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The critical hydration reactions of NO^+ and NO_2^+

L. Angel and A. J. Stace^{a)}

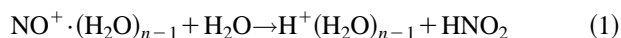
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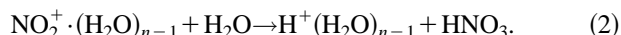
The reactions of NO^+ and NO_2^+ with water are considered to make an important contribution to the formation of proton hydrates in the upper atmosphere. There have been several recent studies of the relevant reactions, with the result that discrepancies have arisen in each case over the critical number of water molecules required to promote the appearance of a proton hydrate. Presented here are new results based on the collision-induced reactions of $\text{NO}^+ \cdot (\text{H}_2\text{O})_n$ and $\text{NO}_2^+ \cdot (\text{H}_2\text{O})_n$ cluster ions, which we believe clarify the situation. © 1998 American Institute of Physics. [S0021-9606(98)01429-9]

I. INTRODUCTION

Several studies have been undertaken recently on reactions in clusters of the form $\text{NO}^+ \cdot (\text{H}_2\text{O})_n$ and $\text{NO}_2^+ \cdot (\text{H}_2\text{O})_n$, where important changes are seen for n in the range 2–5.^{1–4} Each of these species is considered to be an intermediate in an atmospheric reaction sequences; $\text{NO}^+ \cdot (\text{H}_2\text{O})_n$ in the D -region of the ionosphere and $\text{NO}_2^+ \cdot (\text{H}_2\text{O})_n$ in the stratosphere.⁵ In both systems the first steps are the successive hydration of either ion, NO^+ or NO_2^+ . At a critical number (n) a chemical reaction is initiated within each cluster to produce a proton hydrate of the form $\text{H}^+ (\text{H}_2\text{O})_{n-1}$, which is accompanied by the release of either nitric acid (HNO_3) or nitrous acid (HNO_2).



or



There have been two separate experimental studies of these reactions via cluster intermediates: (i) Laser photofragmentation spectroscopy has been applied to the detection of features associated with the formation of either acid as a function of cluster size (n);^{2,3} (ii) unimolecular fragmentation patterns of the clusters ions have been monitored to detect the loss of either acid.^{1,4} From a comparison of results from the two separate experiments, it is evident that there are small but significant differences between the levels of hydration identified as being necessary to promote reactions (1) and (2). In particular, the laser experiments^{2,3} suggest that each reaction requires one more water molecule than was considered necessary from the experiments on unimolecular decay.^{1,4} Since the two experiments have used different methods for the preparation of clusters, one possibility would be for differences in behavior to be attributed to variations in cluster temperature. In the case of $\text{NO}^+ \cdot (\text{H}_2\text{O})_n$ clusters, the low collision frequency associated with the ionosphere, means that the exact number of water molecules required to drive the hydration reaction will have a very significant effect on the contribution reaction (1) makes to proton hydrate

formation. For the $\text{NO}_2^+ \cdot (\text{H}_2\text{O})_n$ system, the number of water molecules is probably not so important, because the chemistry is considered to take place on polar stratospheric cloud particles.⁵

Presented here is new experimental evidence which we believe helps to explain the small discrepancies observed in previous studies.^{1–4} The new data are in the form of comparisons between the unimolecular (metastable) and collision-induced fragmentation patterns of $\text{NO}^+ \cdot (\text{H}_2\text{O})_{3-5}$ and $\text{NO}_2^+ \cdot (\text{H}_2\text{O})_{2-4}$. The results show that neither reaction (1) nor (2) is promoted by collisional activation. However, once a reaction has taken place, unimolecular decay favors the loss of acid from either cluster at the critical value of n , but not necessarily at larger sizes.

II. EXPERIMENT

The experiment apparatus consists of a pulsed supersonic nozzle coupled to a modified high resolution, double-focusing VG ZAB-E mass spectrometer and has been described in detail elsewhere.⁶ MIKE (Mass-analyzed ion kinetic energy) spectra were recorded for each of the ions under conditions where both unimolecular and collision-induced fragmentation patterns could be identified separately. For the clusters $\text{NO}^+ \cdot (\text{H}_2\text{O})_{3-5}$ and $\text{NO}_2^+ \cdot (\text{H}_2\text{O})_{2-4}$, the parent signals were reduced by approximately one-half through the introduction of collision gas (air at $\sim 10^{-6}$ mbar) into a cell located in the second field-free region between the magnet and the electrostatic analyzer. The cell was floated at a potential of -500 V to distinguish collision-induced processes from normal (metastable) unimolecular decay.

III. RESULTS AND DISCUSSION

A. $\text{NO}^+ (\text{H}_2\text{O})_n$

The MIKE spectrum for $\text{NO}^+ \cdot (\text{H}_2\text{O})_3$ given in Fig. 1(a) shows only two loss channels. The largest peak corresponds to the collision-induced loss of H_2O (~ 6200 eV), and is accompanied by a metastable peak for loss of water at ~ 6300 eV. The peak at ~ 4400 eV is for the collision-induced loss of 2 H_2O . There is no evidence of HNO_2 loss and the spectrum supports the view that the $\text{NO}^+ \cdot (\text{H}_2\text{O})_3$

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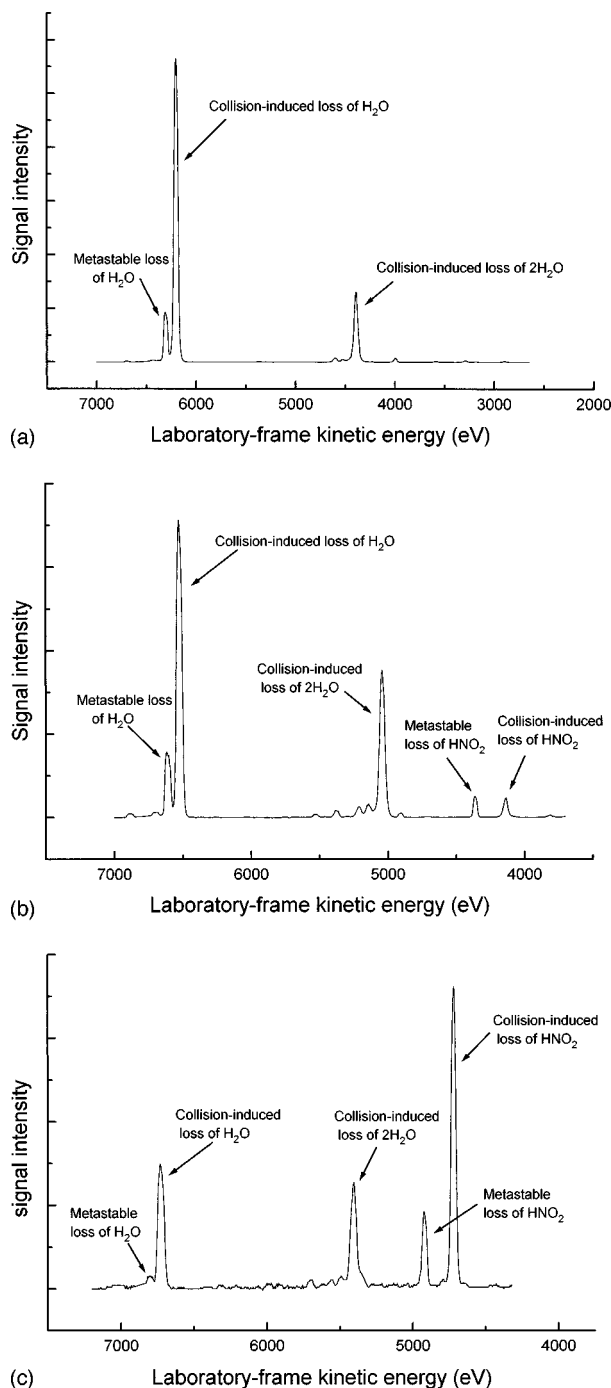


FIG. 1. MIKE (Mass-analyzed ion kinetic energy) spectra recorded following the collisional activation of $\text{NO}^+(\text{H}_2\text{O})_n$ cluster ions for: (a) $n=3$; (b) $n=4$; (c) $n=5$.

cluster adopts one (or possibly both) of the proposed configurations.^{2,7} Choi *et al.*² suggested that the cluster might consist of a central NO^+ ion in association with three H_2O ligands in a first solvation shell. In contrast, recent calculations by Ye and Cheng⁷ show the most stable structure to consist of one water molecule attached directly to NO^+ , with the other two molecules hydrogen bonded in the form a second solvation shell. The experiment is unable to distinguish between these two options.

The MIKE spectrum of the next cluster hydrate in the series, $\text{NO}^+(\text{H}_2\text{O})_4$, shows a more interesting fragmentation

pattern. As seen in Fig. 1(b), the loss of H_2O , metastable at ~ 6600 eV and collision-induced at ~ 6500 eV, are the same as before, but there are two additional peaks at ~ 4300 and ~ 4100 eV, which correspond to the metastable and collision-induced loss of HNO_2 . Note the relative peak intensities for the loss channels of H_2O and HNO_2 as these are of interest in the discussion which follows. In their spectroscopic study, Choi *et al.*² observed a 12% relative yield of HNO_2 compared with loss of H_2O from the cluster $\text{NO}^+(\text{H}_2\text{O})_4$ on absorption of a single IR (infrared) photon (~ 43.9 kJ mol⁻¹). From this result, the authors postulated that the collision of $\text{NO}^+(\text{H}_2\text{O})_3 + \text{H}_2\text{O}$ would lead to the formation of HNO_2 10% of the time. This conclusion contrasts with results from a metastable study by Stace *et al.*,¹ where for $\text{NO}^+(\text{H}_2\text{O})_4$ the formation and loss of HNO_2 from the cluster accounted for $\sim 40\%$ of the signal. In Figure 1(b) both these results can be identified. The metastable peaks for loss of H_2O and HNO_2 , are in the ratio 3:2; however, collision excitation leads to a large increase in the loss of H_2O which is not matched by HNO_2 , and the ratio of the two fragmentation routes (9:1) is now almost identical to that observed in the IR spectroscopic studies.² This evidence would suggest that neither collisional activation nor IR excitation promotes reaction (1), but that they both enhance the loss of water from the cluster. A proposed structure for $\text{NO}^+(\text{H}_2\text{O})_4^2$ shows a central NO^+ ion with three H_2O ligands in the first solvation shell, and a fourth H_2O ligand hydrogen bonded to two water molecules in the first shell. The structure of the cluster is consistent with the observation that excitation will facilitate the loss of the hydrogen-bonded H_2O , and not promote an intracuster reaction to yield HNO_2 and $\text{H}^+(\text{H}_2\text{O})_3$.

The MIKE spectrum of $\text{NO}^+(\text{H}_2\text{O})_5$ in Fig. 1(c) shows that collisional activation leads to an increase in both H_2O and HNO_2 loss when compared with the corresponding metastable signals. However, in each case the loss of acid from the cluster is greater than the loss of water, which is consistent with previous work. A structure suggested for $\text{NO}^+(\text{H}_2\text{O})_5^2$ shows the presence of HNO_2 in association with the stable proton hydrate, $\text{H}^+(\text{H}_2\text{O})_4$, which would account for the observed fragmentation pattern.

B. $\text{NO}_2^+(\text{H}_2\text{O})_n$

The MIKE spectrum recorded for $\text{NO}_2^+(\text{H}_2\text{O})_2$ is shown in Fig. 2(a) and is dominated by loss of H_2O , which as with the previous example, is consistent with the structure proposed for the cluster.³ There is no evidence of either collision-induced or metastable loss of HNO_3 loss from the cluster. The MIKE spectrum for $\text{NO}_2^+(\text{H}_2\text{O})_3$ shown in Fig. 2(b), exhibits a pattern of behavior which is very similar to that seen for $\text{NO}^+(\text{H}_2\text{O})_4$ [Fig. 1(b)]. There is a large peak which corresponds to the collision-induced loss of H_2O and smaller peaks for the metastable loss of H_2O , and both metastable and collision-induced loss of HNO_3 . Again, there is no increase in the collision-induced loss of HNO_3 compared with the metastable channel. The relative intensities of the metastable loss of H_2O and HNO_3 match the results reported by Stace *et al.*⁴ Similarly, the relative intensities of the collision-induced decay channels match those observed in the IR spectroscopic study by Cao *et al.*³

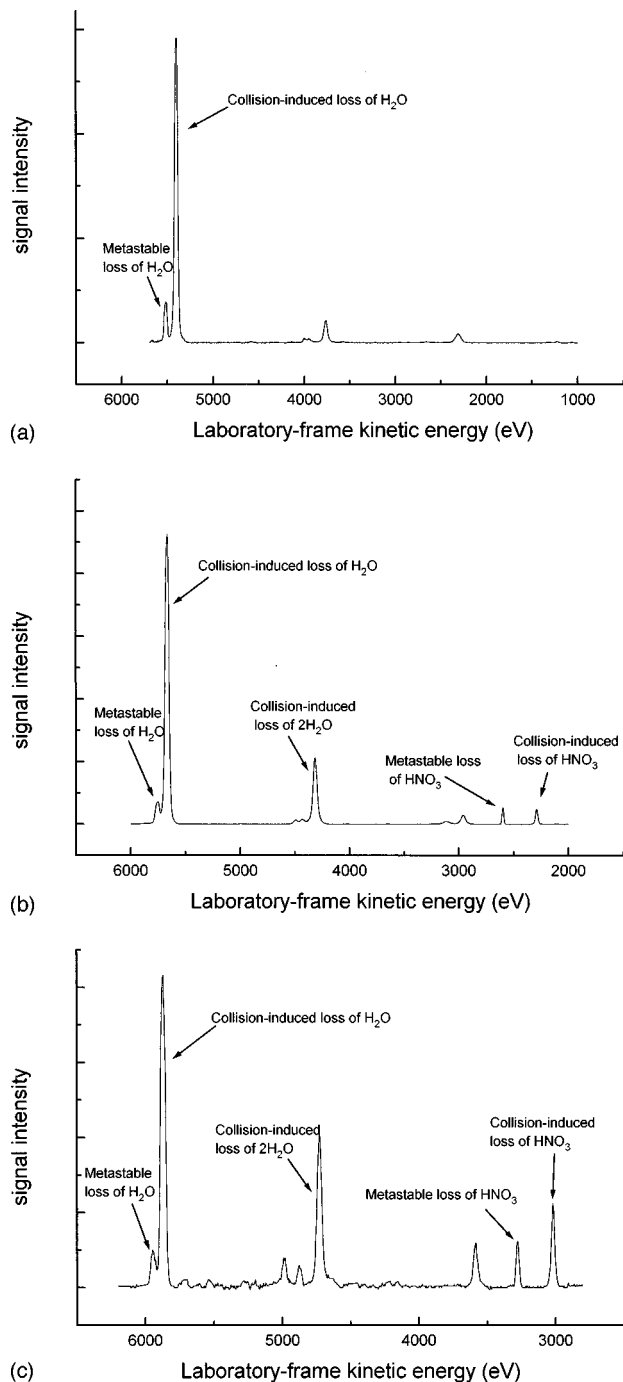


FIG. 2. As for Fig. 1, but for $\text{NO}_2^+(\text{H}_2\text{O})_n$ cluster ions for: (a) $n=2$; (b) $n=3$; (c) $n=4$.

The MIKE spectrum of $\text{NO}_2^+(\text{H}_2\text{O})_4$ shown in Fig. 2(c), exhibits an increase in both the metastable and collision-induced loss channels of HNO_3 . The relative intensities of the metastable channels match those observed by Stace *et al.*,⁴ however, this time the ratio of the collision-induced channels is different from that observed in the IR study by Cao *et al.*³ The latter experiments show a greater degree of HNO_3 loss, which was wavelength dependent, with a ratio of 7:1 in the 3550 cm^{-1} region and 2:1 in the $3600\text{--}3800\text{ cm}^{-1}$ region. This suggests that IR photon excitation may be promoting the formation of HNO_3 and $\text{H}^+(\text{H}_2\text{O})_3$ from the $\text{NO}_2^+(\text{H}_2\text{O})_4$ cluster.

The results do not support the suggestion that initial cluster temperature alone is responsible for observed differences between the laser and metastable studies of NO_x^+ reactions with water. Ion complexes generated by the electron impact ionization of neutral clusters are very likely to be “warmer” than those ions generated directly via the supersonic expansion of an ion beam. The fact that increasing the energy content of the ions through collisional activation leads to results similar to those seen in the laser study, suggests that infrared excitation produces its own internal energy increase, which in turn influences the unimolecular fragmentation pattern. As an alternative explanation of events, we would suggest that the majority of cluster ions at the critical size $[\text{NO}^+(\text{H}_2\text{O})_4]$ and $[\text{NO}_2^+(\text{H}_2\text{O})_3]$ are in an unreacted state (a conclusion supported by the structures suggested in Refs. 2 and 3). However, once an intracuster reaction has taken place, the acid (either HONO or HNO_3) is rapidly lost through unimolecular decay as it is now the most weakly bound species in the complex. Previous studies of competitive metastable decay have found reaction path preference to be sensitive to binding energy differences of just $\sim 2\text{ kcal mol}^{-1}$.^{8,9} The experiments on metastable decay would be particularly sensitive to this aspect of cluster behavior,^{1,4} because they concentrate on recording fragmentation patterns from ions observed over a comparatively long period of time, $\sim 10^{-5}\text{ s}$. In contrast, the laser experiments^{2,3} are searching specifically for the presence of either HONO or HNO_3 in clusters with the (assumed) critical size, and for the reason given above, those species will not be present to any significant degree. Only when clusters contain more than the critical number of water molecules are solvation interactions strong enough to retain either acid, and at that point features due to their presence begin to appear in the laser spectra.^{2,3} For the $\text{NO}_2^+(\text{H}_2\text{O})_n$ system, this latter conclusion would be consistent with the observations of Zhang *et al.*¹⁰ Since reaction time scales in the upper atmosphere are going to be very much longer than those experienced in either of the two experiments discussed here, the lower critical hydration limits of four for NO^+ and three for NO_2^+ are probably going to have the most significant influence.

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