Vibrational spectroscopy of NO$^+(\text{H}_2\text{O})_n$: Evidence for the intracluster reaction NO$^+(\text{H}_2\text{O})_n\rightarrow\text{H}_3\text{O}^+\text{(H}_2\text{O})_{n-2}$ (HONO) at $n\geq4$

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Infrared spectra of mass-selected clusters NO$^+(\text{H}_2\text{O})_n$ for $n=1$ to 5 were recorded from 2700 to 3800 cm$^{-1}$ by vibrational predissociation spectroscopy. Vibrational frequencies and intensities were also calculated for $n=1$ and 2 at the second-order Møller-Plesset (MP2) level, to aid in the interpretation of the spectra, and at the singles and doubles coupled cluster (CCSD) level energies of $n=1$ isomers were computed at the MP2 geometries. The smaller clusters ($n=1$ to 3) were complexes of H$_2$O ligands bound to a nitrosium ion NO$^+$ core. They possessed perturbed H$_2$O stretch bands and dissociated by loss of H$_2$O. The H$_2$O antisymmetric stretch was absent in $n=1$ and gradually increased in intensity with $n$. In the $n=4$ clusters, we found evidence for the beginning of a second solvation shell as well as the onset of an intracluster reaction that formed HONO. These clusters exhibited additional weak, broad bands between 3200 and 3400 cm$^{-1}$ and new minor photodissociation channels, loss of HONO and loss of two H$_2$O molecules. The reaction appeared to go to completion within the $n=5$ clusters. The primary dissociation channel was loss of HONO, and seven vibrational bands were observed. From an analysis of the spectrum, we concluded that the $n=5$ cluster rearranged to form H$_3$O$^+$(H$_2$O)$_3$(HONO), i.e., an adduct of the reaction products.

I. INTRODUCTION

The nitrosium ion NO$^+$ and its hydrates play an important role in the ion chemistry of Earth's upper atmosphere.$^1$ The NO radical possesses a low ionization potential (9.26 eV) and is thus readily ionized by either photodissociation or charge transfer. NO$^+$ is the major primary ion in the D region of the ionosphere, where it is formed by solar Lyman-$\alpha$ radiation. However, measurements of the positive ion composition in the ionosphere, beginning with rocket-borne mass-spectrometric observations by Narcisi and Bailey,$^2$ have revealed that the predominant ionic species in the D region are the hydronium ion hydrates, H$_3$O$^+$(H$_2$O)$_n$. The conversion of NO$^+$ to H$_3$O$^+$(H$_2$O)$_n$ is now known to occur by a hydration mechanism.$^3$ NO$^+$ first undergoes a sequence of solvation steps to form a hydrated cluster ion, NO$^+$,(H$_2$O)$_3$. This cluster subsequently reacts with another water molecule:

$$\text{NO}^+(\text{H}_2\text{O})_3+\text{H}_2\text{O}\rightarrow\text{H}_3\text{O}^+\text{(H}_2\text{O})_3+\text{HONO}$$ (1)

to form the hydrated hydronium ions.

Gas-phase experiments on hydrated NO$^+$ clusters have examined the association kinetics and thermochromism in order to understand the processes occurring in the ionosphere. Several groups used stationary$^4,5$ and flowing afterglow techniques$^6,7$ to measure the rate constants of the successive hydration steps and the final reaction (1). Puckett and Lineberger$^8$ identified the neutral product HONO in their stationary afterglow apparatus from their negative ion mass spectrum. French et al.$^9$ studied the kinetics and equilibria of NO$^+$ hydration by pulsed high-pressure mass spectrometry.

They obtained hydration enthalpies of $\Delta H_{0,1}^r=-18.5\pm1.5$ kcal mol$^{-1}$ for NO$^+$ and $\Delta H_{1,2}^r=-16.1\pm1.0$ kcal mol$^{-1}$ for NO$^+(\text{H}_2\text{O})$. They extrapolated these values to estimate $\Delta H_{2,3}^r=-13.5\pm1.0$ kcal mol$^{-1}$. Burdett and Hayhurst$^{10}$ found a similar value for the hydration of NO$^+$ of $\Delta H_{0,1}^r=-19.3\pm2.4$ kcal mol$^{-1}$ in their studies of boundary layer cooling of ions sampled from flames.

In aqueous solution, NO$^+$ is a key intermediate in the nitrosation reactions of organic compounds.$^{11}$ Studies of nitrosation reactions have established that the mechanism depends on acidity. Both NO$^+$ and protonated nitrous acid are thought to participate in the rate-determining step at high acidity (pH=1). Protonated nitrous acid, H$_2$NO$^+_2$ (nitrosohydrin or nitrous acidium ion), is believed to exist as a weakly bound complex of NO$^+$ and H$_2$O, depicted in Fig. 1(a), in equilibrium with NO$^+$:

$$\text{H}^++\text{HONO}\rightleftharpoons\text{NO}^+(\text{H}_2\text{O})\rightleftharpoons\text{NO}^++\text{H}_2\text{O}.$$ (2)

The equilibrium constants are not accurately known and there has been no direct detection of NO$^+(\text{H}_2\text{O})$ in the condensed phase.

Several theoretical calculations$^{12-17}$ have examined the optimized geometries of protonated nitrous acid, although no theoretical studies of the higher hydrates of NO$^+$ have been performed. The consensus is that the most stable form is an ion–molecule complex between NO$^+$ and H$_2$O, rather than a purely covalently bound cation. De Petris et al.$^{17}$ performed ab initio calculations that included electron correlation and predicted that protonated nitrous acid has six different isomers which are true minima on the potential energy hypersurface. For the lowest-energy form, NO$^+(\text{H}_2\text{O})$, they obtained an enthalpy of formation $\Delta H_f^r=160\pm2$ kcal mol$^{-1}$, in good agreement with the experimental value of 159.0±1.5 kcal mol$^{-1}$ based on the binding energy$^9$ of NO$^+(\text{H}_2\text{O})$. 
They found that the next lowest-energy isomers are formed by protonating either the terminal oxygen to form NO(H₂O)⁺, or the nitrogen atom to form HONO⁻, isomers shown in Fig. 1. Both structures were calculated to have ΔH_f over 41 kcal mol⁻¹ higher than that of the NO⁺(H₂O) complex. Such energetic metastable isomers have not been observed experimentally.

If the complex NO⁺(H₂O) is the lowest-energy isomer of protonated nitrous acid, the proton affinity of HONO is PA= 187.7 kcal mol⁻¹, 11 kcal mol⁻¹ higher than that of H₂O. Direct protonation of nitrous acid has not been observed in the gas phase because of the difficulty in generating pure HONO. Using collisionally activated dissociation (CAD) mass spectrometry, De Petris et al. found that only one isomer of protonated nitrous acid is produced in proton transfer reactions such as H⁺+CH₂ONO. They presented circumstantial evidence that this isomer is the complex NO⁺(H₂O). However, they observed no metastable signal and thus were unable to glean further structural information on protonated nitrous acid from kinetic energy release measurements.

Basic thermodynamic and kinetic data have been measured for reaction (1), but little is known about the mechanism and role of the solvent H₂O in assisting the reaction. The reaction is estimated to be slightly endothermic (~+2 kcal mol⁻¹),9,18 The rate constant 4–7 was found to be k=7×10⁻¹¹ cm³ s⁻¹, based on the disappearance of the NO⁺(H₂O)₃ cluster. The production of H₂O⁺(H₂O)₂ was inferred rather than directly measured because the hydronium ion hydrates equilibrated too rapidly. In speculating about the molecular mechanism of reaction (1), Fuchs and others postulated intermediate cluster configurations in which not all H₂O moieties solvated the NO⁺, but conventional mass-spectrometric and kinetic experiments have shed no further light on their key idea, that the reaction requires solvent reorganization within an activated cluster.

IR photodissociation spectroscopy coupled with tandem mass spectrometry has proven to be a powerful method for investigating cluster ions. 19–22 We have recently investigated similar intracluster reactions in hydrated nitronium ion clusters NO⁺₂(H₂O)ₙ using the technique of vibrational predissociation spectroscopy. 23–24 In these experiments, the infrared spectra of mass-selected ions are obtained by detecting vibrational predissociation spectra of the hydrated clusters n=1 and 2 to confirm our vibrational assignments. Our calculations were undertaken because there were no published theoretical estimates of the vibrational frequencies for n=1, nor of the structure, energetics, and vibrational frequencies for n=2.

II. EXPERIMENT

The apparatus employed in these experiments 20,23 will be described in detail elsewhere, 24 and only a brief account will be presented here. NO⁺(H₂O)ₙ (n = 1 to 5) clusters were generated by a high-pressure, pulsed discharge source. An MKS mass-flow controller was used to produce a mixture of 12% NO (Matheson Gas Co, purity 99%) seeded in ultrahigh purity (99.999%) He or H₂. Hydrate clusters could be readily formed using only the trace water vapor already present in the stainless-steel inlet line. The pressure was 1000 Torr at room temperature in the stagnation volume of a piezo-driven pulsed valve. Gas was pulsed (200 μs width) at a repetition rate of 10 Hz into a 1 mm diameter, 1.5 cm long channel and expanded into the first differential vacuum chamber maintained at 2 to 5×10⁻⁵ Torr by a 10 in. diffusion pump. A discharge was struck as the gas flowed through the channel by applying a high voltage pulse (~1.5 to ~3 kV, 100 μs wide) between two electrodes near the entrance. The ions formed in the plasma were thermalized as the gas flowed through the channel and further cooled in the supersonic expansion. The expanding plasma was skimmed and entered a second region (6 in. diffusion pump, 1×10⁻⁶ Torr) containing the time-of-flight ion optics. The ions were extracted by a pulsed electric field 15 μs in duration and accelerated to 1.3 kV, focused by a pair of einzel lenses. The ions passed through an additional stage of differential pumping (4 in. diffusion pump, 1×10⁻⁶ Torr) and entered the photolysis chamber (500 L/s turbomolecular pump, 3×10⁻⁶ Torr).
Parent ions of a specific mass were selected by a 1 cm long mass gate which rejected all ions of other m/e. The ions were vibrationally excited by a collimated infrared beam, which was generated by a pulsed LiNbO₃ optical parametric oscillator (OPO) and timed to intersect the selected ions at the spatial focus of the time-of-flight mass spectrometer. The OPO was pumped by a Quanta Ray GCR 12S Nd:YAG laser whose 1.06 μm output was propagated 3 m to achieve a nominally Gaussian transverse mode at the input of the OPO. The OPO was tunable from 2700 to 6700 cm⁻¹ by simultaneously adjusting the crystal and grating angles. Typical OPO pulse energies were about 3 to 5 mJ with a linewidth of 1.5 cm⁻¹. The laser beam path from the OPO to the vacuum chamber was purged with dry air to eliminate absorption by water vapor.

The fragment ions resulting from IR excitation were separated from the parent ions using a reflectron energy analyzer, and then detected by a microchannel plate detector. The signal was preamplified and then collected by a transient digitizer. Predissociation spectra were obtained by stepping the OPO wavelength and averaging the photofragment ion signal for 200 shots at each wavelength. Fragment ion background arising from dissociation of metastable parents was subtracted to obtain the fragment signal due solely to photodissociation. The data were then normalized with respect to the OPO pulse energy. Between 2 and 14 such scans were averaged, depending on the photofragment signal intensity. The OPO laser wavelength was calibrated during the scan by simultaneously recording the rovibrational spectra of either methane or hydrogen chloride in a photoacoustic cell.

III. EXPERIMENTAL RESULTS

A typical time-of-flight mass spectrum of nitrosonium ion hydrate clusters is shown in Fig. 2. While this distribution peaked at NO⁺(H₂O)₂, it could be shifted by varying the stagnation temperature and pressure, source voltage, and pulsed valve settings. Two additional series of hydrates can be seen in Fig. 2, H₃O⁺(H₂O)₁ and, very weakly, (NO)⁺(H₂O)₁. The relative intensities of these species also varied, but did not interfere with the measurements reported here.

![FIG. 2. Time-of-flight mass spectrum of hydrated nitrosonium clusters (n =0–4). The ions were formed in a glow discharge of 12% NO seeded in ultrahigh purity H₂ at 1000 Torr. The formation of hydrates is due to the presence of a trace of H₂O vapor.](image)

We recorded infrared spectra of mass-selected clusters NO⁺(H₂O)ₙ for n=1–5 in the 2700–3800 cm⁻¹ region. Figure 3 presents the infrared spectra for n=1–5 over the entire frequency range and Table I lists the observed band maxima.

![FIG. 3. Vibrational predissociation spectra of NO⁺(H₂O)ₙ (n=1–5). The photofragment ions detected were NO⁺(H₂O)ₙ₋₁ (n=1–4) and H₂O⁺(H₂O)₁ (n=5), respectively.](image)

A. Photodissociation behavior

The only photofragment ions detected upon infrared excitation of the clusters NO⁺(H₂O)ₙ (n=1 to 3) were NO⁺(H₂O)ₙ₋₁, indicating that a single water molecule evaporated upon vibrational excitation:

\[
\text{NO}^+(\text{H}_2\text{O})_{n} \rightarrow \text{NO}^+(\text{H}_2\text{O})_{n-1} + \text{H}_2\text{O}, \quad n = 1-3.
\]

Figure 4 shows the dependence of the photodissociation signal on laser pulse energy for these three clusters when exciting the band observed at \(\sim 3620 \text{ cm}^{-1}\). The dissociation signal for \(n=1\) exhibited a quadratic dependence, as seen from the linear dependence of the square root of the signal plotted against laser pulse energy in Fig. 4(a). The dissociation of \(n=1\) clusters thus involved two-photon excitation. The rollover at high fluence probably resulted from saturation. In the case of \(n=2\), the fragment ion signal showed both linear and nonlinear behavior depending on source conditions. In Fig. 4(b), the signal was a sum of linear and quadratic terms, since the plot of the square root of signal vs pulse energy...
TABLE I. Observed vibrational frequencies of NO+(H2O)\textsubscript{n} ion clusters.

<table>
<thead>
<tr>
<th>Cluster</th>
<th>Frequency (cm\textsuperscript{-1})</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO+(H2O)\textsubscript{2}</td>
<td>3599, 3611</td>
<td>H\textsubscript{2}O sym. stretch</td>
</tr>
<tr>
<td>NO+(H2O)\textsubscript{2}</td>
<td>3622</td>
<td>H\textsubscript{2}O sym. stretch</td>
</tr>
<tr>
<td></td>
<td>3695</td>
<td>H\textsubscript{2}O antisym. stretch</td>
</tr>
<tr>
<td>NO+(H2O)\textsubscript{3}</td>
<td>3630</td>
<td>H\textsubscript{2}O sym. stretch</td>
</tr>
<tr>
<td></td>
<td>3712</td>
<td>H\textsubscript{2}O antisym. stretch</td>
</tr>
<tr>
<td>NO+(H2O)\textsubscript{4}</td>
<td>3230</td>
<td>H-bonded OH stretch</td>
</tr>
<tr>
<td></td>
<td>3375</td>
<td>H-bonded OH stretch</td>
</tr>
<tr>
<td></td>
<td>3635</td>
<td>H\textsubscript{2}O sym. stretch</td>
</tr>
<tr>
<td></td>
<td>3713</td>
<td>H\textsubscript{2}O antisym. stretch</td>
</tr>
<tr>
<td>NO+(H2O)\textsubscript{5}</td>
<td>2800</td>
<td>H-bonded H\textsubscript{2}O\textsuperscript{+} stretch</td>
</tr>
<tr>
<td></td>
<td>3190</td>
<td>H-bonded H\textsubscript{2}O\textsuperscript{+} stretch</td>
</tr>
<tr>
<td></td>
<td>3550</td>
<td>H-bonded H\textsubscript{2}O donor OH stretch</td>
</tr>
<tr>
<td></td>
<td>3576</td>
<td>HONO OH stretch</td>
</tr>
<tr>
<td></td>
<td>3644</td>
<td>H\textsubscript{2}O sym. stretch</td>
</tr>
<tr>
<td></td>
<td>3710</td>
<td>H-bonded H\textsubscript{2}O free OH stretch</td>
</tr>
<tr>
<td></td>
<td>3734</td>
<td>H\textsubscript{2}O antisym. stretch</td>
</tr>
<tr>
<td>H\textsubscript{2}O monomer\textsuperscript{b}</td>
<td>3575</td>
<td>sym. stretch, \nu\textsubscript{1}</td>
</tr>
<tr>
<td></td>
<td>3756</td>
<td>antisym. stretch, \nu\textsubscript{3}</td>
</tr>
<tr>
<td>HONO (trans) monomer\textsuperscript{c}</td>
<td>3591</td>
<td>OH stretch</td>
</tr>
<tr>
<td></td>
<td>3426</td>
<td>OH stretch</td>
</tr>
</tbody>
</table>

\textsuperscript{a}Band assignments are based on the structure of Fig. 7(c).
\textsuperscript{b}Reference 33.
\textsuperscript{c}Reference 28.

approached a straight line only at higher energies. Under alternate source conditions, shown in Fig. 4(c), the signal depended linearly on the pulse energy. The detected signal for \( n=3 \) depended linearly on laser power as shown in Fig. 4(d), indicating that the predissociation of this cluster was a single photon process.

Infrared excitation of the \( n=4 \) cluster produced photofragments at three masses, corresponding to NO+(H2O)\textsubscript{3}, NO+(H2O)\textsubscript{2}, and H\textsuperscript{+}(H\textsubscript{2}O)\textsubscript{3}. Thus, the following photodissociation processes were competing:

\[
\begin{align*}
\text{NO}^{+}(\text{H}_2\text{O})_4 & \rightarrow \text{NO}^{+}(\text{H}_2\text{O})_3 + \text{H}_2\text{O}, \quad (4a) \\
\rightarrow & \text{NO}^{+}(\text{H}_2\text{O})_2 + 2\text{H}_2\text{O}, \quad (4b) \\
\rightarrow & \text{H}_3\text{O}^{+}(\text{H}_2\text{O})_2 + \text{HONO}. \quad (4c)
\end{align*}
\]

The major dissociation channel was loss of one water, channel (4a). The minor NO+(H2O)\textsubscript{2} product in Eq. (4b) is likely due to evaporation of a neutral water dimer (H\textsubscript{2}O\textsubscript{2}), although an alternative is the secondary spontaneous dissociation of the primary product ion in channel (4a), a process which requires more energy. The observation of channel (4c) signaled the onset of a new dissociation channel, loss of a nitrous acid molecule. The relative yields were wavelength dependent. When exciting absorption bands observed in the 3600–3800 cm\textsuperscript{-1} region, the branching ratio of channels (4a), (4b), and (4c) was 8:1.5:1. Contributions from channels (4b) and (4c) were negligible when exciting bands in the 3400 cm\textsuperscript{-1} region.

There was a significant change in the photofragmentation pattern of the \( n=5 \) cluster, NO+(H2O)\textsubscript{4}. We detected photofragments at three masses: H\textsuperscript{+}(H\textsubscript{2}O)\textsubscript{3}, H\textsuperscript{+}(H\textsubscript{2}O)\textsubscript{3}, and NO+(H\textsubscript{2}O)\textsubscript{4}. The dominant channel throughout the observed spectral region was

\[
\text{NO}^{+}(\text{H}_2\text{O})_5 \rightarrow \text{H}_2\text{O}^{+}(\text{H}_2\text{O})_3 + \text{HONO}. \quad (5)
\]

Thus, unlike the smaller clusters, infrared excitation of \( n=5 \) led almost exclusively to loss of neutral nitrous acid.

B. Vibrational predissociation spectra

The infrared spectrum of protonated nitrous acid (\( n=1 \)) exhibited a single vibrational band in the 2700–3800 cm\textsuperscript{-1} range [Fig. 3(a)]. This band was only 50 cm\textsuperscript{-1} lower in frequency than the symmetric stretch of the water monomer (Table I). Closer examination revealed that the band was a doublet with maxima at 3599 and 3611 cm\textsuperscript{-1}, as seen in Fig. 5(a).

The clusters NO+(H\textsubscript{2}O)\textsubscript{n} (\( n=2 \) and 3) had two absorption bands in the 2700–3800 cm\textsuperscript{-1} region [Figs. 3(b) and 3(c), Table I]. The lower frequency bands at \( \sim 3630 \) cm\textsuperscript{-1} were sharp and resembled in shape and position the band observed for NO+(H\textsubscript{2}O). The higher frequency bands at \( \sim 3700 \) cm\textsuperscript{-1} were broad. Based on the proximity of these bands to the H\textsubscript{2}O monomer stretch frequencies,\textsuperscript{26} we assigned these bands to the symmetric and antisymmetric stretch modes of water ligands, respectively.

The spectrum of \( n=4 \), shown in Fig. 3(d), consisted of four bands. Two bands at 3635 and 3713 cm\textsuperscript{-1} were similar.
The strongest band, at 2800 cm⁻¹, was broad and had the appearance of the stretching band of an ionic OH group participating as a donor in hydrogen bonding. Such bands were first observed in H₂O⁺(H₂O)ₙ clusters by Schwarz²⁷ Lee and co-workers¹⁹ in their studies of H₃O⁺(H₂O)ₙ clusters and Cao et al.²³ in their studies of NO⁺⁺(H₂O)ₙ observed similar bands and assigned them to the hydrogen-bonded OH antisymmetric stretch of the H₂O⁺⁺ ion. In general, these vibrations occurred below 2700 cm⁻¹ unless the hydronium ion was fully solvated. We therefore concluded that the n=5 clusters possessed a hydronium ion core, with ligands bonded to all three OH bonds.

The strong H₂O⁺ band is often accompanied by a broad but weaker band at higher frequency. We assigned the weaker 3190 cm⁻¹ band as this companion mode. The exact assignment of such bands (symmetric stretch of H₂O⁺, bending overtone, combination band) is still a matter of uncertainty.¹⁹,²⁷

The five higher-frequency bands of the n=5 spectrum can be assigned as OH stretches of the ligands bound to the H₂O⁺ core. One of the two bands near the OH stretching frequency of the trans nitrous acid monomer²⁸,²⁹ (3591 cm⁻¹) could be assigned to the free OH stretch of HONO; the remaining bands we assigned to H₂O. Detailed assignments based on a proposed structure will be discussed below.

IV. AB INITIO CALCULATIONS ON THE n=1 AND n=2 CLUSTERS

A. Computational approach

To help interpret the predissociation spectra of the n = 1 and n = 2 clusters, we performed ab initio calculations at the Hartree–Fock (HF) and the second-order Möller–Plesset³¹ (MP2) level using the 6-31G** basis set³² to compute geometries and vibrational frequencies. Single point energies were also computed at the coupled cluster with single and double excitations (CCSD) level of theory using the 6-31G** basis set for n =2, and the 6-31G(2df,2pd) basis set for n = 1 and its isomers (see Table II). All electrons were correlated at the MP2 level, but core electrons were frozen at the CCSD level. Calculations were done using the GAUSSIAN 92 system of programs³² on a Cray Y-MP supercomputer.

The geometries of NO⁺⁺(H₂O), N(OH)⁺, and HON(H)O⁺ were optimized at the MP2/6-31G** level using the geometries of De Petris et al.¹⁴ as the initial guesses. We found substantially the same results as De Petris et al. for all three isomers. Harmonic vibrational frequencies and infrared intensities for NO⁺⁺(H₂O), N(OH)⁺, and HON(H)O⁺ (Tables

<table>
<thead>
<tr>
<th>Cluster</th>
<th>MP2</th>
<th>MP2+ZPE</th>
<th>CCSD</th>
<th>CCSD+ZPE*</th>
<th>ΔE₀ (kcal mol⁻¹)</th>
<th>ΔH₂₀ (kcal mol⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO⁺⁺(H₂O)</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>HON(H)O⁺</td>
<td>37.8</td>
<td>40.8</td>
<td>32.8</td>
<td>35.8</td>
<td>39.6</td>
<td>34.6</td>
</tr>
<tr>
<td>N(OH)⁺⁺</td>
<td>38.3</td>
<td>41.2</td>
<td>29.7</td>
<td>32.7</td>
<td>40.1</td>
<td>31.5</td>
</tr>
</tbody>
</table>

*Using the MP2 harmonic vibrational frequencies.
TABLE III. Ab initio harmonic frequencies (MP2/6-31G**) for NO+(H₂O).

<table>
<thead>
<tr>
<th>Mode (a')</th>
<th>Approx. description</th>
<th>Frequencies (cm⁻¹)</th>
<th>[Intensities (km mol⁻¹)]</th>
</tr>
</thead>
<tbody>
<tr>
<td>v₁(a')</td>
<td>O–H sym. stretch</td>
<td>3389(156)</td>
<td></td>
</tr>
<tr>
<td>v₂(a')</td>
<td>N–O sym. stretch</td>
<td>2099(20)</td>
<td></td>
</tr>
<tr>
<td>v₃(a')</td>
<td>H₂O bend</td>
<td>1682(65)</td>
<td></td>
</tr>
<tr>
<td>v₄(a')</td>
<td>H₂O wag</td>
<td>472(272)</td>
<td></td>
</tr>
<tr>
<td>v₅(a')</td>
<td>N–O sym. stretch</td>
<td>281(101)</td>
<td></td>
</tr>
<tr>
<td>v₆(a')</td>
<td>O–N–O–O bend</td>
<td>248(10)</td>
<td></td>
</tr>
<tr>
<td>v₇(a')</td>
<td>O–H antisym. stretch</td>
<td>3942(159)</td>
<td></td>
</tr>
<tr>
<td>v₈(a')</td>
<td>H₂O rock</td>
<td>470(56)</td>
<td></td>
</tr>
<tr>
<td>v₉(a')</td>
<td>H₂O twist</td>
<td>116(36)</td>
<td></td>
</tr>
</tbody>
</table>

III, IV, and V) were then determined using analytic second derivatives. All frequencies found were real, which confirmed that the optimized structures obtained were true minima of the potential energy hypersurface.

There has apparently been no previous theoretical work on the n = 2 clusters. For our calculations, then, we assumed that the isomer of interest would be of the form NO+(H₂O)₂, with at least C₁ and perhaps C₂ᵥ symmetry. The structure was fully optimized under these symmetry constraints at both the HF and the MP2 levels. In addition, due to the presence of several low-frequency (<200 cm⁻¹) modes, it was necessary to use more stringent convergence criteria. The minimum calculation was converged to an rms force of less than 1×10⁻⁷ a.u. and to an rms displacement of 4×10⁻⁶ a.u. Both the HF and MP2 structures had C₁ symmetry, although the HF structure was nearly C₂ᵥ. Harmonic vibrational frequencies (Table VI) showed that both the HF and the MP2 optimized structures were potential energy minima.

In order to relate the ab initio frequencies to experimental values, we also computed the vibrational frequencies of H₂O at the MP2/6-31G** level. We obtained scaling factors by comparing the computed values of 3894 (a') and 4032 cm⁻¹ (b₂) with the experimental values of 3657 (a') and 3756 cm⁻¹ (b₂).

To estimate the binding energies and enthalpies of NO+(H₂O)n (n = 1 and 2), CCSD/6-311G(2df,2pd) energies were calculated for NO+(H₂O)₂, NO+(H₂O)₁ NO⁺, and H₂O at their MP2 optimized geometries. Because both the MP2 and CCSD levels of theory are size-consistent, binding energies may be calculated simply as the sum and difference of the point vibrational energy were made to both the MP2 and CCSD energies using the MP2 level vibrational frequencies. Finally, binding enthalpies at 298.15 K were also estimated using the MP2 frequencies. Our enthalpy corrections differ from those of Ref. 17. Results are listed in Table VII.

B. NO⁺(H₂O) and its isomers

The optimized geometry of NO⁺(H₂O) obtained at the MP2/6-31G** level is essentially identical to that obtained by De Petris et al.¹⁷ As shown in Fig. 1(a), the oxygen atom of the water binds to the nitrogen end of the cation, which carries ~70% of the charge; the N–O separation is 2.202 Å, and the O–N–O bond angle is 100.2°. The geometries of the NO⁺ and H₂O moieties do not differ significantly from those of free NO⁺ and H₂O.

The binding enthalpy at the CCSD/6-311G(2df,2pd)/MP2/6-31G** level is ΔΗ₂₉₈°=20.9 kcal mol⁻¹ (see Table VII), slightly higher than the experimental enthalpy of 18.5 kcal mol⁻¹. The scaled MP2 frequencies of the H₂O vibrations are 3587 cm⁻¹ for the symmetric stretch and 3671 cm⁻¹ for the antisymmetric stretch, and the band strengths are comparable.

TABLE IV. Ab initio harmonic frequencies (MP2/6-31G**) for N(OH)₂⁺.

<table>
<thead>
<tr>
<th>Mode (a')</th>
<th>Approx. description</th>
<th>Frequencies (cm⁻¹)</th>
<th>[Intensities (km mol⁻¹)]</th>
</tr>
</thead>
<tbody>
<tr>
<td>v₁(a')</td>
<td>O–H antisym. stretch</td>
<td>4213(259)</td>
<td></td>
</tr>
<tr>
<td>v₂(a')</td>
<td>O–H sym. stretch</td>
<td>4114(14)</td>
<td>3859(75)</td>
</tr>
<tr>
<td>v₃(a')</td>
<td>N–O sym. stretch</td>
<td>2600(101)</td>
<td>2087(36)</td>
</tr>
<tr>
<td>v₄(a')</td>
<td>H₂O bend</td>
<td>1794(20)</td>
<td>1698(63)</td>
</tr>
<tr>
<td>v₅(a')</td>
<td>H₂O rock</td>
<td>425(165)</td>
<td>423(126)</td>
</tr>
<tr>
<td>v₆(a')</td>
<td>H₂O wag</td>
<td>378(764)</td>
<td>307(487)</td>
</tr>
<tr>
<td>v₇(a')</td>
<td>N–O sym. stretch</td>
<td>202(2)</td>
<td>254(52)</td>
</tr>
<tr>
<td>v₈(a')</td>
<td>N–OH bend</td>
<td>27(0)</td>
<td>201(14)</td>
</tr>
<tr>
<td>v₉(a')</td>
<td>H₂O twist</td>
<td>65(6)</td>
<td>105(22)</td>
</tr>
<tr>
<td>v₁₀(a')</td>
<td>O–N–O–O bend</td>
<td>85(0)</td>
<td>33(0)</td>
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<tr>
<td>v₁₁(a')</td>
<td>O–H antisym. stretch</td>
<td>4213(32)</td>
<td>3977(66)</td>
</tr>
<tr>
<td>v₁₂(a')</td>
<td>O–H sym. stretch</td>
<td>4112(179)</td>
<td>3857(132)</td>
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<tr>
<td>v₁₃(a')</td>
<td>H₂O bend</td>
<td>1793(194)</td>
<td>1693(69)</td>
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<td>v₁₄(a')</td>
<td>H₂O wag</td>
<td>360(0)</td>
<td>379(118)</td>
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<td>v₁₅(a')</td>
<td>H₂O rock</td>
<td>414(36)</td>
<td>375(84)</td>
</tr>
<tr>
<td>v₁₆(a')</td>
<td>N–O antisym. stretch</td>
<td>238(23)</td>
<td>224(40)</td>
</tr>
<tr>
<td>v₇(a')</td>
<td>N–OH bending</td>
<td>318(41)</td>
<td>207(1)</td>
</tr>
<tr>
<td>v₁₈(a')</td>
<td>H₂O op twist</td>
<td>28(0)</td>
<td>26(7)</td>
</tr>
</tbody>
</table>
TABLE VII. Ab initio thermochemical data for NO+(H2O)n → NO+(H2O)n−1 + H2O.

<table>
<thead>
<tr>
<th>Cluster</th>
<th>$\Delta E_0$ (kcal mol$^{-1}$)</th>
<th>$\Delta H_{298}$ (kcal mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>MP2 6-31G**</td>
<td>MP2+ZPE 6-31G**</td>
</tr>
<tr>
<td>$n=1$</td>
<td>25.1</td>
<td>23.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$n=2$</td>
<td>19.5</td>
<td>18.0</td>
</tr>
</tbody>
</table>

$^a$Using the MP2/6-311G** harmonic vibrational frequencies.

$^b$EXT refers to the 6-311G(2d,s,2pd) basis set.

Two higher lying isomers formed by protonation of alternate sites were also computed at the CCSD/6-31G(2df,2pd)/MP2/6-31G** level. The "W" shaped isomer, HONOH+, shown in Fig. 1(b), had an enthalpy $\Delta H_{298}^a = 31.5$ kcal mol$^{-1}$ above that of the NO+(H2O) isomer. The enthalpy of the HON(H)O+ isomer, formed by protonating the nitrogen atom of cis HONO, was $\Delta H_{298}^a = 34.6$ kcal mol$^{-1}$ above the cluster isomer. These energies are somewhat lower than the values of 41.5 and 41.7 kcal mol$^{-1}$ calculated by De Petris et al.$^7$ at the MP4/6-311G** level. Both of these isomers possessed strong X-H (X=N, O) absorption bands, but the scaled vibrational frequencies all were below 3500 cm$^{-1}$ (see Tables IV and V).

C. NO+(H2O)$_2$

Figure 6 shows the optimized $C_2$ geometry obtained for the minimum energy structure of NO+(H2O)$_2$ at the MP2/6-31G** level. The H2O molecules both bind to the nitrogen atom. The ion–solvent bond lengths are 2.318 Å and, at this level of theory, the O···N···O angle is 109.9°. The NO bond is predicted to be only 5.9° from perpendicular with respect to the O···N···O plane. The dipole–dipole interaction between the H2O molecules at the computed geometry is repulsive. This effect alone would favor by 0.5 kcal mol$^{-1}$ having the H2O on opposing sides of the nitrogen atom. However, at the MP2 level, this latter geometry ($C_{2v}$ symmetry, with the H2O molecules on opposite sides and the O···N···O angle close to 180°) is 0.5 kcal mol$^{-1}$ higher in energy; thus, the weak dipole repulsion is offset by other factors. The low frequency of the O···N···O bend, 33 cm$^{-1}$, indicates that the potential energy surface is flat along this coordinate. The equilibrium O···N···O bond angle, calculated with this basis set and constrained to $C_2$ symmetry, should therefore be treated with caution.

The CCSD binding enthalpy calculated at the MP2/6-311G** level (Table VII) is 17.5 kcal mol$^{-1}$, in good agreement with the value of 16.1±1.0 kcal mol$^{-1}$ measured by French et al.$^5$ The predicted OH stretch spectrum consists of the symmetric and antisymmetric H2O bands at scaled frequencies of 3623 and 3706 cm$^{-1}$ with similar intensities.

V. DISCUSSION

A. Protonated nitrous acid, NO+(H2O)

The experimental results on the $n=1$ cluster are most consistent with the structure of a weakly bound ion–molecule complex, NO+(H2O). We find that photodissociation of protonated nitrous acid leads to NO++H2O products. The frequency of the observed vibrational band, 3605 cm$^{-1}$, agrees within 5% of the scaled MP2 frequency of the H2O symmetric stretch, 3587 cm$^{-1}$. However, we do not observe an antisymmetric stretch band, which our calculations predict would occur at 3671 cm$^{-1}$ (scaled) with an intensity 80% of that of the symmetric stretch.

From the quadratic fluence dependence, we find that dissociation requires at least two photons, placing a lower limit of 10.3 kcal mol$^{-1}$ on the NO+···(H2O) binding energy. This lower bound is consistent with the dissociation enthalpy measured by French et al.$^5$ of 18.5±1.5 kcal mol$^{-1}$, and with our CCSD estimate of the dissociation enthalpy, $\Delta H_{298} = 20.9$ kcal mol$^{-1}$. Our result places a lower bound on the proton affinity of nitrous acid of PA$>179.5$ kcal mol$^{-1}$, consistent with the theoretical value of PA=187 kcal mol$^{-1}$ calculated by De Petris et al.$^17$

The O···N···O angle predicted by the MP2/6-31G** calculation is sharply bent, and the water molecule is oriented with a lone pair pointed towards the N atom. This geometry can be understood as the lone pair electrons of the O atom of H2O donating density into the empty $\pi^*$ orbitals of NO+, which have significant $p$ character on the N atom.

The $ab initio$ structure for NO+(H2O) is a near prolate top with rotational constants of $A = 1.96$ cm$^{-1}$, $B = 0.239$ cm$^{-1}$, and $C = 0.219$ cm$^{-1}$, yielding an asymmetry parameter of $\kappa = -0.977$. Using this calculated geometry, we can simulate the rotational envelope of the H2O symmetric stretch band. The symmetry axis of the H2O moiety is approximately collinear with the $a$ axis of the cluster; therefore,
excitation of the symmetric H$_2$O stretch will result in approximate \( a \)-type selection rules. We have modeled the rotational contour by deriving a predicted rovibrational spectrum for a semirigid rotor and then convoluting it with a Gaussian linewidth function. We used centrifugal distortion constants and differences between upper and lower state constants similar to those in HONO, although the NO$^+(H_2O)$ complex will be floppier. Figure 5 compares the observed band contour with a simulation of the rovibrational spectrum at a rotational temperature, 120 K, convoluted with our laser linewidth function. We used centrifugal distortion constants and weighted towards the \( n \)-type transition. The doublet structure stems from the \( P \) and \( R \) branches, with the relatively weak \( Q \) branch blending into the \( P \) branch. The band intensity is weighted towards the \( P \) branch, indicating that the rotational constant \( \langle B^i + C^i \rangle \) increases slightly in the upper state. Such a change can occur if the \( 0 = \text{N} \cdots \text{O} \) angle decreases slightly upon excitation. In summary, the rotational contour is consistent with both the predicted rotational constants and selection rules, and provides further confirmation in support of the proposed structure.

The only discrepancy between the experimental results and the proposed structure is the absence of the antisymmetric stretch in the experimental spectrum. Our \textit{ab initio} calculations predict that in NO$^+(H_2O)$, both OH stretch bands have intensities considerably enhanced over those in neutral H$_2$O. However, the antisymmetric band intensity, normally significantly stronger than that of the symmetric stretch, is calculated to be slightly weaker.

An explanation for the observation of only one OH stretch band is that the structure is the covalently bound N(OH)$_2^+$ [Fig. 1(b)], for which the two OH vibrations are nearly degenerate. We discount this possibility for several reasons. First, it is unlikely that this isomer is formed. N(OH)$_2^+$ is calculated to be a highly energetic metastable lying \( \Delta E_0 = 32.7 \text{ kcal mol}^{-1} \) above the ion–molecule complex. Previous experiments find no evidence for this isomer in flow tubes, stationary afterglows, and high-pressure discharges. Our source is also a high-pressure discharge with the plasma occurring in a narrow channel followed by supersonic expansion, and the chemistry is similar. Second, in order for two-photon excitation to dissociate N(OH)$_2^+$, an intramolecular hydrogen atom transfer over two atoms, from one O atom to the other, must occur followed by cleavage of the NO$^+$. This barrier for what is essentially a 1,3 hydrogen shift must be less than \( 21 \text{ kcal mol}^{-1} \). Third, our MP2 calculations predict that the OH stretches for this isomer are not actually degenerate, but are rather split by \( 50 \text{ cm}^{-1} \). Furthermore, the scaled OH symmetric and antisymmetric stretching frequencies of N(OH)$_2^+$ are predicted at 3390 and 3338 cm$^{-1}$, respectively, i.e., more than 200 cm$^{-1}$ below the observed transition, and thus disagree with experiment.

Similar reservations apply to the covalent structure formed by protonating the nitrogen atom, HON(H)O$^+$. This isomer is predicted to be \( \Delta E_0 = 35.8 \text{ kcal mol}^{-1} \) above the NO$^+(H_2O)$ energy, and it can only dissociate to NO$^+$+H$_2$O following isomerization by a hydrogen shift. The barrier for this shift, with the proton bridging an N—O sigma bond, is also likely to be high. Furthermore, our calculations predict that there will be two bands in the region scanned, the OH and NH stretches, both having scaled frequencies 280 cm$^{-1}$ or more to the red of the observed band.

The reason for the absence of an antisymmetric H$_2$O stretch absorption may lie in the fact that the spectra are not absorption spectra, but rather two-photon dissociation spectra. A discrepancy can come about if (a) the multiphoton absorption process is highly inefficient for \( v_3 \) relative to \( v_1 \) absorption, or (b) clusters excited in this mode do not efficiently dissociate.

There is a physical basis for a larger two-photon absorption cross section for the \( v_1 \) absorption. Multiphoton absorption occurs either by sequential absorption, e.g., \( 0 \rightarrow v_1 \rightarrow 2v_3 \), or nonresonantly via an intermediate virtual state. In the free H$_2$O monomer, the anharmonicity constants are \( x_{11} = -43 \text{ cm}^{-1}, x_{13} = -155 \text{ cm}^{-1}, \) and \( x_{33} = -46 \text{ cm}^{-1} \). Thus, the \( v_1 \rightarrow 2v_1 \) and \( v_3 \rightarrow 2v_3 \) transitions are off-resonance from the fundamentals by over \( 170 \text{ cm}^{-1} \). However, the \( v_1 \rightarrow v_3 \) transition is at \( 3600 \text{ cm}^{-1} \), close to the \( v_1 \) frequency of \( 3650 \text{ cm}^{-1} \). Thus, two-photon excitation of the symmetric stretch will be far more efficient because the second photon can excite the red-shifted antisymmetric stretch hot band transition. The \( 0 \rightarrow v_1 \rightarrow v_1 + v_3 \) process is therefore a near-resonant two-photon process. While the frequencies differ in the \( n = 1 \) cluster, this effect should still be qualitatively correct. Thus, two-photon dissociation was observed for \( v_1 \), while the \( v_3 \) band was too weak to be detected experimentally. We plan to test this hypothesis in a two-color photodissociation experiment.

The weakness of two-photon \( v_3 \) absorption is also consistent with the appearance of the antisymmetric stretch band in all larger hydrates of NO$^+$ and its increases in intensity with cluster size relative to the \( v_1 \) band. As discussed in Sec. V B, this result can be explained if the \( v_3 \) signal in the larger clusters arises from one-photon dissociation.

The absence of a band due to the \( v_3 \) vibration could also arise because this mode relaxes more slowly than \( v_1 \). The \( v_3 \) mode has \( A' \) symmetry and will be not be as strongly coupled to the intermolecular stretch as the \( v_1 \) mode, which possesses \( A'' \) symmetry. The differences in coupling could then lead to variations in predissociation rates. If clusters prepared by exciting the \( v_3 \) band predissociate with lifetimes greater than \( 10 \mu s \), they would be undetected. Alternatively, relaxation rates could affect the observed action spectra if two-photon absorption takes place by the following three-step process: excitation of a \( 0 \rightarrow 1 \) transition, intramolecular vibrational relaxation (IVR) of the O–H stretch, and subsequent reexcitation of the \( 0 \rightarrow 1 \) transition of the hot cluster. If IVR from the \( v_3 \) levels occurs on time scales longer than the laser pulsewidth (\( 10^{-8} \) s), the second photon would not be absorbed, and no dissociation would occur. IVR from \( v_1 \) mode must then occur at rates faster than \( 10 \text{ ns} \) to account for the observed band. This possibility could be tested by exciting clusters at \( v_3 \) with two pulses separated by \( 100 \text{ ns} \).
B. NO\textsuperscript{+}(H\textsubscript{2}O)\textsubscript{n}, n = 2 and 3

The predissociation spectra and the photoproducts of NO\textsuperscript{+}(H\textsubscript{2}O)\textsubscript{n} (n = 2 and 3) suggest that these clusters also have water ligands bound to an NO\textsuperscript{+} ion core. Unlike the n = 1 cluster, both symmetric and antisymmetric stretch bands are observed. These vibrations gradually shift to higher frequencies with cluster size in going from n = 1 to 3 (Fig. 3), as expected for the increasing hydration of the NO\textsuperscript{+} core.

The reduction in binding energy with n is also evident in the fluence dependence of the photodissociation yield when exciting the ν\textsubscript{1} band. This dependence can be either linear or nonlinear for n = 2, and becomes linear for n = 3. In the n = 2 case, the photon energy is less than the cluster dissociation energy and the linear dependence arises from dissociation of vibrationally hot complexes, resulting in both linear and quadratic contributions to the fluence dependence. When the distribution is colder, then signal from two-photon dissociation is comparable to onephoton dissociation of a smaller population of vibrationally fully hot complexes, resulting in both linear and quadratic contributions to the fluence dependence. When the distribution is hotter, one-photon dissociation dominates.

In the ab initio structure of the n = 2 complex, the water ligands both bind to the nitrogen atom of the NO\textsuperscript{+}, as in n = 1. The N==O bond is directed almost perpendicular to the ONO plane, indicating that the water molecules interact with the p orbitals of the N atom, one H\textsubscript{2}O donating lone pair density into the π\textscript{a} orbital, the other into the π\textscript{b} orbital. The n = 3 spectrum indicates that all three H\textsubscript{2}O are equivalent, and a postulated structure for NO\textsuperscript{+}(H\textsubscript{2}O)\textsubscript{3} is shown in Fig. 7(a). The third H\textsubscript{2}O also binds to the N atom of NO\textsuperscript{+}, with a lone electron pair of each of the H\textsubscript{2}O molecule donating into the π\textscript{a} orbital. We expect that the three water ligands will be symmetrically positioned about the ion.

The H\textsubscript{2}O antisymmetric stretch transitions appear as broad features that grow in intensity with cluster size relative to the narrower symmetric stretch band. Indeed, there appears to be a progression from a complete absence in n = 1, to a relatively weak shoulder in n = 2, to a strong band in n = 3. This result can be understood if the ν\textsubscript{3} signal primarily arises from one-photon dissociation of vibrationally excited clusters. For the n = 1 cluster, few of the ions are hot enough to dissociate after absorption of a single photon and no ν\textsubscript{3} band is observed. For the n = 2 cluster, the H\textsubscript{2}O binding energy is 2.4 kcal/mol\textsuperscript{-1} lower and a detectable fraction of the clusters is able to dissociate upon absorption of a photon. The ν\textsubscript{3} dissociation signal becomes even larger for n = 3, since the binding energy decreases and the total internal energy increases with the increase in cluster size. Alternatively, if the absence of the ν\textsubscript{3} band is due to low predissociation rates, this effect could arise from the decreases in predissociation lifetime with n.

C. NO\textsuperscript{+}(H\textsubscript{2}O)\textsubscript{4} and opening of the reactive channel

The observed spectrum (Fig. 3) of the n = 4 cluster suggests that this complex is also comprised of water ligands bound to an NO\textsuperscript{+} core; however, the fourth water ligand does not apparently bind directly to the NO\textsuperscript{+} ion. The appearance of bands at 3375 and 3230 cm\textsuperscript{-1} indicate that hydrogen bonds have formed and that the fourth H\textsubscript{2}O binds to the other water ligands, beginning a second solvation shell. Below, we discuss several plausible solvent configurations.

The simplest configuration involves the fourth water forming a hydrogen bond with one of the first shell H\textsubscript{2}O molecules, as depicted in Fig. 7(b). The binding energy for a second shell H\textsubscript{2}O should be on the order of 6–10 kcal mol\textsuperscript{-1}, and thus will be comparable to the estimated energy for binding a fourth water ligand directly to the NO\textsuperscript{+} core. The dissociation channel leading to two water molecules can then be understood as evaporation of (H\textsubscript{2}O)\textsubscript{2}, with a first solvation shell water carrying along its second shell partner. However, this configuration will give rise to only one hydrogen-bonded OH absorption band.

Small water clusters are well known for forming cyclic structures in order to maximize stabilization by hydrogen bonding.\textsuperscript{34} The second shell energy would be more favorable if the fourth H\textsubscript{2}O could form hydrogen bonds with two H\textsubscript{2}O ligands, as depicted in Fig. 7(c). In this structure, the water bridges two adjacent ligands to form a ring of four heavy atoms (three water O atoms and the N\textsuperscript{+}). If we assume that the H\textsubscript{2}O•••N•••OH\textsubscript{2} angle is 120° and the N•••O bond length is 2.4 Å (slightly longer than calculated for n = 2), the separation between O atoms on the H\textsubscript{2}O ligands is 4.2 Å, comparable to the 4.48 Å distance in ice. The hydrogen-bonded rings in ice I are six-membered, but tetrahedral structures similar to those proposed here exist in ice VI. The strain will be lower in the unconstrained cluster, because the soft N•••O stretches and O•••N•••O bend allow the cluster to readily deform. By forming two hydrogen bonds, the second shell H\textsubscript{2}O should bind by at least 6–10 kcal mol\textsuperscript{-1}. This structure should be at least comparable in stability to having four waters in the first shell. The bands observed at 3230 and 3375 cm\textsuperscript{-1} could then be assigned as symmetric and antisymmetric stretch modes of the two hydrogen-bonded OH bonds.

An alternative structure, shown in Fig. 7(d), consists of the adducts of the reaction products, with a HONO molecule and two H\textsubscript{2}O bound to a central hydronium ion core. This structure is not in accord with the observed spectrum. The hydronium ion OH bonds would all be red-shifted below 2700 cm\textsuperscript{-1}, and thus unobserved. The two bands above 3600 cm\textsuperscript{-1} can be assigned to the H\textsubscript{2}O molecules, but the 3375 and 3230 cm\textsuperscript{-1} bands cannot be accounted for. Furthermore, an OH stretch band of the HONO ligand is not observed.

The structure we propose in Fig. 7(d) is topologically equivalent to the structure proposed by Fehsenfeld et al.\textsuperscript{6} (shown in Fig. 7(e)]. This structure was suggested as an intermediate in reaction (1) from NO\textsuperscript{+}(H\textsubscript{2}O)\textsubscript{2}+H\textsubscript{2}O to H\textsubscript{2}O\textsuperscript{+}((H\textsubscript{2}O)\textsubscript{2}+HONO). They proposed that one (first shell) H\textsubscript{2}O was bound to NO\textsuperscript{+}, with a single H\textsubscript{2}O in turn bound to that. The remaining two H\textsubscript{2}O molecules were in the third shell, hydrogen-bonded to the second shell H\textsubscript{2}O. This structure is more consistent with our observed spectrum, since there are three hydrogen-bonded OH groups, as well as two H\textsubscript{2}O ligands with free OH groups. If the charge remains localized on the N atom, however, this configuration will be highly energetic, and unlikely to be formed.
Fehsenfeld et al. also proposed a "linear" structure, in which the four $\text{H}_2\text{O}$ molecules form a single hydrogen-bonded chain with the $\text{O}$ atom on a terminal water binding to the $\text{NO}^+$:

$$\begin{align*}
\text{H} & \quad \text{H} & \quad \text{H} & \quad \text{H} \\
\text{ON}^+ & \cdots & \text{O} \cdots & \text{O} \cdots & \text{O} \cdots & \text{O} \cdots & \text{O} \cdots & \text{O} \cdots & \text{O} \cdots & \text{O} \cdots \\
\end{align*}$$

This structure is not consistent with the observed spectrum. We would expect to observe a progression of three hydrogen-bonded $\text{OH}$ stretches of increasing red-shift and intensity, and the $v_1$ band of $\text{H}_2\text{O}$ should be significantly weaker, since only one water molecule is not a donor. Such a structure, while possibly a local energy minimum, is also energetically unfavored. Two of the water molecules are over 7 Å from the charge, and will contribute little to the solvation energy. Furthermore, if we postulate a structure in which HONO is formed and a proton is transferred to the second $\text{H}_2\text{O}$ to form $\text{H}_3\text{O}^+$, $\sim5$–10 kcal mol$^{-1}$ are lost in having the last water in a second shell position, making the reaction significantly endothermic.

From the observation of HONO products in the absence
of a HONO absorption band, we conclude that one IR photon can induce the reaction
\[ \text{NO}^+(\text{H}_2\text{O})_4 \rightarrow \text{H}_2\text{O}^+(\text{H}_2\text{O})_2 + \text{HONO}. \] (4c)
French \textit{et al.} estimate that the two channels, loss of H$_2$O (4a) and loss of HONO (4c), are almost identical in energy, but we find that the yield of HONO is significantly lower (10%). There are several plausible reasons why unimolecular decay of excited NO$^+$(H$_2$O)$_4$ favors H$_2$O loss. First, the estimated dissociation energies are comparable to the photon energy; if the molecule is excited close to threshold, differences of even a few kcal mol$^{-1}$ can greatly influence the branching ratio. Second, the reaction (4c) may have an activation energy significantly larger than the H$_2$O binding energy, $E_{bind} > 10$ kcal/mol. A barrier between NO$^+$(H$_2$O)$_4$ and H$_2$O$^+$(H$_2$O)$_2$(HONO) is plausible, especially if the solvent H$_2$O must rearrange as the charge is transferred. Finally, unimolecular decay via the reactive channel may also be limited by the entropy of activation. Evaporation of H$_2$O from NO$^+$(H$_2$O)$_4$ proceeds by simple bond fission, but formation of HONO may occur by a concerted reaction. In particular, substantial solvent rearrangement within the cluster may inhibit the reaction even if the HONO channel is energetically accessible.

D. The $n=5$ cluster: H$_2$O$^+$(H$_2$O)$_3$(HONO)

The large differences in the spectrum of $n=5$ compared to the spectra of the smaller clusters signal a qualitative change in the nature of the clusters. The broad, strong absorption band near 2800 cm$^{-1}$ and the weaker band at 3190 cm$^{-1}$, which we assigned as the OH stretches of H$_2$O$^+$, provide clear evidence that the $n=5$ complex has an H$_2$O$^+$ ion core hydrogen-bonded to three solvating ligands. The appearance of the higher-frequency bands of the $n=5$ cluster is also distinct, with several sharp bands instead of the pattern of a sharp $v_1$ and broad $v_2$ bands observed in the smaller clusters. Because HONO is the dominant dissociation product, we infer that HONO forms weaker hydrogen bonds than H$_2$O. We thus propose that the $n=5$ clusters have the structure shown in Fig. 7(f), with the H$_2$O$^+$ bound to three water molecules in the first solvation shell and a HONO molecule in the second shell hydrogen-bonded to one of the first shell waters.

Given this structure, we can assign the five bands observed in the 3500 to 3800 cm$^{-1}$ region (shown in more detail in Fig. 8). We distinguish between the two H$_2$O ligands which do not act as donors in a hydrogen bond, and the third H$_2$O ligand, which forms a hydrogen bond with the HONO in the second solvation. The bands at 3644 and 3734 cm$^{-1}$ are close to the free H$_2$O monomer bands, and are assigned as the symmetric and antisymmetric OH stretches of the two water ligands (not bound to HONO). The third H$_2$O will have one OH stretch significantly red-shifted, while the other will remain essentially unperturbed. We assign the 3710 cm$^{-1}$ band to the free OH of this perturbed molecule, and the broader band at 3530 cm$^{-1}$ (shifted 125 cm$^{-1}$ from the $v_1$ band of the H$_2$O monomer) to the HO-H-O bond. The remaining band is the sharp, strong feature at 3576 cm$^{-1}$, 15 cm$^{-1}$ to the red of the t-HONO monomer band. We assign this feature as the OH stretch of the nitrous acid ligand.

The frequency of the OH stretch of the nitrous acid ligand suggests that it is the trans conformer, since the t-HONO monomer stretch has a frequency of 3591 cm$^{-1}$, while c-HONO absorbs at 3426 cm$^{-1}$. The effect of hydrogen bonding on the OH stretch of HONO is unknown. Thus, the issue of how the HONO is hydrogen-bonded to the cluster (terminal oxygen, N atom, hydroxy group O atom, or bridging) remains uncertain.

E. The intracluster reaction of NO$^+$

The clusters we observed are intermediate complexes along the pathways for the reaction
\[ \text{NO}^+(\text{H}_2\text{O})_{n-1} + \text{H}_2\text{O} \rightarrow \text{H}_2\text{O}^+(\text{H}_2\text{O})_n + \text{HONO}. \] (6)
The energetics along the reaction coordinates for $n = 2$ to $5$ are illustrated in Fig. 9. From their hydration enthalpy measurements, French \textit{et al.} show that the reaction is endothermic for $n=2$ and $3$ by 23.6 and 8.1 kcal mol$^{-1}$, respectively. Using their estimated value of $\Delta H_{298}^\circ$, the reaction for $n=4$, i.e., reaction (1), is slightly endothermic ($-2$ kcal mol$^{-1}$). If we continue their extrapolation, then $\Delta H_{298}^\circ \approx -10$ kcal mol$^{-1}$, and we estimate that the reaction enthalpy for $n=5$ is $-6$ kcal mol$^{-1}$.

Our results are consistent with the thermodynamics. For reactions which are endothermic ($n \leq 4$), the complexes we observed are adducts of the reactants NO$^+$ and H$_2$O. The structure of the $n=5$ cluster, H$_2$O$^+$(H$_2$O)$_3$(HONO), reflects the fact that the reaction for $n=5$ is exothermic. Although the cluster NO$^+$(H$_2$O)$_5$ may be stable, it is probably higher in energy than the observed cluster (see Fig. 9).

While the reaction goes to completion for five water molecules, we find evidence for the onset of reaction in the $n=4$ cluster, even though the reaction is probably endothermic. Absorption of one IR photon ($\sim 10.5$ kcal mol$^{-1}$) leads to $\sim 12\%$ yield of HONO formation. The photon energy is approximately equal to the internal energy of the activated complex formed in the thermal collision NO$^+$(H$_2$O)$_3$+H$_2$O. Thus, we would expect that such collisions would lead to reaction approximately 10% of the time. This reaction effi-

![FIG. 8. Details of the vibrational predissociation spectrum of NO$^+$(H$_2$O)$_3$ in the 3500-3800 cm$^{-1}$ region. The ordinate is the yield of photofragment ions H$_2$O$^+$(H$_2$O)$_3$.](image-url)
FIG. 9. Energy level diagram for the reactions NO+(H₂O)_n+1 + H₂O → NO+(H₂O)_n + H³O+(H₂O)_2 + HONO. Dashed lines indicate hypothesized reaction paths and transition states. Each reaction pathway for a cluster n is lowered relative to the n-1 pathway by the hydration enthalpies. Numbers are hydration enthalpies in kcal mol⁻¹, those in parentheses are estimates only.

Scarcity is consistent with the observed rate constant, 7 × 10⁻¹¹ cm³ s⁻¹, which is about one order of magnitude lower than the rate constant for ion–dipole collisions.

In the earlier static and flow tube experiments, NO⁺(H₂O)_4 was not observed. This can be understood since the reaction rate is greater than three-body stabilization of the adduct. Furthermore, once H₃O⁺(H₂O)_2 is formed, it quickly equilibrates to form larger hydrates. The backreaction is inhibited by the reduced concentration of H₃O⁺(H₂O)_2 and the negligible concentration of HONO.

Reorganization of the H₂O molecules is almost certainly required for the reaction to proceed, because the charge is transferred from the nitrogen atom to an H₃O⁺ moiety. The barrier for this process is still relatively high in n=4, but is readily overcome in n=5. Additional experiments on the n=4 cluster, aided by computational studies, may provide further insights into the activation steps of this reaction.

VI. SUMMARY

Our results provide clear evidence for a rearrangement of NO⁺(H₂O)_n at larger cluster sizes. The experimental results indicate that the smaller clusters are nitrosonium ions bound by water ligands and are in accord with the theoretical calculations for n=1 and 2. The cluster n=4, however, begins to deviate from this picture with the appearance of new hydrogen-bonded OH stretch absorptions and the opening of a minor photodissociation channel giving rise to loss of HONO. This behavior presages the large changes in the vibrational spectrum and photodissociation behavior observed after adding a fifth water molecule. The n=5 cluster forms an adduct of the reaction products, H₃O⁺(H₂O)_3(HONO).

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