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Ammonia–Acetone Mixed Clusters: Internal Ion–Molecule Reactions, Structure, and Bonding

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Abstract: Internal ion–molecule reactions in mixed ammonia–acetone clusters are studied by use of multiphoton ionization. Some differences in the branching ratios that arise in the clusters produced by using three clustering methods serve to elucidate reaction mechanisms. In experiments involving the coexpansion of the vapors, the ion intensity ratio $[(C_3H_6O)_{m+1}^+]/[(C_3H_6O)_m^+H^+]$ increases as the ammonia/acetone mixing ratio increases. The result indicates that the unprotonated cluster ions $(C_3H_6O)_{m+1}^+$ result from the ionization of the mixed clusters $(NH_3)_p(C_3H_6O)_q$ and, most importantly, suggests that the keto form of the ion is responsible for photon transfer in this system. In the second method, involving the attachment of acetone to preformed ammonia clusters, the acetone molecules strongly interact with the preformed neat ammonia clusters to form long-lived mixed neutral acetone–molecule clusters $(NH_3)_p(C_3H_6O)_q$. When mixed neutral clusters are formed by the addition of ammonia to preexisting acetone clusters, only small signals of $\{(NH_3)_n(C_3H_6O)_m\}H^+$ ion peaks for $n = 1$ and $m = 1-4$ are observed, even at high ammonia flow rates. This indicates that the incoming ammonia molecule is not well accommodated in the preformed acetone clusters to form mixed acetone–ammonia clusters. The observed $\{(NH_3)_n(C_3H_6O)_m\}H^+$ ions evidently result from the intracuster ion–molecule reaction between two like molecules accompanying an electron-transfer reaction in a heteromolecular cluster ion.

Studies of the properties, structure, and reactivities of molecular clusters contribute to an understanding of the chemical dynamics and bonding in systems lying between the gaseous and condensed state.¹⁻⁴ Although various techniques are available for their study, multiphoton ionization in conjunction with time-of-flight mass spectrometry (TOFMS) has been found to be a particularly useful method for obtaining information regarding the composition, structure, bonding, and detailed intracuster ion–molecule reactions in clusters.⁵⁻⁹

In the majority of experiments reported to date,¹⁰⁻¹⁴ results have been obtained with mixed neutral clusters formed by expanding a gas mixture through a pulsed nozzle. In some cases it has been possible to systematically vary the cluster composition by varying the mixing ratio of the two components. It has also been shown that mixed neutral clusters can be prepared by crossed beam,¹⁵ pickup,¹⁶ and dual nozzle source methods.¹⁷ In this paper we

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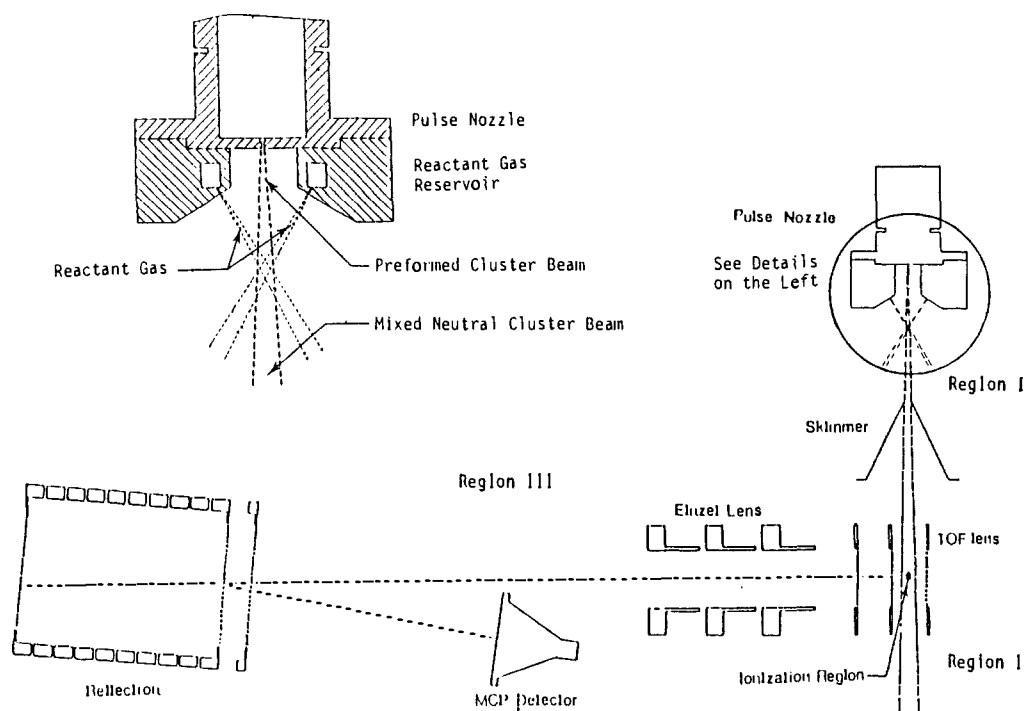


Figure 1. Schematic of the laser multiphoton ionization time-of-flight mass spectrometer with reflection.

report results obtained on clusters produced by three different methods for forming the mixed system $(\text{NH}_3)_p(\text{C}_3\text{H}_6\text{O})_q$ with p and q up to 18 and 5, respectively. Interesting differences in the reaction products are obtained. The three methods used in forming the mixed neutral clusters are (1) the coexpansion of a mixture of ammonia and acetone vapors (with a proper mixing ratio) through a pulsed nozzle, (2) the expansion of ammonia through a pulsed nozzle and crossing the ammonia cluster beam with acetone from a reactant gas reservoir, and (3) the expansion of acetone through a pulsed nozzle and crossing the acetone cluster with ammonia from the reactant gas reservoir.

Ammonia clusters^{5,18,19} and acetone clusters^{6,20-22} formed by supersonic expansion have been investigated previously. Both clusters can be ionized by laser light at a wavelength of 355 nm^{5,6} via multiphoton ionization processes. This allows one to confirm that in formation methods 2 and 3, the neat neutral clusters are produced (from the pulsed nozzle) before adding the reactant gas molecules (from the reactant gas reservoir).

Experimental Section

The apparatus used in these studies has been described in previous publications.^{6,7} However, for the present study, the mixed-cluster source has been modified as described below.

Besides the source pressure and temperature, the nozzle geometry is also an important factor for producing clusters of different sizes.²³ A hypersonic nozzle (modified from a commercial pulsed valve, General Valve Series 9), which has a throat diameter of 150 μm , an apex angle of 30°, and a length of 1.5 mm, is used in the present experiments.

In order to prepare mixed clusters by methods 2 and 3, a reactant gas reservoir is adjoined to the pulsed valve, as shown in Figure 1. The reactant gas reservoir consists of four concentric orifices, each having a diameter of 200 μm . The pulsed nozzle and the reactant gas reservoir

enable the mixed neutral clusters $(\text{NH}_3)_p(\text{C}_3\text{H}_6\text{O})_q$ to be formed through interactions between the preformed clusters and the reactant gas, as well as by the traditional coexpansion method.

The reactant gas crosses the main supersonic (preformed neutral cluster) beam at an angle of 30° and at a distance of 1.7 cm from the tip of the pulsed nozzle. Both the interaction angle and the distance between the interaction region and the pulsed nozzle are crucial factors for the case where the mixed clusters are formed by methods 2 and 3. A small crossing angle reduces beam-scattering problems and thus facilitates the formation of mixed clusters. However, if the angle is too small, the interaction region will be far from the pulsed nozzle. Since both concentrations of the preformed cluster and the reactant gas decrease roughly as the square of the distance from the nozzle, the overall concentration of mixed neutral clusters is then greatly reduced. A crossing angle of 30° has been found to be satisfactory for our mixed-cluster studies.

Another consideration is to ensure that molecular addition of a second component occurs downstream of the formation region of the main cluster. In order to assure that the mixed neutral clusters are formed through collisions between the preformed clusters and the reactant gas, the interaction region has to be outside the "freeze-in" surface.²⁴ For a continuous isentropic flow, the freeze-in surface from the nozzle, x_{FI} , can be estimated by

$$x_{\text{FI}} = \left(\frac{M_T}{A} \right)^{1/(\gamma-1)} D \quad (1)$$

where D , M_T , A , and γ , are nozzle diameter, terminal Mach number, proportionality constant, and heat capacity ratio, respectively. For a nonlinear molecule, A and γ are 3.82 and 1.33, respectively.²⁵ For a gas of nonlinear polyatomic molecules at a stagnation pressure of 2000 Torr, the freeze-in surface is located at ~ 20 times the nozzle diameter and hence is estimated to be 3 mm for a nozzle of 150- μm diameter. In our experimental setup, the designed interaction location at a distance of 17 mm away from nozzle is beyond the freeze-in surface. Therefore, one can be assured that the mixed neutral clusters are made by the interaction between preformed neat clusters and the second component gas.

The distances from the tip of the pulsed nozzle to the tip of the skimmer, and to the center of the ionization zone, are 3.8 and 8.8 cm, respectively. The beam of mixed neutral clusters passes through a conical skimmer (diameter at tip is 1 mm) and spreads to a width of ~ 4 mm in the ionization region.

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The mixed neutral clusters are ionized by 355-nm light from a frequency-tripled Nd:YAG laser. The ions are accelerated to ~ 2 keV and directed through a 130 cm long field-free region toward a reflecting electrostatic field (reflection).⁵ Ions are then reflected through an 85-cm field-free region to a chevron microchannel plate (MCP) detector. The signal received by MCP is fed into a 100-MHz transient recorder coupled to an IBM PC/AT microcomputer. The experiments operate at 10 Hz and typically TOF spectra are accumulated for 1000 laser shots. The voltage applied to the center plate of the reflection is set at 2050 V in order to reflect all ions.

Under normal operational conditions, the base pressure in the source chamber is 2×10^{-7} Torr. In the coexpansion experiment (mixed cluster formation method 1), the pressure in the source chamber is raised to 9×10^{-7} Torr when a nozzle stagnation pressure of 4000 Torr is applied. In the second formation method, 2200 Torr ammonia is typically expanded through the pulsed nozzle to produce the preformed neat ammonia clusters. The pressure in the chamber where the source is housed is increased from 2×10^{-7} to 5×10^{-7} Torr when the neat ammonia clusters are generated. The acetone gas released through the reactant gas reservoir at a flow rate of 3 standard cubic centimeters per minute (scm) raises the pressure in the source chamber to 4×10^{-5} Torr. In mixed cluster formation method 3, pure acetone clusters are formed by expanding a gas mixture containing 10% acetone in argon gas through the pulsed nozzle at a stagnation pressure of 2200 Torr. The ammonia gas issuing from the reactant gas reservoir at a flow rate of 8 scm brings the source chamber pressure from 5×10^{-7} to 1×10^{-4} Torr.

The ammonia (anhydrous, minimum purity of 99.99%) used in these experiments was obtained from Linde Specialty Gases, whereas the acetone liquid sample was a certified ACS spectranalyzed grade obtained from Fisher Scientific. Both chemicals were used without further purification.

Results

Some very distinct features have been observed in the spectra of mixed ammonia–acetone clusters when they are formed by the three different methods. Parts a–c of Figure 2 show the same portions of TOF spectra for cases where the mixed ammonia–acetone clusters are prepared by methods 1–3, respectively.

(A) Coexpanding a Gas Mixture of Ammonia and Acetone. The ratio of partial pressures of ammonia and acetone in the gas mixture is crucial for the formation of mixed ammonia–acetone clusters. It is found that a partial pressure ratio of ammonia to acetone of 4:1 produced maximum signals of the mixed clusters. In the mixed cluster formation method 1, experiments are typically made with a gas mixture consisting of 5.00% ammonia, 1.25% acetone, and 93.75% argon expanded through the pulsed nozzle at a stagnation pressure of 4000 Torr. As shown in Figure 2a the observed major homomolecular cluster ions are $(\text{NH}_3)_n\text{H}^+$, $(\text{C}_3\text{H}_6\text{O})_m^+$, and $(\text{C}_3\text{H}_6\text{O})_m\text{H}^+$ (designated as E, F, and P, respectively), and the heteromolecular cluster ions are $\{(\text{NH}_3)_n(\text{C}_3\text{H}_6\text{O})_m\}^+$ (designated as X for $m = 1$ and Y for $m = 2$).

The ion intensity distributions of $(\text{NH}_3)_n\text{H}^+$ are similar to those observed in the multiphoton ionization of neat ammonia clusters.⁵ A sharp drop in the ion intensity between $n = 5$ and $n = 6$ shows that the cluster ion $(\text{NH}_3)_4\text{NH}_4^+$ is a relatively stable species indicating bonding to the four hydrogens around the ammonium ion.^{26,27}

Interestingly, the unprotonated cluster ions $(\text{C}_3\text{H}_6\text{O})_m^+$ are present in significant amounts; only the protonated acetone monomer ions show high intensities while the $(\text{C}_3\text{H}_6\text{O})_m\text{H}^+$, $m \geq 2$, ions are seen in trace amounts. The ion intensity distribution of $(\text{C}_3\text{H}_6\text{O})_m^+$ decreases smoothly as a function of the number m of acetone molecules. In addition, $(\text{C}_3\text{H}_6\text{O})_m\text{CH}_3^+$ and $(\text{C}_3\text{H}_6\text{O})_m\text{CH}_3\text{CO}^+$ ions are not observed. This result is noticeably different from that in the multiphoton ionization study of pure acetone clusters,⁶ where the $(\text{C}_3\text{H}_6\text{O})_m\text{H}^+$, $(\text{C}_3\text{H}_6\text{O})_m\text{CH}_3^+$, and $(\text{C}_3\text{H}_6\text{O})_m\text{CH}_3\text{CO}^+$ are dominant cluster ions and the $(\text{C}_3\text{H}_6\text{O})_m^+$ ions are not seen.

Both protonated mixed-cluster ions $\{(\text{NH}_3)_n(\text{C}_3\text{H}_6\text{O})_m\}^+$ and the unprotonated species $\{(\text{NH}_3)_n(\text{C}_3\text{H}_6\text{O})_m\}^+$ are observed. However, the intensities of the $\{(\text{NH}_3)_n(\text{C}_3\text{H}_6\text{O})_m\}^+$ ions are much

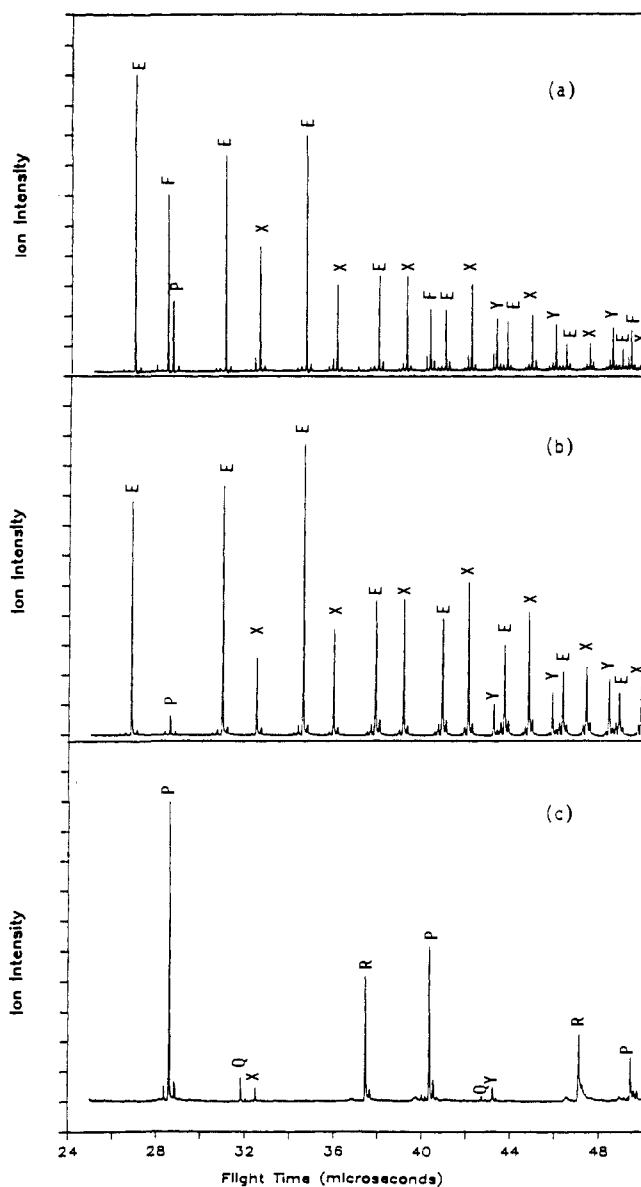


Figure 2. Time-of-flight spectra when mixed neutral ammonia–acetone clusters were formed by three different methods: (a) method 1, (b) method 2, (c) method 3. The experimental conditions were included in the text. $E \equiv (\text{NH}_3)_n\text{H}^+$, $n = 3-10$; $F \equiv (\text{C}_3\text{H}_6\text{O})_m^+$, $m = 1-3$; $X \equiv \{(\text{NH}_3)_n(\text{C}_3\text{H}_6\text{O})\}^+$, $n = 1-7$; $Y \equiv \{(\text{NH}_3)_n(\text{C}_3\text{H}_6\text{O})_2\}^+$, $n = 1-3$; $P \equiv (\text{C}_3\text{H}_6\text{O})_m\text{H}^+$, $m = 1-3$; $Q \equiv (\text{C}_3\text{H}_6\text{O})_m\text{CH}_3^+$, $m = 1-2$; $R \equiv (\text{C}_3\text{H}_6\text{O})_m\text{C}_2\text{H}_3\text{O}^+$, $m = 1-2$.

lower compared to the corresponding protonated species, $\{(\text{NH}_3)_{n-1}(\text{C}_3\text{H}_6\text{O})_m\}^+$ or $\{(\text{NH}_3)_n(\text{C}_3\text{H}_6\text{O})_{m-1}\}^+$. The ion intensity distributions of $\{(\text{NH}_3)_n(\text{C}_3\text{H}_6\text{O})_m\}^+$, $n = 1-18$, $m = 1-4$, show a gradually declining trend as a function of n , as shown in Figure 3a.

(B) Reacting Acetone with Neat Ammonia Clusters. In method 2, 2200 Torr ammonia is expanded through the pulsed nozzle to produce the neat ammonia clusters. The acetone gas releases through the reactant gas reservoir then interacts with the preformed neat ammonia clusters to form mixed neutral ammonia–acetone clusters. Figure 2b displays the TOF spectrum for the mixed ammonia–acetone clusters prepared by method 2. The intensity distributions of the $(\text{NH}_3)_n\text{H}^+$ ions are similar to those seen in the multiphoton ionization of neat ammonia clusters and in the coexpansion experiment (mixed cluster formation method 1). These $(\text{NH}_3)_n\text{H}^+$ ions probably originate from the ionization of the unreacted neat ammonia clusters.

Ion signals corresponding to $(\text{C}_3\text{H}_6\text{O})_m^+$ and $(\text{C}_3\text{H}_6\text{O})_m\text{H}^+$ are negligible when mixed clusters are formed by method 2. This result is not surprising since the reactant gas reservoir is the only

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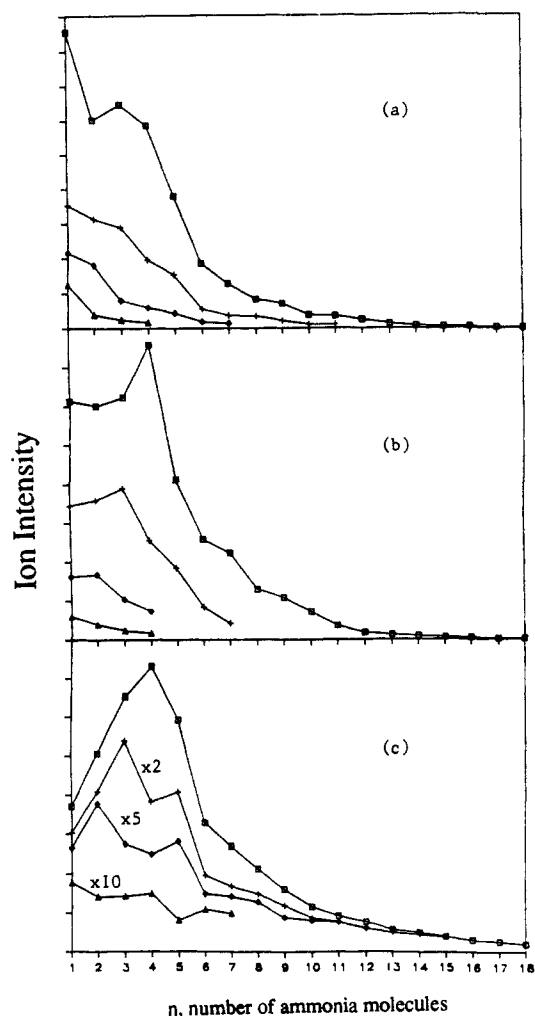


Figure 3. Ion intensity distributions of $\{(NH_3)_n(C_3H_6O)_m\}H^+$ for (a) method 1, mixing ratio ammonia/acetone = 4/1, (b) method 1, mixing ratio ammonia/acetone = 8/1, (c) method 2. \square , $+$, \diamond , and Δ , designate $m = 1, 2, 3,$ and $4,$ respectively.

source of acetone. Recall that the acetone gas from the mixing nozzle intersects the axis of the preformed ammonia cluster beam at an angle of 30° (see Figure 1). Clearly, neat acetone clusters cannot be formed under this experimental condition. The small ion signal of $C_3H_6O \cdot H^+$ as seen in Figure 2b probably results from the ionization (and fragmentation) of $(NH_3)_p(C_3H_6O)_q$. The origin of this peak is discussed in the last paragraph of the Discussion, section B.

An interesting feature is found in the distributions of the mixed-cluster ions $\{(NH_3)_n(C_3H_6O)_m\}H^+$. Figure 3c shows ion intensity distributions of $\{(NH_3)_n(C_3H_6O)_m\}H^+$, for each m from 1 to 4 as a function of the n ammonia molecules contained in the cluster ions. Note that each curve displays a maximum at $n + m = 5$, indicating that the $\{(NH_3)_n(C_3H_6O)_m\}H^+$ $n + m = 5$ ions have a very stable structure.

(C) Reacting Ammonia with Neat Acetone Clusters. In mixed cluster formation method 3, pure acetone clusters are formed by expanding a gas mixture consisting of 220 Torr acetone (its vapor pressure at room temperature) and 1980 Torr argon through the pulsed nozzle. The ammonia gas from the reactant gas reservoir then crosses with the preformed pure acetone cluster beam to form mixed ammonia-acetone clusters. Figure 2c displays the TOF spectrum for the mixed ammonia-acetone clusters prepared at an ammonia flow rate of 5 sccm. As expected, no pure ammonia clusters are seen since ammonia gas effusing from the reactant gas reservoir would not form neat ammonia clusters.

The $(C_3H_6O)_m \cdot H^+$, $(C_3H_6O)_m \cdot CH_3^+$, and $(C_3H_6O)_m \cdot CH_3CO^+$ (designated as P, Q, and R, respectively) are dominant cluster ions whereas the unprotonated ions $(C_3H_6O)_m^+$ are not observed.

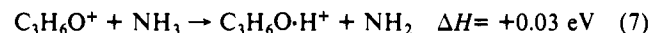
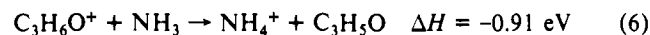
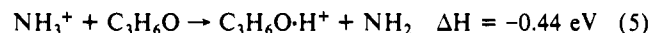
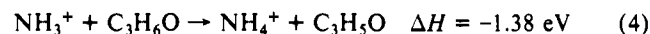
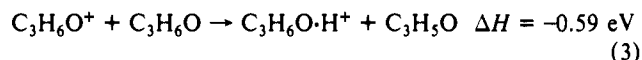
The ion intensities of $(C_3H_6O)_m \cdot H^+$, $(C_3H_6O)_m \cdot CH_3^+$, and $(C_3H_6O)_m \cdot CH_3CO^+$ decrease as cluster size increases. These results resemble those found in the multiphoton ionization of pure acetone clusters,⁶ suggesting that the cluster ions originate from the ionization of the unreacted neat acetone clusters.

It is difficult to form mixed ammonia-acetone clusters by method 3. No mixed-cluster ions were observed except those with only one ammonia molecule, $NH_4^+(C_3H_6O)_m$, (designated as X and Y for one and two acetone molecules, respectively, in Figure 2c).

Discussion

The ionization potentials of neat acetone monomer, dimer, trimer, and tetramer were measured to be 9.694, 9.26, 9.10, and 9.02 eV, respectively,²⁰ whereas those of neat ammonia monomer, dimer, trimer, tetramer, and pentamer were reported^{7,28} to be 10.166, 9.54, 9.30, 9.06, and 8.82 eV, respectively. No values of the ionization potentials of mixed clusters (ammonia)_p(acetone)_q have been reported. However, in the multiphoton ionization experiments of neat ammonia²⁹ and acetone⁶ clusters, we found that there was no distinct difference in the applied laser power under similar experimental conditions. Therefore, it is expected that the same number of photons is involved in the ionization of these neutral clusters. With currently available information, it is not certain whether the ionization process involves ejection of an electron from an ammonia molecule, acetone molecule, an aggregated ammonia unit, or mixed ammonia-acetone one within the neutral mixed clusters (ammonia)_p(acetone)_q.

Since an intracuster ion-molecule reaction may occur in the ionization of mixed ammonia-acetone clusters, one may consider the simplest analogous cases of ion-molecule reactions of (a) $NH_3^+ + NH_3$, (b) $C_3H_6O^+ + C_3H_6O$, (c) $NH_3^+ + C_3H_6O$, and (d) $C_3H_6O^+ + NH_3$. The enthalpies of the four possible proton- (or hydrogen-) transfer reactions estimated from known values of proton affinities of ammonia and acetone (204.0, 196.7 kcal/mol³⁰), ionization potentials of H, NH_3 , and C_3H_6O ,³¹ and bond energies of NH_2-H and CH_3COCH_2-H (107.4 and 93 kcal/mol^{32,33}) are as follows:



All of the above reactions are exothermic except process 7, which is essentially thermal neutral. Although rate constants have not been measured for all of the above reactions, the reported value for reaction 2 is $2 \times 10^{-9} \text{ cm}^3/\text{s}$ ³⁴⁻³⁷ and those for reaction 3 range from 0.5 to $0.8 \times 10^{-9} \text{ cm}^3/\text{s}$,^{38,39} all such reactions are generally

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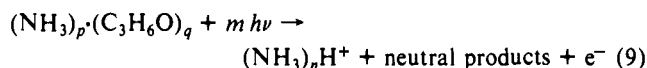
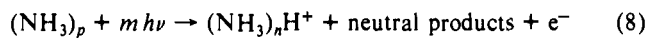
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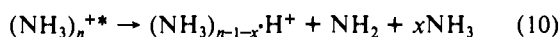
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within a factor of 2 of the collision rate for isolated gas-phase reactions. Hence, it is likely that the observed channels proceed following the ionization of any of the cluster moieties. In the following discussions we will use the above analogous reactions to interpret our observation on protonated species.

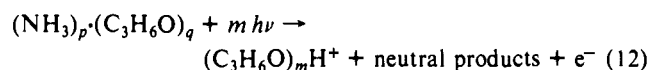
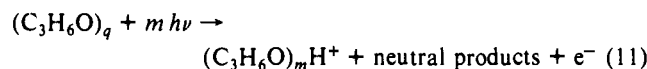
(A) **Ammonia Cluster Ions.** In the mixed cluster formation methods 1 and 2, protonated ammonia cluster ions $(\text{NH}_3)_n\text{H}^+$, $n = 1-18$, are observed as shown in Figure 2a and b. There are two possible routes to the production of these cluster ions:



The ion intensity distributions of $(\text{NH}_3)_n\text{H}^+$ shown in Figure 2a and b resemble those found in the multiphoton ionization of the pure ammonia cluster system,^{5,29} strongly suggesting formation via process 10. Hence, following ionization, the protonated ammonia cluster ions originate by loss of NH_2 and undergo subsequent evaporative loss of NH_3 .⁵

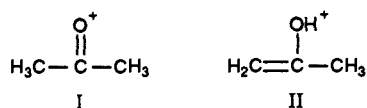


(B) **Acetone Cluster Ions.** In the coexpansion experiment (method 1) the protonated species $(\text{C}_3\text{H}_6\text{O})_m\text{H}^+$ may come from the ionization of either $(\text{C}_3\text{H}_6\text{O})_q$ or $(\text{NH}_3)_p \cdot (\text{C}_3\text{H}_6\text{O})_q$ neutral species:

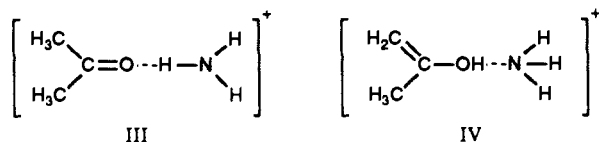


Even though the mixing ratio of ammonia to acetone is 4:1, the possible presence of homomolecular acetone clusters in the gas mixture should be considered. It has been found that the $(\text{C}_3\text{H}_6\text{O})_m\text{H}^+$, $(\text{C}_3\text{H}_6\text{O})_m\text{C}_2\text{H}_3\text{O}^+$, and $(\text{C}_3\text{H}_6\text{O})_m\text{CH}_3^+$ are the major cluster ions and the $(\text{C}_3\text{H}_6\text{O})_{m+1}$ are not seen in the multiphoton ionization of pure acetone clusters.⁶ Thus, the intensities of the $(\text{C}_3\text{H}_6\text{O})_m\text{H}^+$, $(\text{C}_3\text{H}_6\text{O})_m\text{C}_2\text{H}_3\text{O}^+$, and $(\text{C}_3\text{H}_6\text{O})_m\text{CH}_3^+$ ions should reflect the amount of homomolecular acetone clusters $(\text{C}_3\text{H}_6\text{O})_q$ in the gas mixture. The fact that there is neither $(\text{C}_3\text{H}_6\text{O})_m\text{C}_2\text{H}_3\text{O}^+$ nor $(\text{C}_3\text{H}_6\text{O})_m\text{CH}_3^+$ observed in the coexpansion experiment indicates that there is very little neutral cluster $(\text{C}_3\text{H}_6\text{O})_q$ present in the gas mixture. Consequently, the observed $(\text{C}_3\text{H}_6\text{O})_m\text{H}^+$ ions are the products of ionization of mixed clusters $(\text{NH}_3)_p \cdot (\text{C}_3\text{H}_6\text{O})_q$.

Similar arguments suggest that the unprotonated cluster ions $(\text{C}_3\text{H}_6\text{O})_m^+$ result from the ionization of the mixed clusters $(\text{NH}_3)_p \cdot (\text{C}_3\text{H}_6\text{O})_q$. In order to explain the above observation, we first consider the simplest case, which involves ionization of the neutral mixed dimer. The excited acetone monomer ion may have a keto (structure I) or an enol (structure II) form,⁴⁰ where the



enolic form is thermochemically more stable by 14 kcal/mol.⁴¹ In the case of the excited mixed dimer, one can propose possible structures III and IV. The ionization potential³¹ of acetone (9.69



eV) is lower than that of ammonia (10.166 eV), and it may be that the charge is initially localized in the acetone molecule of

the excited dimer ion $(\text{NH}_3 \cdot \text{C}_3\text{H}_6\text{O})^{+\bullet}$. Among the four analogous ion-molecule reactions (4-7), the possible processes are 6 and 7. If the $(\text{NH}_3 \cdot \text{C}_3\text{H}_6\text{O})^{+\bullet}$ has a form of structure III, the product of reaction 6 is structurally not favored in a straightforward process. Since reaction 7 is thermoneutral, the protonated acetone ion can be produced through this mechanism. Another mechanism involving a direct bond breaking between the O and H in the $\text{O} \cdots \text{H}-\text{N}$ bridge in structure III may well account for our observation of the unprotonated acetone cluster ions.

On the other hand, if the $(\text{NH}_3 \cdot \text{C}_3\text{H}_6\text{O})^{+\bullet}$ has a form of structure IV, reaction 6 can occur by a simple O-H bond cleavage, giving rise to the production of NH_4^+ . If the charge is localized in the ammonia molecule of the excited dimer ion $(\text{NH}_3 \cdot \text{C}_3\text{H}_6\text{O})^{+\bullet}$, reactions 4 and 5 are possible. As a result, both NH_4^+ and $\text{C}_3\text{H}_6\text{OH}^+$ can be product ions.

Since the neutral acetone molecule has a structure of keto form but not enol form,⁴² it is more likely that the mixed neutral ammonia-acetone dimer has a configuration similar to structure III. Although the structure of the ionic species may be very different from that of the original neutral, it is unlikely that the methyl hydrogen of the acetone will change position to form the O-H-N bridge as structure IV. The experimental observation of the unprotonated acetone cluster ions suggests that the keto form (structure III) of the ion is responsible for the internal ion-molecule reaction in the mixed ammonia-acetone cluster system.

Recently the observation of $(\text{H}_2\text{O})_n^+$ and $(\text{Ar})_m(\text{H}_2\text{O})_n^+$ was reported in the photoionization of supersonic cluster beam of argon-water mixtures by vacuum UV discharge⁴³ and synchrotron radiation.⁴⁴ It was proposed that the unprotonated cluster ion species were produced through "intracluster excess energy dissipation" of the excited cluster ion $[(\text{Ar})_k(\text{H}_2\text{O})_n]^{+\bullet}$ and evaporations of argon atoms. In the ionization of mixed ammonia-acetone clusters, a question concerning whether the carrier gas (e.g., argon) plays any role in the ionization/dissociation processes is raised. To answer this question, we have conducted coexpansion experiments (mixed cluster formation method 1) under similar conditions as described under Results, section A, except replacing argon with helium as the carrier gas. Our results show that the carrier gas has no effect on the observed cluster ions. Therefore, in the present work where a hydrogen-bonded system is involved, the observation of unprotonated acetone cluster ions in the photoionization of ammonia-acetone gas mixture is governed by the configuration of a preferred excited cluster ion.

In the mixed cluster formation method 2, a small peak of $\text{C}_3\text{H}_6\text{O} \cdot \text{H}^+$ (labeled P) is clearly seen in Figure 2b. The observed $\text{C}_3\text{H}_6\text{O} \cdot \text{H}^+$ ions probably result from the ionization (and fragmentation) of $(\text{NH}_3)_p \cdot (\text{C}_3\text{H}_6\text{O})_q$ in the time-of-flight lens (ionization and ion acceleration) region. Considering the simplest case, which involves ionization of the mixed neutral dimer $\text{NH}_3 \cdot \text{C}_3\text{H}_6\text{O}$, the electron can be ejected from either the ammonia or acetone molecule since the sum of the energy of three photons (10.49 eV) is greater than the ionization potentials of ammonia and acetone molecules. The observed $\text{C}_3\text{H}_6\text{O} \cdot \text{H}^+$ ions can be the products of intracluster ion-molecule reactions as the analogous expressions in (5) and (7). In the case of ionizing a neutral mixed cluster $(\text{NH}_3)_p \cdot \text{C}_3\text{H}_6\text{O}$, a similar internal proton (or hydrogen) transfer between the ammonia cluster and the acetone molecule may occur and lead to the final products of $\text{C}_3\text{H}_6\text{O} \cdot \text{H}^+$ ions and other neutral products.

(C) **Ammonia-Acetone Mixed-Cluster Ions. (1) Formation, Composition, and Bonding.** Both $\{(\text{NH}_3)_n \cdot (\text{C}_3\text{H}_6\text{O})_m\text{H}^+\}$ and $\{(\text{NH}_3)_n \cdot (\text{C}_3\text{H}_6\text{O})_m\}^+$, $n = 1-18$, $m = 1-5$ ions are detected in the coexpansion experiment (method 1). The intensities of the unprotonated species $\{(\text{NH}_3)_n \cdot (\text{C}_3\text{H}_6\text{O})_m\}^+$ are about one-tenth of those of the corresponding protonated ones, $\{(\text{NH}_3)_{n-1} \cdot$

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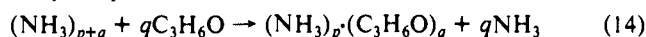
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$(\text{C}_3\text{H}_6\text{O})_m\text{H}^+$ or $\{(\text{NH}_3)_n(\text{C}_3\text{H}_6\text{O})_{m-1}\}\text{H}^+$. There is not enough thermodynamic data available in the literature on clusters to determine the energetics of the two fragmentation channels leading to the formation of $\{(\text{NH}_3)_n(\text{C}_3\text{H}_6\text{O})_m\}\text{H}^+$ and $\{(\text{NH}_3)_n(\text{C}_3\text{H}_6\text{O})_{m-1}\}\text{H}^+$. However, based on our experimental results, the pathway leading to the formation of the protonated species appears to be energetically more favorable.

As discussed above, the $\{(\text{NH}_3)_n(\text{C}_3\text{H}_6\text{O})_m\}\text{H}^+$ ions evidently originate from the ionization of the mixed neutral clusters $(\text{NH}_3)_p(\text{C}_3\text{H}_6\text{O})_q$. The formation of the $(\text{NH}_3)_p(\text{C}_3\text{H}_6\text{O})_q$ by method 2 implies that the acetone molecules effusing from the reactant gas reservoir can easily "stick" on the preformed neutral ammonia clusters. Sticking may occur by either a simple "addition" reaction between the acetone molecule and the neat ammonia clusters



or by "displacement" reaction



Due to a complication in the ionization and fragmentation processes, the observed cluster ion distribution may not reflect the distribution of neutral clusters. Because of this, one cannot distinguish "addition" from "displacement" reactions based on the observed cluster ion intensity distributions.

The binding energy of $(\text{NH}_3)_p$ has been experimentally measured to be lower than 2.8 kcal/mol^{45,46} and the binding energies for the addition of each additional NH_3 to the neutral homogeneous clusters $(\text{NH}_3)_p$ have been estimated to be in the range of 3.4–6.2 kcal/mol for $p = 2$ –6.⁴⁷ The collision energy depends on reduced mass, relative velocity, and intersection angle of the two beams. For an interaction angle of 30° (see Figure 1), the collision energies of $(\text{NH}_3)_p$ and acetone are estimated to be 0.06–0.21 kcal/mol for p ranging from 1 to 10. Since the collisional energy is much lower than the binding energy, the collision between acetone molecules and neat ammonia clusters will not result in a direct ejection of ammonia molecules from the cluster. However, the interaction (or binding) energy upon accommodation of the acetone molecule in the ammonia cluster may cause ejection of ammonia molecules.

The results of electric deflection experiments⁴⁸ indicate that the $(\text{NH}_3)_p$, $p = 3$ –6, have a cyclic ring structure. Qualitatively, a reasonably large sticking coefficient between an ammonia cluster and an acetone molecule is expected. In addition, the lifetime of the formed mixed acetone–ammonia clusters must exceed 100 μs where the distance from the interaction region to the ionization region is 7.1 cm and the beam velocity is $\sim 5 \times 10^4$ cm/s. The observation of the $\{(\text{NH}_3)_n(\text{C}_3\text{H}_6\text{O})_m\}\text{H}^+$, $n = 1$ –18, $m = 1$ –5 ions in mixed-cluster formation by method 2 (at an acetone flow rate of 1–5 sccm) suggests that the acetone molecules can strongly interact with the neutral ammonia clusters to form "long-lived" mixed neutral acetone–ammonia clusters $(\text{NH}_3)_p(\text{C}_3\text{H}_6\text{O})_q$.

In method 3 of preparing mixed ammonia–acetone neutral clusters, ammonia gas flowing from the reactant gas reservoir reacts with preformed homomolecular acetone clusters to form mixed neutral ammonia–acetone clusters. Only small signal of $\{(\text{NH}_3)_n(\text{C}_3\text{H}_6\text{O})_m\}\text{H}^+$ ion peaks for $n = 1$ and $m = 1$ –4 are observed; see Figure 2c. A further study (section C3) shows that the amounts of the neutral clusters $(\text{NH}_3)_p(\text{C}_3\text{H}_6\text{O})_q$, $p \geq 2$, are negligible. In contrast to the mixed cluster preparation method 2, the formation of $(\text{NH}_3)_p(\text{C}_3\text{H}_6\text{O})_q$ clusters is less favorable using method 3.

No experimental value for the neutral acetone dimer binding energy has been reported. The calculated binding energy values

for $(\text{C}_3\text{H}_6\text{O})_2$ are in the range of 1.6–2.4 kcal/mol.^{48–52} Those for the larger neutral acetone clusters have not been reported. The collision energies of $(\text{C}_3\text{H}_6\text{O})_q$ and ammonia are estimated to be 0.06–0.08 kcal/mol for q ranging from 1 to 4. Since the collisional energy is much lower than the binding energy, collision between ammonia molecules and acetone clusters also is not expected to cause acetone molecule ejection from the cluster. Our observation of small signals of $\{(\text{NH}_3)_n(\text{C}_3\text{H}_6\text{O})_m\}\text{H}^+$ ion peaks suggests that the incoming ammonia molecule is not well accommodated in the preformed acetone clusters to form mixed acetone–ammonia clusters even at an ammonia flow rate as high as 8 sccm.

The difference in behavior between methods 2 and 3 may be due to the type of "surface" the cluster presents to the incoming molecule. In method 2, the surface of a hydrogen-bonded ammonia cluster provides many hydrogen sites for forming $\text{NH}\cdots\text{O}$ bonds with the incoming acetone molecule. In method 3, there are fewer oxygen sites on the surface of an acetone cluster to interact with the incoming ammonia molecules to form "long-lived" neutral mixed ammonia–acetone clusters.

(2) Size Distribution, Stability, and Structure. As shown in Figure 3, the ion intensity distributions of $\{(\text{NH}_3)_n(\text{C}_3\text{H}_6\text{O})_m\}\text{H}^+$ are different when the mixed neutral clusters are prepared by formation methods 1 and 2. In the case of formation method 1, the ion intensity of $\{(\text{NH}_3)_n(\text{C}_3\text{H}_6\text{O})_m\}\text{H}^+$ shows a generally decreasing trend with n , number of ammonia molecules for $m = 1$ –4. Recall that the TOF spectrum shown in Figure 2a is taken in the case of coexpanding a gas vapor of ammonia to acetone ratio of 4:1. It is interesting to observe that when the ammonia to acetone ratio is changed to 8:1 in the gas vapor, the intensity distribution of $\{(\text{NH}_3)_n(\text{C}_3\text{H}_6\text{O})_m\}\text{H}^+$ always shows a maximum at $n + m = 5$; see Figure 3b. In method 2, the distributions of ion signals corresponding to $\{(\text{NH}_3)_n(\text{C}_3\text{H}_6\text{O})_m\}\text{H}^+$ display a maximum intensity at $n + m = 5$ as shown in Figure 3c. This variation in cluster size distribution for both cases is probably due to the different size distributions of mixed neutral clusters $(\text{NH}_3)_p(\text{C}_3\text{H}_6\text{O})_q$ prepared by two different formation methods.

One may question whether the amount of acetone gas was added to the preformed ammonia clusters will change the ion intensity distribution of $\{(\text{NH}_3)_n(\text{C}_3\text{H}_6\text{O})_m\}\text{H}^+$. To answer this question, an experiment was done by varying the flow rate (1–5 sccm) of acetone and monitoring the pressure in the source chamber as it changed from 2×10^{-5} to 9×10^{-5} Torr. Distinct ion signals of $\{(\text{NH}_3)_n(\text{C}_3\text{H}_6\text{O})_m\}\text{H}^+$ can only be seen for flow rate of acetone of ≥ 1 sccm. When the flow rate of acetone is higher than 4 sccm, the scattering of the preformed ammonia neutral cluster beam by the acetone gas from the mixing nozzle is evident by the decrease in the ion intensities of $(\text{NH}_3)_n\text{H}^+$. However, for flow rates of acetone between 1 and 3 sccm (normal experimental conditions), the ion intensity distribution of $\{(\text{NH}_3)_n(\text{C}_3\text{H}_6\text{O})_m\}\text{H}^+$ remains unchanged.

The structure of the stable cluster ion $(\text{NH}_3)_4\text{NH}_4^+$ can be pictured as ammonia molecules hydrogen bonded to each hydrogen of the ammonium ion NH_4^+ .^{26,27} The proton affinity of NH_3 is 204.0 kcal/mol, which is higher than that of acetone (196.7 kcal/mol).³⁰ A study of the unimolecular decomposition of mixed ammonia–acetone cluster ions⁵³ has shown that the metastable cluster ions $\{(\text{NH}_3)_n(\text{C}_3\text{H}_6\text{O})_m\}\text{H}^+$, $m = 1$ –4, lose an ammonia molecule for $n = 2$ –14, whereas they lose an acetone molecule for $n = 1$. The finding also supports the proposed picture that the proton is bound to an ammonia molecule in $\{(\text{NH}_3)_n(\text{C}_3\text{H}_6\text{O})_m\}\text{H}^+$ ions. Therefore, it is reasonable to picture the $\{(\text{NH}_3)_n(\text{C}_3\text{H}_6\text{O})_m\}\text{H}^+$ as $\{(\text{NH}_3)_{n-1}(\text{C}_3\text{H}_6\text{O})_m\}\text{NH}_4^+$. Hence, the discrete maximum intensities of $\{(\text{NH}_3)_n(\text{C}_3\text{H}_6\text{O})_m\}\text{H}^+$ at $n +$

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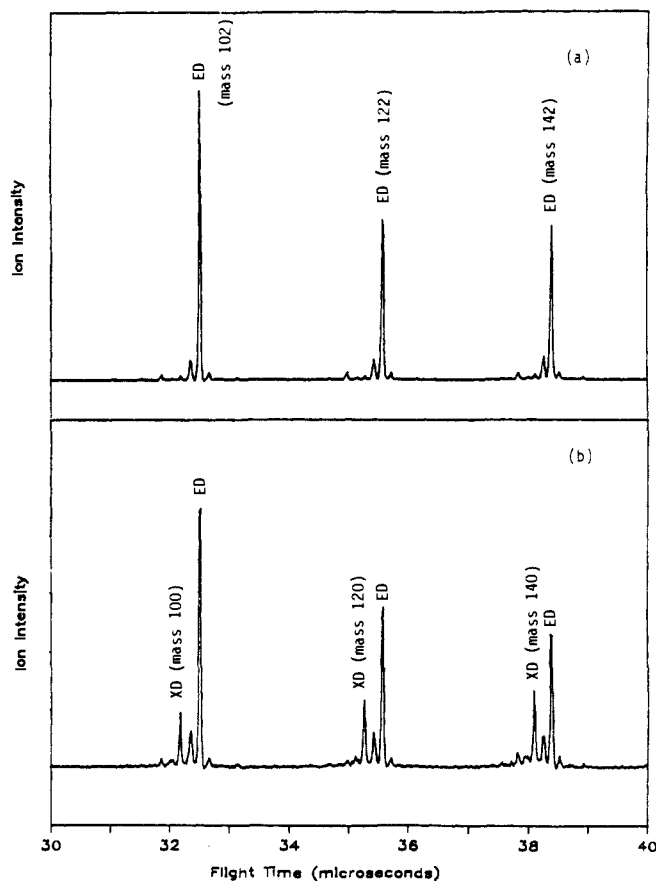


Figure 4. (a) TOF spectrum of neat $(\text{ND}_3)_n$ clusters. The three major peaks are $(\text{ND}_3)_n\text{D}^+$, $n = 5-7$, (labeled as ED). (b) TOF spectrum of $(\text{ND}_3)_n(\text{C}_3\text{H}_6\text{O})_m$ clusters formed by method 2. Besides the $(\text{ND}_3)_n\text{D}^+$, $n = 5-7$ (masses 102, 122, and 142) three ion peaks corresponding to $\{(\text{ND}_3)_n(\text{C}_3\text{H}_6\text{O})\text{D}^+, n = 2-4$ (labeled as XD, masses 100, 120, and 140) are seen.

$m = 5$ can be accounted for by picturing a similar stable structure in which a central ammonium ion is bound to four constituents in any combination of ammonia and acetone molecules. A similar observation has also been found in the multiphoton ionization studies of mixed ammonia-acetonitrile and ammonia-acetaldehyde⁵⁴ clusters.

(3) Origin of Solvated Proton in $\{(\text{NH}_3)_n(\text{C}_3\text{H}_6\text{O})_m\}\text{H}^+$. Another question concerns the origin of the solvated proton in the $\{(\text{NH}_3)_n(\text{C}_3\text{H}_6\text{O})_m\}\text{H}^+$ ions. Isotopic labeling can, in principle, provide an answer to this question. However, due to rapid H/D exchange, the ionization of mixed hydrogen and deuterated clusters formed by coexpansion (method 1) will not provide an answer. In contrast, mixed cluster formation methods 2 and 3 can give a satisfactory answer. Four isotopic labeling experiments have been carried out; each involves a second component gas molecule interacting with the preformed neutral clusters.

First of all, the mixed clusters $(\text{ND}_3)_p(\text{C}_3\text{H}_6\text{O})_q$ are produced by reacting $\text{C}_3\text{H}_6\text{O}$ molecules with $(\text{ND}_3)_p$ clusters. When the mixed clusters $(\text{ND}_3)_p(\text{C}_3\text{H}_6\text{O})_q$ are formed by this method, the unreacted neutral clusters $(\text{ND}_3)_p$ also coexist. In order to identify the ion peaks resulting from the ionization of the mixed species $(\text{ND}_3)_p(\text{C}_3\text{H}_6\text{O})_q$, it is necessary to compare the cluster ion spectra of the neat $(\text{ND}_3)_p$ and the $(\text{ND}_3)_p(\text{C}_3\text{H}_6\text{O})_q$ (prepared by mixed cluster formation method 2). Figure 4a is a portion of the TOF spectrum of $(\text{ND}_3)_n\text{D}^+$. Three sharp peaks are the $(\text{ND}_3)_n\text{D}^+$, $n = 5-7$, (masses 102, 122, and 142). The small peaks on the left side of them are the $(\text{ND}_3)_n\text{H}^+$ ions (1 mass unit lower) resulting from impurity in the sample system. Figure 4b displays the same portion of TOF spectrum for the ionized $(\text{ND}_3)_p$

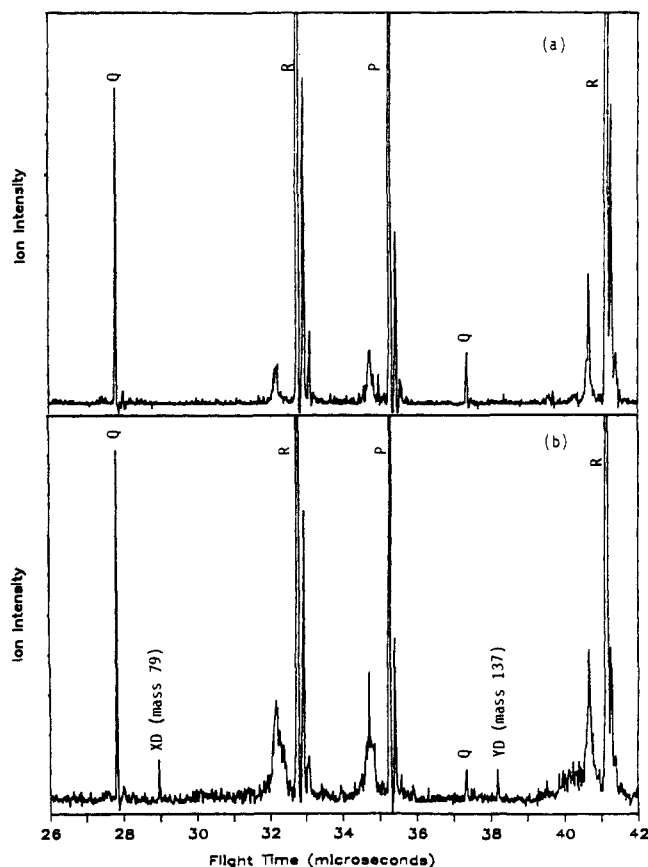


Figure 5. (a) TOF spectrum of neat $(\text{C}_3\text{H}_6\text{O})_m$ clusters. The major peaks are $\text{P} \equiv (\text{C}_3\text{H}_6\text{O})_2\text{H}^+$, $\text{Q} \equiv (\text{C}_3\text{H}_6\text{O})_m\text{CH}_3^+$, $m = 1-2$; $\text{R} \equiv (\text{C}_3\text{H}_6\text{O})_m\text{C}_2\text{H}_3\text{O}^+$, $m = 1-2$. (b) TOF spectrum of $(\text{ND}_3)_n(\text{C}_3\text{H}_6\text{O})_m$ clusters formed by method 3. In addition to those peaks observed in (a), two ion peaks corresponding to $\{(\text{ND}_3)_n(\text{C}_3\text{H}_6\text{O})_m\}\text{H}^+$, $m = 1-2$ (labeled as XD and YD, masses 79 and 137) are observed.

$(\text{C}_3\text{H}_6\text{O})_q$. The peaks corresponding to the $\{(\text{ND}_3)_n(\text{C}_3\text{H}_6\text{O})_m\}\text{D}^+$, $n = 2-4$ (masses 100, 120, and 140) ions can be clearly seen. From a careful investigation of these spectra one can conclude that only the $\{(\text{ND}_3)_n(\text{C}_3\text{H}_6\text{O})_m\}\text{D}^+$ rather than the $\{(\text{ND}_3)_n(\text{C}_3\text{H}_6\text{O})_m\}\text{H}^+$ are present.

Secondly, deuterated acetone $\text{C}_3\text{D}_6\text{O}$ molecules flowing from the reactant gas reservoir are directed to react with the neat $(\text{NH}_3)_p$ clusters formed by supersonic expansion to produce $(\text{NH}_3)_p(\text{C}_3\text{D}_6\text{O})_q$ clusters. The photoionization results show that only the $\{(\text{NH}_3)_n(\text{C}_3\text{D}_6\text{O})_m\}\text{H}^+$ rather than the $\{(\text{NH}_3)_n(\text{C}_3\text{D}_6\text{O})_m\}\text{D}^+$ ions are produced.

A peculiar observation is that the proton in the mixed-cluster ion always originates from the preformed cluster species. To further confirm this observation, the third approach, which involves preparing mixed clusters $(\text{ND}_3)_p(\text{C}_3\text{H}_6\text{O})_q$ by method 3, is undertaken. Parts a and b of Figure 5 display cluster ion spectra taken under conditions where the neat $(\text{C}_3\text{H}_6\text{O})_q$ and the $(\text{ND}_3)_p(\text{C}_3\text{H}_6\text{O})_q$ are photoionized. Comparing the two spectra one can readily identify the peaks corresponding to the $\{(\text{ND}_3)_n(\text{C}_3\text{H}_6\text{O})_m\}\text{H}^+$, $n = 1$, $m = 1-2$, (masses 79 and 137) cluster ions as shown in Figure 5b. The unassigned broad peaks on the left side of the peaks corresponding to $(\text{C}_3\text{H}_6\text{O})_m\text{H}^+$ and $(\text{C}_3\text{H}_6\text{O})_m\text{C}_2\text{H}_3\text{O}^+$ (labeled as P and Q, respectively) are their daughter ions resulting from "bleed-through" in the reflection of the time-of-flight mass spectrometer.⁶ It should be noted that $\{(\text{ND}_3)_n(\text{C}_3\text{H}_6\text{O})_m\}\text{H}^+$, $n \geq 2$, are not seen. The fact that only $\{(\text{ND}_3)_n(\text{C}_3\text{H}_6\text{O})_m\}\text{H}^+$, $n = 1$, ions are observed indicates that the amounts of the neutral $(\text{ND}_3)_p(\text{C}_3\text{H}_6\text{O})_q$, $p \geq 2$, are negligible.

Lastly, the $(\text{NH}_3)_p(\text{C}_3\text{D}_6\text{O})_q$ neutral clusters are produced by reacting NH_3 molecules with preformed $(\text{C}_3\text{D}_6\text{O})_q$ neutral clusters (method 3). The results of photoionization of $(\text{NH}_3)_p(\text{C}_3\text{D}_6\text{O})_q$ also confirm the formation of $\{(\text{NH}_3)_n(\text{C}_3\text{D}_6\text{O})_m\}\text{D}^+$. Based on the experimental results of above four different experiments (sum-

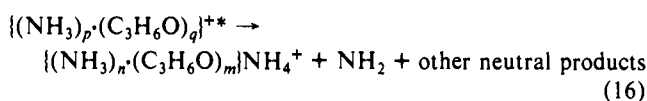
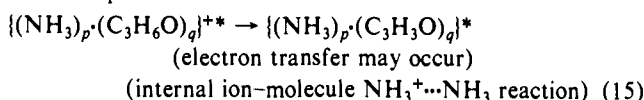
(54) Tzeng, W. B.; Wei, S.; Castleman, A. W., Jr. Ammonia-Acetonitrile and Ammonia-Acetaldehyde Mixed Cluster Ions: Stability, Structure and Metastable Decomposition. To be submitted.

Table I. Formation of Mixed Clusters and Observed Protonated Mixed-Cluster Ions

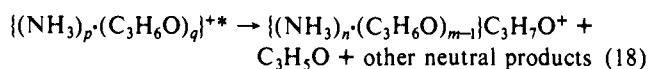
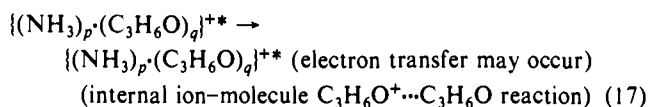
reactant cluster	reactant gas	formation method	observed cluster ion
(ND ₃) _p	C ₃ H ₆ O	2	{(ND ₃) _n (C ₃ H ₆ O) _m }D ⁺
(NH ₃) _p	C ₃ D ₆ O	2	{(NH ₃) _n (C ₃ D ₆ O) _m }H ⁺
(C ₃ D ₆ O) _q	NH ₃	3	{NH ₃ (C ₃ D ₆ O) _m }D ⁺
(C ₃ H ₆ O) _q	ND ₃	3	{ND ₃ (C ₃ H ₆ O) _m }H ⁺

marized in Table I), the proton in the observed {(ammonia)_n(acetone)_m}H⁺ ions clearly originates from the preformed clusters.

The fact that the proton in the observed {(NH₃)_n(C₃H₆O)_m}H⁺ ions originates from the preformed clusters can be explained by the following two situations. When the mixed neutral clusters (NH₃)_p(C₃H₆O)_q are produced by method 2 (preformed ammonia neutral clusters), the {(NH₃)_n(C₃H₆O)_m}H⁺ ions are produced through internal ion-molecule NH₃⁺...NH₃ reaction if the ammonia is initially ionized. However, if the electron is initially ejected from the acetone molecule, a rapid electron-transfer reaction from the collective of ammonia molecules that have lower ionization potentials²⁸ to the acetone molecule in the cluster will take place. It follows that a proton transfer or a hydrogen atom transfer occurs in the collective of ammonia molecules, leading to a formation of NH₄⁺...NH₂. A bond cleavage between the NH₄⁺ and NH₂ gives rise to the protonated mixed clusters {(NH₃)_{n-1}(C₃H₆O)_m}NH₄⁺ and neutral species. The processes can be expressed as



In the second case, when the mixed neutral clusters (NH₃)_p(C₃H₆O)_q are produced by method 3 (preformed acetone neutral clusters), very few neutral clusters (NH₃)_p(C₃H₆O)_q, $p \geq 2$, are formed as discussed in a previous section. In general, there are more acetone molecules than ammonia molecules in the cluster and it is more likely the electron is ejected from the acetone molecule. It follows that the {(NH₃)_n(C₃H₆O)_m}H⁺ ions are produced through intracuster ion-molecule reaction between two neighboring acetone molecules in the cluster ion {(NH₃)_p(C₃H₆O)_q}⁺. Alternatively, if the ammonia molecule in the cluster is initially ionized, a rapid electron-transfer reaction from the acetone to the ammonia molecule will occur before the internal ion-molecule C₃H₆O⁺...C₃H₆O reaction. Similarly, a proton transfer or a hydrogen atom transfer may occur and form C₃H₇O⁺ + C₃H₅O. This yields the protonated mixed clusters {(NH₃)_n(C₃H₆O)_{m-1}}C₃H₇O⁺ and neutral fragments. The processes can be expressed as follows:



The findings concerning the origin of the solvated proton in the {(NH₃)_n(C₃H₆O)_m}H⁺ ions provide insights into reaction dynamics within heteromolecular cluster ions.

Conclusion

The present experiment demonstrates that different methods for preparing mixed neutral clusters can lead to observable differences in the cluster ions produced from the neutral precursors, which depends on the relative concentration of each type of neutral cluster in various formation methods. This provides a method for studying the composition, structure, bonding, and detailed intracuster ion-molecule reactions in the mixed cluster systems.

In the expansion experiment (method 1), the ion intensity ratio [(C₃H₆O)_{m+1}⁺]/[(C₃H₆O)_m·H⁺] increases as the ammonia/acetone mixing ratio increases. The result indicates that the unprotonated cluster ions (C₃H₆O)_{m+1}⁺ result from the ionization of the mixed clusters (NH₃)_p(C₃H₆O)_q and suggests that the keto form of the ion is responsible for proton transfer in this system.

The observation of the {(NH₃)_n(C₃H₆O)_m}H⁺, $n = 1-18$, $m = 1-5$ ions in mixed cluster formation method 2 suggests that the acetone molecules can strongly interact with the neutral ammonia clusters to form long-lived mixed neutral acetone-ammonia clusters (NH₃)_p(C₃H₆O)_q. In contrast, when mixed neutral clusters are formed by method 3, only small signals of {(NH₃)_n(C₃H₆O)_m}H⁺ ion peaks for $n = 1$ and $m = 1-4$ are observed even at high ammonia flow rate. This indicates that the incoming ammonia molecule is not well accommodated in the preformed acetone clusters to form mixed acetone-ammonia clusters.

In formation method 2, stable cluster ions {(NH₃)_n(C₃H₆O)_m}H⁺, $n + m = 5$, are observed. These cluster ions can be pictured as a central ammonium ion bound to four constituents in any combination of ammonia and acetone molecules.

The experimental results in the studies of the origin of the solvated proton in the {(NH₃)_n(C₃H₆O)_m}H⁺ ions show that the proton generally comes from the preformed neat cluster because of the excess number of such species in the neutral precursors. They are formed through the internal ion-molecule reaction between two like molecules accompanying an electron-transfer reaction in a heteromolecular cluster.

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