

Electronic Supplementary Information

Infrared Spectroscopy of Large-Sized Neutral and Protonated Ammonia Clusters

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1. Evaluation of the maximum number of evaporated ammonia molecules upon the ionization of large-sized $(\text{NH}_3)_n$

Ionization of a $(\text{NH}_3)_n$ cluster causes intracluster proton transfer and the cluster becomes $\text{H}^+(\text{NH}_3)_{n-1}\cdot\text{NH}_2$.¹ Figure S1 shows the schematic energy diagram on the photoionization and dissociation. When we assume sequential evaporation of single ammonia (or NH_2) molecules following the resonant two-photon ionization, the maximum number of evaporated molecules upon the ionization (Δn_{max}) is given by

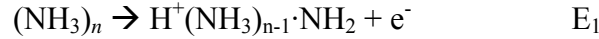
$$\Delta n_{\text{max}} = E_{\text{excess}}/D(\text{D}_0),$$

where E_{excess} is the maximum excess energy upon the ionization and $D(\text{D}_0)$ is the dissociation energy of the one ammonia loss channel in $\text{H}^+(\text{NH}_3)_{n-1}\cdot\text{NH}_2$.

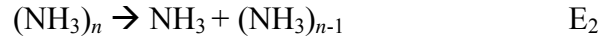
The energy scheme in Figure S1 shows

$$E_{\text{excess}} = 2E_{\text{UV}} - [E(\text{D}_0) - E(\text{S}_0)],$$

where E_{UV} is the energy of the UV photon used to ionize the cluster, $E(\text{D}_0)$ and $E(\text{S}_0)$ are the electronic potential energies of the cationic and neutral ground states, respectively. $[E(\text{D}_0) - E(\text{S}_0)]$ is equivalent to the enthalpy change of the reaction



This reaction can be decomposed to the following steps



From the thermodynamical cycle,

$$[E(\text{D}_0) - E(\text{S}_0)] = E_1 = E_2 + E_3 + E_4 + E_5$$

E_2 and E_5 are dissociation and association energies of one molecule and a cluster, respectively. In the association of $\text{H}^+(\text{NH}_3)_n$,



the association energy becomes a constant, $E_6 = -20$ kJ/mol, in large clusters of $n \geq 8$.² This value would be a good approximation to neutral clusters and association with NH_2 . Thus we evaluate E_2 and E_5 to be +20 and -20 kJ/mol, respectively. E_3 is the appearance energy of H^+ from NH_3 and has been reported to be +1792 kJ/mol.³ E_4 is the proton affinity of $(\text{NH}_3)_n$, and it has been determined for $n = 1$ (-857 kJ/mol) to $n = 5$ (-1054 kJ/mol).⁴ We extrapolate the convergence value and estimate E_4 to be -1079 kJ/mol. From these evaluations, E_1 is finally evaluated to be 712 kJ/mol.

In the present measurement, $E_{\text{UV}} = 46070 \text{ cm}^{-1} = 551$ kJ/mol. Thus, E_{excess} is evaluated to be 390 kJ/mol. From E_6 , the dissociation energy of $\text{H}^+(\text{NH}_3)_n$

($\approx H^+(NH_3)_{n-1} \cdot NH_2$) is 20 kJ/mol. Then, $\Delta n_{\max} = 390/20 = \sim 20$.

As noted in the main text, this is evaluation of 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 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 different spectra, we estimate that Δn_{\max} is actually less than 10.

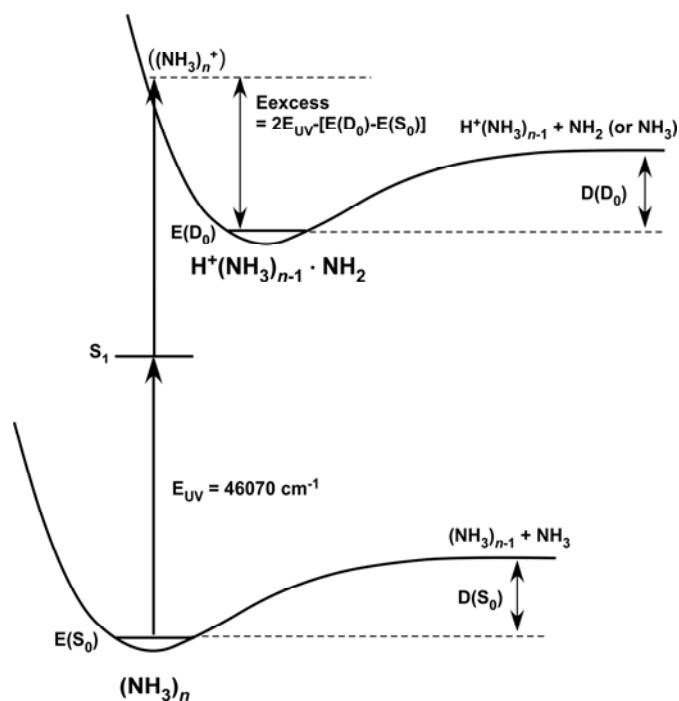


Figure S1

Schematic energy diagram of the resonant two-photon ionization and following dissociation of large-sized $(NH_3)_n$

References

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