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Proton sharing in hydronium–nitrogen clusters probed with infrared spectroscopy

B. Bandyopadhyay, T.C. Cheng, M.A. Duncan *

Department of Chemistry, University of Georgia, Athens, GA 30602, United States

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ABSTRACT

Cluster ions containing hydronium and multiple nitrogen molecules, e.g., $H_3O^+(N_2)_n$ ($n = 1–4$) are produced in a supersonic molecular beam using a pulsed discharge source. Ions are mass analyzed and size-selected using a reflectron time-of-flight mass spectrometer. Selected ions are investigated with infrared laser photodissociation spectroscopy in the 2000–4000 cm^{-1} region. Photodissociation occurs by the loss of a single nitrogen molecule from each cluster. The infrared spectra contain free-OH vibrations, hydrogen bonding O–H vibrations, combination bands between the latter vibrations and the low-frequency intermolecular stretches, and an N–N stretch in the $n = 4$ clusters. The $n = 1$ cluster has partially resolved rotational structure, confirming that its structure is that of end-on addition of N_2 to one of the hydrogens of hydronium. The hydrogen bonding bands have broad linewidths and are significantly red-shifted from the free-OH vibrations. The red-shift decreases when more nitrogens are added, as the shared-proton interaction is distributed over the three hydrogen binding sites. Proton sharing in this system is highly biased toward the water moiety, but the nitrogen interaction is significant enough to induce significant vibrational shifts compared to other weakly bound complexes with hydronium (e.g., argon).

1. Introduction

Protonation and proton transfer processes are important throughout Chemistry and Biology, and the mechanistic details of these processes have been investigated extensively [1–7]. Protonated molecular ions, which can be studied with mass spectrometry, provide models for the intermediates in these processes [8,9]. Proton transfer processes also form the basis for chemical ionization [10], and therefore have had a longstanding role in mass spectrometry. Key structures in proton transfer reactions are proton-shared dimers, and these systems have also been the subject of much recent work. In the last few years, infrared spectroscopy measurements have become possible that allow the structures of proton-bound dimers to be measured [11–26]. Many of these studies have examined protonated water and its proton sharing interactions with other small molecules [12–15,18,20,25]. Theory has focused on these systems, particularly the protonated water dimer [27–29]. More recent experiments have examined proton sharing in mixed dimer species having different proton affinities, polarizabilities, dipole moments, etc. [16,18–20]. In the present study, we use infrared spectroscopy to examine the mixed system having the hydronium ion interacting with one or more nitrogen molecules.

Recent interest in the infrared spectroscopy of proton-bound dimers began with the work of Asmis et al., who used the free electron laser "FELIX" to probe the low-frequency shared-proton-based vibrations of the protonated water dimer [12]. Following that initial work, Johnson and coworkers, in a collaboration with our group, used IR optical parametric oscillator lasers to probe the protonated water dimer and other small protonated water clusters [14]. More recent studies by the Johnson group explored isotopic variants of the protonated water dimer [15]. Numerous theoretical investigations have explored this system, including reduced-dimensional and full-dimensional anharmonic treatments [27,29]. Our group has recently reported an in-depth study of the small protonated water clusters, $H^+(H_2O)_n$, $n = 3–5$, investigating the role of tagging with argon on these systems and the effects of deuteration [25]. A central focus of these protonated water studies has been the shared-proton stretch vibration, which occurs for symmetrically shared water structures in the 1000–1200 cm^{-1} region. Such symmetrically shared-proton vibrations have now also been studied for many other small molecules, including CH_3OH [16], NH_3 [17], CO_2 [21], acetylene [22], acetone [23], N_2 [24], etc. Johnson and coworkers performed a systematic study of asymmetric proton-bound dimers, concluding that the shared-proton stretching vibration varies over a wide range depending on the difference

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* Corresponding author. Tel.: +1 706 542 1998; fax: +1 706 542 1234.
E-mail address: maduncan@uga.edu (M.A. Duncan).

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in the two proton affinity values, ΔPA, and that a linear plot of ΔPA can be used to predict this vibration [18]. Burt and Fridgen have recently commented about special cases in which the proton stretches may not follow this ΔPA trend, such as systems in which one component molecule has an especially high dipole moment [19]. Johnson and coworkers have studied one such example in the case of the proton-bound dimer of water and acetonitrile [20].

The infrared spectroscopy of the hydronium ion was studied with high resolution measurements in the gas phase by Oka, Saykally and others [30–32]. The detailed potential energy surface of this prototype ion has also been studied with theory [33,34]. Hydronium is also the central ion in many small protonated water clusters, although the proton-bridged dimer structure, known as the Zundel ion, is also the charged species in some of these systems [14,25,35]. Small clusters of water containing the hydronium or Zundel ion moieties have been studied extensively in recent work [14,15,25,35], and mixed dimers of water and selected small molecules have been investigated [15,16,18,20,35]. Likewise, the protonated nitrogen ion N_2H^+ has been studied with high resolution spectroscopy [36,37]. Our research group has recently reported the spectrum of the proton-bound nitrogen dimer [24]. The proton affinity of water is 691.0 kJ/mol, while that of nitrogen is 493.8 kJ/mol [38]. In the mixed system, then, the proton is expected to reside mostly on water, and these clusters can be viewed to a good approximation as hydronium ions solvated by nitrogen molecules. The $H_3O^+(N_2)_n$ ($n = 1–3$) system has been studied in mass spectrometry measurements, providing the binding energies [39]. Johnson and coworkers have studied the infrared spectroscopy of selected mixed complexes of hydronium–nitrogen with attached argon [40]. The IR spectra reported here support the solvated hydronium picture, but show that there is also partial proton sharing in this system whose importance varies with the progressive solvation.

2. Experimental

Cluster ions for this experiment are produced with a pulsed discharge source employing needle electrodes situated downstream from the output of a pulsed valve (General Valve series 9). The expansion gas included water at its ambient vapor pressure seeded into a pure nitrogen expansion with a few percent of hydrogen added. Without added hydrogen, the mass spectrum contained clusters of the form $(H_2O)(N_2)_n^+$ in addition to the desired protonated $H_3O^+(N_2)_n$ species, making clean mass selection difficult. The addition of hydrogen enhanced the protonation process, producing only the latter ion series.

Ions are mass analyzed and size-selected using a specially designed reflectron time-of-flight spectrometer [41]. Selection is accomplished with pulsed deflection plates located in the first flight tube section. The selected ions are excited in the turning region of the reflectron field with a tunable infrared laser. The IR laser is a Nd:YAG pumped infrared optical parametric oscillator (IR-OPO; LaserVision), with tuning range of 2000–4500 cm^{-1} and linewidth of about 1.0 cm^{-1}. The OPO provides several mJ/pulse of output in the region of this experiment. The intensities of one or more fragment ions resulting from IR excitation are recorded versus the IR photon energy to obtain a spectrum. The signal is collected with a digital oscilloscope (LeCroy) interfaced to a PC computer.

Computational studies on the ions in this experiment are carried out with the Gaussian 03 program package [42] using density functional theory at the B3LYP/6-311+G** level. The $n = 1$ complex was also investigated with MP2/aug-cc-pVDZ calculations to investigate the dependence of binding energies on the computational method. Computed IR frequencies are scaled by a factor of 0.961 for comparison to the experiment. This factor was chosen because it brings the frequencies for the isolated hydronium ion computed in this same way into agreement with the known experimental frequencies.

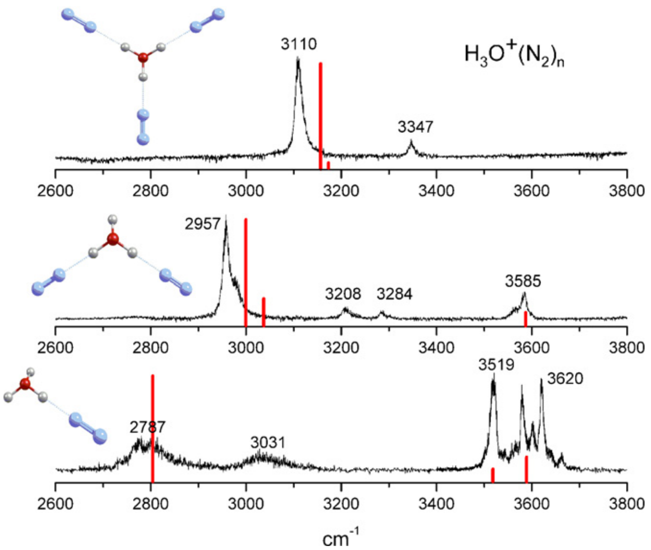

Fig. 1. The photodissociation spectra of $H_3O^+(N_2)_n$ complexes for $n = 1–3$. In each case the spectrum is measured in the N_2-loss mass channel. The red bars indicate the computed vibrational bands, which are scaled by a factor of 0.961.

3. Results and discussion

The mass spectrum of the ions produced in this experiment contains primarily protonated water clusters and protonated water–nitrogen mixed species. The $H_3O^+(N_2)_n$ complexes ($n \leq 6$) are prominent, and the mass peak corresponding to the $n = 3$ complex is relatively more intense than others. This is perhaps not surprising, because three nitrogens can bind to the O–H bonds of hydronium forming the first solvation sphere. El-Shall and coworkers measured the binding energies of $H_3O^+(N_2)_n$ complexes, finding values of 7.8, 7.3 and 6.3 kcal/mol (2730, 2550 and 2200 cm^{-1}) for the $n = 1, 2, 3$ species [39]. Consistent with these energetics, we find that these complexes dissociate efficiently upon photoexcitation with the infrared laser in the 2500–4500 cm^{-1} range, losing a single nitrogen molecule. However, they do not photodissociate in the lower energy range where the N–N stretch resonance is expected (2330 cm^{-1} in the isolated molecule [43]). Studies in this region and at lower frequencies are therefore precluded for the $n = 1–3$ complexes here. Dissociation at the N–N stretch might be expected for the $n = 3$ complex based on its previously determined dissociation energy, but it is not detected, indicating that the actual dissociation energy is greater than 2330 cm^{-1}.

Fig. 1 shows the infrared photodissociation spectra of the $H_3O^+(N_2)_n$ complexes with $n = 1$, 2 and 3, measured in the respective mass channels corresponding to the loss of a single nitrogen molecule from the selected parent ion. The computed structures of these complexes are shown in the inset and their predicted vibrations are shown as solid lines in the figure. The $n = 1$ complex has broad bands centered at 2787 and 3031 cm^{-1} and several sharper features in the 3500–3700 cm^{-1} range. The $n = 2$ spectrum has a more intense band in the lower frequency region at 2957 cm^{-1}, and weaker bands in the higher frequency region at 3208, 3284 and 3585 cm^{-1}. The spectrum of the $n = 3$ complex is quite simple, with a single strong band at 3110 cm^{-1} and a weaker one at 3347 cm^{-1}. These various vibrations can be assigned qualitatively based on the results of previous infrared studies of protonated water clusters [14,15,25,35]. The bands in the higher frequency region of 3500–3700 cm^{-1} are associated with "free-OH" stretch-

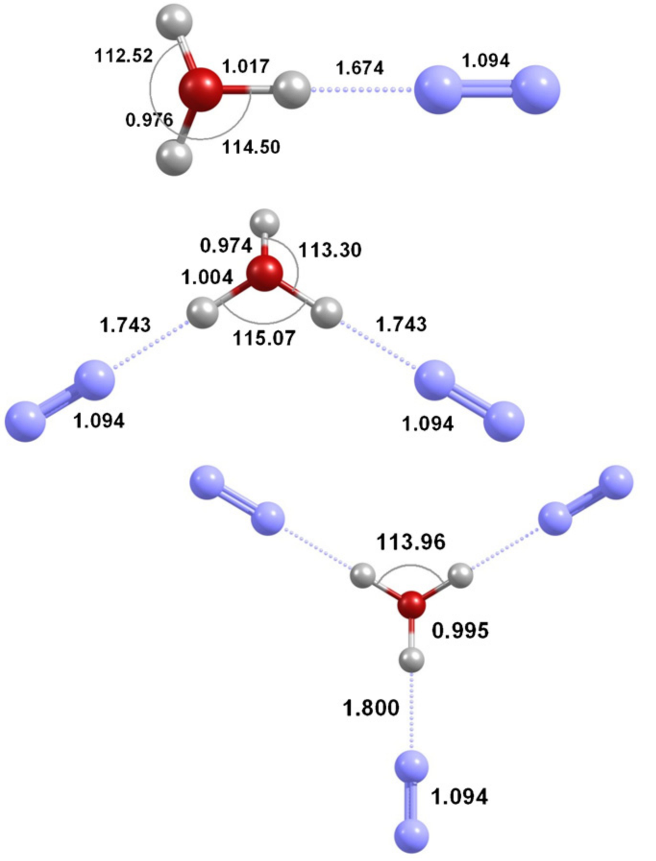

Fig. 2. The structures resulting from theory (DFT/B3LYP) for the $H_3O^+(N_2)_n$ complexes for $n = 1–3$.

ing vibrations of hydronium, while the more red-shifted bands are those associated with hydrogen-bonded or "solvated" OH vibrations. For comparison to these spectra, the isolated hydronium ion has its symmetric and asymmetric OH stretch vibrations (ν_1 and ν_3) at 3445/3491 and 3514/3530 cm^{-1} (inversion doublets) [30,31], and the symmetric and asymmetric O–H stretches of the isolated water molecule occur at 3657 and 3756 cm^{-1} [44]. The inversion or "umbrella" vibration of the isolated hydronium ion, split by the tunneling dynamics, is expected below 1000 cm^{-1} [31], which is well below the dissociation limit of these complexes. Like the N–N stretching motions, this bending vibration is outside the range of this photodissociation experiment. However, Johnson and coworkers have recently studied selected $H_3O^+(N_2)_n$ complexes mixed with argon, which have resonances in the region of the water bending/scissors mode near 1500–1800 cm^{-1} [40].

To investigate these systems in more details, we have performed computational studies on the $n = 1–3$ complexes. The structures resulting from the computations are shown in Fig. 2, and the vibrational frequencies for these complexes are presented in Table 1. The binding energies for the elimination of one nitrogen from each of these complexes are computed to be 9.6, 7.2 and 5.9 kcal/mol (3360, 2520, 2065 cm^{-1}), respectively, for the $n = 1–3$ species at the DFT/B3LYP level. Using the MP2/aug-cc-pVDZ level for the $n = 1$ species, this binding energy was reduced to 8.7 kcal/mol (3045 cm^{-1}). These binding energies are roughly comparable to those determined experimentally by El-Shall and coworkers, as mentioned above [39]. However, quantitative agreement is not expected for the DFT computations because of the well-known difficulties that this method has with dispersion interactions. However, past experience has shown that DFT is reliable for reproducing the structures of such complexes and their vibrational spectra.

Table 1
Vibrational frequencies (unscaled) computed for the $H_3O^+(N_2)_n$ complexes studied here. Intensities and symmetries are in parentheses.

$H_3O^+(N_2)$	157.8(2)(a″), 159.9(5)(a′), 246.1(85)(a′), 411.1(2)(a″), 483.9(180)(a′), 914.8(330)(a′), 1662.8(44)(a′), 1703.6(92)(a″), 2464.3(49)(a′), 2920.9(2090)(a′), 3662.1(238)(a′), 3734(415)(a″).
$H_3O^+(N_2)_2$	38.4(4)(a′), 145.0(7)(a′), 147.6(1)(a″), 148.0(0)(a″), 169.8(4)(a′), 215.7(23)(a′), 235.8(110)(a″), 337.4(93)(a′), 498.0(7)(a″), 690.9(66)(a″), 924.5(338)(a′), 1682.1(29)(a″), 1712.4(63)(a′), 2461.2(57)(a″), 2462.0(15)(a′), 3121.1(2819)(a″), 3161.9(760)(a′), 3730.6 (329)(a′).
$H_3O^+(N_2)_3$	31.8(1)(e), 31.8(1)(e), 45.7(5)(a_1), 139.6(1)(a_1), 139.6(1)(a_1), 140.7(0)(a_1), 144.3(2)(a_1), 162.7(5)(e), 162.7(5)(e), 185.2(1)(a_1), 228.8(76)(e), 228.9(76)(e), 584.9(0)(a_2), 635.4(69)(e), 635.5(69)(e), 918.9(336)(a_1), 1707.7(33)(e), 1707.7(33)(e), 2460.1(41)(e), 2460.1(41)(e), 2460.1(2)(e), 3283.8(2305)(e), 3283.8(2305)(e), 3300.8(114)(a_1).

The $H_3O^+(N_2)$ complex is expected to have a structure with nitrogen binding to a single OH of hydronium in a near-linear O–H–N–N configuration. Following the logic described above, this complex should have higher frequency vibrations for the free-OH groups on the hydronium and a lower frequency OH stretch corresponding to the hydrogen bound to the nitrogen, which is then essentially a shared-proton motion. Theory predicts the symmetric and asymmetric free-OH stretches at 3519 and 3588 cm^{-1} and the complexed O–H stretch at 2807 cm^{-1}. As shown in Fig. 1, the predicted shared-proton stretch matches nicely with the broad experimental band centered at 2787 cm^{-1}, and this band can then be assigned to this vibration. The integrated intensity of this band is high, consistent with the strong IR intensity computed (2090 km/mol) for the proton stretch. However, only two bands are predicted in the free-OH region, but three intense peaks and at least two weaker ones are actually observed here. Fortunately, this pattern of bands in the OH stretching region is familiar and occurs often for complexes containing a water molecule bound in a complex with near-C_{2v} symmetry having the heavy atoms on this C_2 axis. In these complexes, only the light hydrogen masses are off the C_2 axis and contribute to the moment of inertia along this axis. The complex is therefore a near-prolate symmetric top, and the multiple bands here can be assigned to the partially resolved K-type rotational sub-band structure expected for such a system. For example, this same behavior has been seen by our group in the infrared spectra of several metal cation–water complexes [45,46].

In this picture of the band structure, the symmetric stretch has a parallel-type rotational contour, resembling a single band slightly broader than usual, and the asymmetric stretch has a perpendicular-type contour, with two main intense bands and a weaker central one. Fig. 3 shows an expanded view of this region of the spectrum compared to a spectrum simulated for such partially resolved rotational structure using the program AsyRotWin [47]. For this simulation, we use the computed structure for this complex to derive rotational constants, and these are employed in the simulation. Good agreement is obtained between the simulated spectrum and the experimental one if we assume that the temperature is low and we apply the 3:1 intensity alternation for K = odd:even expected for equivalent hydrogens. Because of the low resolution, other rotational constants varying slightly from these also give an acceptable match with the experimental spectrum. Therefore, we cannot determine any detailed structural information, but can conclude that the spectrum is consistent with the

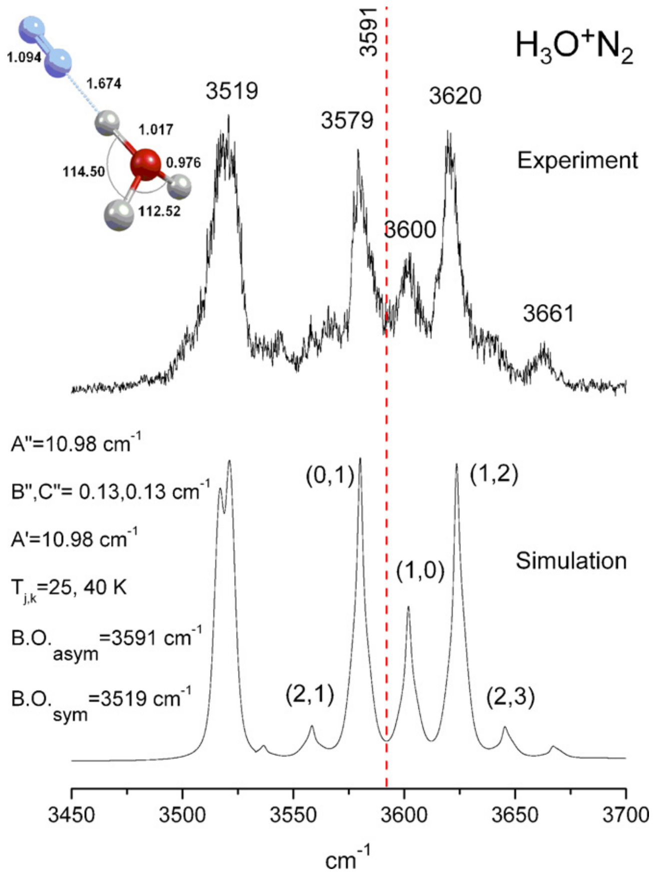

Fig. 3. An expanded view of the free-OH stretching region, showing the partially resolved rotational structure in this region. The lower trace shows a simulation of the rotational structure expected based on the computed structure for this complex. The (K′,K″) levels are indicated.

computed structure. The symmetric stretch band is therefore the one at 3519 cm^{-1} and the asymmetric stretch band center, taken from the origin of the simulated band, is at 3591 cm^{-1}. These compare nicely with the computed band positions of 3519 and 3588 cm^{-1}. Several other comments are in order about this simulation. As shown in the figure, two different temperatures are employed in the simulation, i.e., $T_J = 25$ K and $T_K = 40$ K. The J temperature affects the widths of the sub-bands measured, as it applies to the unresolved J structure. The K sub-bands are resolved, and so the K temperature affects the relative intensities of the sub-bands for the asymmetric stretch. This behavior has been seen previously [45,46] and is reasonable because the K levels are more widely spaced and do not relax as efficiently as the J levels in the supersonic expansion. Another aspect of the simulation concerns the 3:1 intensity alternation, which should apply strictly only for a planar C_{2v} symmetric species. However, we have investigated the H–O–H bending potential computationally by fixing the remainder of the structure and varying this angle with respect to the C_2 axis. Although this is a very approximate procedure, we find that the barrier to non-planarity is low (about 2 kcal/mol) and that the zero point energy lies close to the barrier height. The system therefore may be vibrationally averaged to planarity. Of course tunneling also occurs on this double-well potential even if the zero point energy lies below the barrier.

The only remaining vibrational feature not yet accounted for in the $n = 1$ spectrum is the broad band in the hydrogen bonding region centered at about 3031 cm^{-1}. Because of its position at lower frequency and its width, this band is likely to involve a hydrogen bonding vibration, but only one such vibrational fundamental is predicted by theory and this was already assigned to the band at 2787 cm^{-1}. The other possibility is a combination band involving the main hydrogen bonding stretch with another vibration whose frequency corresponds to the difference between the 2787 and 3031 cm^{-1} bands. Such a combination band would not be predicted by harmonic theory, but it could be identified using harmonic theory intervals. The 244 cm^{-1} interval lies close to the (unscaled) frequency of 246 cm^{-1} computed for the intermolecular H_3O^+–N_2 stretch vibration, which lies along the same axis as the hydrogen bond/proton stretch. It then makes sense that these vibrations could couple effectively together, and so we assign this second band to the proton stretch–intermolecular stretch combination. Strong anharmonicity effects and prominent combination bands are a general feature of other shared-proton dimers [11–26], and so such a combination band in this system is not too surprising.

The $H_3O^+(N_2)_2$ complex is expected to have a structure with nitrogens binding to two of the hydronium hydrogens. This structure is shown in Fig. 2 and the computed vibrations are shown in Table 1. In this configuration, there is only one free-OH, and there is no longer a single axis containing all the heavy atoms. Consequently, there is only one free O–H stretch and the widely spaced rotational structure seen for the $n = 1$ complex is not expected. Consistent with this, there is only one band in the free-OH region at 3585 cm^{-1}, and the position of this band agrees perfectly with the frequency computed for this vibration (3585 cm^{-1}). In the hydrogen bonding region, there are now two IR-active fundamentals expected, which are the symmetric and asymmetric stretches of the two O–H's connected to nitrogens. These vibrations are predicted at 2999 and 3039 cm^{-1}, and are assigned to the main band in this region at 2957 and its shoulder noticeable on the higher frequency side. There are this time two additional weak bands in this hydrogen bonding region that are not near any predicted vibrational fundamentals, and so we again consider the possibility of combination bands. The bands at 3208 and 3284 cm^{-1} lie 251 and 327 cm^{-1} above the main hydrogen bonding O–H stretch band. Three low-frequency vibrational fundamentals are predicted by theory in this frequency range. The (unscaled) frequency of 215.7 cm^{-1} is the symmetric intermolecular (N_2)–H_3O^+–(N_2) stretch, the 235.8 cm^{-1} frequency is the asymmetric intermolecular stretch, and the 337.4 cm^{-1} band is the free-OH bending mode. Each of these motions appear on inspection to be viable candidates for coupling with the hydrogen-bonded O–H stretch. If we assume that the vibrational combinations do not have high anharmonicities (consistent with the assignment for the $n = 1$ complex), then the latter two frequencies correspond to the intervals that we see above the main hydrogen bonding O–H stretch band. We therefore assign these features to the hydrogen-bonded O–H stretch/asymmetric intermolecular stretch and hydrogen-bonded O–H stretch/free-OH bend combinations, respectively. Anharmonic vibrational calculations would of course be necessary to confirm this proposed assignment. Another conceivable assignment for bands in this vicinity is the overtone of one of the bending modes predicted in the 1600–1700 cm^{-1}. However, the bands in question only fall near the overtone region of 3200–3400 cm^{-1} for the $n = 2$ and 3 species. Because similar intervals are observed for all three complexes, the combination of the hydrogen bonding stretch with lower frequency modes seems to be a more likely assignment.

The $H_3O^+(N_2)_3$ complex is predicted to have a structure with nitrogens binding to each of the three hydrogens of hydronium. This structure is shown in Fig. 2 and its computed vibrational frequencies are shown in Table 1. Because this complex has each hydronium hydrogen atom complexed to a nitrogen molecule, it may be regarded as having a filled first coordination sphere. In this configuration, there is no free-OH, and consequently no free O–H stretch. Instead, there are symmetric and asymmetric hydrogen-bonded O–H stretches, with nearly the same frequen-

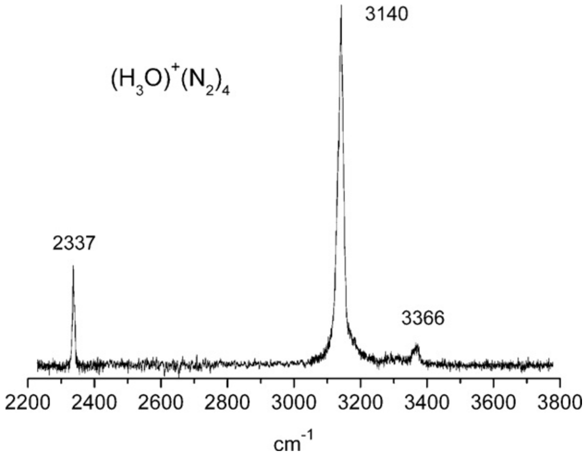

Fig. 4. The IR photodissociation spectrum for the $H_3O^+(N_2)_4$ complex. Because there is a more weakly bound external N_2 molecule present, photodissociation is possible in the lower energy region where the N–N stretch is expected, and this band is observed.

cies. The spectrum is noticeably simpler than those for the $n = 1$ and 2 complexes, consistent with this higher symmetry. The band at 3110 cm^{-1} is assigned to the asymmetric stretch, which is predicted to have the much greater IR intensity. As for the smaller complexes, this band is noticeably broadened, and there is very weak signal on the higher frequency side of this that could be attributed to a broad and much weaker symmetric stretch band. The 3347 cm^{-1} band is in about the same relative position as the combination bands assigned for the $n = 1$ and 2 complexes, lying 237 cm^{-1} above the 3110 cm^{-1} band. Again, since no other fundamental is expected here, we consider the possibility of a combination band. There is a doubly degenerate intermolecular stretching mode predicted (unscaled) at 229 cm^{-1}, whose frequency compares well with this interval. As we noted above, this kind of motion seems to be one which could couple effectively with the hydrogen-bonded O–H stretch, and therefore we again assign the 3347 cm^{-1} to this kind of combination.

The last cluster size studied here is the $H_3O^+(N_2)_4$ complex, whose spectrum is shown in Fig. 4. The $n = 3$ complex was concluded above to have a filled first coordination sphere, and therefore the $n = 4$ complex should have one nitrogen molecule binding more weakly in a remote site. Past experience has shown us that theory on such systems is difficult because of multiple binding sites with close energies for the external molecule, and therefore we have not pursued computational studies on this complex. However, the nature of the spectrum confirms that there is a weakly bound nitrogen molecule present, as the dissociation efficiency is high and dissociation can be measured down to energies including the N–N stretch vibration. By analogy to the $n = 3$ spectrum and its computed and experimental frequencies, the bands present in this spectrum are therefore assigned to the N–N stretch at 2337 cm^{-1}, the hydrogen-bonded O–H stretch at 3140 cm^{-1} and the combination of this latter vibration with the intermolecular H_3O^+–(N_2) stretch at 3366 cm^{-1}. The latter two bands are shifted 30 and 19 cm^{-1}, respectively, to the blue from the corresponding frequencies in the $n = 3$ complex. The nitrogen stretch was not detectable in the smaller clusters, but because of the external nitrogen and its weak binding energy, this vibration can be measured here. The N–N vibration is that of the asymmetric stretch of the three nitrogens bound to hydronium, which then looks much like a stretch of a single nitrogen; the external molecule is not expected to have significant IR intensity. The frequency here is only 7 cm^{-1} higher than that in the isolated nitrogen molecule. The proton sharing interaction apparently has little affect on the N–N stretch, consistent with a similar effect seen for the protonated nitrogen dimer [24].

Having assigned these vibrational spectra, it is interesting to consider how they may shed light on the proton sharing interactions in this system. For this discussion, it is convenient that structural information is available for the isolated hydronium ion, and that the proton-shared homo-molecular dimers of both H_2O and N_2 have been studied recently. The first qualitative observation is that these spectra are significantly different from that of the isolated hydronium cation, which has symmetric and asymmetric stretch vibrations at 3445/3491 and 3514/3530 cm^{-1} [30,31]. The frequencies of the free-OH vibrations for the $n = 1$ and 2 complexes are similar to or slightly higher than these values. The greatest vibrational shift occurs for the hydrogen-bonded O–H stretches. For the $n = 1$ complex, the frequency of 2787 cm^{-1} lies over 700 cm^{-1} to the red from the vibrations of hydronium, and over 400 cm^{-1} to the red from the vibrations of the argon complexes of H_3O^+, which have been studied by our group [48] and that of Johnson and coworkers [40]. This is an indication that this complex has a partially shared-proton interaction rather than just that of a weakly bound complex. This is also evident from the structure computed here for the H_3O^+–N_2 complex, which is shown in Fig. 2. In this structure, the proton lies much closer to water than it does to nitrogen, consistent with the much greater proton affinity of water, but there is noticeably variation in the structure compared to isolated hydronium. The O–H bond distance toward the N_2 is lengthened (1.017 å) compared to that in hydronium (0.979 å) or to the remote O–H bonds in the complex (0.976 å). Additionally, the H–O–H angle opposite the shared proton is computed to be reduced to 112.52°, compared to the 114.9° value in hydronium. This smaller angle is closer to that of 104.7° for the isolated water molecule. Polarization effects such as this which affect the H–O–H bond angle in water have been measured previously for singly and doubly charged metal cation complexes with water, although in those systems the induction effect caused the angle to expand [45,46].

Perhaps the best indicator for the nature of the shared-proton interaction is the O–H stretch associated directly with this. Vibrational shifts resulting from hydrogen bonding interaction have been known for many years, and these shifts are often associated with the strength of the hydrogen bond, the bond distance between donor and acceptor, or the relative proton affinity values [49]. Johnson and coworkers have investigated a series of hetero-molecular proton bound dimers and have compared the proton stretch frequency to the relative proton affinity values of the two molecules [18]. Based on their measured infrared spectra of 19 complexes they made a plot of shared-proton stretch (ν_{sp}) versus the proton affinity difference (ΔPA) between the two species competing for the proton, concluding that the frequency of the shared-proton stretch is linearly correlated with ΔPA. According to this analysis, the proton stretch of H_3O^+–N_2, which has a ΔPA value of 197 kJ/mol, is predicted to appear at 2800 cm^{-1}. This is in fact roughly where we observed this band. In the protonated water dimer, the symmetrically shared proton has a stretch vibration near 1000 cm^{-1} [12–15,18,27–29], while that of the protonated nitrogen dimer is at 743 cm^{-1} [24]. Therefore, although there is indeed significant variation for these homo-molecular (ΔPA = 0) species, the trend for higher proton stretch in the mixed systems is reproduced qualitatively here.

The shared-proton interaction is also interesting to consider in the $n = 2$ and 3 complexes, in which (according to the computed Mulliken charges) the charge is progressively more delocalized. In the $n = 2$ complex, there are two hydrogen bonds, each computed to be slightly longer than the free O–H bond distance. The shared-proton interaction is then distributed over these two binding sites, and the strength of each interaction is therefore less than in the single interaction for the $n = 1$ complex. Consistent with this, and the idea that the red-shift varies with the hydrogen bond strength, the hydrogen-bonded O–H vibration is less red-shifted for the $n = 2$ complex than it is for the $n = 1$. The $n = 3$ complex has a completed coordination and a symmetric environment around the central hydronium. The O–H bond distance and H–O–H bond angles are computed to be quite close to those in the isolated hydronium ion. Consistent with the three-fold distribution of hydrogen bonding, the O–H stretch is again less red-shifted than this vibration for the $n = 1$ and 2 complexes. The position of this vibration in the $H_3O^+(N_2)_3$ complex is still about 110 cm^{-1} to the red from the corresponding frequency (3220 cm^{-1}) in the $H_3O^+Ar_3$ complex [40,48] and about 400 cm^{-1} to the red from this vibration in isolated hydronium. Although the solvation environment is symmetric in all cases, the nitrogen proton affinity (493.8 kJ/mol) is significantly higher than the value for argon (computed to be 380 kJ/mol [50]) and thus there is still partial proton sharing sufficient to induce a considerable shift on the O–H stretches.

The infrared spectroscopy of these hydronium–nitrogen complexes therefore provides a consistent picture of proton sharing interactions not unlike those seen previously in other systems. The 1:1 complex has a proton stretching mode whose frequency can be predicted based on the relative proton affinity values of water and nitrogen. Consistent with other hydrogen bonding interactions, this O–H stretch is significantly red-shifted with respect to the vibrations in the isolated hydronium ion. As additional nitrogens are added, the charge delocalization dilutes the strength of this interaction, and the OH stretches are progressively less red-shifted. However, even in the symmetric system, the shift is greater than the comparable value for argon solvation, consistent with the greater proton affinity of nitrogen. The vibration of nitrogen is remarkably unaffected by this proton sharing interaction, falling at virtually the same value as for gas phase N_2. The hydrogen bonding bands in these systems are broadened, as seen for other hydrogen-bonded systems, and combination bands coupling the shared-proton stretch with low-frequency intermolecular stretches are also found. This system is small enough for full-dimensional anharmonic theoretical treatments, and it may therefore provide a relatively simple model system with which to investigate the subtle details of proton-shared potentials.

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