REACTION DYNAMICS IN CLUSTERS AND CONDENSED PHASES

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J. JORTNER The Israel Academy of Sciences and Humanities, Jerusalem, Israel

R. D. LEVINE The Fritz Haber Center for Molecular Dynamics, The Hebrew University of Jerusalem,

> Jerusalem, Israel and

B. PULLMAN Institut de Biologie Physico-Chimique (Fondation Edmond de Rothschild), Paris, France



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PREFACE

The Twenty Sixth Jerusalem Symposium reflected the high standards of these distinguished scientific meetings, which convene once a year at the Israel Academy of Sciences and Humanities in Jerusalem to discuss a specific topic in the broad area of quantum chemistry and biochemistry. The topic at this year's Jerusalem Symposium was reaction dynamics in clusters and condensed phases, which constitutes a truly interdisciplinary subject of central interest in the areas of chemical dynamics, kinetics, photochemistry and condensed matter chemical physics.

The main theme of the Symposium was built around the exploration of the interrelationship between the dynamics in large finite clusters and in infinite bulk systems. The main issues addressed microscopic and macroscopic solvation phenomena, cluster and bulk spectroscopy, photodissociation and vibrational predissociation, cage effects, dynamics, reaction dynamics and transfer interphase energy in clusters, dense fluids, liquids, solids and biophysical systems. The interdisciplinary nature of this research area was deliberated bv intensive and extensive interactions between modern theory and advanced experimental methods. This volume provides a record of the invited lectures at the Symposium.

Held under the auspices of the Israel Academy of Sciences and Humanities and the Hebrew University of Jerusalem, the Twenty Sixth Jerusalem Symposium was sponsored by the Institut de Biologie Physico-Chimique (Fondation Edmond de Rothschild) of Paris: We wish to express our deep thanks to Baron Edmond de Rothschild for his continuous and generous support, which makes him a true partner in this important endeavour. We would also like to express our gratitude to the Adminitrative Staff of the Israel Academy and, in particular, to Mrs. Avigail Hyam for the efficiency and excellency of the local arrangements.

> Joshua Jortner Raphael D. Levine Bernard Pullman

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ELUCIDATING THE INFLUENCE OF SOLVATION ON THE DYNAMICS OF CLUSTER REACTIONS

A. W. Castleman, Jr., S. Wei, J. Purnell, S. A. Buzza

Department of Chemistry Pennsylvania State University University Park, PA 16802 USA

1. Introduction

The ionization of neutral ammonia clusters mainly leads to the formation of protonated cluster ions,¹⁻⁹ although unprotonated species (intact $(NH_3)_n^+$) are sometimes observed in single photon experiments conducted under varying conditions.⁴⁻⁶ By contrast, unprotonated species $(NH_3)_n^+$ are not observed in typical nanosecond multiphoton ionization experiments, and they have only been detected under very low fluence conditions. Some fraction of unprotonated clusters is always observed in femtosecond MPI, for which there is no dependence on fluence over a wide range of values.

In the formation of protonated cluster ions under multiphoton ionization conditions, two possible processes¹⁻³ have been proposed: an absorption-dissociation-ionization¹⁰⁻¹² (ADI) mechanism and an absorption-ionization-dissociation^{12,13} (AID) mechanism. The ADI mechanism is proposed to involve formation of long-lived¹⁴ radicals (NH₃)_nNH₄ in the intermediate state, followed by photoionization of these species. On the other hand, the AID mechanism assumes that the protonated clusters are formed through intracluster ion-molecule reactions which proceed upon direct ionization of ammonia clusters.

In order to elucidate these mechanisms we have investigated the ionization of ammonia clusters through the \tilde{C}' and \tilde{A} states using femtosecond pump-probe techniques.¹⁵ The present paper summarizes our findings which resolve the mechanisms that have been the subject of some controversy.

2. Experimental

The apparatus used in these experiments is a reflectron time-of-flight (TOF) mass spectrometer¹⁶ coupled with a femtosecond laser system. An overview of the laser system is shown in Fig. 1(a), and a schematic of the TOF mass spectrometer is presented in Fig.

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is shown in Fig. 1(a), and a schematic of the TOF mass spectrometer is presented in Fig. 1(b). Femtosecond laser pulses are generated by a colliding pulse mode-locked (CPM) ring dye laser. The cavity consists of a gain jet, a saturable absorber jet, and four



Figure 1(a). A Schematic of the Femtosecond Laser System



Figure 1(b). A Schematic of the Reflectron Time-of-Flight Apparatus

recompression prisms. The gain dye, rhodamine 590 tetrafluoroborate dissolved in ethylene glycol, is pumped with 5 W, all lines, from an Innova 300 argon ion laser. In order to generate short pulses, passive mode-locking is performed with DODCI, also

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dissolved in ethylene glycol, acting as the saturable absorber. Four recompression prisms are used to compensate for group velocity dispersion (GVD). The output wavelength, pulse width, and energy are \sim 624 nm, \sim 100 fs, and \sim 200 pJ, respectively.

In order to supply the large photon flux needed for multiphoton ionization (MPI), the laser pulses are amplified through three stages. Each of these is pumped with the second harmonic (532 nm) from an injection seeded GCR-5-30Hz Nd:YAG laser, which is synchronized with the femtosecond laser. The three sequential pump energies for the amplification stages are \sim 33 mJ, \sim 100 mJ, and \sim 250 mJ.

The first stage of amplification is a bowtie amplifier. The gain dye, sulforhodamine 640, is dissolved in a 50/50 mixture of methanol and water. The beam makes six passes through the dye cell giving a total amplification of ~10 μ J. The laser configuration to this point is the same for both the \tilde{A} state and \tilde{C}' state experiments, but the remaining arrangement varies depending on the state to be pumped. For the \tilde{C}' state experiments, a wavelength of 624 nm is used while for the \tilde{A} state experiments, the third harmonic of wavelengths--642 nm, 633 nm, and 624 nm--are used for accessing the v=0, v=1, and v=2 vibrational levels of ammonia molecules, respectively. The wavelength corresponding to the v=2 vibrational level is the third harmonic of the CPM fundamental wavelength; however, the wavelengths for the v=0 and v=1 vibrational levels are obtained by generating a white light continuum in a water cell. After continuum generation, the appropriate wavelength is selected with a 10 nm bandwidth interference filter.

The second and third stages of amplification are performed with 6mm bore prism dye cells, termed Bethune cells. For the amplification of 624 nm wavelength light, the gain dye is sulforhodamine 640 which is dissolved in a 50/50 mixture of methanol and water. For amplification of the 633 nm and 642 nm wavelengths, DCM, dissolved in methanol, is used. The output energy for the 624 nm wavelength light is ~200 μ J after the first dye cell and ~1.5 mJ after the second, with ~10% amplified spontaneous emission (ASE) and a pulse width of ~350 fs. The output energy for the second, with ~10% as and 642 nm is ~50 μ J after the first dye cell and ~1 mJ after the second, with ~10% ASE and ~350 fs pulse width. The second stage of amplification for the \tilde{C}' state is the same as for the \tilde{A} state (v=2); however, the third stage utilizes a 12 mm bore instead of another 6mm bore Bethune cell. The gain dye for the 12 mm bore cell is also sulforhodamine 640. The output energy and pulse width are the same as for the \tilde{A} state; however, the effective pulse width involved in the multiphoton process is considerably shorter, depending on the number of photons absorbed in the excitation and ionization steps.

After amplification, the beam is split into pump and probe beams. For the \tilde{A} state experiment, the pump beams are frequency-tripled and the probe beams are frequency-doubled. This gives pump wavelengths of 214 nm (v=0), 211 nm (v=1), and 208 nm (v=2) and probe wavelengths of 321 nm, 316.5 nm, and 312 nm. Using a 45° high

beam and transmitting the probe beam. The probe beam is sent through a delay stage which can be varied from 0.1 μ m to 1 nm. Thereafter, the beams are recombined using another 45° high reflector. For the \tilde{C}' state experiment, the laser beam is split into identical pump and probe beams at a wavelength of 624 nm. A Michelson interferometric arrangement is used to set the time delay between the pump and probe beams.

After recombination, the laser beams are focused into the interaction region with a 50 cm lens, where they intersect the molecular beam containing the neutral ammonia clusters which are produced via supersonic expansion through a pulsed valve. The ions formed in the multiphoton ionization process are accelerated in a standard Wiley-McLaren doubleelectric field arrangement to an energy of 2000V. (See Figure 1(b).) The ions are directed through the first field free region, which is ~1.5 m long, toward a reflectron. Ions are then reflected, whereupon they travel through a second field free region which is ~0.5 m long. They are thereafter detected by a chevron microchannel plate detector. The signals received by the detector are directed into a digital oscilloscope coupled to a personal computer.

3. Elucidating the Mechanisms

Two mechanisms (Figure 2) have been proposed to account for the formation of rotonated ammonia clusters under multiphoton resonant ionization conditions. The ADI

Reaction Schemes of Ammonia Clusters

$$\begin{array}{c}
\stackrel{mh\nu}{\longrightarrow} (\mathrm{NH}_{3})_{\mathrm{m}}\mathrm{H}^{+} + \mathrm{e}^{-} \\
\stackrel{k_{d}}{\longrightarrow} (\mathrm{NH}_{3})_{\mathrm{m}}\mathrm{H} + \mathrm{NH}_{2} + (\mathrm{n-m-1})\mathrm{NH}_{3} \\
\stackrel{nh\nu}{\longrightarrow} (\mathrm{NH}_{3})_{\mathrm{n}}^{*} \qquad Absorption-Dissociation-Ionization \\
\stackrel{mh\nu}{\longrightarrow} (\mathrm{NH}_{3})_{\mathrm{n}}^{+} + \mathrm{e}^{-} \\
\stackrel{k_{\mathrm{im}}}{\longrightarrow} (\mathrm{NH}_{3})_{\mathrm{m}}\mathrm{H}^{+} + \mathrm{NH}_{2} + (\mathrm{n-m-1})\mathrm{NH}_{3}
\end{array}$$

Figure 2. Two Possible Reaction Mechnisms of Ammonia Clusters

mechanism was initially proposed¹⁰ based on theoretical calculations, and supported¹⁴ by findings that hydrogenated ammonia clusters can have lifetimes of a few microseconds following neutralization of the cluster cations. Recent nanosecond pump-probe studies by

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Mizaizu et. al.¹¹ also provided some evidence for the ADI mechanism for the case of large clusters ionized through the \tilde{A} state. However, the fact that protonated ammonia clusters are formed under electron impact⁷⁻⁹ and single photon ionization⁴⁻⁶ conditions provides support that the AID mechanism must be operative at least under some situations. As discussed in what follows, the femtosecond pump-probe studies reported herein provide detailed insight into the mechanisms of formation of protonated ammonia cluster ions through the \tilde{C}' state and \tilde{A} state.

The possible profiles of intensity versus the delay between the pump and probe photons for the several potential processes operative in the mechanism of ionization are shown in Figures 3(a), (b) and (c). The ionization schemes employed in the present study are



Figure 3. Possible Intensity Profiles for Two Mechanisms (a) Ionization Through AID Mechanism. (b) Ionization Through ADI Mechanism. The signal would persist for long times due to the lifetime of the NH_4 in the cluster, and its ensuing ionization. (c) Ionization Through both AID and ADI Mechanisms.

shown in Figure 4. The results of these studies presented in the next section reveal that different processes are operative in the \tilde{C}' compared to the \tilde{A} state.

4. Results and Discussion

In the first series of experiments, ammonia clusters are ionized by femtosecond laser pulses at 624 nm through intermediate states at energies corresponding to the \tilde{C}' state of the monomer.¹⁷ Pump-probe experiments are employed to distinguish these two



Figure 4. Ionization Schemes of the Present Experiments

mechanisms. Since the ADI mechanism involves a long-lived intermediate $(NH_3)_nH$ to the formation of the protonated species $(NH_3)_nH^+$, varying the delay time of the pump-probe laser (up to 1 picosecond) would have little influence on the protonated cluster signal, which should then persist for long times as shown in Figure 3(b). Note, since the protonated and unprotonated species have different intermediates, the lifetime of the unprotonated species would be expected to be much shorter. However, the measured lifetime for the intermediate to the formation of both $(NH_3)_m^+$ and $(NH_3)_nH^+$ would be expected to be identical if the AID mechanism is operative since there would be a common intermediate for the formation of both $(NH_3)_mH^+$, (n < m). See Figure 3(a).

To ascertain whether the ionization involves resonant or non-resonant multiphoton ionization, we carried out studies of the ionization signal versus the laser power dependence. Contrary to the case in typical nanosecond experiments,³ it is found that the cluster distribution does not shift to small sizes with increasing fluence of the femtosecond laser pulses. A linear relationship between logarithm (laser power) and logarithm (ion intensity) is found¹⁸ for all cluster ions studied and for laser powers ranging from the minimum power for observable ionization up to the maximum power obtainable in the current setup. The ionization potential⁴ of ammonia is 10.17 eV, and depending on cluster size, a minimum of five to six photons are required for ionization. Hence, a slope of 4 which is observed for all five lines, indicates that ionization is achieved through a four-photon resonant intermediate state. This energy corresponds to the \tilde{C}' (v=1) state of the ammonia monomer (8.04 eV).¹⁹

In order to find out whether the protonated cluster ions formed through the \tilde{C}' state follow the absorption-ionization-dissociation mechanism or the absorption-dissociationionization mechanism, we performed femtosecond pump-probe experiments. One beam was used to excite the neutral clusters to the intermediate state, and the second laser beam to ionize the excited clusters. The laser power of each beam is carefully controlled so that the ion intensity resulting from either laser beam alone is less than 5%. Figure 5 shows a typical pump-probe spectrum. Since the pump and probe pulses are identical, the ion



Pump-Probe Spectrum of Ammonia Clusters

Figure 5. Pump-Probe Spectrum of Ammonia Clusters Through the \tilde{C}' State

signal is symmetric at the zero time delay. It is seen that the response curves for all ions are identical within the experimental error. This finding suggests that the lifetime of the state leading to the formation of both the unprotonated and protonated clusters is the same. Since the lifetimes of the neutral species $(NH_3)_nH$ are measured to be on the order of microseconds,¹⁴ the present results which show a rapid increase and decay in the signal versus pump-probe delay can only be explained on the basis of the absorption-ionization-dissociation mechanism. Otherwise, the signal arising from the ionization of $(NH_3)_nH$ would persist for long times corresponding to the microsecond lifetime of this intermediate. The rapid change in signal and the failure to observe ionization through NH₄ is attributed to the fact that the predissociation of ammonia through the \tilde{C}' state has a dominant channel²⁰ via the formation of NH + H₂.

Studies to reveal the mechanisms operative through the \tilde{A} state were conducted in a similar fashion, using the scheme given in Figure 4. Figure 6 shows typical pump-probe

Pump-Probe Spectrum of (NH₃)₂H+



Figure 6. Pump-Probe Spectra of $(NH_3)_2H^+$ through the \tilde{A} (v=0,1,2) States

spectra of protonated cluster ions $(NH_3)_nH^+$, n=2, through different vibrational levels of \tilde{A} states (v=0,1,2) of ammonia molecules, at a time step-size of 200 fs/point. The zero-oftime is defined as the time when the pump and probe pulses are temporarally overlapped which results in the maximum protonated cluster ion signals. It is evident that when the probe is ahead of the pump (negative pump-probe delay), the signal retains a constant value. After that, the signal decreases in an exponential fashion and thereafter levels off to a finite, non-zero value. It is found that this pump-probe signal persists longer than 1 ns. To understand these common time response features which are generally in accord with Figure 3(c), we propose the following dynamical processes in the electronically excited \tilde{A} state of ammonia clusters. The dominant predissociation channel in the \tilde{A} state leads to NH₂ and H.

1. The neutral clusters are excited to the à state through absorption of the first photon,

 $(\mathrm{NH}_3)_{\mathrm{n}} + \mathrm{hv}_1 \rightarrow (\mathrm{NH}_3)_{\mathrm{n}}^*$

The excited clusters undergo intracluster reactions as follows:

2. Predissociation of the excited ammonia moiety

$$(NH_3)_n^* \rightarrow (NH_3)_{n-2} \bullet H_3 N \bullet (H \bullet \bullet \circ NH_2)$$

3. The intermediate species can lead to the loss of H or NH₂, or reaction of the H to form NH₄.

$$(NH_3)_{n-2} \bullet H_3 N \bullet (H \bullet \bullet \bullet NH_2) \rightarrow (NH_3)_{n-2} \bullet NH_4 + NH_2$$

- 4. Ionization of either $(NH_3)_n^*$ or the radicals $(NH_3)_{n-2} \bullet NH_4$ leads to formation of protonated cluster ions as follows:
 - a. $(NH_3)_n^* + hv_2 \rightarrow (NH_3)_n + e^- \rightarrow (NH_3)_{n-2}NH_4^+ + NH_2 + e^-$

b.
$$(NH_3)_{n-2} \bullet NH_4 + h\nu_2 \rightarrow (NH_3)_{n-2} \bullet NH_4^+ + e^{-2}$$

It should be noted that the rapid intensity drop observed for all protonated cluster ions when $n\geq 2$ is attributed to reaction 2, where the NH₂ or H containing species cannot be readily ionized. Reaction 3 leads to formation of long-lived radicals in accordance with the findings of non-zero ion intensity values at long pump-probe delays observed in the data for the \tilde{A} state. The relative importance of the ionization of the NH₄ in the overall ionization of ammonia through the \tilde{A} state at different vibrational levels is seen in Figure 6 and by comparing other data for the trimer and hexamer, detected as the protonated dimer and pentamer cluster ions.²² The overall dependence of the decaying signal intensity on the vibrational level is indicative of the influence of the energetics on the predissociation and reaction forming NH₄, while the trend in the long-time tail reflects effects due to solvation and retainment of NH₄.

Proposed pseudo-potential wells, which are consistent with all of the experimental findings from our studies, are shown in Figure 7. Our findings that ionization through the A state (v>0) displays a peak followed by rapid decay leveling off to a non-zero value of ion intensity, suggest that two processes are operating simultaneously. Since it is known²¹ that ammonia clusters rapidly predissociate into $NH_2 + H$, the rapid decay that we observe would suggest that a similar predissociation mechanism is taking place in the clusters. It is also known¹⁴ that the radicals $(NH_3)_nNH_4$ have long lifetimes (greater than 1 ns). Evidence suggests that formation of these radicals is taking place through intracluster reactions. For the case of \tilde{A} (v>0), this is seen in the leveling off to a non-zero value of ion intensity which persists for longer than 1 ns. Unlike the \tilde{C}' state which follows only the AID mechanism, it appears that the processes in the à state compete between both the AID and ADI mechanisms. The AID is the dominant process when the pump and probe pulses are overlapped (t = 0), while the ADI is the major mechanism when the probe is at a longer time delay. The failure to see a definitive long-time tail for \tilde{A} (v = 0) is attributable to the likelihood that the predissociation is probably endothermic for this situation.11



MPI of Ammonia Clusters

Figure 7. Proposed Potential Surfaces of Ionization of Ammonia Clusters; the dashed potential curve represents a different reaction coordinate for species formed by predissociation in the à state (see text). The probe beam (dash-dot) is time delayed by a selected value.

5. Conclusions

Femtosecond pump-probe techniques have revealed the mechanisms of ionization operative for multiphoton ionization involving the \tilde{C}' and \tilde{A} states of ammonia clusters. In the case of the \tilde{C}' state, lifetimes of less than 100 fs for the species $(NH_3)_n^+$, and $(NH_3)_nH^+$, (n = 1-4) establish the AID as the sole operative mechanism in the \tilde{C}' state. For the \tilde{A} state (n=2-5), the pump-probe experiments show two distinct features with respect to the pump-probe delays: a fast decay process, followed by a leveling off to a non-zero value of ion intensity. These observations support a competing process between the AID and ADI mechanisms. The first process, a maximum peak at t = 0 followed by a rapid decay, supports the AID mechanism. These observations are consistent with those observed for the \tilde{C}' state. The second process, leveling off to a non-zero value persisting for longer than 1 ns, supports the ADI mechanism. Work is in progress to model the lifetimes of the individual steps in the reaction mechanisms.

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