

## Notes

### Structure and Stability of Unprotonated Ammonia Cluster Cations $[(\text{NH}_3)_n]^+$ ( $n = 1-6$ )

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Photoionization experiments on ammonia clusters have been widely conducted using various methods combined with molecular beam techniques.<sup>1-11</sup> A diagrammatic representation of the reaction mechanism of ammonia cluster cations was first suggested by Nishi *et al.*<sup>4,7</sup> According to this mechanism, the unprotonated cations  $[(\text{NH}_3)_n]^+$  are very unstable, and these species are quickly transformed into protonated cations  $[\text{NH}_4^+(\text{NH}_3)_{n-2} + \text{NH}_2]$  via intracuster proton-transfer  $[(\text{NH}_3)_{n-2}(\text{H}_3\text{N}^+-\text{HNH}_2)]$ . As a result, the peak intensities of unprotonated cluster cations are very weak. Recently, Fuke and Takasu<sup>8</sup> and Castleman, Jr. *et al.*<sup>9</sup> performed photoionization experiments on unprotonated and protonated ammonia clusters. In their experiments, the peaks of unprotonated cations were observed to be very weak. Although the photoionization processes of ammonia clusters have already been studied, the geometrical structure and stability of unprotonated ammonia cluster cations, except for  $n=2$ , are investigated in this study for the first time.

To analyze the above experimental findings, we carried out systematic calculations both for unprotonated and protonated ammonia cluster cations with the same accuracy. We discuss the stability and binding energy of unprotonated and protonated ammonia cluster cations. The geometrical structures of unprotonated ammonia cations  $[(\text{NH}_3)_n]^+$  ( $n=1-6$ ) as well as protonated ammonia clusters  $[\text{NH}_4^+(\text{NH}_3)_{n-1}]$  ( $n=1-6$ ) are fully optimized using the Hartree-Fock (HF) and second-order Møller Plesset perturbation (MP2) methods with the 6-31+G\*\* basis set. After the optimization, the harmonic vibrational frequencies of those molecules are evaluated at the HF and MP2 levels to confirm the true minimum.

Optimized geometrical structures of unprotonated ammonia cluster cations are shown in Figure 1. In the structures, a planar  $\text{NH}_3^+$  ion is located at a core part in the first ammonia solvation shell and the shell is completed at  $n=6$ . The ammonia cluster cations are the ion-neutral interaction complexes. Therefore, as the cluster size increases, the charge-dipole interaction becomes weaker and the bond length ( $R_{\text{NN}}$ ) between two nitrogen atoms increases regularly.

In unprotonated dimer cations, there are two types of isomers. One is a head-to-head complex. For this structure, two different results are reported in previous experiments.<sup>10-11</sup> Posey *et al.*<sup>10</sup> observed a stable geometry as a nonsymmetric complex ( $C_s$ ), which is separated by the positive charge, *i.e.*, a dipole-charge interaction form. A positively-charged nitro-

gen of  $\text{NH}_3^+$  is directly interacted with a lone pair orbital of  $\text{NH}_3$ . Another experimental result, observed by Ganghi *et al.*,<sup>11</sup> gives a totally symmetric structure with  $D_{3d}$ -symmetry. In the symmetric structure, the respective nitrogens have a half charge,  $[\text{H}_3\text{N}^{(1/2)+} \cdots \text{N}^{(1/2)+}\text{H}_3]$ . On the other hand, according to previous theoretical results,<sup>13-17</sup> the geometrical structure is sensitive to the N-N internuclear distance. At a short distance, a totally symmetric form is more stable, while at a long distance, a nonsymmetric complex is more stable.

The other isomer is a hydrogen-bonded type, which results from two kinds of process mechanisms. In the first mechanism, a lone pair orbital of the nitrogen atom of neutral ammonia is directly interacted with a hydrogen atom of  $\text{NH}_3^+$ , and then the proton-transfer takes place from the  $\text{NH}_3^+$  cation to  $\text{NH}_3$  without an energy barrier, forming a complex such as  $[\text{NH}_4^+ \cdots \text{NH}_2]$ . In the second mechanism, a single occupied *p*-orbital of the charged nitrogen of  $\text{NH}_3^+$  is combined with a hydrogen atom of neutral ammonia. In a complex, the electron- and proton-transfers take place sequentially from  $\text{NH}_3$  to  $\text{NH}_3^+$ , and finally the complex is also optimized as a hydrogen-bonded type. But, in the other unprotonated cluster cations ( $n \geq 3$ ), except for dimer, the proton- and electron-transfer reactions do not take place. Our optimized structures of unprotonated ammonia dimer cation are in good agreement with previous results.<sup>11-15</sup>

In unprotonated trimer cations, two types of isomers exist, as in the dimer (head-to-head and hydrogen-bonded interactions). The head-to-head type is a sandwich complex with  $D_{3h}$ -symmetry. A single occupied *p*-orbital of the  $\text{NH}_3^+$  core is combined with each lone pair orbital of two  $\text{NH}_3$  monomers at both sides. The hydrogen-bonded type demonstrates  $C_{2v}$ -symmetry, and two monomers each pair with a hydrogen of a  $\text{NH}_3^+$  core. In terms of energy, the hydrogen-bonded type is more stable than the head-to-head.

In unprotonated tetramers, the core cation undergoes only the interaction of the hydrogen-bonded type, that is, three hydrogens of  $\text{NH}_3^+$  interact with three ammonia monomers. The geometry of this complex is coplanar with  $C_{3h}$ -symmetry. The head-to-head complex in unprotonated tetramer cations does not exist. On the other hand, in unprotonated pentamer and hexamer, both types of interactions exist in a complex. In the head-to-head type of unprotonated pentamer, the  $\text{NH}_3^+$  core is combined with a monomer at one side, while in hexamer the core is combined with two

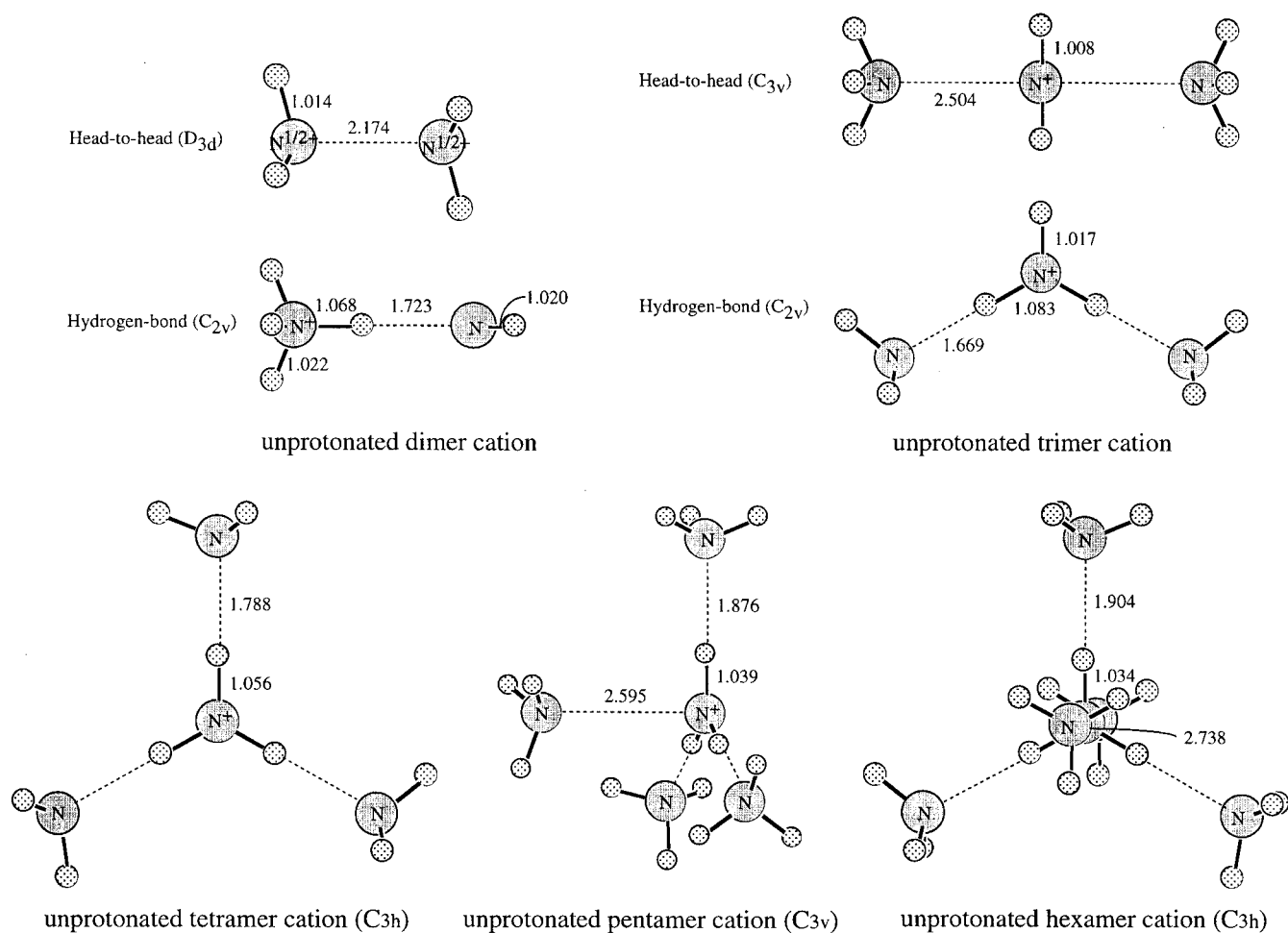
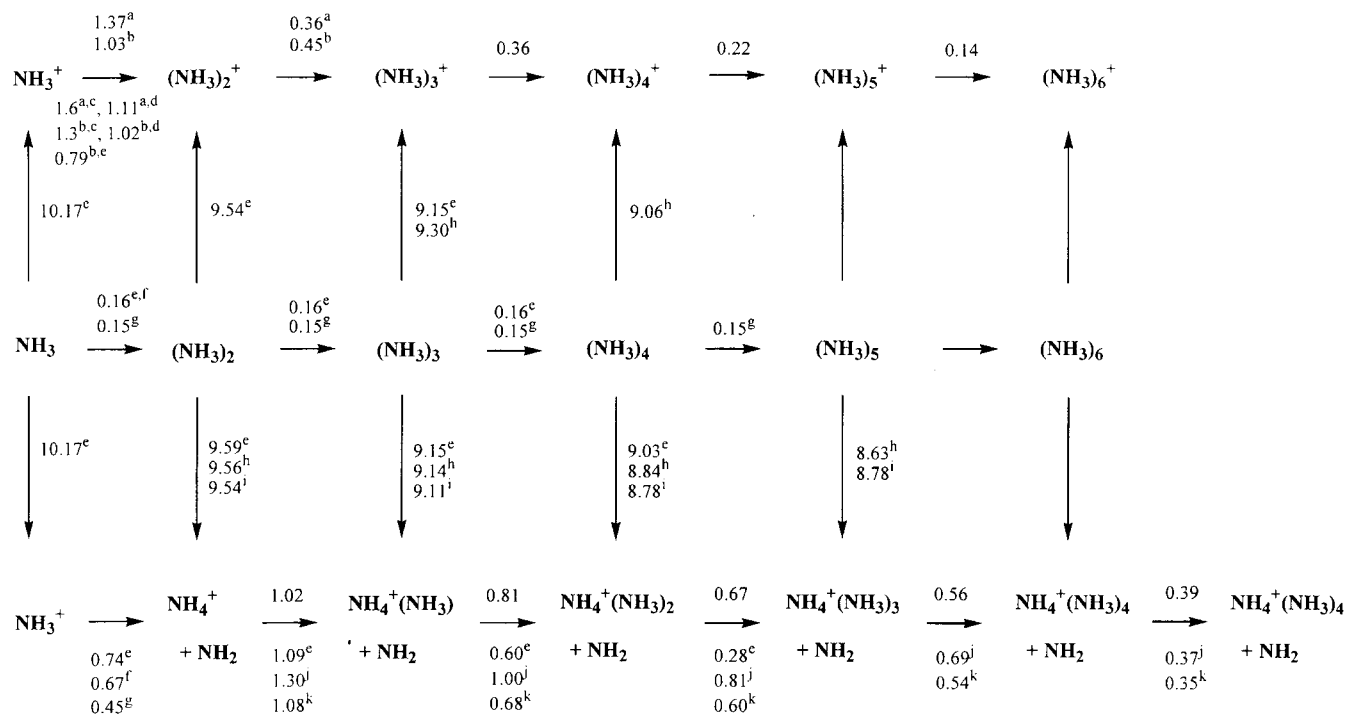


Figure 1. Optimized geometrical structures of unprotonated ammonia cluster cations  $[(NH_3)_n]^+$  ( $n=1-6$ ) at the MP2/6-31+G\*\* level.



<sup>a</sup>head-to-head type. <sup>b</sup>hydrogen-bonded type. <sup>c</sup>Ref. 13. <sup>d</sup>Ref. 10. <sup>e</sup>Ref. 3. <sup>f</sup>Ref. 12. <sup>g</sup>Ref. 1. <sup>h</sup>Ref. 7. <sup>i</sup>Ref. 5,6. <sup>j</sup>Ref. 15. <sup>k</sup>Ref. 8.

Figure 2. Binding energies (eV) of unprotonated and protonated ammonia cluster cations  $[(NH_3)_n]^+$  ( $n=1-6$ ) at the MP2/6-31+G\*\* level.

ammonia monomers at both sides. Pentamer has a trigonal pyramidal structure, and hexamer has a trigonal bipyramidal structure. In unprotonated cations, a magic number of the first solvation shell is  $n=6$ . Because the first ammonia solvation shell is complete at  $n=6$ , the geometrical structure of unprotonated hexamer cation is stable thermodynamically.

A schematic diagram of the binding energies ( $E_{n,n-1}$ ) of unprotonated and protonated ammonia cluster cations is shown in Figure 2. Except for unprotonated dimer cation, the geometrical structures and binding energies for unprotonated ammonia cations are calculated for the first time here. Thus, our binding energies can not be compared with previously reported values. In the hydrogen-bonded dimer cation, since the proton-transfer takes place from  $(\text{NH}_3 \cdots \text{NH}_3^+)$  to  $(\text{NH}_4^+ \cdots \text{NH}_2)$ , the binding energies decrease irregularly. In the head-to-head type of dimer cation, our binding energy is 1.37 eV. This value is in line with other results.<sup>10,13</sup> Because of the competitive interaction of the two types (head-to-head, hydrogen-bonded) in unprotonated cluster cations, the binding energy decreases sharply from  $n=2$  to 3. From unprotonated trimer cation to hexamer, the complexes are relatively stable and the binding energies are larger than those of the corresponding neutral ammonia clusters.

In protonated ammonia trimer cation, Ceyer *et al.*<sup>3</sup> observed a binding energy of 0.28 eV. This value is smaller than the others. In protonated hexamer cation, although the sixth monomer is located at the second shell, the binding energy decreases at a regular rate. That is, since the cationic character of the  $\text{NH}_4^+$  core cation is transmitted to the terminal hydrogen, the growth of the second shell cluster is easily combined without the loss of cationic character. Our binding energy of unprotonated dimer and protonated cluster cations are in good agreement with other theoretical<sup>12,13,15</sup> or experimental<sup>1,3,5-8,10</sup> results.

In the photodissociation of unprotonated pentamer and hexamer cations into protonated cations, the Nishi group<sup>4,7</sup> used the photodissociation mechanism of unprotonated dimer cation as a model. Because of the structural stability of  $\text{NH}_4^+(\text{NH}_3)_4$ , the unstable  $(\text{NH}_3)_6^+$  cation easily dissociates into  $\text{NH}_4^+(\text{NH}_3)_4 + \text{NH}_2$  and the unstable  $(\text{NH}_3)_5^+$  cation transforms into a proton-transferred structure  $[(\text{NH}_3)_3\text{H}_3\text{N}^+ \cdots \text{H}\text{NH}_2]$ , which is bonded between a positively charged nitrogen and a hydrogen of the fifth monomer. The above reactions, however, do not occur by the proton-transfer mechanism. If the proton-transfer takes place, a nitrogen of

the central  $\text{NH}_4^+$  ion should be a dication charge. In the dimer case, the proton-transfer process holds true. But in the other cluster cations  $[(\text{NH}_3)_n]^+$  ( $n \geq 3$ ), the proton-transfer and  $\text{NH}_2$  dissociation does not take place automatically.<sup>12</sup>

Although the Fuke group<sup>8</sup> and Castleman *et al.*<sup>9</sup> observed very weak peaks of unprotonated ammonia cluster, except for  $n=2$ , we have optimized the geometrical structures of unprotonated ammonia cluster cations. The binding energies are relatively large. With increasing cluster cation size, the interaction becomes weaker. As a result, the bond lengths of  $R_{\text{NN}}$  and the distances of the hydrogen-bonds increase monotonously and the binding energies decrease in step.

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