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Delayed ionization following resonant photon absorption and intracluster electron transfer

P. D. Dao and A. W. Castleman, Jr.

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

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Ionization of clusters comprised of paraxylene (PX) bound to NH₃ and N(CH₃)₃ is studied following the absorption of photons through the perturbed S_1 state of PX. In the case of PX \cdot NH₃ where the ionization potential of PX (8.445 eV) lies below that of NH₃ (10.16 eV), ionization of the cluster near the ionization threshold of PX leads to the formation of the cluster ion (PX \cdot NH₃)⁺. By contrast, for clusters of PX \cdot N(CH₃)₃ where the ionization potential of N(CH₃)₃ (7.82 eV) lies below that of PX, resonance absorption through high Rydberg states of PX below its I.P. leads to the production of N(CH₃)₃⁺ and H⁺ \cdot N(CH₃)₃, but no parent cluster ions. In this case, following photon absorption the ionization and formation of N(CH₃)₃⁺ is substantially delayed for times ranging from 160–200 ns, the longer values being obtained at lower photon energies.

INTRODUCTION

Ionization of atoms or molecules following the absorption of a photon can proceed through various well-known processes which depend on the nature of the system and the wavelength of the light, and of course, the selection rules for the case under consideration.¹ Direct ionization is prompt, and for allowed transitions autoionization typically occurs in the range of 10^{-15} – 10^{-13} s; but, for unallowed cases significantly longer times are found.²

Atoms and molecules that become excited below their ionization threshold can also cause ionization through collisions with other constituents in the system; two such processes are associative ionization,³ where bond formation is involved, and Penning ionization^{3,4} where an electron is transferred from the colliding partner of lower ionization potential to the excited atom or molecule, whereupon electron ejection ensues. In atomic systems Penning ionization is rapid and occurs with high cross section,^{3–5} although in molecular systems steric factors can significantly reduce the probability.

An interesting comparison to these well-known gas phase bimolecular collision processes is provided by results of studies on molecular clusters of specific composition. Findings from such studies are expected to also bear on related investigations made in the condensed state. Investigation of the multiphoton ionization of clusters, including observation of reactions in clusters and fragmentation, have been reported in the literature for a number of systems⁶⁻¹²; but, to the best of our knowledge none have dealt with the case of absorption through the well-defined (perturbed) states of one component of a cluster, leading to ionization of a bound partner having a lower ionization potential.

Herein, we report the results of a study that may be considered to be an internal Penning ionization process within a cluster. Evidence is presented for unusually long delays in ionization following photon absorption, which we believe is the first such finding for a gas phase system. Experimental data showing that delays in ionization lengthen with lower photon energy is given for the case of paraxylene (PX) bound to $N(CH_3)_3$, leading largely to the production of $N(CH_3)_3^+$ following photoexcitation. Contrasting results are presented for the analogous system $PX \cdot NH_3$ where $PX \cdot NH_3^+$ is the dominant product ion.

EXPERIMENTAL

The details of the experimental apparatus have been described elsewhere.¹⁰⁻¹² Briefly, it consists of a pulsed source used to produce clusters via supersonic expansion through a 0.2 mm diameter nozzle from high pressure into vacuum. The molecular beam is collimated using a Beam Dynamics skimmer having a 1 mm diameter hole 1.5 cm away from the nozzle. Ions are formed by multiphoton ionization using a pulsed Nd:YAG-pumped dye laser (Quanta Ray DCR1A and PDL) system. The time-of-flight lens (TOF) where the ions are born is located 16 cm away from the nozzle in a second vacuum chamber which is differentially pumped.

The ions are accelerated out of the ionization region toward the ion collector by two uniform electric fields (see Fig. 1). If all ions of a given mass-to-charge ratio (m/q) are



FIG. 1. Detailed schematic of the time-of-flight (TOF) electrodes. Laser ionization occurs at point S_0 and the photoions are accelerated by the double acceleration stage towards the ion detector.

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TABLE I.	Typical ex	perimental	parameters	in	this	TOFMS.
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the second se	
Electric potential (V):	$U_i = 1250 \text{ V} \text{ (at electrode 1)}$
•	$U_2 = 1100 \text{ V}$ (at electrode 2)
	$U_3 = 0$ (at electrode 3)
	$U_T = 1160 \text{ V} \text{ (ion energy)}$
	$U_0 = 0.03 \text{ eV}^*$ (axial energy spread)
Distances:	D = 48 cm (distance TOF lens to
	detector)
	d = 1.0 cm (distance between 2 adjacen electrodes)
	s = 0.4 cm (between location of ion
	birth and electrode 2)
Electric	Time (us)

	Mass (amu)	$\Delta T(\mu s)^{\circ}$
$E_1 = 150 \text{V/cm}$	$T_1 = 0.0745 \text{ m}^{1/2}$	$\Delta T_1 = 0.003 \ 33 \ \mathrm{m}^{1/2}$
$E_2 = 1100 \text{V/cm}$	$T_2 = 0.0345 \text{ m}^{1/2}$	$\Delta T_2 = 0.000 \ 04 \ \mathrm{m}^{1/2}$
	$T_3 = 1.01648 \text{ m}^{1/2}$	$\Delta T_3 = 0.000 014 \mathrm{m}^{1/2}$
	$E_1 = 150 \text{ V/cm}$ $E_2 = 1100 \text{ V/cm}$	$E_1 = 150 \text{ V/cm} \qquad T_1 = 0.0745 \text{ m}^{1/2}$ $E_2 = 1100 \text{ V/cm} \qquad T_2 = 0.0345 \text{ m}^{1/2}$ $T_3 = 1.01648 \text{ m}^{1/2}$

^a Energy spread of supersonic beam (argon, Mach 10), J. B. Anderson, R. P. Andres, and J. B. Fenn, *Advances in Atomic and Molecular Physics*, edited by D. R. Bates (Academic, New York, 1965).

^b Time spread due to distribution of initial velocities (for argon beam).

born in a plane parallel to the electrodes 1 and 2 (at potentials U_1 and U_2 as listed in Table I), and with zero initial velocity, they will arrive at the ion detector at the same time. In contrast to the case of a stagnant gas where there is a thermal distribution of initial velocities, in a supersonic expansion all neutral products essentially travel at the beam velocity and have a narrow axial spread of kinetic energy.

Ions born within the first electric field have approximately the same kinetic energy just before entering the fieldfree drift region. The flight time is a function of distance and the parameters d, D, E_1 , and E_2 which are defined in Table I. (Also see Fig. 1.) The overall time is composed of the time T_1 , for an ion to get to the middle grid, the time T_2 , the ion spends in the second acceleration stage, and T_3 , the drift time in the field-free region. Based on standard equations for ion motion in a uniform electric field, these times are given by

$$T_1 = \frac{(2m)^{1/2}}{qE_1} \left[(U_0 + qsE_1)^{1/2} \pm U_0^{1/2} \right], \qquad (1)$$

$$T_2 = \frac{(2m)^{1/2}}{qE_2} [(U_0 + qsE_1 + qdE_2)^{1/2} - (U_0 + qsE_1)^{1/2}], (2)$$

$$T_3 = D \left[\frac{2(\mp U_0 + qsE_1 - qdE_2)}{m} \right]^{-1/2},$$
 (3)

where U_0 denotes initial energy. The times obtained with our operating conditions are calculatable from the parameters given in Table I.

The laser beams are intersected between the first and second electrodes of the TOF lens (see Fig. 1). When one YAG harmonic beam is used for both dye lasers, the beam is split 30/70 by dichroic elements. Dividing the pumping laser into unequal parts enables one dye laser output (ionizing beam) to be more intense than the other (probe laser for exciting the perturbed S_1 state). The dye laser outputs can be frequency doubled, mixed with the 1.06 μ , or doubled and mixed with the 1.06 μ as appropriate.

A set of six crystals contained in two modules (WEX-1)

extend the wavelength range of the pulsed dye laser into the ultraviolet (432-216 nm). In many instances the crystal in the second module are used to frequency double another dye laser output. Whenever both tunable outputs are used in the multiphoton ionization of the beam molecules, they are crossed at right angles with the molecular beam between the first two electrodes of the TOF lens. In the two-color experiments, the laser beams are left unfocused (cross section $\sim 0.3 \text{ cm}^2$) to avoid undesirable nonresonant multiphoton excitation and ionization. The laser bandwidth of the dye output is measured by a Fabry-Perot etalon to be ~ 0.6 cm^{-1} ; however, with a pressure-tuned intracavity etalon, the resolution is improved to 0.1 cm^{-1} . The temporal width of the fundamental output is 6-9 ns. In order to monitor the laser shot-to-shot fluctuation and normalize the ion signal to the laser power, two fast pyroelectric joulemeters (Molectron, model J3) are used. These joulemeters have a flat response over a wavelength range of 1 nm to $1000 \,\mu$.

RESULTS

Two cluster systems were chosen for detailed investigation, one comprised of paraxylene bound to a species with higher ionization potential (NH₃) and a second one of paraxylene bound to N(CH₃)₃, a molecule which has a lower ionization potential than paraxylene. Dramatically different results were obtained in these two systems by effecting ionization through absorption of photons in paraxylene via the S_1 state.

PX-NH₃ cluster system

As an extension of our studies of spectral shifts in the electronic states of substituted benzenes upon clustering with various molecules^{11,12} we undertook an investigation of the resonance enhanced ionization of $PX \cdot NH_3$ through the S_1 state of paraxylene. Based on findings of appreciable red shifts in the electronic origin of the S_1 state in phenyl acetylene due to clustering with rare gas atoms as well as a variety of other molecules including NH_3 , and similar results for the case of rare gas atoms bound to paraxylene, a red-shifted spectrum was anticipated. As discussed below, this is precisely what is observed.

The origin of the S_1 electronic state of paraxylene is 36 740 cm⁻¹. Since this is more than half the first ionization energy of 8.445 eV^{13,14} one color resonant enhanced two-photon ionization results in an excess energy of more than 0.66 eV¹⁵ in the cluster ion formed between PX and another atom or molecule. In order to probe the PX \cdot NH₃ system near the ionization threshold, two-color techniques were employed as discussed in the preceding section.

Ionization of ammonia to the ${}^{2}A_{1}$ state requires 10.16 eV, 16 a little over 1.7 eV higher than for ionizing paraxylene. For purposes of discussion, a pseudo-two-dimensional potential energy diagram along the dissociation coordinate for paraxylene bound to ammonia is shown in Fig. 2; well depths are schematic. One of the asymptotic limits lying about 0.1 eV^{17,18} higher than the ionization potential of paraxylene is that corresponding to the removal of an H atom from paraxylene leading to a protonated ammonia ion, namely NH₄⁺.



FIG. 2. Laser-induced processes in PX-NH₃ complexes.

The resonant two-photon ionization (R2PI) spectrum of $PX \cdot NH_3^+$ shows multiple absorption peaks at energies close to the S_1 state of paraxylene. The dominant product is the parent cluster ion $PX \cdot NH_3^+$. Figure 3 displays the spectrum taken with 300 Torr of NH_3 behind the nozzle and the ionizing photon energy at 3.89 eV. For a range of stagnation pressures (200–450 Torr), the spectrum remains uncongested from photofragmentation and displays five absorption lines red-shifted by 4 (strong), 26 (strong), 47 (medium), 67



FIG. 3. R2PI spectrum of $(PX \cdot NH_3)^+$. The spectrum is recorded with a stagnation pressure of 300 Torr (NH_3) . The photon energy of the ionizing laser is fixed at 3.89 eV.

(weak), and 78 cm⁻¹ (strong) from the S_1 state of unclustered paraxylene.

Since the sum of photon energies is at the dissociation threshold of $C_8H_{10}^+(PX^+) + NH_3$, and approximately 0.1 eV lower than the $C_8H_9 + NH_4^+$ limit, there is a possibility of observing fragmentation into the $C_8H_{10}^+$ channel (see Fig. 2). A careful study over the two-photon energy range from 8.42 to 9.09 eV revealed no evidence of dissociations yielding either $C_8H_{10}^+$ or NH_4^+ . However, by increasing the laser fluence of the ionizing photon, enhancing the 1 + 2 ionization, we are able to induce fragmentation into both channels. R2PI spectra of both mass-to-charge ratios show the spectral fingerprint of $PX \cdot NH_3$ (see Fig. 4). The findings are in accord with what is expected for the ionization of a simple cluster as found in earlier investigations of related systems.^{11,12}

PX · N(CH₃)₃ cluster system

The energetics of the PX \cdot trimethylamine (TMA) is favorable for studying laser-induced reactions in a complex where intracluster Penning ionization and electron transfer might occur. The right-hand asymptotes (Fig. 5) depict the energetics of the ion-molecule reactions that can occur.¹⁶⁻¹⁸ Because of the lower ionization potential of the amine [I.P.(TMA) = 7.82 eV¹⁶], the normal gas phase charge transfer reaction:

$$\mathbf{PX}^{+} + \mathbf{TMA} = \mathbf{PX} + \mathbf{TMA}^{+} \tag{4}$$

is exothermic by 0.62 eV. The proton transfer reaction shown in Eq. (5) is even more exothermic:

$$C_8H_{10}^+ + TMA = C_8H_9 + TMA \cdot H^+$$
 (5)

It has been observed in the $PX \cdot NH_3$ and other van der



FIG. 4. Two-photon ionization and three-photon dissociative ionization of PX·NH₃.



FIG. 5. Laser-induced charge transfer in PX-TMA complexes.

Waals (vdW) complexes that, for ionization near threshold, PX⁺ ions remain bound to the clustering partner.¹² The binding is the sum of pure vdW interactions and electrostatic forces. In the TMA case, however, the existence of the PX + TMA⁺ potential surface renders the PX⁺ · TMA bound state unstable, perhaps repulsive. In cases where the characteristic crossing time is shorter than that for mass selection, (PX · TMA)⁺ complexes would not be observed. Schematic two-dimensional potential energy diagrams along the cluster dissociation coordinate are shown in Fig. 5.

Three energetic situations need to be considered: (a) the two-photon energy is higher than the $PX^+ + TMA$ dissociation limit, (b) the energy range probed is approximately between the $PX^+ + TMA$ dissociation and the bound state energy of $(PX \cdot TMA)^+$, and (c) the energy available is much lower than the mentioned limit, but still higher than the PX + TMA⁺ limit.

The first situation (a) corresponds to the half-collision between PX^+ and TMA, resulting in the ion-molecule reactions shown in Eqs. (4) and (5). (Similar bimolecular ionmolecule reactions have been studied and are discussed later.) Due to the relative ionization potentials of PX and TMA, excitation of the complex through high Rydberg states¹³ of paraxylene, yet below its ionization threshold, should enable intracluster electron transfer analogous to Penning ionization to occur and be investigated.

Another possible reaction to the $PX^+ \cdot TMA$ system is that of proton transfer shown in Eq. (5). If proton transfer is exothermic and if there are no competing reactions, it should in general be very fast. (Note that similar gas-phase reactions which occur at rates close to collisional are not uncommon.) Therefore, experiments on the PX^+/TMA system enable study of the two parallel reactions, charge and proton transfer, in a half-collision of an ion-molecular pair.

Situation (b), where the two-photon energy lies below the ionization of PX and approximately higher than the zero-point energy of the vdW well, has no analog in gas phase ion-molecule reactions. Even in this case, the exothermicity of the intracluster reaction provides enough energy to dissociate the cluster ion. And, finally, situation (c) corresponds to two-photon energies several thousand cm^{-1} below the ionization energy of PX.

Experiments generally were conducted at a stagnation pressure of less than 150 Torr in order to minimize the production of larger clusters ($\mathbf{PX} \cdot \mathbf{TMA}_n$). No parent ions correspond to PX · TMA⁺ were detected under any ionizing conditions; the only products were the dominant ion TMA⁺ and a small signal due to the protonated amine. Figure 6 shows the ion yield (TMA⁺) from exciting the vdW complex by a photon red shifted by 28 cm⁻¹ from the S_1 state of paraxylene, and scanning the wavelength of the ionizing laser. The one-color R2PI signal is subtracted from the overall two-color signal plotted in the figure. The ion yield curve is seen to be a slow rising threshold; the ion yield at 2330 cm^{-1} below the appearance potential of PX⁺ is still approximately 10% of the yield obtained when the wavelength of the photon is tuned to the main resonance. The ion yield at the third harmonic of the YAG output (3547 Å, which is red shifted by 3170 cm⁻¹), not shown in Fig. 6, is still finite. Since the relative laser fluence at 3547 Å with respect to the tunable UV output used is not known, the 355 nm data point is omitted from the figure.

Figure 7 shows the TOF ion mass spectrum corresponding to TMA^+ and $TMA \cdot H^+$. The ion peak is asymmetrically broadened into a tail to the longer time side, an effect which is increased as the two-photon energy is lowered. A slow ion production process compared to the typical ion residence time in the TOF lens is shown to be responsible for this interesting finding.

Larger complexes with more than one TMA attached to the aromatic center might be considered to be the precursor of TMA⁺ ions and this must be considered first. Therefore, a series of experiments were performed to investigate this possibility. The stagnation pressure was kept low in all scans, and for measurements over the range of P_0 from 100–150



FIG. 6. Ion yield curve of TMA⁺ ion via the perturbed S_1 state of PX. The vdW complex PX·TMA is excited to S_1 and subsequently, by a second laser, to dissociative reaction. The total photon energy is relative to AP(PX⁺).



FIG. 7. Ion mass peaks at different two-photon energies. Broadening of TMA⁺ ion peaks as a function of the ionization energy. The broadenings in B and C correspond to time constants of 160 ± 20 and 200 ± 20 ns, respectively. The peaks corresponding to TMA·H⁺ are also observable.

Torr [trace PX: TMA (5%): He (95%)] the R2PI spectra remained identical. To further disprove the contribution of larger complexes, the stagnation pressure dependences of TMA⁺, PX · NH₃⁺, and PX · (NH₃)₂⁺ ion signals were studied at $\lambda_1 = 2723.5$ Å and $\lambda_2 = 3190$ Å. The excitation laser λ_1 was tuned to a common resonance of all three cluster species and the ionizing photon λ_2 was fixed such that the two-photon energy was 8.44 eV, i.e., just below the ionization threshold of paraxylene. Figure 8 displays the ion signals of TMA⁺ and PX · (NH₃)₂⁺ relative to PX · NH₃⁺. It is seen that the TMA⁺/PX · NH₃⁺ ratio remains constant, while the TMA⁺/PX · (NH₃)₂⁺ ratio decreases with in-



FIG. 8. Stagnation pressure dependence of TMA⁺ and PX- $(NH_3)_2^+$ ion signals relative to PX- NH_3^+ . The latter shows a stronger dependence of stagnation pressure. The results suggest that in the low stagnation pressure range, the precursor of TMA⁺ is a binary complex (PX-TMA).

creasing P_0 . These findings show that the TMA⁺ signal is attributable to a bimolecular precursor.

Furthermore, the possibilities of free ion-molecule reactions and Penning ionization between laser-produced PX⁺ (or PX^{**}) with beam TMA molecules can also be eliminated from consideration as causes of the delayed ion tail. By studying the effects of varying the pulsed nozzle-laser time delay one can monitor the ion-molecule reaction contribution. No dependence on the nozzle-laser delay times was found. (Note that it is possible for drawn-out PX⁺ ions to also reactively collide with beam TMA molecules.) Additionally, Rydberg molecules PX^{**}, because of their large electronic clouds, can Penning-ionize TMA. Since the TMA R2PI spectra shows absorption features different from the S_1 origin of PX, we discard both possibilities (see Fig. 9).

It is possible for the fragmentation of larger ions to cause a delayed ion signal. However, in this case the shape of the "tail" must display an irregular break.¹⁹ In our TOF acceleration stage, the ions are accelerated through two distinct regions, 1 and 2, which are 0.5 and 1.0 cm long, respectively (Fig. 1). Optimum operating conditions dictate the use of a low field strength in region 1 (150 V/cm) and a higher field (1100 V/cm) in region 2. (See typical experimental parameters in Table I.) All values quoted below correspond to the normal operation of the TOF-MS and the dissociation of the metastable ($PX \cdot TMA$)⁺ ion to give a TMA⁺ daughter ion. If the parent ion dissociates (as shown) as it is accelerated through regions 1 and 2, it will appear in the TOF spectrum at a time intermediate between the parent and daughter flight times. From Table I it is also found that the first 0.96



FIG. 9. R2PI spectra of complexes leading to the production of TMA⁺ and TMA·H⁺. Both spectra are recorded simultaneously with 150 Torr of trimethylamine (5%): He (95%) and a trace amount of *p*-xylene (PX).

 μ s of the parent ions life (residence time in region 1) is mapped into a spread of 544 ns in the TOF spectrum. Note that the difference in residence times in region 1 of mass 59 and 165 is 384 ns, and the differences in flight times due to different kinetic energies is 160 ns. The next 0.44 μ s of the parent ion lifetime, however, is spread into the interval of 5.85 μ s that separates the TOF's of daughter and parent ions. Consequently, any first-order decay of the parent ions should induce a sharp break in the daughter mass peak; furthermore, the break should occur at about 544 ns after the correct TOF of the daughter ion. This feature has been exploited by Zare and co-workers¹⁹ to measure dissociation rates of ions formed in a TOF mass spectrometer.

Clearly, slow ion production causes the asymmetric broadening of the TMA⁺ ion peak. The shape of the tail can be analyzed to obtain the time constant of the information. Regardless of their times of birth (t = 0 at laser excitation) all TMA⁺ ions carry the neutral beam energy, the only difference in their times of flight is due to their ion birth potential. If the ionization delay is ∂t , then its ion birth potential is lower than the potential of the ions born at the laser crossing. The potential difference is proportional to the neutral beam velocity, the electric field strength (V/cm) and the time delay itself. The reduction of the birth potential results in a lower ion kinetic energy in the drift region. From Table I it is evident that the dominant contribution to the overall time-offlight is the residence time in the field-free region. To figure out the change of TOF due to delay ion production, only the flight in the drift region is considered. From Eq. (3), the time lag is approximated as

$$\frac{\Delta T}{T} \simeq \frac{\partial t}{T} + \frac{v_b E_1 \partial t}{2\left[(s - v_b \partial t)qE_1 + qdE_2\right]} \,. \tag{6}$$

In Eq. (6), t = 0 corresponds to the occurrence of the laser, v_b is the neutral beam velocity, and ∂t is the ionization delay. For realistic operating conditions, the second term on the right-hand side is approximately $1.27 \times 10^{-2} \partial t$, and (6) becomes

$$\Delta T \simeq \Delta t + (1.27 \times 10^{-2}) (T) \Delta t . \tag{7}$$

From Eq. (7), it is evident that ΔT can be approximated by Δt . Based on this approximation, the ion production time constants measured at 8.24 and 8.16 eV are estimated to be 0.16 and 0.20 μ s, respectively.

The interestingly long lifetimes of two-photon excited $PX \cdot TMA$ are attributed to the time needed to cross from the $PX^+ + TMA$ to the $PX + TMA^+$ electronic surfaces. It is considered likely that at 0.3 eV below the $PX^+ + TMA$ limit, the laser-induced reaction corresponds to an intracluster Penning ionization. This should correlate with Penning processes in which the neutral species is in direct contact with the ion and the Rydberg electron remains inactive.²⁰

The origin of the TMA⁺ signal is established to be the bimolecular complex PX \cdot TMA. Within the two-photon energy range where the broadening is not too excessive, the branching ratio between charge transfer and proton transfer products remains constant around 9:1 with charge transfer as the dominant channel. Tiernan and Hughes²¹ impacted cyclobutane ions (C₄H₈⁺, 9.6 eV) with various amines and observed charge transfer to increase by a factor of ~ 10 from methylamine $(I.P. = 8.97 \text{ eV}^{16})$ to trimethylamine $(I.P. = 7.82 \text{ eV}^{16})$. They measured a charge transfer reaction rate of 1.3×10^{-9} cm³ molecule⁻¹ s⁻¹ at a kinetic energy of 0.3 eV. The branching ratio of the free reaction of $C_4H_8^+$ + TMA at 0.3 eV kinetic energy was measured to be 18.5:1 in favor of the charge transfer product.²¹ Since it is generally found that a long collision complex lifetime favors proton transfer, it is interesting that half-reactions starting from a stable complex do not dramatically do so. Symmetrical proton transfer of the $TMA^+ + TMA$ system shows effects of ionic internal energy, as measured by Hellner and Sieck.²² They found that the proton transfer rates vary as a function of photon energy used to produce TMA⁺. The rate decreases by 40% as the photon energy increases from 8.4 to 11.7 eV.

In charge transfer reactions between rare gas ions and simple molecules, at least two reaction mechanisms have been observed: At low kinetic energies, the molecules are allowed to distort at the approach of the ion. Because of this perturbation, the charge transfer cross sections do not follow the photoelectron envelopes of the molecules. This situation is possible when the electron is transferred at distances where the ion starts interacting strongly with the molecule to allow the energy mismatch to be transferred from the internal degrees of freedom to the product kinetic energy. At low energies this momentum transfer explains large nonresonant rate constants. At high kinetic energies, these systems show the importance of vertical Franck-Condon processes. But, because the molecular ion can dissociate after charge-transfer reactions, the recoil energy of its fragments can accommodate the energy mismatch.

In the case of molecular ion-molecule charge transfer reactions, strict adherence to an energy resonance condition is observed even less often. In some cases electron transfer can proceed without formation of collision complexes as evidenced by the existence of charge transfer reactions having rate constants comparable to the collision rate. However, in other reactions of thermal ions with molecules, charge transfer is found to proceed through the formation of well-defined complexes.²³ The lifetime of an ion-molecule complex increases as the kinetic energy is decreased, the lifetimes of about 10^{-7} s have been recorded.²⁴ The general trends observed for the charge transfer reactions of systems which form complexes are typified by results for monosubstituted benzene ions with anisole where the cross sections are found to increase with increasing recombination energies.²⁵ In light of these gas-phase findings, in cases where strong interactions do exist between the ion-molecule pair, one might expect that intracluster charge transfer reactions are governed by the exothermicity.

A remaining question concerns whether the tail in Fig. 7 is actually associated with TMA⁺ or rather with the protonated species TMA \cdot H⁺. The peak to the right of the main one in the figure is the time-of-flight of TMA \cdot H⁺, and the time delay might be due to the rearrangement step necessary for proton transfer. Conversely, a tail on the primary TMA⁺ peak would suggest a delay in the electron transfer involving an intracluster Penning ionization process.

In order to resolve this crucial point, experiments were performed with fully deuterated PX. The results are shown in Fig. 10. The first main peak (at the left) is due to TMA⁺; the second (minor peak) arises because of the ¹⁵N isotope in TMA. Finally, the third peak is due to TMA \cdot D⁺. Clearly, the long-time tail originates from the primary parent ion TMA⁺, providing the role of charge transfer in the delayed ionization process. In agreement with the findings for the nondeuterated system, the tail, and hence the delay in ionization, lengthens for lower values of the photon energy as seen by comparing curves A and B.

Due to the fact that the ionization potential of PX is greater than that of TMA by about 0.6 eV, crossover between the two core ion states is expected when probing with photons in high Rydberg states just below the ionization threshold at PX. Hence, because of the instability of the $PX^+ \cdot TMA$ potential well, a definite threshold of TMA^+ production could not be determined (see Fig. 6).

Slow rising ionization thresholds have been measured for weakly bound complexes such as water dimer²⁶ and fluorobenzene-CCl₄.²⁷ In those cases, the unfavorable Franck-Condon factors are due to the geometry change upon ionization. Poor Franck-Condon overlaps are responsible for the FB \cdot CCl₄⁺ ionization threshold which has a width of $\sim 2000 \text{ cm}^{-1}$. The bond refraction of C-N (in TMA) is 4.2 times smaller than C-Cl (in CCl_4)²⁸; the stabilization energy of PX^+ in $PX^+ \cdot TMA$ is accordingly smaller. The bad Franck-Condon overlap cannot be the only reason behind the threshold width observed in the PX · TMA system (width > 3170 cm^{-1}). We suggest that coupling to a low-

FIG. 10. Ion peaks at m/e = 59 (TMA⁺), 60 (¹⁵N·Me₃⁺), and 61 (TMA·D⁺). The first laser is tuned into the S_1 excited state of $(d_{10}$ -PX)·TMA $(\lambda_1 = 2712.75 \text{ Å})$. The second laser is fixed at -965 cm^{-1} (case A) and at - $1565 \,\mathrm{cm}^{-1}$ (case B), i.e., red shifted relative to the ionization threshold of paraxylene.

lying electronic potential surface has smeared out the ionization threshold.

CONCLUSIONS

Studies of the formation of product ions resulting from the ionization of PX · TMA through the absorption of photons via the perturbed S_1 state of PX are reported. No intact parent ions are detected, the major product ion being TMA+ with the protonated species TMA \cdot H⁺ as a minor product. Probing the system through high Rydberg states in the neutral paraxylene leads to TMA⁺ via charge transfer.

The finding of a transfer of charge between the two partners in the cluster due to photoabsorption bears a similarity to the studies of Bowers and co-workers²⁹ on the photodissociation of KrO_2^+ . Their dissociation study is related to the charge transfer reaction

$$Kr^+ + O_2 = O_2^+ + Kr$$
. (8)

Since reaction (8) is exothermic by 1.94 eV for the $Kr^{+}({}^{2}P_{3/2})$ state, the production of $Kr^{+}(^{2}P_{3/2})$ and O_{2} from KrO_{2}^{+} by absorption of a visible photon of energy higher than 1.94 eV is energetically accessible. Since they reported the Kr⁺ signal as the product, the corresponding charge transfer reaction is the reverse of Eq. (8). Before photon absorption, the positive charge largely resides on the oxygen molecule; hence, the dissociation yield curves are related to the cross sections of the charge transfer reaction.

The particular significance of the present work is not only the observation of TMA ionization within a cluster through photoexcitation of the paraxylene partner, but more importantly the long time delay associated with the ionization step (electron transfer). Interestingly, Hatano³⁰ has found that evidently orientational effects in the liquid phase, where motion is restricted, lead to a significant reduction in the rate of Penning ionization. Whether there is some analogy with the long delays in ionization for NH₃ on silver electrode surfaces that has been observed by Harris³¹ is unknown, but represents an important question worthy of study.

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