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**ION-MOLECULE CHEMISTRY WITHIN
DOUBLY CHARGED AMMONIA CLUSTERS**

by

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Ion-Molecule Chemistry Within Doubly Charged Ammonia Clusters

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We present in this paper the observation of "intramolecular" ion-molecule reactions within doubly charged clusters produced via electron impact ionization of neat beams of ammonia molecules. The fragmentation pattern strongly suggests that reactions occurring within these doubly charged clusters are similar to those observed for singly charged ammonia clusters. This behavior implies that these cluster ions consist of two separate, singly charged ammonia cations which act separately within the bulk neutral cluster. That is, either one, both, or neither of the ammonia cations may react with the neutrals solvating them within the doubly charged cluster.

1. Introduction

The study of clusters is one of the most exciting fields of modern experimental and theoretical physics and chemistry. Clusters afford an opportunity to directly observe the effects of stepwise solvation on a system's physical and chemical properties as well as providing a unique environment to observe novel chemistry. The study of cluster ions [1,2] in particular has an important place in this field since mass spectrometry is one of the most frequently utilized tools in cluster studies.

In the case of ammonia clusters the dominant intracluster ion-molecule reaction is the formation of the NH_4^+ ion [3-17] via the following exoergic reaction:

$$(NH_3)_n^+ \Rightarrow (NH_3)_{n-2}NH_4^+ + NH_2 \qquad \Delta H = -1.1 eV \qquad (1)$$

In addition to observing this expected protonation peak from eq. (1) it is also possible to observe ion signal arising from ionized but unreacted ammonia clusters.[13] Additional peaks observed in the mass spectrum correspond to a sequence of peaks resulting from unimolecular fragmentation of the unreacted cation [15]:

$$(NH_3)_n^+ \Rightarrow (NH_3)_{n-1}NH_2^+ + H \qquad (2)$$

Lastly, a sequence of low intensity peaks has also been observed which has been attributed to either water impurity [16,17] or a solvated NH_5^+ specie formed via an intramolecular cluster reaction.[18] More recently, it has been proposed that this sequence of peaks is due to the creation of solvated

Rydberg radical cation pair (i.e. an $NH_4NH_4^+$ species) [19,20]. Two possible reactions which could lead to the production of this "NH_5^+" species are [18]:

$$(NH_3)_n^+ \Rightarrow (NH_3)_{n-2}NH_5^+ + NH \qquad (3)$$
$$\text{or} \qquad (NH_3)_n^+ \Rightarrow (NH_3)_{n-3}NH_5^+ + N_2H_4 \qquad (4)$$

Reactions like (3) and (4) above, which have not been observed in bimolecular collisions, but appear to occur only within the solvated environs of clusters [21-24] provide an important bridge between bimolecular gas-phase reaction dynamics and solution chemistry.

A recent development in the study of cluster ions is the characterization of multiply charged clusters $\{(A_n)^{z+}\}$. Experimentally critical sizes, $\{n_c(z)\}$, have been observed [25,26] for these cluster ions which have been modeled by several theoretical studies [27,28]. Recently Whetten and co-workers attempted to explain the ionization mechanism within clusters in terms of an exciton annihilation model [29].

In the case of doubly charged ammonia clusters, a critical size $\{n_c(2)\}$ of 51 has been reported [30,31] for the $(NH_3)_{n-2}(NH_4)_2^{2+}$. In this paper we report, for the first time, the observation that the peaks attributed to doubly charged ammonia clusters are each composed of seven individual peaks separated by 0.5 amu. These peaks are shown to be analogous to the peaks observed in the singly charged ammonia cluster spectrum. This sequence of seven doubly charged peaks arises due to processes occurring at two separate and independent cation centers within the doubly charged cluster. That is, two distinct cations are formed which can each have its own separate chemistry within the same cluster.

2. Experiment

The molecular beam apparatus consists of a Campargue type beam source [32] where the source chamber is pumped by a $1000m^3/h$ roots blower package. The cluster beam is generated by a neat, adiabatic expansion of anhydrous NH_3 (Linde, 99.99% pure) at 1 atm stagnation pressure (source chamber pressure = 50 mtorr) through a 250 µm nozzle which is kept at 253K by a circulating chiller, as measured by a thermocouple within the nozzle.

Following collimation by a 5 mm diameter skimmer 7.5 mm from the nozzle, the cluster beam passes into a differentially pumped chamber (p = 1 x 10^{-5} torr). The cluster beam then travels through a second collimating skimmer before entering the differentially pumped mass spectrometer chamber (P = 5 x 10^{-7} torr). The collimating and mass spectrometer chambers are each pumped by a 360 l/s turbo pump and the two chambers are separated by an electromagnetic gate valve which also serves as a beam
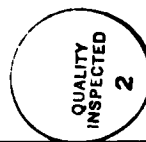
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The skimmed beam enters into the mass spectrometer chamber in a direction collinear with the ion optic axis. The electron impact ionizer of the mass spectrometer is located 22 cm from the nozzle. The mass spectrometer is an Extrel C-50, (200 watt, 3/8" diameter rods, open design ionizer) which is capable of unit mass resolution up to $m/z = 1400$, and with electron impact energies varying from 15 to 150 eV. The electron emission current for these experiments was kept at 1 mA. Ions formed in the source are mass filtered and detected by an off-axis channeltron. The amplified signal from the channeltron is then averaged by a LeCroy 9400 digital oscilloscope.

3. Results and Discussion

Figure 1 shows the expanded view of the seven doubly charged cluster peaks observed for three different cluster sizes. The peaks are individually labeled at the bottom and in each case normalized with respect to the parent peak (p). As other workers have previously shown [30,31] for doubly charged ammonia cluster ions, a rapid onset is observed at $n_c(2) = 51$ which is independent of instrumental parameters (electron energy, stagnation pressure, etc..). This intensity then falls off montonically with increasing n. We observe that the steepness of this fall-off decreases with decreasing electron energy. We interpret this effect in that at reduced electron energies evaporative processes within the cluster become less efficient thereby broadening the cluster distribution at large n.

Figure 2 illustrates the dependence of the ion intensity as a function of electron energy for a particular cluster size (n = 59). All the curves are normalized with respect to the parent peak (p) intensity. As can be seen, peaks to the left (a and b) and right (c,d,e and f) of the parent peak fall off with decreasing electron energy.

Figure 3 illustrates a simple model to explain the appearance of the three major peaks observed in both Figures 1 and 2. Through electron impact ionization, two singly charged cations are formed within the neutral cluster. If the cluster size is below some critical size, the doubly charged cluster undergoes a coulombic explosion which generates two singly charged clusters. However, if the cluster is large enough to accommodate these two cations, reorganization (presumbly by rapid charge transfer) occurs within the cluster to separate the two cation centers as far apart as possible. This accounts for the appearance of the parent ion with the empirical formula $(NH_3)_{n-2}(NH_3)_2^{2+}$ (peak p, Fig 1&2).

Once this cluster ion has been formed, each of the separated cation

centers can react with one of the neutral NH_3 solvating it by reaction 1. These reactions then produce either a singly (peak **c**) or doubly (peak **d**) protonated, doubly charged ammonia cation. As with the singly charged cations, we observe that the intensity of these protonated ion peaks (**c** & **d**) falls off more rapidly with increasing n in comparison with the parent peak (**p**). This effect we feel is due in part to the the bath modes of the larger clusters effectively quenching the ion molecule reaction (reaction (1)). This same effect has also been observed for singly charged cluster of methyl halides [21,22].

The smaller peaks to the left of the parent peak can be explained as a unimolecular fragmentation process (reaction (2)) which occurs at either one (peak **b**) or both (peak **a**) of the NH_3^+ centers which did not react. The smaller peaks to the right of the three major peaks can be explained by either water contamination or an intracluster reaction (reactions (3) and (4)) occurring at one or both of the cation centers. It is interesting to note that if water contamination is prominent, then peak **e** would arise from the presence of 1 water molecule [(n-1)-mer **d** + H_2O] while peak **f** arises from the presence of 2 water molecules [(n-2)-mer **d** + $2H_2O$]. However, for singly charged ammonia clusters only one such peak is observed. This would mean that if the only explanation was water contamination, then there is, at most, only one water molecule in the ammonia cluster.[17] Assuming similar contamination in the doubly charged cluster peaks, we then should see only one peak (**e**) but in fact observe two (peaks **e** and **f**). The presence of peak **f** in the doubly charged mass spectrum suggests that it arises not from water contamination but rather from two separate reaction having occurred at both of the cation centers, generating in both cases "NH_5^+".

To summarize, the mass spectrum of doubly charged ammonia clusters can be interpreted as two distinct ammonia cations (peak **p**) separated within the bulk cluster, which may then either fragment (peaks **a** and **b**) or undergo a bimolecular ion-molecule reaction (peaks **c** and **d**), independent of each other. There is also a set of peaks which appear to be due to additional cluster reactions (peaks **e** and **f**). The situation is further complicated by the possibility of mixed species (ie. the formation of $(NH_3)_{n-2}(NH_4)^+(NH_2)^+$ would appear as a parent peak, **p**) which are not possible to easily deconvolute, but would certainly constitute only a minor addition to the observed intensity.

It is interesting to compare the behavior of the doubly charged ammonia clusters with that of doubly charged water clusters recently studied by Stace [33]. In that paper Stace reported the observation of _two_ stable forms of doubly charged water clusters, $(H_2O)_n^{2+}$ and $H_3O^+(H_2O)_{n-2}H_3O^+$, but did not

observe the $H_3O^+(H_2O)_n\text{-}2H_2O^+$ cluster ion. In contrast, we observe for ammonia cluster ion <u>three</u> major peaks of the form $(NH_3)^{2+}$, $NH_4^+(NH_3)_n\text{-}2NH_4^+$, and $NH_4^+(NH_3)_n\text{-}2NH_3^+$. We can now ask why in the ammonia system it is possible to have a reaction at one or two of the cation centers while with water there is only reaction at both? The reason may lie on the simple basis of thermochemical arguments in that the water protonation reaction is 8 kcal/mole more exoergic than the analogous ammonia reaction [34]. In addition, it is expected that the water cations within the cluster are closer together then in the case of ammonia (12 A vs. 16 A respectively). [30] This suggests that for the water system the two cations may be more easily coupled and energy may transfer between the two centers. Therefore, the excess reaction energy at one water cation may in turn trigger the reaction at the second water cation.

In the case of the ammonia clusters it appears that the two cations act independently of each other. If this is true then this uncorrelated reactivity would imply that the probability of reaction at either ammonia cation would be the same. This can be written in terms of the observed ion intensities as follows:

$$I_c^2 = I_d \qquad (5)$$

where I_c and I_d are the ion intensities of the singly and doubly protonated doubly charged cluster peaks, normalized to the appropriate parent peak (p). As can be seen in figure 2, in the limit of low electron energy, equation 5 does indeed hold, consistent with the idea that the reactivity of the two ammonia cations are not coupled. However, at higher electron energies we observe that the intensities of both c and d increase and become equivalent, suggesting that the additional electron energy serves to promote the reaction at both cation centers. Work is currently in progress to further quantify this relationship.

We also intend to now utilize these doubly charged ammonia clusters as a probe of the internal structure of the cluster itself. Many workers have recently suggested that neutral clusters generated by an expansion can undergo a "phase" transition from a solid framework to a more fluid-like geometry [35,36] depending on the expansion conditions (pressure, temperature, geometry, etc...)[37]. If this should be the case, the stability of these doubly charged clusters may be a sensitive test of this transition. That is the intensities of these doubly charged peaks may be expected to shift as a function of the expansion conditions, thereby reflecting a change in the cluster medium.

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Figure Captions

Figure 1) Raw data of electron impact mass spectra of doubly charged NH_3 cluster ions taken at 100 eV electron energy for three separate cluster sizes (n = 61, 73, 85), and normalized with respect to the most intense peak (peak **p**).

Figure 2) Ion intensity as a function of electron energy for n = 59. Each trace is normalized with respect to the parent peak, **p**. Each trace was signal averaged for 200 scans under identical operating conditions, which accounts for the decrease in signal-to-noise at lower electron energy (lower ion intensity). Processes coresponding to chemical reaction and fragmentation are indicated in the figure.

Figure 3) Schematic which indicates possible mechanism for the three most intense peaks observed in figures 1 & 2. The ellipsoidal shape of the parent cluster is deliberately exaggerated to indicate the mutual separation of the two cations within the cluster ion.