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Infrared Spectroscopy of Large-Sized Neutral and Protonated Ammonia Clusters[†]

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†Electronic supplementary information (ESI) available: Evaluation of the maximum number of evaporated ammonia molecules upon the ionization of large-sized $(NH_3)_n$

Abstract

Size-selective infrared spectroscopy was applied to neutral and protonated ammonia clusters, $(NH_3)_n$ (n = ~5 – ~80) and $H^+(NH_3)_n$ (n = 8 – 100), to observe their NH stretching vibrations. The moderate size selection was achieved for the neutral clusters by the infrared – ultraviolet double resonance scheme combined with mass spectrometry. The size dependence of the observed spectra of $(NH_3)_n$ is similar to that of the average size-controlled clusters doped in He droplets. The ν_1 (NH sym stretch)/ν_3 (NH asym stretch) band intensity ratio shows rapid decrease in the size range $n \leq$ ~20. This demonstrates that ammonia begins to form crystalline like hydrogen bond networks at the much smaller size region than water. The precise size selection was achieved for $H^+(NH_3)_n$ by infrared photodissociation spectroscopy combined with a tandem type quadrupole mass spectrometer. The spectra of the protonated clusters become almost identical with those of the corresponding neutral clusters at $n \geq \sim 40$, demonstrating that the radial chain structures, which are characteristic in the small-sized protonated clusters, develop into the crystalline like structures seen in the neutral clusters up to $n = \sim 40$.

I. Introduction

One of the important factors which determine hydrogen bond (H-bond) network structures in pure substances is the ratio of the numbers of proton donating and accepting sites in the molecule. [1] In the case of water, for example, a molecule has two donating protons and two accepting sites (non-bonding orbitals), and the numbers of the donating and accepting sites are balanced. As a result, a water molecule can be tetrahedrally coordinated by four H-bonds and water prefers forming three-dimensional cage-like networks, as seen in ice. [2] On the other hand, methanol has only one donating proton but has two accepting sites. Though the maximum H-bond coordination number of a methanol molecule is three, methanol prefers being two-coordinated and forming one-dimensional (chain-like) networks. [3]

From such a view point of H-bond networks, ammonia is an interesting system. Ammonia has three donating protons but has only one accepting site. Because of this significant unbalance, the one-to-one relation between a donor and an acceptor is not necessarily kept in H-bond networks of ammonia. In crystalline ammonia, a molecule is six-coordinated as schematically seen in Figure 1a; all the three protons are donated and the single non-bonding orbital accepts three other protons from surrounding molecules.[4] The spectral signature of this compact multi-ring H-bond network structure in crystalline ammonia is seen in its NH stretching vibration bands.[5-9] An ammonia monomer has two normal modes of NH stretching vibrations; symmetric stretch (ν_1) and doubly degenerated asymmetric stretch (ν_3). The ν_1 fundamental is strongly coupled with the overtone of the NH bending mode ($2\nu_4$). The infrared (IR) transition intensity ratio between the ν_1 (with coupled $2\nu_4$) and ν_3 bands is ~2.5 : 1 in the monomer.[10] In the crystalline structure, however, the IR intensity of the ν_1 band is almost cancelled among molecules while the ν_3 band intensity is enhanced by H-bond formation. Therefore, the ν_3 band is dominant over the ν_1 (+ $2\nu_4$) band in crystalline ammonia. In other words, the decrease of the ν_1 band intensity relative to the ν_3 band indicates the progress of the crystallization process of ammonia. A variety of spectroscopic and theoretical studies have been performed for ammonia clusters in the gas phase to elucidate H-bond structures of ammonia and their development process with increasing cluster size.[11-26] The minimum energy structures of the clusters have been determined in the small size region of $n = 2 – 4$.[17] The cluster size dependence of the NH stretch bands has been studied in the very wide range, $<n> = 2 - 10^5$ (here, $<n>$ is the average size of the cluster), under the various conditions such as cold gas condensation,[18] molecular beam,[19] He droplet,[20] and supersonic free jet expansion.[21] The rapid decrease of the ν_1 band intensity has been reported in the size range of $<n> \leq$

40 and this suggests that (at least partially) crystalline-like compact structures can be formed in this size range.[19, 20] This size range is much smaller than the case of water, which requests at least ~100 molecules to show the sign of the partially crystalline structure formation.[27, 28] However, there has been no method to achieve definitely size-selective IR spectroscopy of large-sized neutral clusters (n > ~10). All the previous reports on IR spectroscopy of large $(NH_3)_n$ clusters ($n > 5$) employed the average size control by the conditions of the cluster sources.[18-21] Therefore, the size-dependence of the previously reported IR spectra has the uncertainty due to the size distributions.

Another interesting system of ammonia is protonated ammonia clusters, $H^+(NH_3)_n$.[29-37] Addition of an excess proton to neutral clusters largely changes their H-bond network structures. The protonated site becomes ammonium ion, NH_4^+, and strongly prefers being four-coordinated. Because of the excess charge, IR dissociation spectroscopy combined with a tandem type mass spectrometer enables definitely size-selective IR spectroscopy of protonated clusters. Lee and coworkers have pioneered this type of IR spectroscopy and they have reported the IR spectra of $H^+(NH_3)_n$ ($n = 2 - 11$) in the NH stretch region.[29, 30] They have demonstrated that the solvation of the ammonium ion core is completed at $n = 5$ to form the first shell (i.e.,

$NH_4^+(NH_3)_4$) and extension of the four H-bonded chains form the first shell occurs to form the second shell in the size region of $n = 6 – 9$. A schematic representation of such a radial chain structure is shown in Figure 1b. The mid IR spectra (the NH bending vibrations and the excess proton vibration) of $n = 2 - 8$ and the theoretical studies have also supported this picture of the H-bond network development. [31-37] No ring motifs are included in these radial chain type H-bond networks of the protonated clusters, and this contrasts with the networks of the neutral ammonia clusters, which prefer having ring motifs even in the small sizes. It is reasonably expected that structures of protonated clusters finally converge to those of neutral clusters with increasing cluster size since the influence of the excess proton is enough diluted in large clusters. However, no IR spectra of $H^+(NH_3)_n$ larger than $n = 11$ have been reported, and the size of the practical convergence to neutral structures has not yet been known.

In this paper, we report size-selective IR spectra of $(NH_3)_n$ ($n = \sim5 – \sim80$) and $H^+(NH_3)_n$ ($n = 8 – 100$) in the NH stretch region. For the neutral clusters, we applied the infrared – ultraviolet double resonance scheme combined with mass spectrometry, and achieved the moderate size-selectivity. [3, 38, 39] In comparison with the previously reported IR spectra of the clusters in He droplets, [20] we discuss the size dependence of the crystalline-like structure formation. For the protonated clusters, we employed IR dissociation spectroscopy by using a tandem quadrupole mass spectrometer. [3, 27] The convergence of the spectra of the protonated clusters to those of the neutrals is demonstrated.

II. Experimental

Two different size-selective IR spectroscopic techniques were applied to $(NH_3)_n$ and $H^+(NH_3)_n$, respectively. Moderately size-selective IR spectra of neutral $(NH_3)_n$ in the NH stretch region were measured by the infrared-ultraviolet (IR-UV) double resonance technique combined with time-of-flight mass spectrometry. [3, 38, 39] An UV light pulse, of which frequency was tuned to the broadened $S_1(\tilde{A})$ - $S_0(X)$ origin band of the clusters (46070 cm^{-1}), ionized all the sizes of the produced clusters simultaneously. All the cluster ions produced by one-color resonance enhanced two-photon ionization (RE2PI) with the UV pulse were mass analyzed by a Wiley-McLaren type time-of-flight mass spectrometer. Because of the intracluster proton transfer and following fragmentation upon the ionization, [40, 41] $H^+(NH_3)_n$ (or $H^+(NH_3)_{n-1}\cdot NH_2$; we did not distinguish these two species in mass spectrometry) can be produced from $(NH_3)_{n+\Delta n}$. Here, Δn is the number of evaporated ammonia molecules upon the ionization process. This means that the intensity of $H^+(NH_3)_n$ can be a measure of the population of neutral $(NH_3)_n$ with the size uncertainty of less than Δn_{max} (here, Δn_{max} is the maximum Δn). By monitoring the $H^+(NH_3)_n$ intensity, a tunable IR pulse was introduced prior to the UV pulse and its frequency was scanned. When an IR transition occurs in $(NH_3)_{n+\Delta n}$, the monitored $H^+(NH_3)_n$ signal intensity decreases because of vibrational predissociation of the neutral clusters. An IR spectrum of $(NH_3)_{n+\Delta n}$ was measured as an ion-dip spectrum with the size uncertainty of less than Δn_{max} (there is certainly no contribution of smaller clusters than $(NH_3)_n$). The Δn_{max} value upon one-color RE2PI is roughly estimated to be 20 (on the evaluation of Δn_{max}, see electronic supplementary information). However, we should note that this is the maximum value based on the simple energetics and the actual uncertainty is expected to be much less (in addition, the monitoring cluster ion was every time adjusted to be almost the largest size produced by adjusting the jet expansion condition). Because the difference of the monitoring size of 10 (e.g., $n = 10$ and 20) is enough to observe clearly different spectra as shown later, we estimate that Δn_{max} is effectively less than 10.

The $(NH_3)_n$ clusters were formed by a pulsed supersonic jet expansion of a gaseous mixture of ammonia/helium. The total stagnation pressure of the mixture gas was 0.3 MPa. A pulsed valve (*General Valve* series #9) was used for the jet expansion. Coherent IR light was generated by difference frequency mixing between the second harmonic of a YAG laser (*Continuum* PL-8000) and the fundamental output of a dye laser (*Continuum* ND-6000, DCM dye). A $LiNbO_3$ crystal was used for the frequency mixing. All the IR spectra were normalized with the intensity of the IR light.

On the other hand, IR spectra of precisely size-selected $H^+(NH_3)_n$ were measured by IR predissociation spectroscopy using a mass spectrometer equipped with linearly aligned tandem quadrupole mass filters connected by an octopole ion guide.[3, 27, 42] The $H^+(NH_3)_n$ clusters were produced by a pulsed supersonic jet expansion and electro ionization at the collisional region. Ammonia vapor seeded in helium (total pressure 7 MPa) was expanded into an ion source chamber through a high pressure pulsed valve (*Even-Lavie* valve).[43] The gas pulse was crossed by an electron beam of 200 eV generated by an electron gun (*Omegatron Co.*) in the collisional region of the jet. Protonated clusters grew with collision and were also cooled. They were introduced into the first quadrupole mass filter through a skimmer by ion lenses and were size-selected. Only the clusters of the size of interest were introduced into an octopole ion guide and were irradiated by an IR pulse (*Laser Vision* OPO/OPA). When the IR pulse is resonant with a vibrational transition of $H^+(NH_3)_n$, vibrational predissociation occurs. The second quadrupole mass filter was tuned to pass only the parent cluster ion or (n-1) fragment ion. An IR spectrum of the size-selected $H^+(NH_3)_n$ was recorded by measuring the depletion of the parent cluster ion intensity or enhancement of the fragment ion intensity while scanning the IR laser frequency (2600-3800 cm^{-1}). The IR absorption intensities of the NH stretch bands in $H^+(NH_3)_n{}^+$ are much weaker than those of the OH stretch band in large-sized $H^+(H_2O)_n$ and $H^+(CH_3OH)_n$, in which depletion of the parent ion should be employed in the measurement of their IR spectra to avoid the interference by the secondary IR dissociation of fragment ions.[3, 27] In the case of $H^+(NH_3)_n$, the depletion of the parent ion could not be detected in $n \leq 40$, and the (n-1) fragment detection was employed in this size region. In the size rage of $n \geq 50$, the depletion of the parent ion was monitored.

III. Results and discussion

1. IR spectra of neutral $(NH_3)_n$ clusters

Figure 2 shows moderately size-selected IR spectra of $(NH_3)_{n+\Delta n}$ (n = ~5 − ~80) in the NH stretch region. Each spectrum of $(NH_3)_n$ was measured by monitoring the $H^+(NH_3)_n$ ion signal intensity and the magnitude of the signal depletion was plotted as a function of the IR frequency. As seen in Figure 2, difference of monitoring size of 10 (e.g., n = 10 and 20) is enough to observe different spectra. Therefore, we estimate that the effective size uncertainty of the observed spectra is $0 \leq \Delta n \leq$ ~10. In the observed NH stretch region, the $2\nu_4$ ($\ell = 0$ and 2), ν_1, and ν_3 bands are seen. The assignments of the spectra follow those given by Slipchenko *et al*. for $(NH_3)_{<n>}$ in He droplets. [16, 17, 20]

For the size range of a few tens to hundred, there have been two reports on IR spectra of average size-controlled $(NH_3)_{<n>}$ in molecular beams and He droplets. [19, 20] The present size-selective spectra well reproduce the features of these previous spectra, especially those in He droplets. [20] Comparison between the present spectra and the spectra of the clusters in He droplets is shown in Figure 3. The present spectrum of $n = 5$ shows non-negligible broadening, which should be due to the contribution of larger-sized clusters. There might be also the small contribution of somewhat higher temperature of the clusters. We expect the vibrational temperature of the neutral clusters is close to that of typical jet-cooled molecules ($\leq \sim 100$ K) though the evaluation of the temperature is difficult in the present experiment. On the other hand, the spectra of $n \geq 10$ well agree with those in He droplets. We should note that the effective size uncertainty ($0 \leq \Delta n \leq \sim 10$) in the present measurement is almost constant independently of cluster size and therefore the relative size-selectivity ($n/\Delta n$) becomes better with increase of the size. Though the details on the Poisson distribution of the cluster size in He droplets were not given in the paper by Slipchenko *et al.*,[20] the present size-uncertainty ($0 \leq \Delta n \leq \sim 10$) would be narrower than the Poisson distribution under the condition of $<n> \geq \sim 10$. In addition, clusters of $\Delta n < 0$ never contribute to the present spectra while both of smaller and larger clusters should contribute to the spectra under the average size-controlled condition. The good agreement confirms the size dependence of the spectra obtained by the average size-control in He droplets. This also means that the size-averaged spectrum of $<n>$ successfully represents the features of the cluster at n.

The size dependence of the observed band frequencies are summarized in Figure 4. The ratio of the ν_3 band intensity to the total NH band intensity ($\frac{I_{\nu 3}}{I_{\nu 1} + I_{2\nu 4} + I_{\nu 3}}$) is shown in Figure 5. These data of $n \geq 10$ are essentially same as those reported by Slipchenko *et al*. for $(NH_3)_{<n>}$ in He droplets.[20] In the size rage of $n < 100$, the magnitude of the band shifts of ν_1, ν_3, and $2\nu_4$ are small (less than ~20 cm^{-1}). It has been known that the frequency order of the $2\nu_4$ and ν_1 bands is reversed in solid ammonia. [5-9] Steinbach *et al*. have suggested the crossing of the $2\nu_4$ and ν_1 bands in the size range of $n = 10 – 100$ on the basis of the molecular dynamics sampling of stable cluster structures and anharmonic vibrational calculations.[19] Though the ν_1 band shows the low-frequency shift trend with increase of cluster size, the band is still well separated from $2\nu_4$ up to $n = 80$, demonstrating that the crossing would occur in a much larger size.

The suppression of the intensities of the ν_1 and coupling $2\nu_4$ bands (i.e., the rise of the relative intensity of the ν_3 band) is a spectral sign of the multiple-ring motif formation leading to the crystalline structure. The present measurements indicate that the multiple-ring motif is rapidly formed up to n = ~20, and the progress (slop of the ν_3 band intensity increase) is rather moderate in the larger region. This result agrees with that in the average size-controlled clusters in He droplets. [20] In the IR spectroscopic study of average size-controlled clusters in a molecular beam by Steinbach *et al.*, the prominent suppression of the ν_1 and $2\nu_4$ band seems to occur in $\langle n \rangle > 29$. [19] However, this might be due to the broad size distribution (larger contribution of smaller sized clusters) in their beam study. Their IR spectrum of $\langle n \rangle = 80$ in a molecular beam well agrees with the present spectrum of $n = 80$. This agreement would be attributed to the weak size dependence in this size region.

2. IR spectra of protonated $H^+(NH_3)_n$ clusters

Figure 6 shows IR spectra of $H^+(NH_3)_n$ ($n = 8 - 100$) in the NH stretch region. In the case of these spectra of the protonated clusters, the size selection is rigorous ($\Delta n = 0$). The most significant feature in the spectra is the intense band of the NH stretching vibrations of the NH_4^+ ion core moiety, which appears at ~2800 cm^{-1}. [30] The ν_1, ν_3, and $2\nu_4$ bands are also seen in the 3200 – 3400 cm^{-1} region, being similar to those of the neutral clusters. The spectra of n = 8 and 10 are essentially same as those observed by Lee and coworkers.[30] The spectra of $n \geq 12$ are reported for the first time.

The NH frequencies and the intensity of the ν_3 band relative to $\nu_1 + 2\nu_4$ ($\frac{I_{\nu 3}}{I_{\nu 1} + I_{2\nu 4} + I_{\nu 3}}$) are also summarized in Figures 4 and 5, respectively, with those in the spectra of the neutral clusters. In the small size region, n = 8 – 10, the $\nu_1 + 2\nu_4$ band intensity (in the 3200 – 3375 cm^{-1} region) is much stronger than the ν_3 intensity. Lee and coworker has showed that the H-bond networks of $H^+(NH_3)_n$ in this small sized region have the radial chain structures (Figure 1b), in which four H-bonded chains extend from the central NH_4^+ ion core.[30] The low ν_3 intensity relative to $\nu_1 + 2\nu_4$ is the spectral signature of such radial chain structures, in which no ring motif is involved and the intensity cancellation does not occur in the ν_1 (and $2\nu_4$) mode. In this size region, the ν_3 frequency also shows prominent low-frequency shift in comparison with the neutral clusters. The excess charge at the ion core, which slightly attracts the electron density from the surrounding molecules, should account for this frequency shift. In the size region of n = 12 – 15, the $\nu_1 + 2\nu_4$ intensity rapidly decreases and the peak height of the ν_3 band is rather higher in $n \geq 18$. As was discussed on the neutral clusters, this is an indication of the ring motif formation, which finally leads into the crystallization. In other words, additional NH_3 molecules begin to connect the radial chains in the H-bond network development at this size region. The ν_3 frequency also shows the high frequency shift trend, demonstrating the dilution of the influence of the excess charge at the ion core. In $n \geq 30$, as seen in the Figures 4 and 5, the $\nu_1 \sim \nu_3$ region of the spectra is quite similar to that of the neutral clusters at the corresponding sizes. The NH stretch band of the NH_4^+ ion core moiety also becomes weaker with increasing n, and it almost disappears at $n = 40$. The spectra are almost identical to those of the neutral clusters in $n \geq 40$, and this means that the influence of the excess proton is diluted enough and the H-bond networks are essentially same as those of neutral clusters.

The dilution process of the influence of the excess proton on the H-bond network has been studied in the large-sized protonated clusters of water and methanol.[3, 44] We have performed comparison between the IR spectra of the large-sized neutral and protonated clusters of these molecules in the OH stretch region, which is also sensitive to H-bond network structures. The IR spectra of $H^+(H_2O)_n$ become almost identical to those of $(H_2O)_n$ in $n \geq \sim 50$ and $H^+(CH_3OH)_n$ also shows such spectral convergence to the corresponding neutral at $n = \sim 30$. The presently observed critical size of $H^+(NH_3)_n$ is $n = \sim 40$ and this value is just in between the critical sizes of methanol and water. Since the spectral convergence of the protonated cluster to the neutral occurs at the similar size regions in these typical protic molecules, it would be a general trend that the influence of an excess proton to H-bond network structures is effectively limited to surrounding 30 ~ 50 molecules.

Here we briefly comment on the implication of the NH stretching band of the NH_4^+ ion core at ~2800 cm^{-1}. Because of the excess charge in the ion core, the NH stretch band of the ion core has a great intensity. After the completion of the second shell at $n = 9$, no prominent frequency shift occurs in the larger sizes (considering the four-coordinated nature of the NH_4^+ ion core, the excess proton is expected to be located at the center of the cluster). Its band intensity relative to the “neutral“ NH bands (at 3200 – 3400 cm^{-1}) decreases with increasing n. If the relative intensity of the ion core band at $n = 10$ is simply extrapolated to $n = 40$ on the assumption that the intensity of the neutral moiety is simply proportional to the cluster size, the effective disappearance of the ion core band at $n = 40$ seems to be reasonable. This means that no special reason is needed to interpret the disappearance of the ion core band in large $H^+(NH_3)_n$. In the case of $H^+(H_2O)_n$, the OH stretching band of the H_3O^+ ion core has never been observed in the size range of $n > 11$.[45, 46] Especially for $n = 21$, the famous magic number cluster, the ion core band is missing in spite of the extensive searches.

[45-48] The extremely large shift and dynamical broadening of the band have been proposed for the origin of the missing but the origin is still controversial.[49, 50] The present observation of the ion core vibration in large $H^+(NH_3)_n$ is the first one of the excess proton vibration in large protonated clusters of $n >> 10$ and its “normal” behavior is quite contrastive to the proton vibration in large $H^+(H_2O)_n$.

Figure 7 shows the comparison between the IR spectra of $H^+(NH_3)_n$ and neutral $(NH_3)_{<n>}$ in He droplets. It is seen that the spectra are almost identical in $n \geq 40$. In addition to the spectral convergence of the protonated clusters to those of neutrals, this conformity suggests an interesting property of the spectra of $H^+(NH_3)_n$. Because of the large excess energy in the ionization and protonation, protonated clusters are vibrationally warm (typically ~200 K) even if they are produced in a supersonic jet. [51, 52] However, the present spectra of $H^+(NH_3)_n$ ($n \geq 40$) are essentially identical to the spectra of the He droplets at the ultracold temperature of 0.38 K. [20] There are two possible interpretations for this conformity. One is that the temperature dependence of $H^+(NH_3)_n$ is weak and this implies the H-bond network structure distribution does not largely change in the wide vibrational temperature range. An alternative interpretation is that the large clusters are efficiently cooled down by evaporation cooling because of weak H-bond strength among ammonia. At the present stage, we cannot measure temperature of the produced cluster and both the interpretations are plausible.

IV. Summary

In the present work, we measured size-selective IR spectra of neutral and protonated ammonia clusters, $(NH_3)_n$ and $H^+(NH_3)_n$, in the size range of n = ~5 to 100. The spectra of the neutral clusters in the NH stretching vibrational region well agree with the previously reported spectra of the average size-controlled clusters in He droplets and molecular beams. From the intensity suppression of the symmetric NH stretch band (and coupling overtone band of the bending mode), it is confirmed that the multiple-ring motif, which finally leads to the crystalline structure, is rapidly formed up to n = ~20. The protonated clusters have the radial chain structures in the small sized region of $n \leq$ ~10. In the size range of n = 10 – 20, however, the multiple-ring motif formation rapidly occurs in their H-bond networks. In $n \geq$ ~40, the spectra are essentially identical to those of the neutral clusters at the corresponding size. This critical size of the spectral convergence is similar to those in the protonated water and methanol clusters, suggesting a general trend that the influence of an excess proton to H-bond network structures is effectively limited to surrounding 30 ~ 50 molecules.

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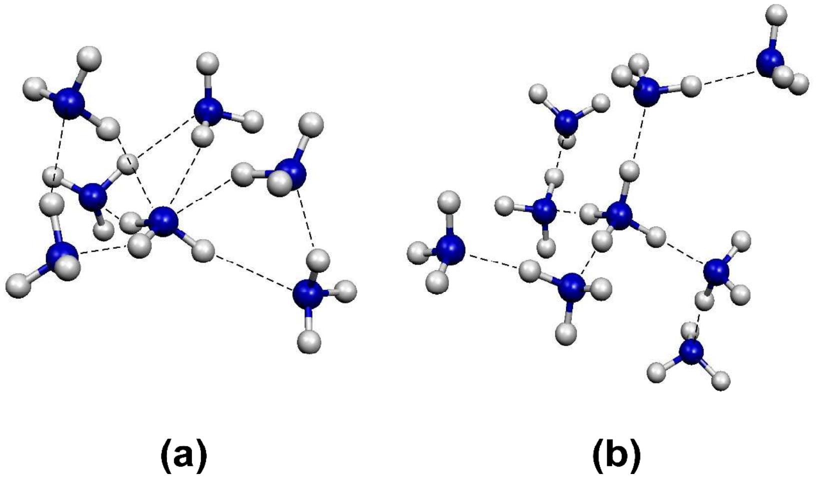

Figure 1 (a) Multiple-ring motif with a six-coordinated ammonia molecule. (b) Radial chain motif seen in small-sized protonated ammonia clusters.

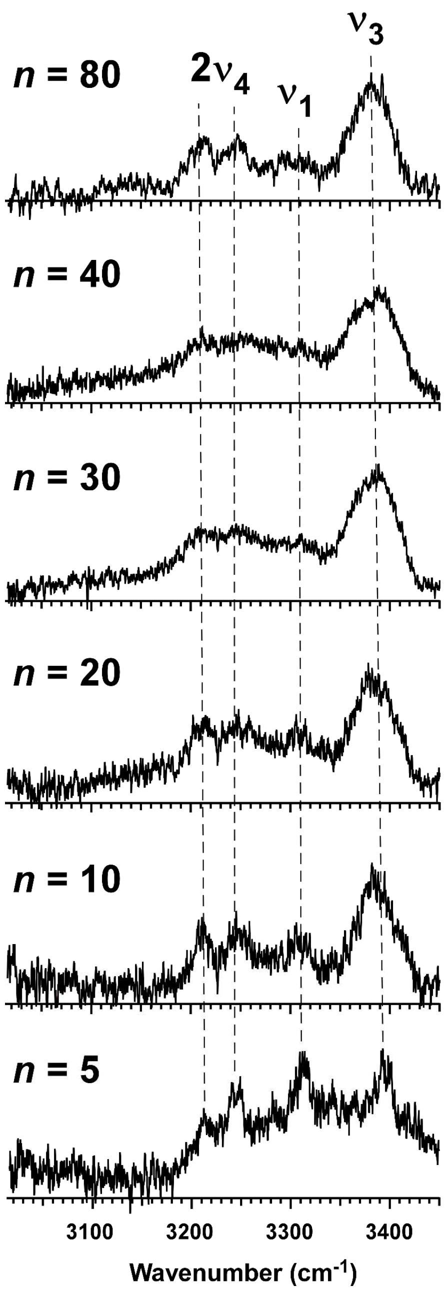

Figure 2 Moderately size-selected IR spectra of $(NH_3)_{n+\Delta n}$ in the NH stretch region. The effective size uncertainty is estimated to be $0 \leq \Delta n \leq {\sim}10$ (see text).

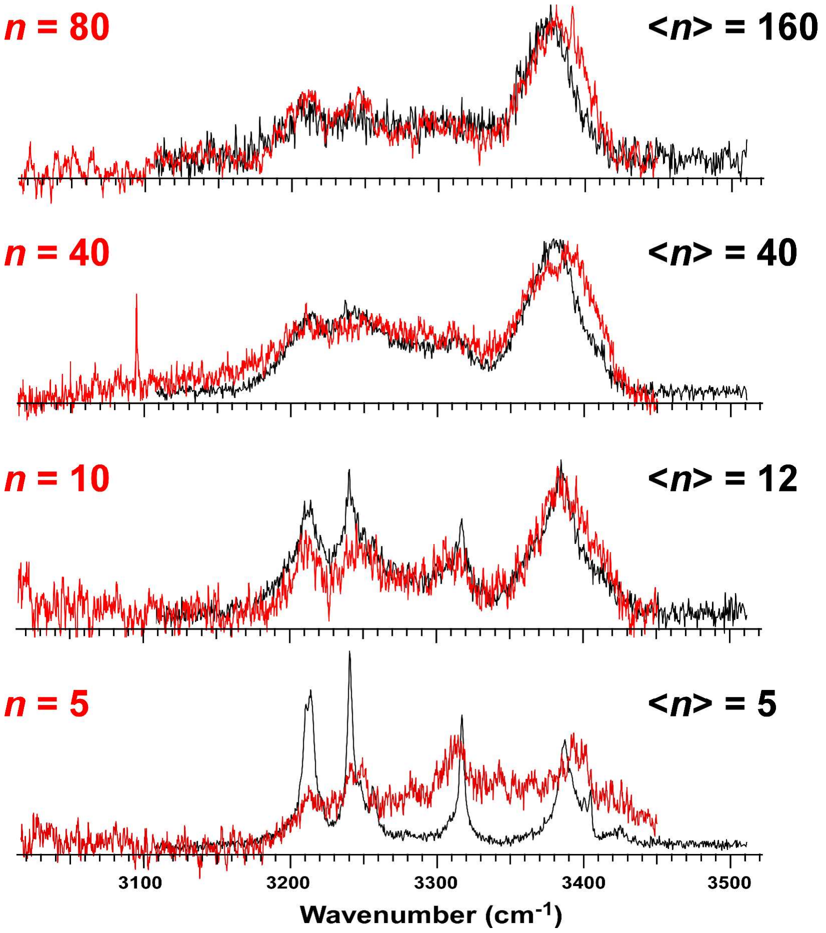

Figure 3 Comparison between the IR spectra of moderately size-selected $(NH_3)_{n+\Delta n}$ (red traces) and average size-controlled $(NH_3)_{<n>}$ in He droplets (black traces). The spectra of $(NH_3)_{<n>}$ in He droplets were taken from the paper by Slipchenko *et al.* (Ref. 20).

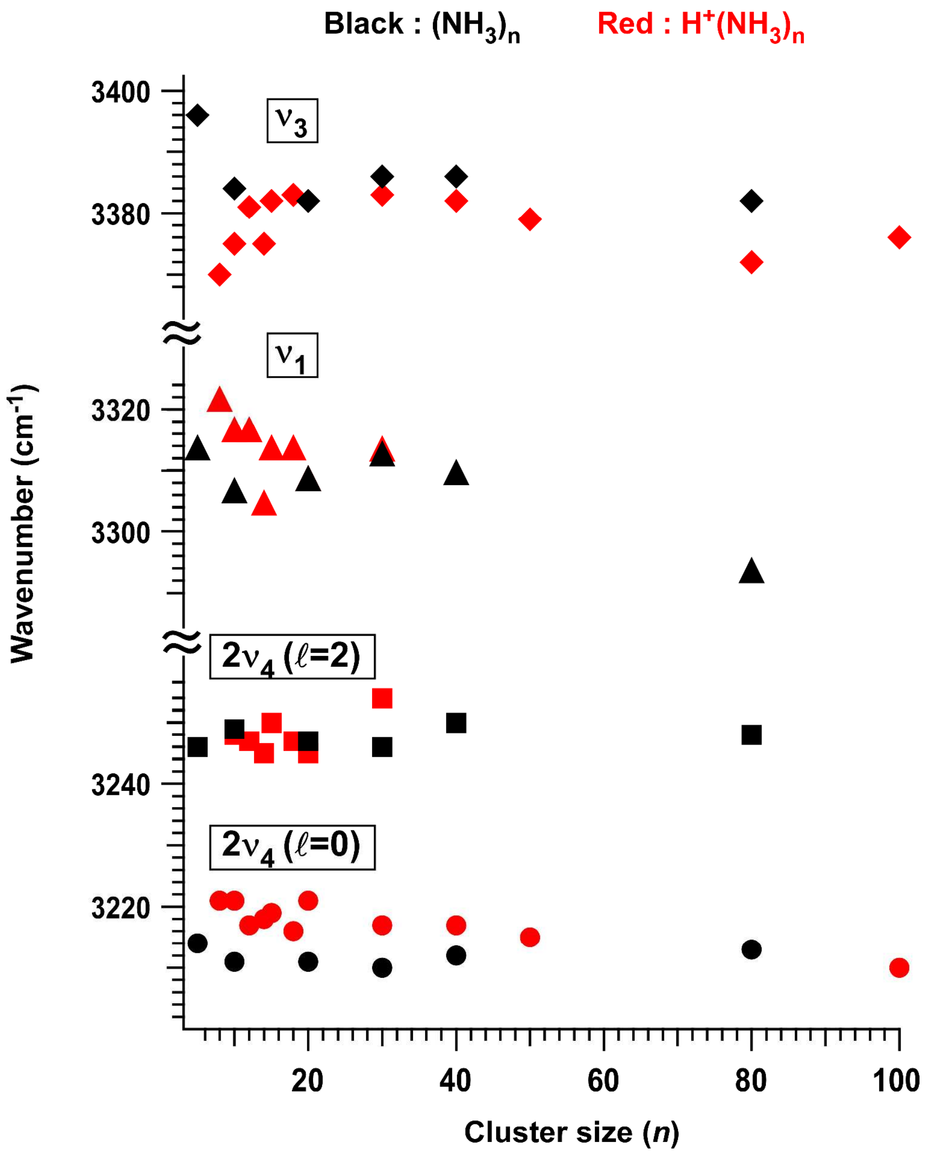

Figure 4 Size dependence of the $2\nu_4$, ν_1, and ν_3 frequencies of $(NH_3)_n$ (black symbols) and $H^+(NH_3)_n$ (red symbols) observed in this work.

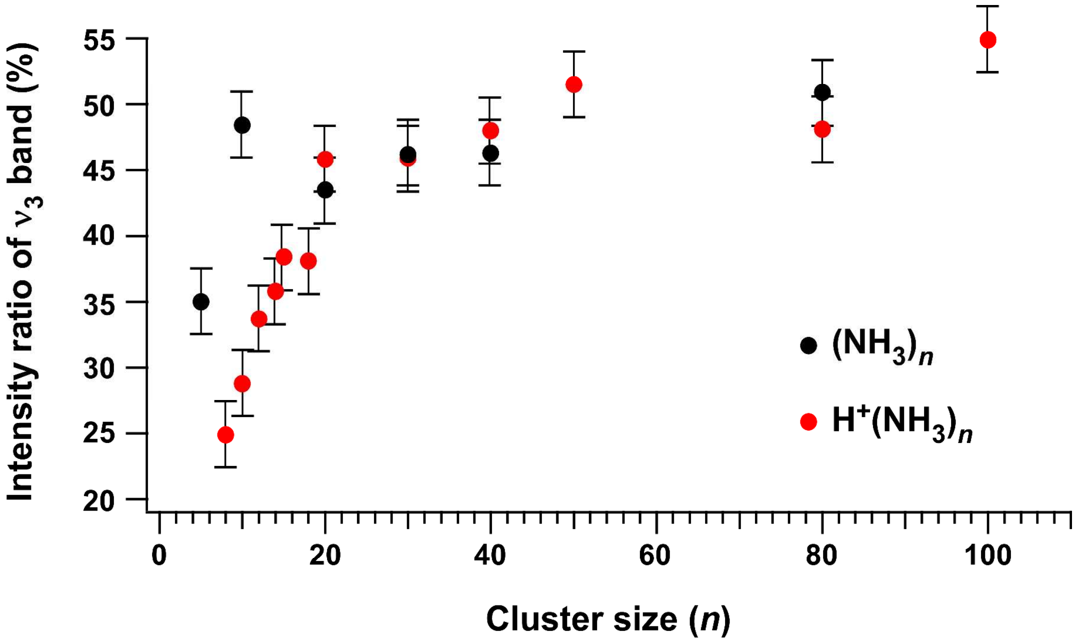

Figure 5 Size dependence of the ratio of the ν$_3$ band intensity to the total NH band intensity ($\frac{I_{\nu 3}}{I_{\nu 1}+I_{2\nu 4}+I_{\nu 3}}$) of $(NH_3)_n$ (black symbols) and $H^+(NH_3)_n$ (red symbols).

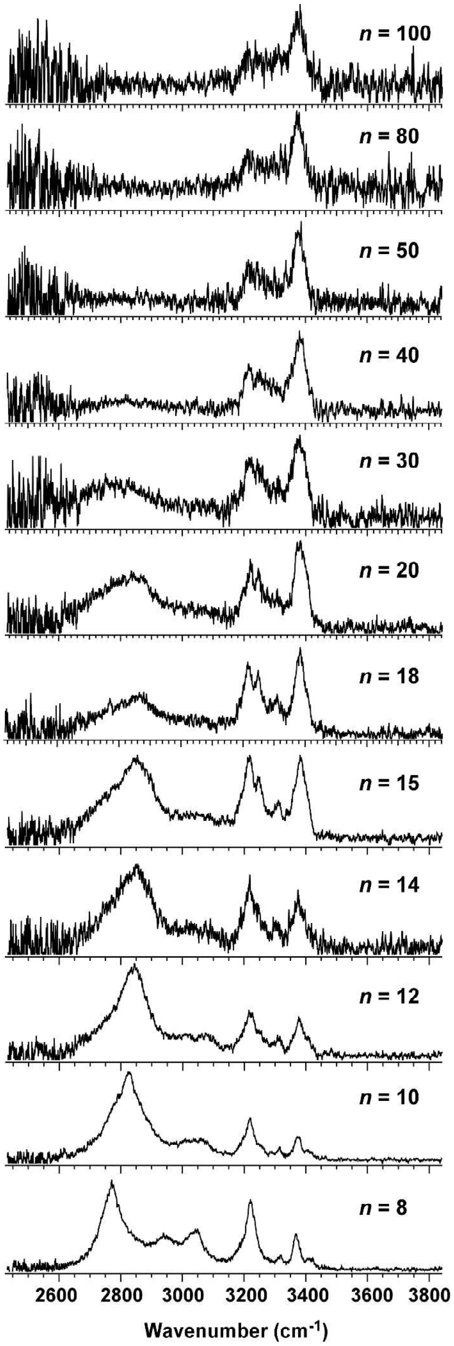

Figure 6 Size-selected IR spectra of $H^+(NH_3)_n$ in the NH stretch region. The enhancement of the (*n*-1) fragment intensity was monitored in the spectra of $n \leq 40$ while the depletion of the parent ion intensity was monitored in $n \geq 50$.

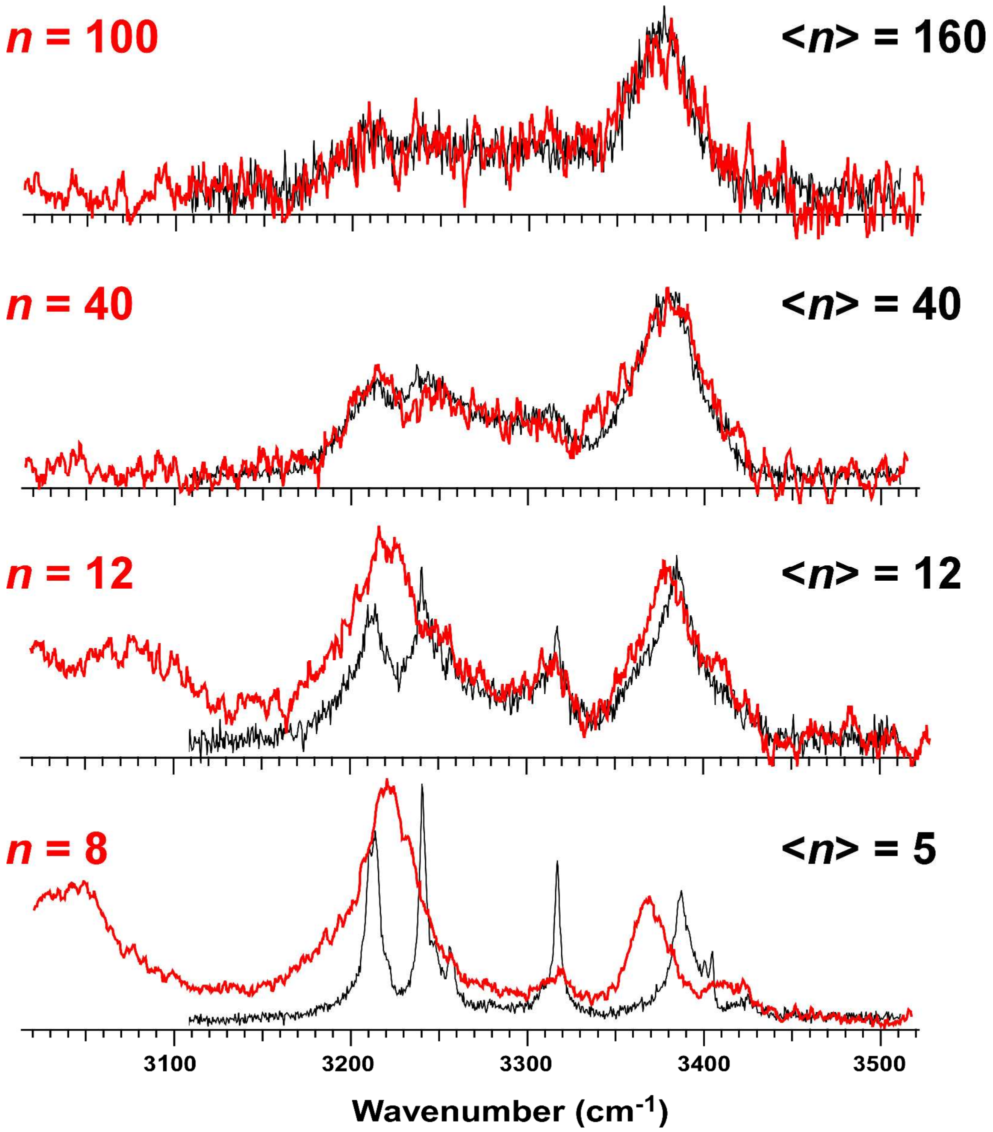

Figure 7 Comparison between the IR spectra of size-selected $H^+(NH_3)_n$ (red traces) and average size-controlled $(NH_3)_{<n>}$ in He droplets (black traces). The spectra of $(NH_3)_{<n>}$ in He droplets were taken from the paper by Slipchenko *et al*. (Ref. 20).

TOC entry

Size selective IR spectroscopy shows the nature of hydrogen bond networks in neutral and protonated ammonia clusters.