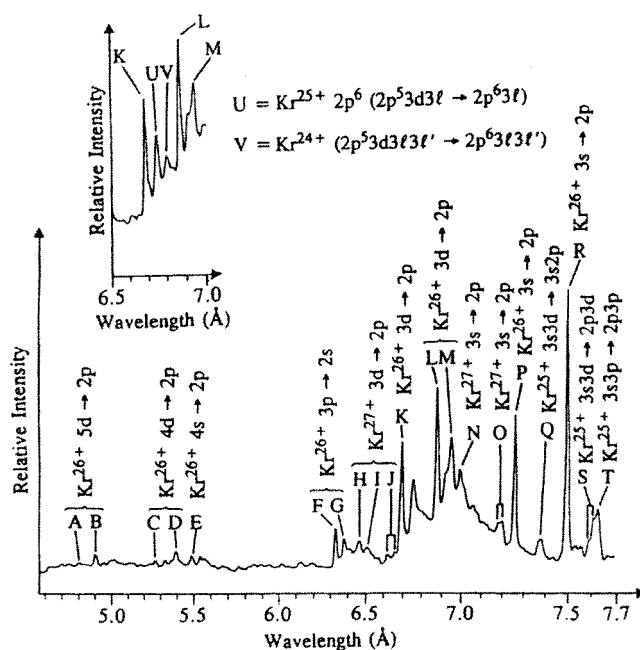


Figure 2. Figure 1 from Boyer, K.; Thompson, B. D.; McPherson, A.; Rhodes, C. K. *J. Phys. B: At. Mol. Opt. Phys.* **1994**, *27*, 4373. (Reprinted with permission from ref 94d. Copyright 1994 IOP Publishing Ltd., Bristol.)

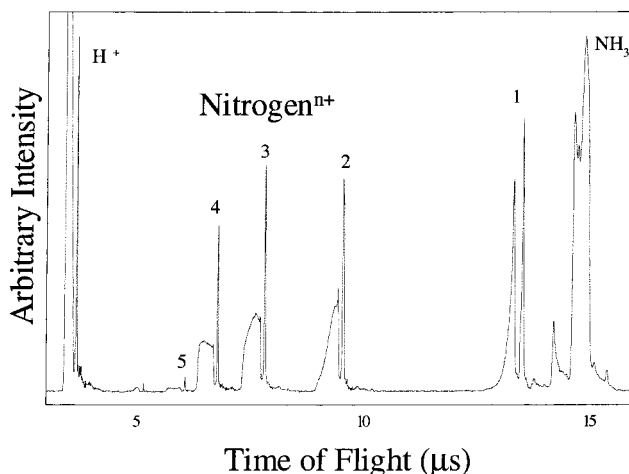


Figure 3. Time-of-flight mass spectrum of multicharged nitrogen atoms resulting from the interaction of intense laser field (wavelength at and power $\sim 10^{15}$ W/cm²) with ammonia clusters.

a. Quantifying Coulomb Explosion

The consequences of like-charge repulsion in clusters has been known for some years, but the fingerprint left by the process was not very detailed. Until recently, most observations of Coulomb phenomena in clusters were confined to the appearance of intact multiply charged clusters that were large enough to retain the presence of more than one charge center and hence could be detected with a mass spectrometer. The implementation of various ionization methods, including the use of lasers along with well-designed mass spectrometers, sometimes enabled the observation of a stability change induced by the laser heating of stable clusters, effecting evaporation and hence a reduction in size to clusters which then would undergo a fission-like disassembly.

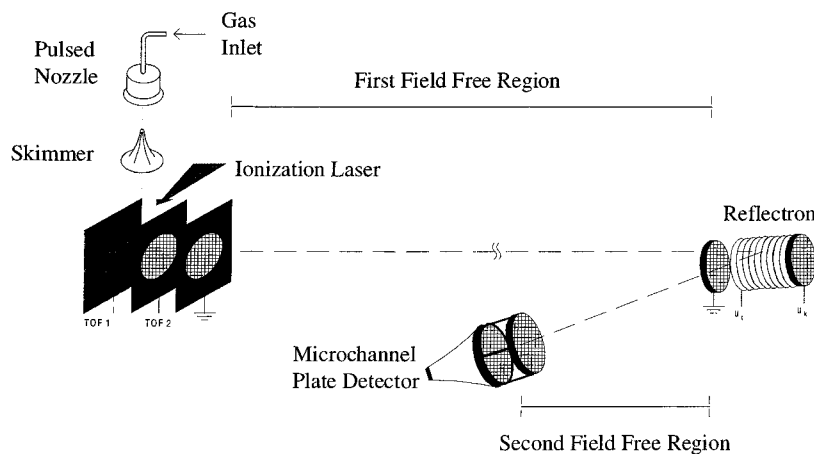


Figure 4. Schematic of the reflectron time-of-flight mass spectrometer.

A time-of-flight mass spectrometer (TOFMS) is especially useful in studying the process. Clusters which Coulomb explode give off highly charged atomic ions uniformly in all directions, and the essence of the value of the TOFMS in these experiments is the fact that a separation occurs in the flight times of the Coulomb-exploded species with the same mass and charge which are ejected to different directions initially. This is due to the experimental arrangement used whereby the particles initially moving away from the detector are electrically reflected to it and hence arrive later than those ejected directly toward the detector during the explosion event. The difference in arrival time is a measure of the repulsion at the moment of Coulomb explosion and can be used to calculate the kinetic energy associated with the explosive event; alternatively, the reflectron which we have incorporated in our TOF system can also yield information on kinetic-energy release through determinations of cutoff potentials for which species with high kinetics are not reflected to a detector. See Figure 4 for a schematic of a reflectron time-of-flight mass spectrometer.

Particularly interesting findings first came in our laboratory from studies of molecular clusters,⁹¹ like $(\text{NH}_3)_n$, $(\text{HI})_n$, X_n ($\text{X} = \text{Ar}, \text{Kr}, \text{Xe}$), and $(\text{CH}_3\text{COCH}_3)_n$, etc. In the case of $(\text{HI})_n$ clusters, when irradiated with a femtosecond laser at 624 nm and a power of $\sim 1 \times 10^{15} \text{ W/cm}^2$, prominent peaks corresponding to multicharged I^{n+} ions were observed, with $n = 17$ being clearly discernible.^{91b} As seen in Figure 5, a broad peak is found for the multicharged fragments having an early arrival time, followed by a sharp peak arising from space focusing for those species corresponding to a later time of arrival. Using the peak splittings from this spectrum, the kinetic energies (KE) are calculated using the following equation

$$\text{KE} = q^2 (\Delta U/d)^2 \cdot \Delta t^2 / (8m)$$

where Δt is the peak splitting, m is the mass of the ion, $(\Delta U/d)$ is the field gradient, q is the charge. The kinetic energy measured by the peak splitting, along with those determined from the voltage cutoffs, are generally found to be in good agreement. The high values of several hundred to several thousand electronvolts which we have measured cannot arise from

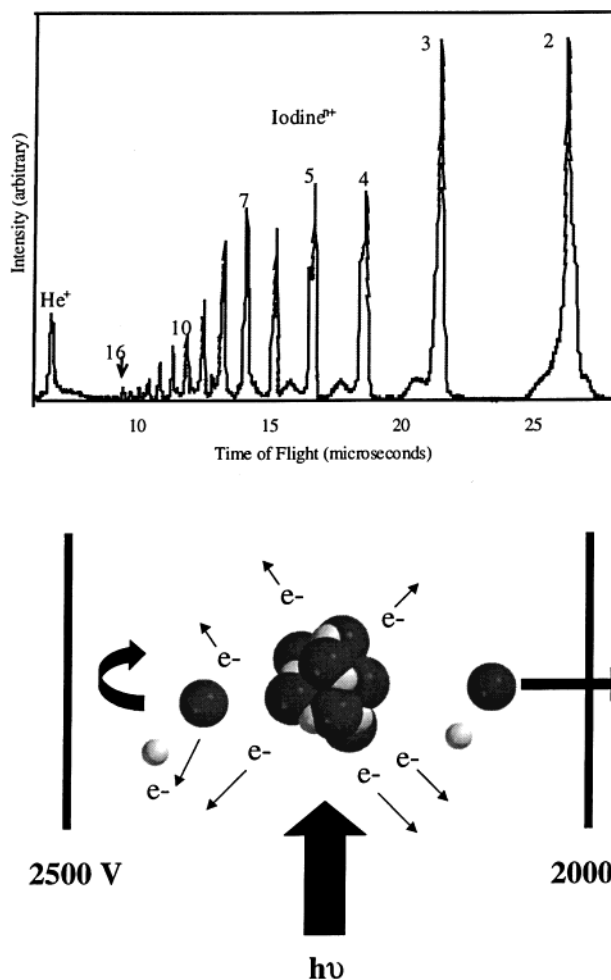


Figure 5. Coulomb explosion processes arising from interaction of HI clusters with intense laser field. Note the formation of high charge states of iodine, i.e., extending at least to $n = +17$.

the Coulomb explosion of HI monomer because they would involve unknowable small internuclear distances between H^+ and I^{n+} . This finding indicates that the large kinetic energies observed in the study result from the Coulomb explosion of HI clusters, a conclusion born out by the covariance studies and other more direct experiments discussed in part b of this section.

While hot ions with kiloelectronvolt energies can be released from the interaction of small clusters

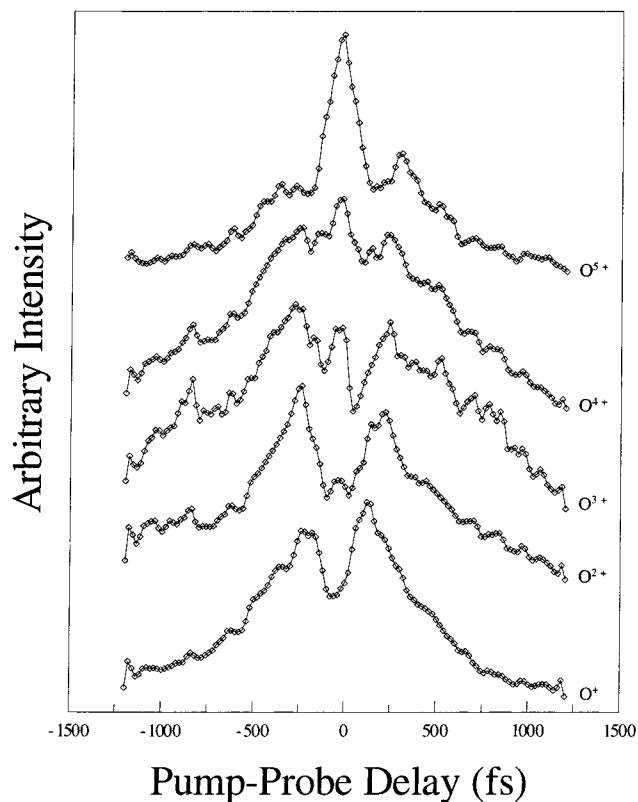


Figure 6. Pump-probe transients of multicharged oxygen ions, O^{n+} ($1 \leq n \leq 5$), formed through the Coulomb explosion of acetone monomer and acetone clusters.

($\sim 10^2$) with moderate laser field ($\sim 10^{15}$ W/cm²), ions with energies up to 1 MeV are observed when significant larger clusters, for example, Xe_n ($n \sim 2500$), are irradiated with stronger laser pulses ($\sim 2 \times 10^{16}$ W/cm²).⁹² The high kinetic energy released during the Coulomb explosion process provides an opportunity to realize substantial nuclear fusion reaction. Indeed, Ditmire et al.⁹² observed the $D + D \rightarrow He^3 + n$ fusion reaction when high-energy deuterium ions (greater than kiloelectronvolts) are created by the interaction of intense laser field ($\sim 2 \times 10^{16}$ W/cm²) with deuterium clusters. An efficiency of about 10^5 fusion neutrons per joule of incident laser energy was obtained, which approaches the efficiency in large-scale laser-driven fusion experiments.

Another aspect of the Coulomb explosion process has been learned from the study of acetone clusters^{91c} where highly charged carbon and oxygen atoms were found to be produced. A unique feature of the work performed on this system was the utilization of pump-probe techniques in the ionization process as a test of theoretical predictions of the possible mechanisms involved. In this case, the pump laser at 624 nm has a power density of $\sim 3 \times 10^{14}$ W/cm², and the probe laser also at 624 nm was slightly ($\sim 10\%$) weaker. The pump-probe transients of the oxygen fragments (O^{n+} , $1 \leq n \leq 5$) are shown in Figure 6. There are several significant features that should be noted. A large dip is observed in the O^+ transient at zero delay, and a peak begins to grow in for each subsequently higher charged species. For the higher charged species (O^{n+} , $2 \leq n \leq 5$), the ion signal drops to a local minimum and then returns to a local maximum at some pump-probe delay. At longer

delay times, the O^{n+} , $3 \leq n \leq 5$, show clear signs of a "beating" pattern. The unequal intensities of the maxima at positive and negative delay times can be attributed to the unequal pump and probe intensities, but significantly, the maxima in O^+ and O^{5+} occur at positive delay times, whereas the maxima in O^{2+} , O^{3+} , and O^{4+} occur at negative delay times. C^{n+} ($1 \leq n \leq 4$) observed in the experiment was found to behave in a similar fashion.

The maxima and minima do not occur at the same delay times for different O^{n+} species, and in all of the pump-probe scans, the transients displayed similar structure. Obviously, the observed beating pattern could not arise from the phasing of the pump and probe optical fields since the period of the laser is about 2 fs. The power of either pump or probe beam is sufficient to multiply ionize the acetone clusters, and it is unlikely that the cluster can stabilize the large amount of potential energy of multiple positive charges within the cluster. Furthermore, there does not appear to be any periodicity in the transients. As the cluster undergoes electron loss, the probe beam arrives at the cluster at some later time. Depending on the time delay of the probe beam, the interatomic spacings have increased to a particular distance as a result of the nuclear motion arising from the Coulomb explosion process. The structure seen for the transients in Figure 6 is due to the varying ionization rates as the interatomic spacing is increased, as predicted by Bandrauk,⁹⁵⁻¹⁰¹ Corkum,¹⁰²⁻¹⁰⁴ Jortner,^{105,106} and co-workers. As the interatomic spacings are varied, the wave function and electron localization is changed, resulting in different ionization rates for the various charge states. In their model, the ionization rate is predicted to be a highly irregular function of interatomic distance. This would result in the observed maxima and minima observed in the transients.

b. Direct Evidence for the Role of Clusters in the Coulomb Explosion Process

Several different types of experiments have provided definitive evidence for the role of clusters in effecting the facile formation of highly charged species at modest laser fluences. The first conclusive evidence was obtained from experiments employing a covariance analysis approach.^{86c,107} Probing various cluster distributions in a pulsed molecular beam and correlating the findings of high charge state formation with cluster size through covariance methods has served to further elucidate the mechanisms responsible for the generation of multiply ionized constituents.

In most photoionization TOF mass-spectroscopic studies, advantage is taken of the fact that the ion intensities produce average intensity values which can be analyzed and interpreted. However, deviations in the ion intensity do occur because of slight fluctuations in the laser or the molecular beam source. The technique of covariance mapping takes advantage of these fluctuations and compares the changes in one measurement with respect to another, thus providing a measure of the connectiveness between two different events.

Covariance is a measure of the deviation in the measurement of two functions, $X_i(x)$ and $Y_i(y)$, which depend on the independent variables x and y . In this application, the functions $X_i(x)$ and $Y_i(y)$ represent the ion intensities and the independent variables, x and y , represent the time-of-flights of the ions.

$$\begin{aligned} C(x,y) &= \langle (X - \langle X \rangle)(Y - \langle Y \rangle) \rangle \\ &= \langle XY \rangle - \langle X \rangle \langle Y \rangle \\ &= \frac{1}{N} \sum_{i=1}^N X_i(x) \cdot Y_i(y) - \left[\frac{1}{N} \sum_{i=1}^N X_i(x) \right] \left[\frac{1}{N} \sum_{i=1}^N Y_i(y) \right] \end{aligned}$$

The correlation coefficient, $\rho(x,y)$ is another closely related term to the covariance; it is a normalized quantitative measure of the correlation of events revealed through the time-of-flight of each ion. It is defined as

$$\rho(x,y) = \frac{C(x,y)}{\sqrt{C(x,x) \cdot C(y,y)}}$$

where $|\rho(x,y)| \leq 1$.

If $\rho(x,y)$ equals 1, 0, or -1 , the ion signals of $X(x)$ and $Y(y)$ are perfectly correlated, not correlated, or anticorrelated, respectively.¹⁰⁴

Covariance analysis of the Coulomb explosion process of ammonia clusters induced by the intense laser field shows that there is an intense anticovariance between the higher mass clusters and the highly charged Coulomb-exploded nitrogen ions, as seen in Figure 7. This indicates that the production of the highly charged nitrogen ions are formed at the expense of the higher mass ammonia clusters. This result provides strong evidence that the appearance of highly charged Coulomb-exploded species indeed originate from clusters.

Despite the very strong evidence from these observations, more direct proof was sought. This was acquired in a series of experiments conducted in a manner which focused on the composition of the molecular beam which produced the most intense highly charged species at a given laser fluence.⁹³ The experiments were made by crossing the laser with the molecular beam at selected delay intervals where clusters or monomers were the major species present. One experiment involved fixing the focal position and changing the delay of the pulse nozzle relative to the laser pulse. This experiment enables scanning of the entire neutral cluster and unclustered molecule packet. Several different factors were examined: charge-state distribution, kinetic-energy release, and integrated signal intensity as a function of the delay between the laser and pulsed valve. All three exhibited the same trend, namely, showing that the highly charged species were only present, and with high kinetic energy release, when clusters dominated the beam. Essentially no highly charged species were observed when monomer alone was present, see Figure 8.

c. Consideration of Models of Coulomb Explosion

Two general theoretical models proposed to explain the high charge states observed are the coherent electron motion model (CEMM⁹⁴) and the ionization ignition model (IIM¹⁰⁹). In CEMM, the multiple electron ejection is envisioned to arise from the coherent motion of the field-ionized electrons; subsequent removal of electrons is considered to occur in a manner similar to electron impact ionization. In the IIM, after the initial ionization events, the parent ion cores are considered to be inertially confined to the cluster, leaving the ion field unscreened. This results in a very large ($>10^{12}$ V/m) and inhomogeneous electric field. This large field lowers the ionization barrier and enables subsequent ionization events to occur, which in turn further increases the field and lowers the ionization barrier. Both propose that barrier suppression and concomitant electron tunneling facilitate the phenomenon.

In their CEMM, Rhodes and co-workers proposed⁹⁴ an expression to approximate the number of ionization events

$$N_x \cong n^{4/3} Z \frac{\sigma_{ei}}{r_0^2} \quad (n \geq 3)$$

where n is the number of atoms in the cluster, Z is the resultant ionic charge, σ_{ei} is the inelastic electron impact ionization cross section, and r_0 is the interatomic spacing. Furthermore, the coherent electrons behave as quasi-particle of mass Zm_e and charge Ze , requiring modification of the electron impact cross section to the form $\sigma_{ei} \rightarrow Z\sigma_{ei}$.

In the IIM,¹⁰⁹ the strong field due to the unshielded ion cores in a cluster are responsible for the high charge states obtained, rather than the large electron density. It was concluded that removal of the outer electrons is not expected to be very sensitive to pulse width, cluster size, or atomic weight. Related quantum mechanical calculations⁹⁸ done earlier in studies of multielectron ionization of small molecules show that the rate of ionization is highly dependent upon the internuclear distance, in a nonmonotonic fashion. Additionally, it has been shown¹⁰³ that the dependence on internuclear separation is due to the role of electron localization in intense field ionization. Such effects are considered in a related dynamical model referred to as charge resonance enhanced ionization (CREI)⁹⁵⁻¹⁰⁶ which would be expected to give rise to an irregular rate of ionization pattern, consistent with observations in acetone clusters studied via pump-probe femtosecond spectroscopy. In this model, electron excitation which becomes in sync with excursions of the nuclei, assists the ionization process.

As the various models predict, multicharged species are not observed to any significant extent unless clusters are present in our molecular beam. The charge states obtained are reasonable in considering both the CEMM and IIM.

Multicharged species abruptly appear in the mass spectra as a certain minimum critical cluster size is obtained, but the charge distribution does not vary with further variation in the cluster distribution.

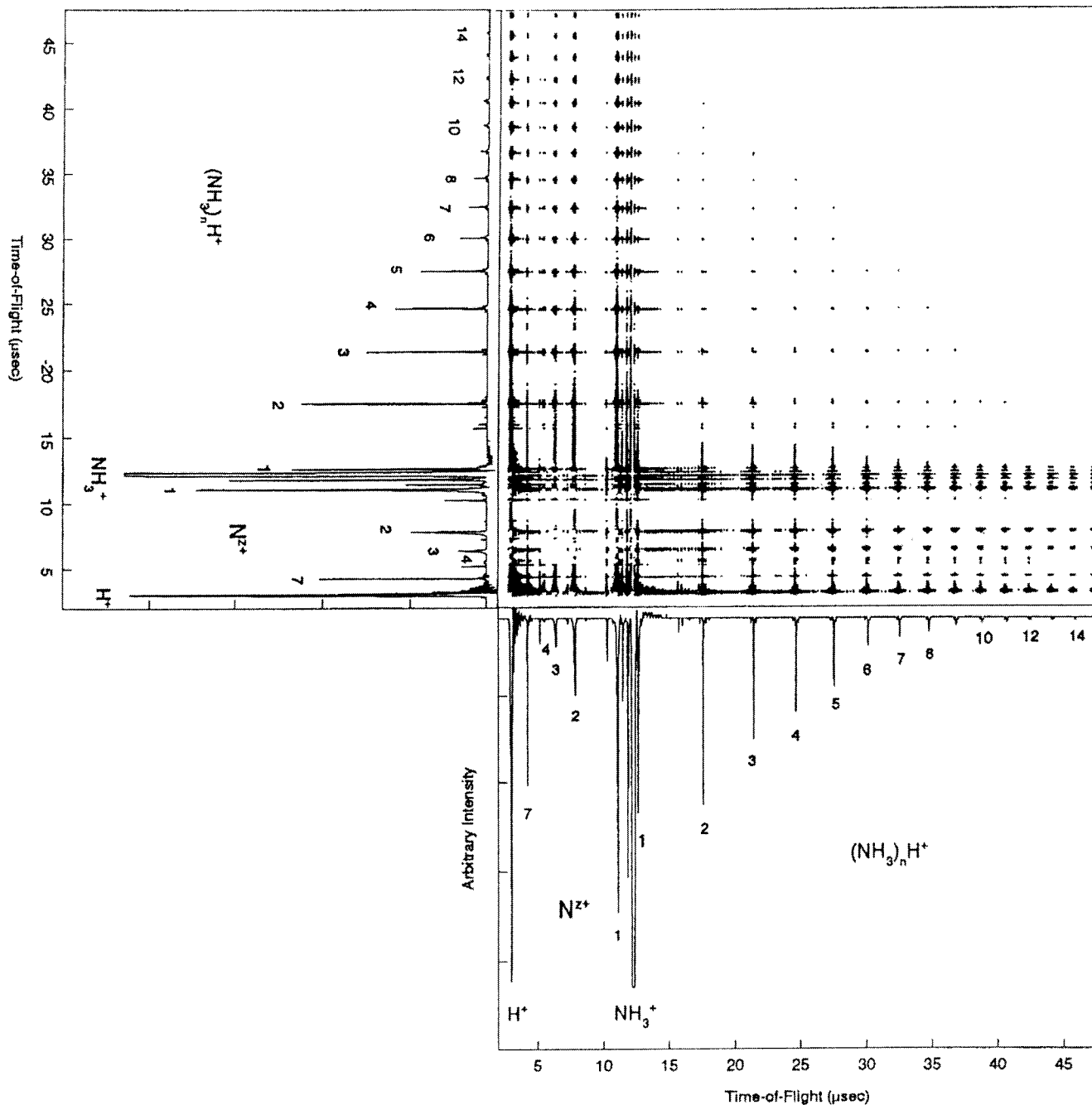


Figure 7. Anticovariance map of ammonia clusters under photoionization at 624 nm, laser pulse width of 120 fs, and a fluence of $\sim 10^{15}$ W/cm². The abscissa and ordinate display a TOF spectrum of ammonia clusters averaged over 10 000 single-shot spectra. The center of the figure displays the calculated anticovariance map as described in the text.

Moreover, under modest ionization conditions, multicharged krypton and argon atoms are only observed when a trace amount of HI is present,^{91a} although pure xenon, ammonia, and acetone clusters are multiply ionized. The fact that neat Kr (IP = 14.00 eV) and Ar (IP = 15.76 eV) clusters do not exhibit multiple ionization, whereas neat Xe (IP = 12.13 eV), HI (IP = 10.39 eV), NH₃ (IP = 10.18 eV), and (CH₃)₂CO (IP = 9.71 eV) clusters do, suggests that the ability to multiply ionize atoms is less sensitive to atomic number and depends more upon the threshold for single ionization.

In the CREI model, the ionization rate is predicted to be a highly irregular function of interatomic distance, in contrast to the CEMM which predicts a

monotonic decrease in the degree of ionization with an increase in interatomic distance (see r_0 in the above equation). Studies on large clusters have been reported which do provide evidence of the operation of CEMM in systems where the wavelength of the optical radiation is comparable to the size of the particles, but this is not the size regime under consideration here.

In conclusion, most studies demonstrate that the high charge states obtained when van der Waals and hydrogen-bonded clusters are irradiated with intense laser fields are well described by the IIM. The lack of dependence on the degree of clustering or atomic weight and the strong dependence on ionization potential and interatomic (or intermolecular) dis-

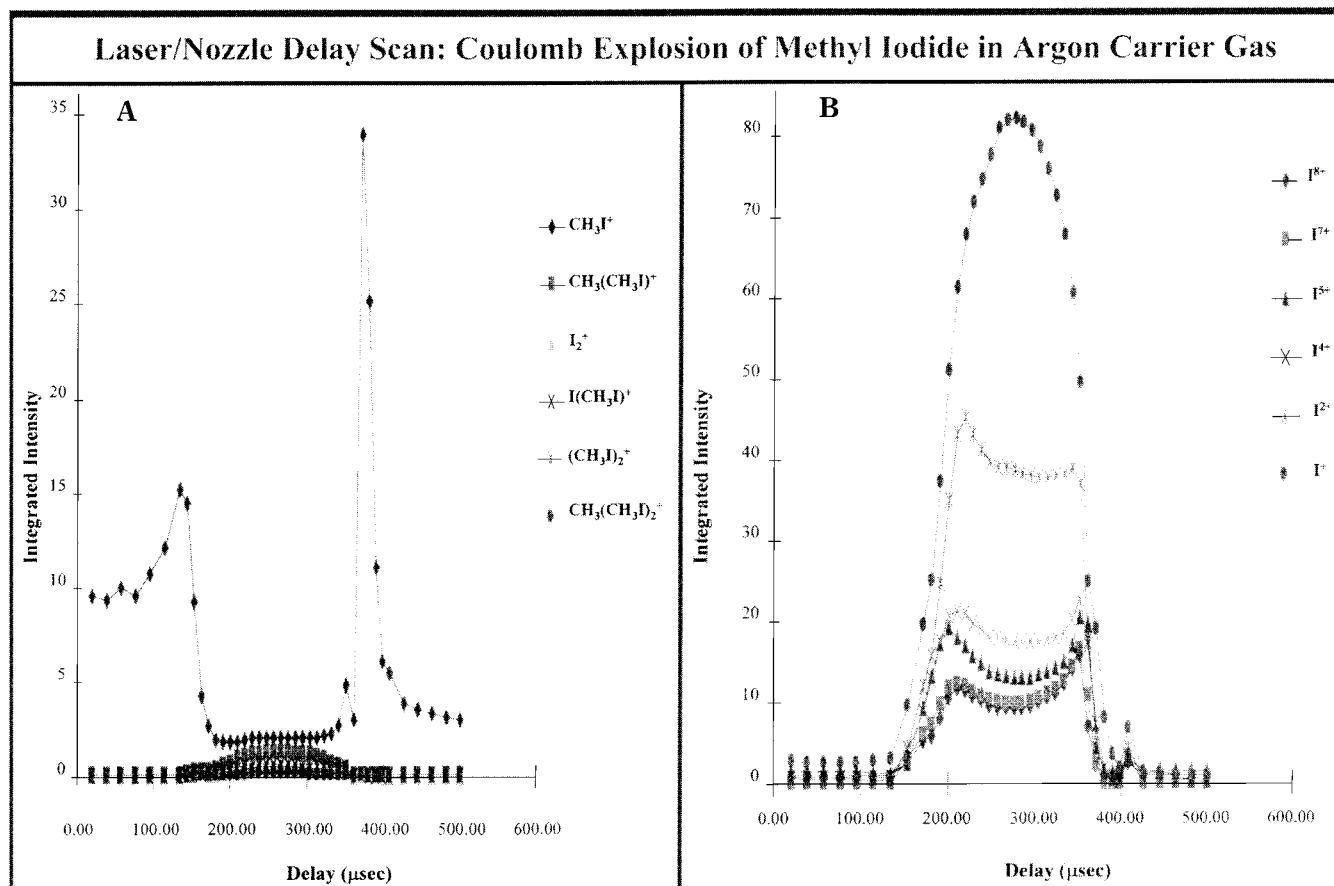


Figure 8. Summary of the nozzle/laser delay experiments. The delay time corresponds to the time between when the pulse nozzle opens and the laser fires. (A) Note the monomer of CH_3I is most intense at the wings of the gas pulse, while the clusters are primarily concentrated at the center of the gas pulse. (B) Note that the high charge state species arise at the center of the gas pulse where the clusters are located.

tances support this conclusion. Present results cannot totally eliminate the possibility of coherent electron motions, but under experimental conditions in which only small clusters are present, it is not a major contribution to the multicharging and subsequent Coulomb explosion of clusters. Clearly, however, the IIM warrants refinement via more elaborate classical and quantum mechanical calculations.

d. Ionization Dynamics and Coulomb Explosion: Chemical Applications

Among the fastest processes of chemical interest are those involving charged species, with the transfer of electrons generally occurring on the shortest of time scales and those involving other ionic constituents being close behind. One particularly important example germane to the present subject is an interaction process involving ionized atoms or molecules. As discussed in detail in the preceding section, due to their electrical charge, ionized particles sense each other over comparatively long distances and accordingly their interactions are generally strong and often give rise to the Coulomb explosion phenomenon which takes place on a very short time scale. If a collection of like charges is suddenly produced in close proximity, the repelling between them is so rapid that it occurs as a nearly explosive event, hence the term Coulomb explosion.

Clusters have a propensity to undergo such processes when exposed to high-intensity light fields

available from pulsed lasers of short duration. We have found that this phenomenon can be taken advantage of to gain information on the time evolution of intermediates produced in chemical reactions occurring within clusters, as we consider further.^{110,111} Calculations¹¹² place the approximate separation times in the neighborhood of 25 fs, so that little further transfer of heavy atoms occurs after the ionization event. Hence, by initiating a reaction with one laser pulse and then initiating the Coulomb explosion with another, the intermediates present at selected reaction time intervals can be interrogated. This has been successfully accomplished in the case of 7-azaindole dimer, as described in detail in the next section. Related methods of studying kinetic energy release have been recently employed¹⁰² in a study of the potential-energy surface for the I^+-I^+ system, and we may expect to see similar applications in the cluster field.

5. Cluster Solvation Effect on Reaction Dynamics

There are several ways in which solvation effects influence reactivity.^{8,20,22} These include (1) solvation effects on the nature of the excited reaction sites, (2) solvation effects on exothermicity (or exoergicity), (3) site-specific solvation blocking, (4) solvation influences on the energy barrier to reaction, and (5) effects due to caging.

The study of cluster dynamics by employing time-resolved spectroscopy is a comparatively new subject of inquiry. Its potential has been brought to fruition due to recent developments in picosecond and especially femtosecond laser pump–probe techniques.^{113,114} Due to the limited length of the paper, here we only focus on a small portion of current research interests, namely, excited-state proton transfer (ESPT^{115,116}), excited-state electron transfer (charge transfer), and caging dynamics.

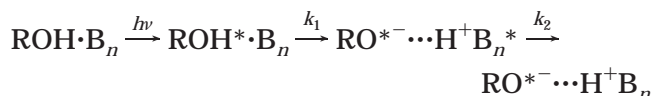
A. Excited-State Proton Transfer

Many molecules exhibit pH changes upon photoexcitation, as in the case of aromatic alcohols, due to the fact that these molecules have electronic state dependent heats of deprotonation. For example, the pK_a of 1-naphthol in its ground electronic state is 9.4 and decreases to 0.5 when excited to its S1 state.¹¹⁷ The large drop in the pK_a makes it possible to photoinduce a proton transfer from the solute molecule to the solvent, which could be initially forbidden in the electronic ground state. The application of femtosecond pump–probe techniques have allowed this excited-state proton-transfer process to be studied and the reaction rate measured in various systems in different environments, e.g., solutions,^{117–120} solid matrixes,^{121,122} and also small clusters.^{115,116,123–127}

In the cluster studies, there are a few common observations: first, the ESPT rate displays a strong dependence on cluster size and solvent structure. For example, in the case of the phenol molecule,^{115,123,125} when ammonia is used as the solvent, $C_6H_5OH \cdot (NH_3)_n$, the proton transfer k^{-1} is measured to be 5 ns for $n = 4$ but increases dramatically to 55 ps at $n = 5$. The dramatic rate change at $n = 5$ is a clear onset for the ESPT reaction. Due to the large energy needed to free a proton from the solute, the proton-transferred ion-pair state is unstable compared to the covalent structure. Solvation of the proton with a high proton affinity solvent enhances the stability of the ion-pair state significantly. The larger the solvent clusters, the larger the gained stability. For solvents with higher proton affinities than ammonia, like trimethylamine, $C_6H_5OH \cdot [N(CH_3)_3]_n$, the ESPT onset is observed at smaller cluster size, $n = 3$. In the case of the 1-naphthol molecule, which is more acidic ($pK_a = 0.5$) in the S1 state than phenol ($pK_a = 4.1$), the onset of ESPT should appear at smaller cluster sizes; as observed in the 1-NpOH $\cdot (NH_3)_n$ clusters,^{124,126} the onset is at $n = 3$, while for 1-NpOH $\cdot (C_5H_{11}N)_n$, the onset is at $n = 5$. For a less basic solvent such as water, experiments show that ESPT occurs with a minimum of hundreds of water molecules and the reaction rate is in the nanosecond regime.¹²⁷ In the experiments involving mixed solvents, the introduction of different solvent molecules can cause changes in the hydrogen-bonding network structure in the ion-pair state, thus affecting the proton-transfer process dramatically. For example, the ESPT of photoexcited $C_6H_5OH \cdot (NH_3)_5$ occurs within 55 ps, whereas when one methanol molecule is added to the clusters, the proton transfer k^{-1} increases to 750 ps.

Second, ESPT displays a strong isotope effect. When hydrogen atoms in $C_6H_5OH \cdot (NH_3)_5$ are replaced by deuterium to give $C_6H_5OD \cdot (ND_3)_5$, the proton transfer k^{-1} slows from 55 ps to 1.5 ns¹²⁵ while the ESPT for 1-NpOH $\cdot (NH_3)_4$ and 1-NpOD $\cdot (ND_3)_4$ are 52 and 150 ps, respectively.¹²⁶ The large isotope effect observed support a tunneling mechanism. The tunneling barrier is formed by the avoided curve-crossing of the covalent $RO-H \cdot B_n$ potential with the solvent-stabilized Coulombic-type ion-pair $RO^{\cdots}H^+B_n$ potential. Experimental evidence of the existence of this barrier is the observation of the slow proton-transfer rate observed even in highly acidic 1-naphthol with high proton affinity solvents, like ammonia and trimethylamine. Solvent type, structure, and cluster size all affect the potential-energy surfaces and thus the barrier shape, influencing the proton-transfer rate profoundly.

Third, ESPT displays biexponential decay characteristics. In the case of 1-NpOH $\cdot (NH_3)_5$, the transient has a distinct double-exponential decay, with a fast component of 25 ps and a slow component of 226 ps. Similar behavior was also observed in the $C_6H_5OH \cdot (NH_3)_n$ system.¹²⁸ The observed fast component is attributed to the proton-transfer process, while the slow component is interpreted to be due to the solvent reorganization following proton transfer.^{125,126} Solvent reorganization involves the rearrangement of the hydrogen-bonded network following the proton-transfer reaction, leading to a more stable ion-pair structure. The process can be described by the following



with k_1 being the proton-transfer rate and k_2 the solvent reorganization rate. k_2 is found to be dependent on cluster size and vibrational excitation and also shows an isotope effect.¹²⁶

ESPT has also been studied extensively in ammonia clusters as well. Ammonia clusters are used as a prototypical hydrogen-bonded system because the ammonia and ammonia clusters have been extensively studied,^{72,74,85,129–135} thus their structures, potential-energy surfaces, and reaction dynamics are well understood. Among these studies, of particular interest is the time-resolved reaction dynamics on the Rydberg state of ammonia clusters.⁷⁵ In this experiment, a pump pulse at 312 nm (two-photon absorption) is used to excite the ammonia clusters to the state and a probe pulse at 624 nm is used to monitor the reaction dynamics by ionizing the clusters. The ions are detected in a reflectron time-of-flight mass spectrometer. Experimentally obtained lifetimes of ammonia clusters are found to be more than one magnitude shorter than the ammonia monomer, which is the opposite of the solvation effect observed on the \tilde{A} state, in which clustering prohibits predissociation, thus prolonging the \tilde{A} state lifetime.^{72,135} Dissociation of ammonia on the Rydberg state occurs through coupling to the lower lying \tilde{A} state, followed by subsequent predissociation. For ammonia clusters, two possible reaction channels open up, namely,

proton transfer and hydrogen-atom transfer. Proton transfer occurs when the photoexcited ammonia chromophore donates a proton to a solvating ammonia, while hydrogen-atom transfer occurs when the excited ammonia chromophore accepts a hydrogen atom from a solvating ammonia. These two reaction channels lead to a population loss from the initial excited Rydberg state and agree with the experimentally observed biexponential decay dynamics for the clusters.⁷⁵ Both reaction pathways display a cluster-size effect. Smaller solvation effects are observed for proton-transfer processes. The proton transfer k^{-1} for $(\text{NH}_3)_n$ increases from 85 fs for $n = 3$ to 135 fs for $n = 40$. Hydrogen-atom transfer processes show a stronger dependence on the degree of clustering. Hydrogen-atom transfer rates increase from 300 fs for $(\text{NH}_3)_3$ to 1500 fs for $(\text{NH}_3)_{40}$. Similar effects are found for the deuterated systems. As with all studies of solvation effects in clusters, there are two competing factors that may affect the reaction dynamics: the ability of the solvent to relax the vibrational and rotational excitation and the solvation stabilization effect on potential-energy surfaces. When ammonia is excited from the ground X state to the state, the out of plane “umbrella” bend is highly excited. The “umbrella” vibration moves along the hydrogen-atom transfer coordinate; therefore, excitation of the umbrella mode would enhance the hydrogen-atom transfer rate. As the cluster size increases, the energy relaxation in this umbrella mode become faster; thus, the lifetime increases, as observed in the hydrogen-atom transfer reaction.⁷⁵ Since the proton-transfer reaction coordinate lies perpendicular to the umbrella vibration, it shows a smaller dependence upon clustering. Related excited-state hydrogen-atom transfer in the ammonia dimer on the Rydberg \tilde{A} state¹³⁶ has also been observed by Hertel's group using the combined femtosecond pump-probe technique and photoelectron-photoion coincidence spectroscopy.¹³⁷

Regarding the ESPT reaction, another particularly interesting system is the 7-azaindole dimer, which has become a model for understanding base pairs such as DNA. In our lab, we have been able to study the excited-state double proton transfer (ESDPT) of the 7-azaindole dimer under conditions ranging from an isolated dimer up to a state of solvation where the hydrogen-bonded dimer is solvated with as many as nine water molecules. As the number of water molecules on the nonreactive dimer increases, we begin to see evidence that the dimer molecule is behaving more as it would in a fully solvated condensed-phase environment.

In the dimer state, particular interest has arisen in the double proton transfer that the 7-azaindole dimer undergoes upon excitation to the S_1 state. This excited-state double proton transfer was first observed by Kasha et al. in solution,¹³⁸ and numerous studies have been undertaken since then by various researchers. The system attracted the attention of Kaya and co-workers, who have performed extensive supersonic jet spectroscopic studies on the 7-azaindole monomer, dimer, and solvated forms of these species.^{139–142} Subsequent dynamical investigations

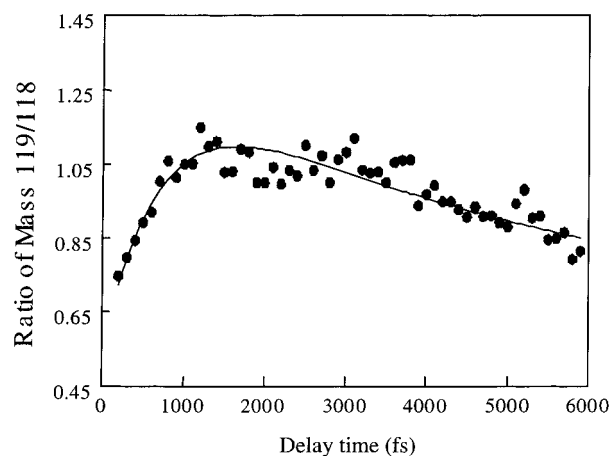


Figure 9. Ratio of mass 119 to mass 118 throughout a typical pump-probe experiment, with the pump laser at 312 nm and the probe at 624 nm. The circles represent experimental data. The solid line represents a fit of the data as described in the text. Time constants of around 660 fs and 5 ps were obtained for the first and second proton transfer, respectively.

have been undertaken in both the gas^{111,143} and condensed phases,^{144,145} leading to a determination of the rate of the excited-state double proton transfer using ultrafast spectroscopic techniques. A major disagreement developed in the literature regarding whether the tautomerization proceeded through a stepwise or concerted process. Gas-phase experiments^{111,143} generally supported a stepwise transfer of protons, while condensed-phase studies made in the presence of a nonpolar liquid were consistent with a suggested one-step mechanism occurring on the order of 1.1–1.4 picoseconds.^{144–146}

Zewail and co-workers initially reported gas-phase measurements of a two-step process for the ESDPT in the 7-azaindole dimer, yielding times of 650 fs and 3.3 ps for the first and second proton transfer times, respectively.¹⁴³ Later, work in our group arrived at similar conclusions by utilizing a Coulomb explosion technique that arrests intermediates in the transfer process. These new experiments provided definitive evidence that a reaction intermediate exists as suggested by Zewail,¹¹¹ confirming a two-step process for the tautomerization of the isolated dimer. The Coulomb explosion method enables the formation of the intermediate to be clearly resolved in the mass spectrum at selected time delays. The stepwise double proton transfer for 7-azaindole dimer can be seen to vary in time with respect to delay between the initiating pump laser and the intense probe laser that serves to instantaneously explode the reactant complex; refer to Figure 9 which shows the variation with time of the 119 and 118 amu species. It is evident that the rise and fall of the 119 amu species with respect to the 118 amu species represents the formation of an intermediate species and subsequent tautomer formation as observed by Coulomb explosion generated mass fragments. Calculations suggest that separation times during such a Coulomb explosion event occur on the order of 25 fs, thus making this method a useful technique for interrogating ultrafast reactions.¹¹² The protonated 7-azaindole monomer arising from the Coulomb explosion event

(mass 119 amu) can only be attributed to a stepwise process with a minimal contribution from isotopic distributions.

During studies of the 7-azaindole dimer, Kaya and co-workers made observations that led them to suggest the possible existence of two isomers of this species, depending upon the stagnation pressure employed in the supersonic expansion.¹⁴⁰ The reactivity of the isomers was found to be dramatically different: one being reactive and the other being nonreactive. The reactive dimer appeared to undergo a normal double proton transfer, whereas the nonreactive dimer did not. Studies by several research groups led to varying explanations for the observed differences, most pointing to the likelihood that geometrically different isomers were responsible for the reported observations.

Some suggestions¹⁴² were made that the attachment of a weakly bonded water molecule might influence the photoexcitation process, thereby accounting for the nonreactive species. However, our experimental results on the water-solvated dimer indicate that the presence of a water molecule is not responsible for the formation of the nonreactive dimer. In fact, our studies show that the presence of a water molecule clustered with the nonreactive dimer actually facilitates proton transfer.

While only the reactive dimer is seen at low backing pressures and the nonreactive dimer at high pressures, both can be observed at certain intermediate pressures. As expected, the reactive dimer and the nonreactive dimer were observed to exhibit very different pump-probe spectra. The transient of the reactive dimer was found to be best fit with a biexponential function having time constants nearly identical to those obtained by Zewail.¹⁴³ The transient of the nonreactive dimer on the other hand showed a long-lived decay with respect to the reactive dimer, which indicated that the double proton transfer had not occurred. The fact that both species are present under the same experimental conditions points toward the original suggestion¹⁴⁰ of different structural isomers being responsible for the different reactive nature of the two experimental situations. This observation leads to the conclusion that the temperature of the molecular beam is responsible for the formation of different isomers rather than a water molecule being responsible for the change in the excited-state double proton-transfer behavior.

To further prove this point, we subsequently investigated hydrated 7-azaindole to examine whether water molecules incorporated with the dimer would promote the formation of a nonreactive dimer. Species composed of $(7\text{-Aza})_2(\text{H}_2\text{O})_n$, where $n = 1-9$, were investigated with pump-probe techniques. Again, both reactive and nonreactive dimer species could be produced in conjunction with higher order clusters exhibiting varying degrees of solvation. As mentioned above, species are considered reactive if they exhibit a fast decay in their pump-probe trace which can be fit best using a biexponential function, while species are considered nonreactive if their pump-probe transients show a long-lived lifetime with respect to the reactive dimer.

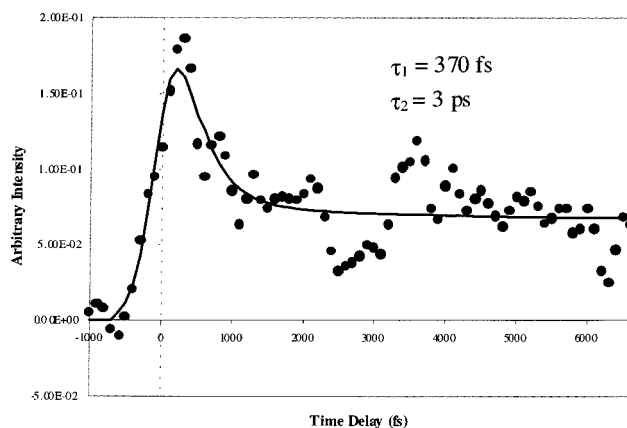


Figure 10. Pump-probe transient of the reactive dimer with one water clustered to it. The pump laser is at 310 nm and the probe at 620 nm. The transient clearly shows that the presence of a water molecule does not inhibit the proton transfer from occurring.

Figure 10 shows data for the case where water molecules were attached to a species corresponding to a reactive dimer, obtained at intermediate backing pressure. If a water molecule was responsible for the formation of the nonreactive dimer, then the species $(7\text{-Aza})_2\text{H}_2\text{O}$ should show a long-lived transient, which is not observed. The findings conclusively establish that double proton transfer also occurs for the monohydrated dimer species. An even more interesting case is seen in Figure 11, where it is seen that solvation of the nonreactive dimer enables it to undergo double proton transfer. Transfer times correspond to 450 fs for the first transfer and about 2.8 ps for the second. As seen from data in Table 1, subsequent hydration has little effect on the transfer times until a change occurs at four waters, and a single transfer step is seen for additional degrees of hydration. This suggests that the double proton transfer is undergoing a transition from a two-step process to a one-step concerted mechanism. It is possible that a change in behavior is being caused through progressive clustering, but alternatively, the proton may become transferred to the waters upon exciting species having higher degrees of solvation. This could be explained by conformational structure changes occurring at the onset of a critical number of water molecules. This consideration would be in accord with suggestions¹⁴⁷ that a change from a hydrogen-bonded dimer to a stacked dimer occurs once enough water molecules become associated with the complex. Further experiments are required to elucidate this unexpected behavior.

B. Electron-Transfer Reactions

Electron-transfer reactions are among the most ubiquitous and elementary of all chemical processes, with wide ranging implications through many areas of chemistry, physics, and biology.¹⁴⁸⁻¹⁵⁰ Photo-induced electron-transfer reactions play a major role in triggering numerous types of chemical and biological processes, and there is a continued and growing interest in determining the molecular-scale details of the initial electron-transfer step. Because electron-transfer processes in natural environments are quite

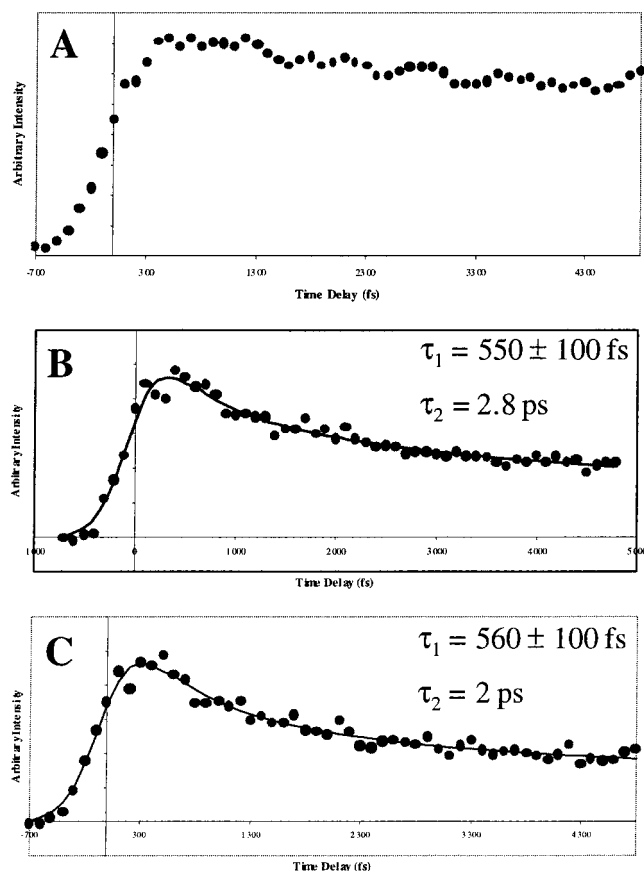


Figure 11. (A) Pump–probe transient of the nonreactive dimer at 1200 Torr. It can be seen from the lack of a fast decay that proton transfer is not occurring in this species. (B) Pump–probe transient of the nonreactive dimer with one water clustered to it. It can be seen here that an attached water molecule actually facilitates the occurrence of the proton transfer in an otherwise nonreactive species. (C) Pump–probe transient of the nonreactive dimer with two waters clustered to it. The second step of the proton transfer can be seen to occur even more quickly with two waters present.

Table 1. Proton-Transfer Times for the Solvated 7-Azaindole Dimers^a

no. of waters	first transfer, fs	second transfer, fs	transfer time, fs
1	550 ± 100	2800	
2	565 ± 100	2000	
3	560 ± 100	2000	
4			
5			1800
6			1600
7			1300
8			1100
9			1000

^a Note that no definite values of lifetimes could be deduced from the data obtained for $n = 4$, a fact attributed to a change in cluster structure at this degree of hydration.

complex, researchers are seeking ways to study the fundamental aspects of these phenomena in simplified model systems using well-characterized optical pulses.

The ease of which iodine accepts an electron from donor molecules, when photoexcited, has made iodine the ideal electron-acceptor molecule for studying the electron-transfer process. When Benesi and Hilde-

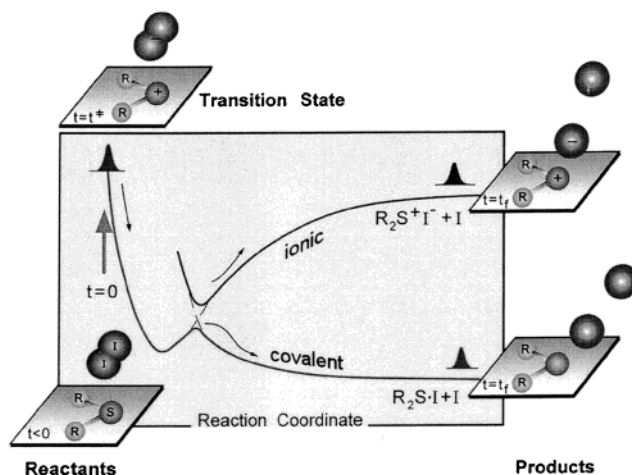


Figure 12. Figure 1 from Zhong, D.; Zewail, A. H. *Proc. Natl. Acad. Sci. U.S.A.* **1999**, *96*, 2602. (Reprinted with permission from ref 154. Copyright 1999 The Academy, Washington, DC.)

brand¹⁵¹ first dissolved iodine and benzene in *n*-heptane, a new absorption band in the ultraviolet range was observed. Mulliken¹⁵² postulated that this absorption band corresponds to an electronic transition from the highest occupied molecular orbital of benzene to the lowest unoccupied molecular orbital of iodine. Since these initial observations, extensive research efforts have been devoted to the study of the electron-transfer process involving the iodine molecule with various electron donors in isolated bimolecular complexes,^{153,154} cluster solvation systems,^{155–157} rare-gas matrixes,¹⁵⁸ and also liquid solutions.^{159–163}

The unique ability to probe the electron-transfer process and the concomitant reaction dynamics through the use of ultrafast laser pump–probe spectroscopy, in which the electron-transfer process is initiated by a femtosecond pulse and the reaction progress is followed with a femtosecond probe pulse, has been demonstrated by Zewail and co-workers.^{154–156} In their studies of electron-transfer reactions in isolated bimolecular complexes or clusters, a femtosecond laser pulse is used to photoinduce the electron transfer from a donor molecule to an iodine molecule, and the subsequent reaction dynamics are followed by monitoring the iodine fragments released from the reaction with a probe pulse, using angular and velocity resolved kinetic-energy time-of-flight mass spectrometry.

Experimental results^{154,156,158} on various D·I₂ (D represents donor molecule like benzene (Bz), diethyl sulfide, or dioxane) systems indicate that the electron-transfer process and the subsequent reactions follow a common mechanism, though there is a strong correlation between the structure of the complex and the observed dynamics. The vertical excitation by a femtosecond pump pulse launches the D·I₂ complex to its ionic potential-energy surface (the so-called charge transfer state). This ionic potential-energy surface is bound in nature and crosses the repulsive covalent potential-energy surface. An avoided crossing of these two potential-energy surfaces forms an upper quasibound potential well and a lower potential well with a barrier at the crossing, as sketched in Figure 12. This kind of ionic-covalent potential-

energy curve crossing is present in many systems. A simple example of this is the case of NaI in which the ground-state ionic curve crosses the covalent curve of the first excited state. The resulting electronic structure along the reaction coordinate of the upper quasibound potential well formed from the avoided crossing of these two states changes from being covalent at short nuclear distances to being ionic at longer distances. When the ground-state NaI molecule is excited with a femtosecond laser pulse to its first excited state, the wave packet, initially prepared on the repulsive covalent potential, propagates within the quasibound well.¹⁶⁴ As the wave packet propagates, the bonding in the NaI molecule oscillates between covalent and ionic character, with an electron being shuttled back and forth from the sodium to the iodine. In the case of the Bz·I₂ complex, following photoexcitation to the charge transfer state, Bz⁺I⁻···I propagates along the ionic curve toward the hybrid region of covalent and ionic potentials. At the crossing barrier, an electron from I⁻ reversibly transfers to the benzene molecule, leaving the I–I bond on its dissociative potential, resulting in the release of an iodine fragment with high translational energy within 450 fs. The other “caged” iodine atom relaxes its energy via collision with the benzene molecule and is released within 1.4 ps with a much lower translational energy compared to the first iodine fragment.¹⁷² Experiments involving different donor molecules such as *o*-xylene, acetone, dioxane, and diethyl sulfide, etc., show that the escape time of the second iodine atom from the single-molecule cage increases when the binding energy of the D–I complex becomes stronger.^{154,155}

Even though size selection in neutral clusters is still an experimental challenge, investigations of electron-transfer reactions under different clustering conditions show clearly that the reaction dynamics have a strong dependence on the degree of solvation.^{154,156} In the (Bz)_{*n*}I₂ cluster system, experimental results as well as molecular dynamics simulations and ab initio calculations show that¹⁵⁸ the benzene molecules tend to cluster around themselves rather than to the iodine molecule; therefore, the iodine protrudes out of the benzene cluster. Following photoexcitation to the charge-transfer state, the cluster moves along the ionic curve toward the ionic-covalent crossing, resulting in an I–I bond rupture. When the I–I bond is broken, the iodine atom that is sticking out of the benzene cluster leaves rapidly, dragging some of the benzene molecules with it. The free iodine fragment was detected within a few picoseconds. The other iodine atom is caged in the remaining benzene cluster, and its escape time from the cluster cage depends on the vibrational energy of the cluster and thus occurs on a much longer time scale, more than a few tens of picoseconds. The dissociation time scales of both steps increase with increasing degree of solvation.

C. Caging Dynamics

Most chemical reactions occur not in isolated but in complex environments. Even weakly bound solvents can perturb reactions significantly. Solvents

can affect the elementary bond-forming and -breaking processes through either enhancing bond formation by encaging reactive species on the reaction time scale or removing the excitation energy of reactants through collisional cooling. To study solvation effects on chemical reactions, cluster methods have taken an important role^{7,165–167} due to the fact that clusters can provide a well-characterized solvation environment on a molecular scale. A wealth of information on solvation effects on reaction dynamics have been obtained via studies of the iodine molecule, which has been investigated in various environments, e.g., clusters, liquid solutions, and solid matrixes, by different research groups employing several different experimental techniques.

An important early experiment on caging dynamics was carried out by Valentini and Cross,¹⁶⁸ who observed a single-atom caging in the I₂·Ar complex upon photodissociation of the I₂ molecule. Zewail's group applied a femtosecond spectroscopic technique to study the dissociation and recombination dynamics of the iodine molecule in large argon clusters^{169–171} as well as in a high-pressure rare-gas cell,¹⁷² in which the gas pressure was varied from essentially ideal gas to that of liquid-like fluid region. Complimentary molecular dynamics simulations¹⁷³ were also performed to aid in interpreting the data. In the experiments involving I₂·Ar_{*n*} clusters,^{169–171} first a femtosecond pump pulse was used to excite the iodine molecules either to the dissociative A state or to the bound B state, and the subsequent dynamics were interrogated by a second femtosecond probe pulse. The signal was detected by laser-induced-fluorescence (LIF). The results show that the mechanism of recombination depends critically on the dissociation dynamics. When the isolated iodine molecule is excited onto the dissociative A state, direct dissociation occurs within 300 fs. The excitation energy is released as the translational energy of the free iodine fragments.

When I₂ is encaged in large Ar clusters, the photodissociated iodine fragments can collide with the solvent cage, relieving its excitation energy. The iodine can coherently recombine onto either the A/A' state or the ground X state within 600 fs after dissociation; subsequent vibrational relaxation would follow. The coherent caging dynamics are found to be dependent on the dissociation time scale, the energy exchange between iodine fragments and cluster cage, and also the collective solvent properties such as geometry and temperature. For example, this coherent dissociation followed by coherent recombination has also been observed in solid rare-gas matrix experiments,^{174–176} whereas in high-pressure gas and liquid solutions at room temperature, due to the lack of collective binding forces, the coherent recombination was not observed.¹⁶⁹

Dissociation and recombination dynamics of an iodine molecule excited to the bound B state are somewhat different. Photoexcitation of isolated iodine molecules to below the dissociation continuum of the B state will not result in dissociation. Predissociation occurs through solvent-induced curve crossing to the lower lying A/A' state or the ground X state, followed

by subsequent vibrational relaxation. The predissociation rate of the B state is solvent dependent and occurs on a much longer time scale when compared to the A state dissociation. Energy transfer from the photoexcited iodine molecule to the cluster cage tends to loosen up the solvent cage during the predissociation, and therefore, the iodine fragments are able to break through the cage and separate far from each other upon dissociation; subsequent recombination occurs through diffusion of the separated iodine fragments. Due to the finite size of the Ar_n clusters, the diffusion of I fragments is confined by the cluster boundary, and therefore, a narrow distribution of recombination rates is observed, compared to high-pressure gas and liquid solution experiments.

Photoinduced reactions and subsequent caging dynamics in methyl iodide clusters is another interesting example.^{177,178} Solvation effects on the electronic states of methyl iodide dimers¹⁷⁹ and clusters^{180,181} have been extensively studied. Evidence from changes in line shapes suggest that the ground state of the methyl iodide is lowered in energy by about 500 cm^{-1} upon dimerization and is lowered up to 1000 cm^{-1} in larger clusters. For excitations from the ground state into the Rydberg B and C states, no spectral shifts can be observed, indicating that these excited states are stabilized in the same way as the ground state. However, the repulsive A state is only stabilized by $\sim 10\text{ cm}^{-1}$ upon clustering. This was suggested to be due to the different strengths of the dipole–dipole interactions of the Rydberg states and the valence states with the solvent shell.¹⁸⁰ Because the Rydberg states and the repulsive A state do not undergo the same amount of energy shift, the coupling between the A state and the Rydberg states is altered. Therefore, the lifetimes of the Rydberg states change upon solvation, as observed experimentally on the $10s$ Rydberg states in our lab.¹⁷⁷ Methyl iodide clusters excited to the $10s$ Rydberg state dissociate within 200 fs through two competing processes: curve crossing to the repulsive A state and internal conversion to the dissociation continuum of the $6s$ Rydberg state. Due to the caging effect on cluster solvation, some of the dissociating CH_3 radicals and I atoms dissipate their excitation energies through collisions with the cluster cage and are able to recombine onto the $6s$ Rydberg state or the lower lying ground X state. Recombination onto the $6s$ Rydberg state occurs on the time scale of picoseconds.¹⁷⁷

Picosecond time-resolved experiments¹¹⁶ on methyl iodide clusters by Syage et al. showed a series of rapid reactions occurring upon photoexcitation to the repulsive A state, resulting in the production of C_2H_6 and I_2 molecules. Interestingly, C_2H_6 was found to evaporate extensively from the clusters after formation, whereas all of the I_2 was caged. Reactions between the photoexcited chromophore and loosely bound solvating molecule have also been observed in femtosecond time-resolved experiments on the methyl iodide dimer by Zewail and co-workers.¹⁷⁸ In this experiment, pump pulse at 277 nm is used to dissociate the methyl iodide molecule and the reaction of the iodine photofragment with the solvating meth-

yl iodide is monitored with a probe pulse at 304 nm by 2+1 REMPI method with a kinetic energy TOF spectrometer. Velocity gating provided the ability for the separation of fast and slow kinetic-energy components of the I^+ ions formed. Pump–probe transients of the slow I^+ ion showed an interesting delayed rise behavior. The time delay was found to be 1.4 ps and the rise time 1.7 ps. The delay of 1.4 ps was interpreted to be due to the formation of the transition-state complex $\text{CH}_3\text{I}_2^\ddagger$, whereas the rise time of 1.7 ps is a measure of the lifetime of the transition-state complex $\text{CH}_3\text{I}_2^\ddagger$.

Time-resolved studies on ionic clusters are also providing insight into the dynamics of photodissociation and caging phenomenon, especially regarding the size-dependent dynamics. Unlike studies involving neutral clusters in which size selection is still an experimental challenge, there is generally no ambiguity concerning the solvent size for clusters with an ionic chromophore, which is an important factor for size-specific investigations. Particularly valuable information regarding ion solvation has been obtained through investigations of the halide dimer anions such as I_2^- , ICl^- solvated with Ar_n ,¹⁸² $(\text{OCS})_n$,¹⁸³ and $(\text{CO}_2)_n$ ^{184–186} clusters. Pump–probe experiments reveal phenomenon having picosecond dynamical events. The caging fraction or quantum yield for formation of the photofragment ions depends strongly on cluster ion size, ranging from zero for small clusters to unity for those of large size. Studies of iodine and bromine anions¹⁸⁷ show that the branching ratio for recombination depends on both the size of the initial cluster and the photodissociation wavelength. The data have shown that the recombination mechanism is dominated by attractive forces in smaller clusters and repulsive interactions in larger ones.

Study of the dynamics of metal clusters employing femtosecond spectroscopic methods has been pursued in depth by several groups, most notably Gerber and co-workers¹⁸⁸ and Wöste and co-workers.^{167,189} A great understanding of ultrafast wave packet dynamics on excited electronic states, size-dependent photodissociation, structural relaxation, and also wave packet dynamics on electronic ground state through NeNePo experiments^{189,190} in particular has been obtained through investigations of small isolated metal clusters. The general subject is beyond the general theme of the present article, where the focus is on van der Waals and hydrogen-bonded systems, and since it has been recently covered in depth by other reviews,^{167,189–191} we do not treat it here.

6. Outlook

Since the advent of femtosecond laser technology, many breakthroughs in the emerging new field, femtochemistry,⁵⁹ have been witnessed over the past decade. The findings discussed in this review are further testimony to the wide-ranging processes that can be explored within the domain of femtochemistry.

Herein, we have demonstrated that clusters exposed to intense laser fields can Coulomb explode giving rise to particles with high-charged states and surprisingly large values of kinetic-energy release. Beyond the interest in the Coulomb explosion phe-

nomenon is the interesting new technique that has emerged from applications that in favorable cases enable intermediates in fast reactions to be arrested and investigated as they undergo transformation from reactants to products. These various findings clearly demonstrate the power of time-resolved spectroscopy in unraveling the dynamics of clusters, and we can expect to observe increasing activity in this field of endeavor. With the development of tabletop solid-state Ti:sapphire lasers, the generation of ultrashort pulses has become relatively simple, allowing the laser experts, as well as nonexperts, to enter this fascinating new field, and many more exciting discoveries are yet to come.

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