J. Phys. Chem. A **2000,** *104,* 5093−5100

Ab Initio Studies for Geometrical Structures of Ammonia Cluster Cations

Jong Keun Park

Department of Chemistry and Central Laboratory, Pusan National University, Pusan 609-735, Korea

Received: November 16, 1999; In Final Form: February 28, 2000

Structures of unprotonated $(NH_3)_n{}^+$ ($n = 1-6$), protonated $NH_4{}^+(NH_3)_{n-1}$ ($n = 1-6$), and proton-transferred $(NH_4{}^+-NH_2)(NH_3)_{n-2}$ ($n = 3-7$)] ammonia cluster cations have been optimized with ab initio Hartree−Fock (HF) and second-order Møller−Plesset (MP2)/6-31+G** levels, and the harmonic vibrational frequencies have also been evaluated. In ammonia cluster cations, $NH_3{}^+$, $NH_4{}^+$, and $NH_4{}^+-NH_2$ form as a central core of the first ammonia solvation shell, respectively. In unprotonated dimer cation, the totally symmetric structure with the head-to-head interaction is optimized to be stable. In the hydrogen-bonded dimer cation, the unprotoned $NH_3\cdots NH_3{}^+$ cation is optimized to the protonated-transferred $NH_4{}^+\cdots NH_2$ cation. In unprotonated trimer cation, there are two types of isomers (hydrogen-bonded and head-to-head). The hydrogen-bonded type of unprotonated trimer cation is more stable. In unprotonated pentamers and hexamers, a $NH_3{}^+$ core has both interactions in a complex. On the other hand, in unprotonated tetramer, protonated, and proton-transferred cations, a core has only the hydrogen-bonded interaction. In unprotonated tetramer and protonated cations, isomers do not exist, while, in the proton-transferred cations, some types of isomers are optimized at the MP2 level. With increasing cluster cation size, the bond lengths [R_{NN}] between two nitrogen atoms and the distances [$R_{N\cdots H}$] of the hydrogen bond increase regularly. The binding energies ($E_{n,n-1}$) of ammonia cluster cations decrease with size. For the dissociation reaction of unprotonated heptamer $(NH_3)_7{}^+$ into protonated tetramers $NH_4{}^+(NH_3)_3$ and $NH_2(NH_3)_2$, the proton-transferred heptamer $(NH_4{}^+-NH_2)(NH_3)_5$ is the most stable one.

Introduction

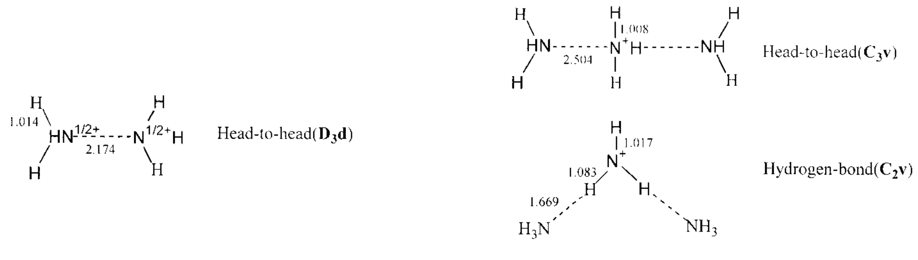
Recently, photoionization experiments on ammonia cluster cations have been extensively performed by electron impact,[1−4] single photon,[5−8] and multiphoton resonant[9−16] ionization spectroscopies. In these experiments, a dominant component is protonated ammonia cluster cations $NH_4{}^+(NH_3)_{n-1}$, while unprotonated ammonia cluster cations $(NH_3)_n{}^+$ are also detected as a byproduct. The unprotonated cluster cations are found to be directly produced from neutral ammonia clusters via photoionization processes. On the other hand, the protonated cluster cations are found to be produced by two other mechanisms. In the first mechanism, the unprotonated cluster cation is formed from the neutral cluster and then it is divided into the protonated cation and NH_2 via the proton-transfer reaction in the cluster cation. This mechanism is often called AID (absorption−ionization−dissociation). In the second one, which is called ADI (absorption−dissociation−ionization), the excited ammonia cluster $(NH_3)_{n-2}(H_3N^*-H\cdots NH_2)$ is formed from the predissociative state of an ammonia molecule in the cluster through the multiphoton absorption process and then the photoionization and photodissociation take place. It seems not to be clearly reported in the literature whether the evaporation of NH_2 takes place before the photoionization process or after it.

The Nishi group[6,9] first suggested the schematic diagram for the mechanism of unprotonated and protonated cluster cations via molecular beam mass spectroscopy and electron impact methods. According to the results, the unprotonated cations $(NH_3)_n{}^+$ are very unstable. These species are quickly transformed into protonated cations $NH_4{}^+(NH_3)_{n-2}$ + NH_2 via intracluster proton transfer $(NH_3)_{n-2}(H_3N^*-H\cdots NH_2)$ or a dissociative reaction $(NH_3)_{n-1}$ + NH_3 takes place simultaneously. As a result, the peak intensities of unprotonated cluster cations are very weak. Additionally, using a model of the proton transfer and dissociation reaction of the ammonia dimer cation, they also explained the mechanism (proton transfer, dissociation reaction) of the photoionization of all ammonia cluster cations.

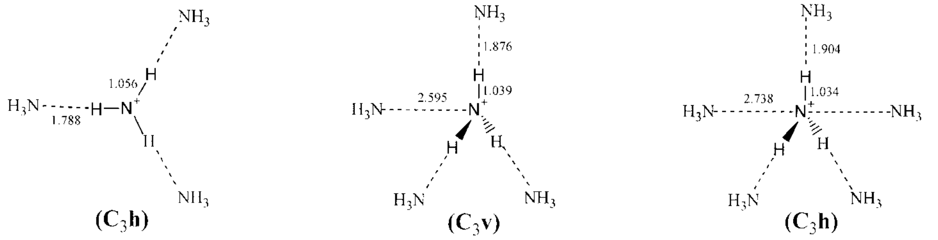
Using ultrafast pump−probe techniques, Fuke and Takasu[16] performed the single photon ionization experiments on unprotonated and protonated ammonia clusters without the relaxation of the intermediate excited states. In this experiment, they pumped the neutral clusters to a vibronic excited state by a 193 nm light, which corresponds to the $\nu' = 5$ vibrational level of free ammonia molecules. And they scanned the delay time of the probe light and observed the time-of-flight mass spectra. By the time profiles of the reaction dynamics of cluster cations, only the peaks of unprotonated monomer and dimer ammonia cations were observed. On the other hand, potential energy representations of the multiphoton ionization processes of unprotonated and protonated cluster cations have been constructed by Castleman, et al.[2,10−13,15] According to the ionization processes, the unprotonated cluster cation is produced by the resonant enhanced multiphoton process and these cations $[(NH_3)_n{}^+]$ dissociate into the protonated cation $(NH_3)_{n-1}H^+$ + NH_2 along the cationic potential curves with a small energy barrier. Therefore, the peaks of unprotonated cations are very weak compared with the protonated cations.

Although the geometrical structure and stability of ammonia cluster cations via the photoionization and photodissociation processes have been investigated by many groups,[1−29] further studies of their structures and stabilities seem to be worth carrying out on the basis of the following points. (i) Do the stable structures of unprotonated cations exist or not? In recent experiments, the unprotonated cluster cations $(NH_3)_n{}^+$ were

10.1021/jp994052q CCC: $19.00



unprotonated dimer cation **unprotonated trimer cation**



unprotonated tetramer cation **unprotonated pentamer cation** **unprotonated hexamer cation**

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

rarely observed except for $n = 1$ and 2. In particular, the peak of the unprotonated pentamer cation is very weak as a noise. (ii) Are there any structural isomers in unprotonated cations? (iii) Are there any stable geometrical structures of proton-transferred cations? (iv) Does the proton transfer reaction takes place in all unprotonated cluster cations? Experiments by Nishi suggest that the proton transfer in all cluster cations takes place from unprotonated to protonated cations. For the dissociation of $(NH_3)_7^+$ into $NH_4^+(NH_3)_3$ and $NH_2(NH_3)_2$, the potential energy curve has energy barriers as an intermediate. To answer these questions, we optimized the structures of ammonia cluster cations at the HF and MP2 levels and also analyzed the harmonic frequencies of the structures to find the local minimum of the structure.

Computational Methods

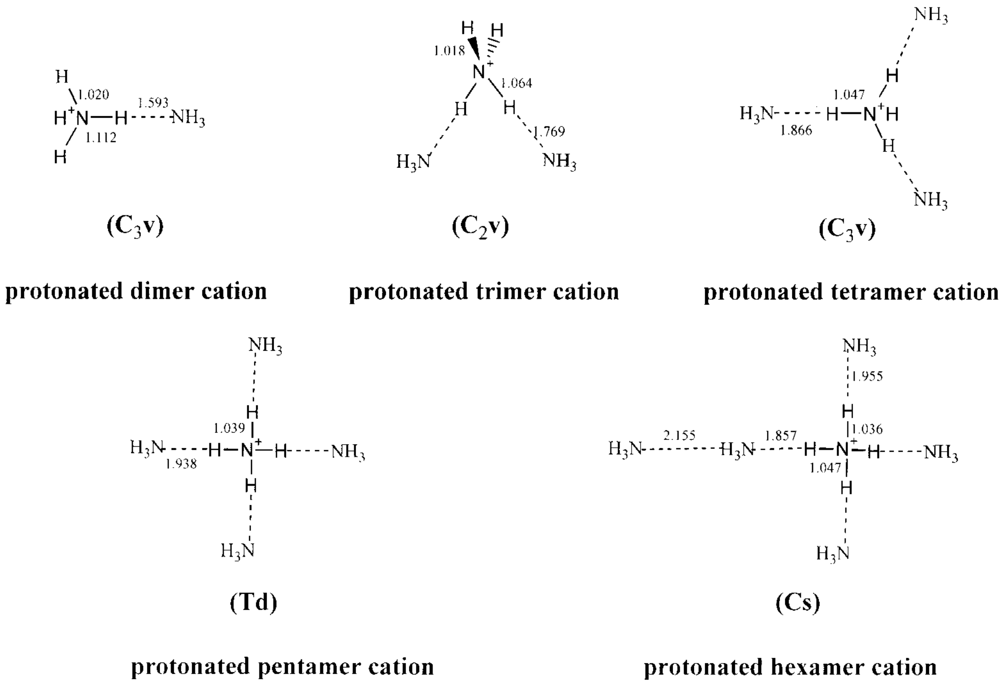
The geometrical structures of unprotonated $(NH_3)_n^+$ ($n = 1-6$), protonated $NH_4^+(NH_3)_{n-1}$ ($n = 1-6$), and proton-transferred $(NH_4^+-NH_2)(NH_3)_{n-2}$ ($n = 3-7$) ammonia cluster cations are fully optimized using the restricted and unrestricted Hartree−Fock (RHF, UHF) and second-order Møller−Plesset perturbation (MP2; all electrons) methods with the 6-31+G** basis set. After the optimization, the harmonic vibrational frequencies are evaluated to confirm the existence of the stable structure at the HF and MP2 levels. To examine the appropriateness of the computational results, the geometrical structures of the cations have also been calculated with coupled cluster with both single and double substitution (CCSD) methods. The program used is Gaussian 94.[30]

Results and Discussion

Geometrical Structures of Unprotonated Ammonia Cluster Cations $[(NH_3)_n^+$ ($n = 1-6$). Optimized geometrical structures of unprotonated ammonia cluster cations are shown in Figure 1. In the cations, a planar NH_3^+ ion is located at a core part in the first ammonia solvation shell and the shell is completed at $n = 6$. In unprotonated dimer cation with a head-to-head interaction (a positively charged nitrogen of NH_3^+ is directly interacted with a lone pair orbital of NH_3), two different results for the geometrical structure are reported in previous experimental[26−29] studies. Posey et al.[27] observed a stable geometry as a nonsymmetric complex which is separated by the positive charge, i.e., a dipole−charge interaction form. They concluded that the system will be split by the exchange interaction into a double-well potential energy surface for the ground electronic state. Another experimental result observed by Ganghi et al.[28] gives a totally symmetric structure with D_{3d} symmetry. In a totally symmetric structure, the respective nitrogens have a half-charge, $H_3N^{(1/2)+}\cdots N^{(1/2)+}H_3$. Recently, the reaction path and structure of this cation were theoretically investigated by Ben Amor et al.[17] and Tomoda et al.[29] According to their results, the geometrical structure is sensitive to the geometrical parameters. Particularly, the most stable geometry is depended by 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. Our optimized geometrical structure of this cation is similar to the previous results; that is, the UHF result gives a nonsymmetric structure with C_s symmetry, while the MP2 result gives a totally symmetric structure with D_{3d}.

In unprotonated trimer cations, two types of isomers with the head-to-head or hydrogen-bonded interactions are optimized to be stable. The head-to-head type is a sandwich complex with C_{3v} symmetry. A single occupied p-orbital of the NH_3^+ core combines with each lone pair orbital of two NH_3 monomers at both sides. An angle $\angle NN^+N$ of three nitrogens of this complex is 180°. In the hydrogen-bonded type, two monomers are combined with two hydrogens of a NH_3^+ core. The hydrogen-bonded complex with C_{2v} symmetry is more stable.

In unprotonated tetramers, this complex undergoes only the interaction of the hydrogen-bonded type; that is, three hydrogens of NH_3^+ interact with three ammonia monomers. The geometrical structure is a coplanar complex with C_{3h} symmetry. To find some local minimum geometries having the head-to-head or both (head-to-head and hydrogen-bond) types in a complex, although each nitrogen of two ammonia molecules is forced to approach to the positively charged nitrogen of the core at both sides (a single occupied p-orbital of the NH_3^+ core is combined with each lone pair orbital of two NH_3 monomers at both sides and a monomer is simultaneously interacted with a



protonated dimer cation

protonated trimer cation

protonated tetramer cation

protonated pentamer cation

protonated hexamer cation

Figure 2. Optimized geometrical structures of protonated ammonia cluster cations $NH_4^+(NH_3)_{n-1}$ ($n = 1-6$) at the MP2/6-31+G** level.

hydrogen of the core), the monomers automatically move to the third free hydrogen of the NH_3^+ core to make a hydrogen bond. Therefore, the other isomer in the unprotonated tetramer cation cannot be optimized.

Meanwhile, in unprotonated pentamers and hexamers, both types of interactions exist in a complex. In a head-to-head interaction of unprotonated pentamer, a single occupied p-orbital of the nitrogen atom of the NH_3^+ core directly combines with a lone pair orbital of the monomer at one side, while, in the hexamer, a nitrogen atom combines with two monomers at both sides. As a result, the head-to-head bond of unprotonated pentamer is stronger. And R_{NN} of the head-to-head bond of the pentamer is shorter than that of the hexamer. Pentamers have a trigonal pyramid structure, and hexamers have a trigonal bipyramid structure. In unprotonated cations, a magic number of the first solvation shell is $n = 6$. On the other hand, in the other unprotonated cluster cations ($n \geq 3$) except for the unprotonated dimer cation, any geometrical structures formed by the proton- and electron-transfer reactions cannot be optimized at the MP2 level.

Spectra of the calculated infrared absorption bands of unprotonated ammonia cluster cations are analyzed, and all values are positive. In unprotonated cations, the spectra are divided into three groups. The first one is the stretching mode of the free N−H between 3000 and 4000 cm^{-1}. The second one is the bending modes between 1000 and 2000 cm^{-1}. The last one is the others (such as the wagging and twist modes of the ammonia monomer unit in a complex) at the low-frequency region. From the trimer of the hydrogen-bonded type to the hexamer, the characteristic peaks of the symmetric and asymmetric stretching vibrational modes of the core involving the hydrogen bonds (N···H) were found between 2306 and 2780 cm^{-1}. The intensities of the peaks are strong. Meanwhile, in the head-to-head type of trimer cation, the characteristic peaks are not found.

Geometrical Structures of Protonated Ammonia Cluster Cations $NH_4^+(NH_3)_{n-1}$ ($n = 1-6$). Optimized geometrical structures of protonated ammonia cluster cations are drawn in Figure 2. NH_4^+ is located at a core of protonated cluster cations. With increasing cluster size, four hydrogen atoms of the NH_4^+ core gradually combine with the neutral ammonia molecule to make the hydrogen-bonded complexes. Our optimized geometrical structures of the protonated cations are in good agreement with the other theoretical[31−37] and experimental[38−47] results. In protonated dimer cation, a geometrical structure with C_{3v} symmetry is optimized at the MP2 level; that is, a nitrogen atom of neutral ammonia is bound to a hydrogen of the NH_4^+ core. A hydrogen atom between two monomers is located at one side. Meanwhile, a structure with D_{3d} symmetry is found to be a transition state with an imaginary frequency at the MP2 frequency analysis. At the CCSD(T) level, the geometrical structure with D_{3d} symmetry cannot be optimized. But Price et al.[38] have concluded that a stable geometrical structure of the protonated dimer cation is D_{3d} symmetry.

In the protonated trimer, two hydrogens of the core interact with two monomers and two hydrogens are free. In the protonated tetramer, three ammonia monomers are bound to three hydrogen atoms of the core. In the protonated pentamer, each of the hydrogen atoms of NH_4^+ combines with four ammonia monomers. That is, the first ammonia solvation shell is completed. In previous theoretical investigations, Kassab and Evleth[31] optimized the geometrical structure of the pentamer with C_{3v} symmetry using the RHF/4-31G** level, while Hirao et al.[33] optimized the structure with T_d symmetry using the RHF/6-31G** level. Experimentally, Echt et al.[45] have observed a peak with strong intensity for the pentamer cation. They concluded that the strong intensity results from a stable geometrical structure $NH_4^+(NH_3)_4$ are due to a closed solvation shell.

In the protonated hexamer, the sixth ammonia molecule is located at the second ammonia solvation shell; that is, a nitrogen of the sixth ammonia molecule is bound to a hydrogen of the fifth ammonia (bridged ammonia) of the first ammonia shell. The distance [$R_{N \cdots H} = 2.155$ Å] of the hydrogen bond between the sixth ammonia and the bridged ammonia of the first shell is longer than that (1.857 Å) between the core and the bridged ammonia. The distance (1.857 Å) of the hydrogen bond between the bridged ammonia and the core is shorter than that (1.955

Å) between the free ammonia and the core. And the distance (1.024 Å) of a bridged N−H bond of the bridged ammonia is shorter than that (1.047 Å) of a bridged N−H bond of NH4$^+$.

Harmonic vibrational frequencies of protonated ammonia cluster cations are also analyzed at the HF and MP2 levels. In the cations, the characteristic peaks made from the symmetric stretching mode of the core are also found from 2033 to 2780 cm^{-1}. With increasing cluster size, the characteristic peaks are found to be blue-shifted regularly. While, the stretching modes of the free N−H bond are found between 3503 and 3656 cm^{-1}. The bending modes between 1321 and 1807 cm^{-1} and the other modes (the wagging and twist modes) at the low-frequency region are found. In the protonated trimer cation, two hydrogens of NH_4^+ are hydrogen bonded with two ammonia monomers. As a result, two characteristic peaks (2500 and 2518 cm^{-1}) are made by the symmetric and asymmetric stretching modes of the core. In Schwarz' experiment,[39] two peaks are broad and weak between 2400 and 2600 cm^{-1}, respectively.

In the protonated tetramer, three vibrational modes are observed from the symmetric stretching vibrational mode (ν'_1) of the core and two asymmetric stretching modes formed from the free N−H bond (ν'_3) of the core and from the hydrogen-bond (ν''_3). In the experiment by Price et al., the frequencies of the symmetric and asymmetric stretching modes (ν'_1, ν''_3) are 2660 and 2692 cm^{-1}, respectively. The frequency of ν'_3 with strong intensity is 2615 cm^{-1}. Meanwhile, in our frequency of the tetramer, two characteristic peaks are analyzed. One (2627 cm^{-1}) is a weak peak which is the symmetric stretching mode (ν'_1) of the core. The other (2670 cm^{-1}) is a strong peak which is made from the degeneracy of the asymmetric stretching modes (ν'_3, ν''_3). Our results are similar to those of Schwarz.[39]

In the protonated pentamer, the asymmetric stretching mode (2762 cm^{-1}) is only active and the IR intensity is strong. By the experimental results of Price et al.[38] and Schwarz,[39] the frequencies of the asymmetric stretching modes are found at 2867 and 2865 cm^{-1}, respectively. In the protonated hexamer cation, three characteristic peaks are made from the three different stretching modes. The middle one (2735 cm^{-1}) is made from the symmetric stretching mode of the core. The lowest one (2650 cm^{-1}) is made from the asymmetric stretching mode of the core due to the hydrogen bond between a bridged monomer and the sixth monomer. By the experimental results,[38] the intensity of this peak greatly increases as the number of solvent molecules at the second shell increases and the position of this peak greatly blue-shifts as the number of solvent molecules at the second shell increases. The highest one (2783 cm^{-1}) is made from the asymmetric stretching mode of the core due to the hydrogen bond between the core and the bridged monomer in the first shell. The spectra of the calculated infrared absorption bands of the protonated ammonia cluster cation are in good agreement with the experimental results.[37−39]

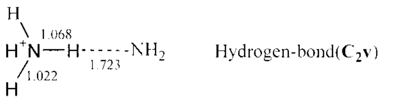
Geometrical Structures of Proton-Transferred Ammonia Cluster Cations [$(NH_4^+{-}NH_2)(NH_3)_{n-2}$ ($n = 3{-}7$)]. Optimized geometrical structures of proton-transferred ammonia cluster cations are drawn in Figure 3. ($NH_4^+{-}NH_2$) is located at a central core. The core is a hydrogen-bonded complex which is obtained from two kinds of mechanisms. In the first mechanism, a lone pair orbital of the nitrogen atom of NH_3 is directly interacted with a hydrogen atom of NH_3^+, and the proton transfer takes place from NH_3^+ to NH_3 without an energy barrier, forming a complex like $NH_4^+\cdots NH_2$]. In the second one, a single occupied p-orbital of the charged nitrogen of NH_3^+ is combined with a hydrogen atom of NH_3. This complex is an intermediate state. In this intermediate state, the electron and proton transfers take place sequentially from NH_3 to NH_3^+, and finally the complex is also optimized as a hydrogen-bonded type. Our result of the hydrogen-bonded type is in good agreement with the theoretical[17] and experimental[27,29] results.

With increasing cluster size, five hydrogen atoms of the core ($NH_4^+{-}NH_2$) gradually combine with neutral ammonia molecules. As a result, some types of isomers in a complex are optimized. The type of isomer is decided on the position of the core combined with the monomers. In a cation, a complex combined with two (one and zero) ammonia molecules at the NH_2 core part is denoted as an A-type isomer (B- and C-types). In the proton-transferred trimer, there are two types of isomers (B- and C-types) with C_s symmetry. The B-type isomer has an interaction between a hydrogen atom of the NH_2 part and a nitrogen atom of the monomer. And the C-type has an interaction between a hydrogen atom of the NH_4^+ part and a nitrogen atom of the monomer. The nitrogen atom of the NH_4^+ side has a positive character, while the nitrogen atom of the NH_2 side has a neutral character. If a hydrogen atom of the NH_4^+ side interacts with an ammonia molecule, the positive charge of the core is more neutralized. As a result, the C-type isomer combined with a monomer at the NH_4^+ side is more stable than the B-type isomer combined with a monomer at the NH_2 side.

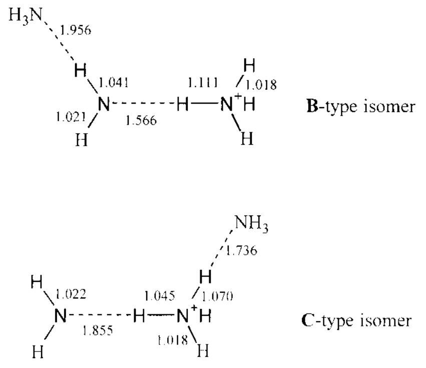
In the proton-transferred tetramer and pentamer, there are three types (A-, B-, and C-types) of isomers. Except for the A-type isomer of pentamer with C_1 symmetry, the geometrical structures of both cations have the C_s symmetry. In the C-type isomer, three ammonia monomers are bound to three hydrogen atoms of the NH_4^+ side. The C-type is more neutralized and more stable than the others. That is, the isomer combined with three ammonia molecules at the NH_4^+ side is the most stable one. In the proton-transferred hexamer, two types (A- and B-types) of isomers are optimized at the MP2 level. The B-type isomer is more stable. The number of the ammonia monomer combined with the NH_4^+ side influences the positively charged character of the core. In the proton-transferred heptamer, each of the hydrogen atoms of the central core ($NH_4^+{-}NH_2$) combines with five ammonia monomers. The first ammonia solvation shell of the proton-transferred cation is completed at the heptamer.

Harmonic vibrational frequencies of the calculated infrared absorption bands of proton-transferred ammonia cluster cations are analyzed, and all values are positive. In proton-transferred cations, the spectra are also divided into three groups. From trimer to heptamer, the characteristic peaks of the symmetric and asymmetric stretching vibrational modes of the core involving the hydrogen bonds (N···H) were found between 2400 and 2800 cm^{-1}. The intensities of the peaks are analyzed to be strong.

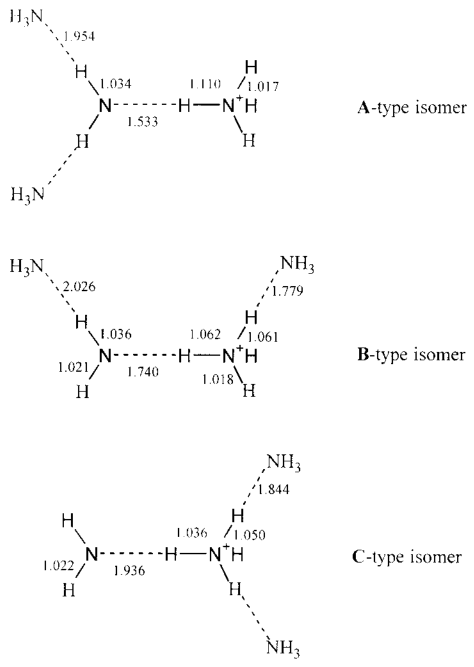
Geometrical Parameters of Ammonia Cluster Cations. Optimized bond lengths of ammonia cluster cations are listed in Table 1. The bond length between two nitrogen atoms of the core and ammonia monomer and bond length of the hydrogen bond between N and H are noted as R_{NN} and $R_{N\cdots H}$, respectively. The bond lengths of the free and bridged N−H bonds of the core NH_3^+ and NH_4^+ cations are indicated as r_{free} and $r_{bridged}$, respectively. The bond lengths of the free N−H bond of NH_3^+, NH_3, and NH_4^+ are listed as a reference. The isomers of the head-to-head and the hydrogen-bonded types of unprotonated cluster cations are noted as H−H and H−B, respectively. The ammonia cluster cations are the ion-neutral interaction complexes. As the cluster size increases, the charge−dipole interaction becomes weaker and R_{NN} between two nitrogen atoms



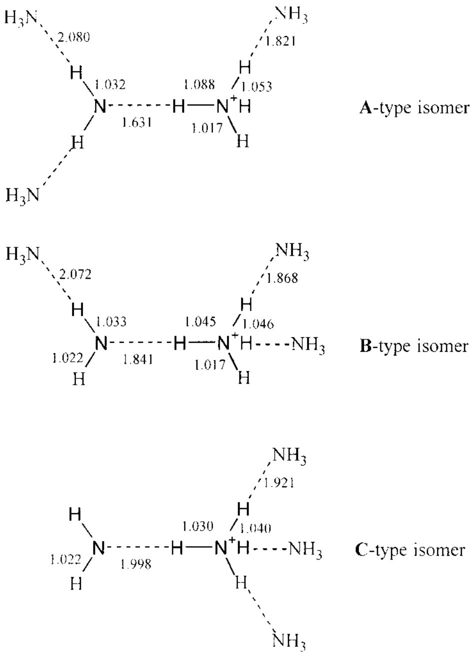
proton-transferred core cation



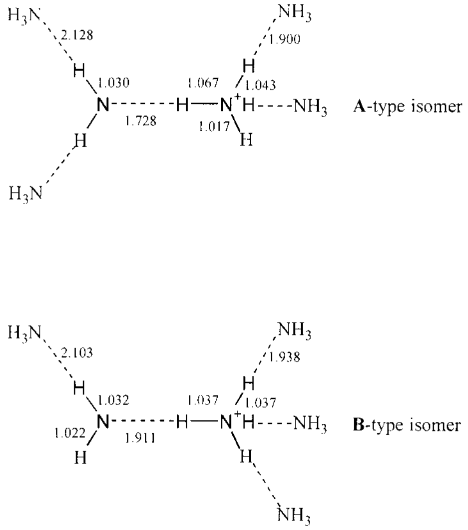
proton-transferred trimer cation (Cs)



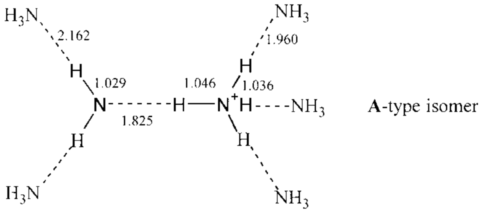
proton-transferred tetramer cation (Cs)



proton-transferred pentamer cation (Cs)



proton-transferred hexamer cation (Cs)



proton-transferred heptamer cation (Cs)

Figure 3. Optimized geometrical structures of proton-transferred ammonia cluster cations $(NH_4^+{-}NH_2)(NH_3)_{n-2}$ ($n = 3-7$) at the MP2/6-31+G** level.

increases regularly. And r_{bridged} of the bridged N−H bond stepwisely decrease with size, while the distances $R_{N\cdots H}$ of the hydrogen bond increase regularly. R_{NN} and $R_{N\cdots H}$ of unprotonated cluster cations having a planar NH_3^+ core are shorter than

TABLE 1: Bond Lengths (Å) of Ammonia Cluster Cations

	MP2				MP2[a]				exptl[b]
	R_{NN}[c]	r_{free}[d]	$r_{bridged}$[e]	$R_{N\cdots H}$[f]	R_{NN}[c]	r_{free}[d]	$r_{bridged}$[e]	$R_{N\cdots H}$[f]	r_{free}[d]
NH_3^+		1.021							
NH_3		1.012				0.991			1.012
NH_4^+		1.023				1.012			1.032[g]
unprotonated ammonia cations									
$(NH_3)_2^+$ (H−H)	2.174[h]	1.014			2.204[i]	1.017[i]			
$(NH_3)_2^+$ (H−B)	2.791	1.022	1.068	1.723	2.770[i]	1.023[i]	1.07[i]	1.70[i]	2.8[j]
$(NH_3)_3^+$ (H−H)	2.504[h]	1.008							
$(NH_3)_3^+$ (H−B)	2.752	1.017	1.083	1.669					
$(NH_3)_4^+$	2.844		1.056	1.788					
$(NH_3)_5^+$	2.595[h]								
	2.915		1.039	1.876					
$(NH_3)_6^+$	2.738[h]								
	2.938		1.034	1.904					
protonated ammonia cations									
$(NH_4^+)(NH_3)$	2.706	1.020	1.112	1.593	2.732	1.008	1.085	1.647	
$(NH_4^+)(NH_3)_2$	2.833	1.018	1.064	1.769	2.828	1.006	1.051	1.777	
$(NH_4^+)(NH_3)_3$	2.914	1.017	1.047	1.866	2.902	1.005	1.036	1.860	
$(NH_4^+)(NH_3)_4$	2.976		1.039	1.938	2.967		1.027	1.940	
$(NH_4^+)(NH_3)_5$	2.991		1.036	1.955					
proton-transferred ammonia cations									
$(H_2N{-}HNH_3^+)(NH_3)$(B)	2.997[k]	1.021[l]	1.041[m]	1.956[n]		1.018[p]			
$(H_2N{-}HNH_3^+)(NH_3)$(C)		1.022[l]			2.806[o]	1.018[p]	1.070[q]	1.736[r]	
$(H_2N{-}HNH_3^+)(NH_3)_2$(A)	2.988[k]		1.034[m]	1.954[n]		1.017[p]			
$(H_2N{-}HNH_3^+)(NH_3)_2$(B)	3.062[k]	1.021[l]	1.036[m]	2.026[n]	2.840[o]	1.018[p]	1.061[q]	1.779[r]	
$(H_2N{-}HNH_3^+)(NH_3)_2$(C)		1.022[l]			2.894[o]	1.017[p]	1.050[q]	1.844[r]	
$(H_2N{-}HNH_3^+)(NH_3)_3$(A)	3.112[k]		1.032[m]	2.080[n]	2.874[o]	1.017[p]	1.053[q]	1.821[r]	
$(H_2N{-}HNH_3^+)(NH_3)_3$(B)	3.104[k]	1.022[l]	1.033[m]	2.072[n]	2.914[o]	1.017[p]	1.046[q]	1.868[r]	
$(H_2N{-}HNH_3^+)(NH_3)_3$(C)		1.022[l]			2.961[o]		1.040[q]	1.921[r]	
$(H_2N{-}HNH_3^+)(NH_3)_4$(A)	3.158[k]		1.030[m]	2.128[n]	2.943[o]	1.017[p]	1.043[q]	1.900[r]	
$(H_2N{-}HNH_3^+)(NH_3)_4$(B)	3.134[k]	1.022[l]	1.032[m]	2.103[n]	2.975[o]		1.037[q]	1.938[r]	
$(H_2N{-}HNH_3^+)(NH_3)_5$(A)	3.191[k]		1.029[m]	2.162[n]	2.996[o]		1.036[q]	1.960[r]	

[a] Reference 31. [b] Reference 45. [c] Bond length between two nitrogen atoms of the core and ammonia monomer is noted as R_{NN}. [d] Bond length of the free N−H bond in the core ions NH_3^+, NH_4^+, and $NH_4^+{-}NH_2$. [e] Bond length of the bridged N−H bond of the core ions. [f] Bond length of the hydrogen bond between N and H. [g] Reference 47. [h] Bond length between two nitrogens in the head-to-head interaction. [i] Reference 17. [j] Reference 26. H−H indicates the isomer of the head-to-head type. H−B indicates the isomer of the hydrogen-bonded type. [k] Bond length between two nitrogen atoms of the NH_2 core and ammonia monomer. [l] Bond length of the free N−H bond at the NH_2 core. [m] Bond length of the bridged N−H bond at the NH_2 core. [f] Bond length of the hydrogen−bond between N and H at the NH_2 core. [o] Bond length between two nitrogen atoms of the NH_4^+ core and ammonia monomer. [p] Bond length of the free N−H bond at the NH_4^+ core. [q] Bond length of the bridged N−H bond at the NH_4^+ core. [r] Bond length of the hydrogen bond between N and H at the NH_4^+ core.

those of protonated cations having a tetrahedral NH_4^+ core and proton-transferred cations having a $(NH_4^+{-}NH_2)$ core.

In the head-to-head type of unprotonated dimer cation, its stable geometry is not clear still. From one experiment by Posey et al.,[27] it was reported that the positive charge of the dimer cation is localized and the complex is C_s symmetry, while the other[28] observed a symmetric complex with D_{3d} symmetry. Meanwhile, by the experiment of Tomoda et al.,[29] the geometrical structure of the dimer cation is dependent on the three geometrical parameters [angle, R_{NN}, and $r_{bridged}$] of the cation. And by the theoretical result,[17] the most stable structure of the dimer cation is dependent on the bond length of R_{NN}. In the head-to-head type, our R_{NN} (2.174 Å) is shorter than that (2.204 Å) of Ben Amor et al.[17] calculated with the MP2/DZP level, but, longer than that (2.151 Å) of Radom et al.[19,20] using the MP2/6-31G* level. Our results of unprotonated dimer and protonated ammonia cluster cations are in good agreement with the other theoretical[17−25,31,33] and experimental[26−29] results.

In proton-transferred ammonia cluster cations, ammonia monomer can be combined with two sides NH_4^+, NH_2 of the core $NH_4^+{-}NH_2$. In the core cation, our R_{NN} (2.791 Å) is longer than some results [2.770 Å from Ben Amor et al.,[17] 2.776 Å from Tomoda,[21,22] and 2.783 Å from Tachibana et al.[18]] but shorter than others [2.877 Å from Tachikawa and Tomoda,[23] 2.80 Å from Tomoda and Kimura,[21] 2.80 Å from Cao et al.,[24] and 2.816 Å from Gill and Radom[19]]. In each isomer (A-, B-, and C-types) of the cluster cations, R_{NN} and $R_{N\cdots H}$ increase with cluster size, while $r_{bridged}$ decreases regularly. In the $NH_4^+{-}NH_2$ core, a nitrogen atom of NH_4^+ has the cationic character, while a nitrogen atom of NH_2 has the neutral. As a result, in each cluster cation, the bond lengths (R_{NN}, $R_{N\cdots H}$) between NH_2 and ammonia monomer are longer than those between NH_4^+ and monomer, while $r_{bridged}$ between NH_2 and ammonia monomer are shorter than that between NH_4^+ and monomer.

Binding Energies and Reactions of Ammonia Cluster Cations. A schematic diagram of the binding energies ($E_{n,n-1}$) of ammonia cluster cations is shown in Figure 4. Except for unprotonated dimer and protonated cluster cations, the binding energies for unprotonated and proton-transferred ammonia cations are calculated for the first time here. Thus, our binding energies cannot be compared with previously calculated values. In the head-to-head type of unprotonated dimer cation, our binding energy of 1.37 eV is larger than those of Ceyer et al. (0.79 eV)[5] and Tachibana et al. (1.21 eV),[18] while it is smaller than those of the other results.[17,21,22] This value is in line with other results.[10,13] Because of the competitive interaction of two types (hydrogen-bonded, head-to-head) in unprotonated cluster cations, the binding energy decreases sharply from $n = 2$ to 3. From the unprotonated trimer cation to the hexamer, the binding energies are larger than those of the corresponding neutral ammonia clusters. In unprotonated pentamer and hexamer cations, our calculated binding energies are 0.22 and 0.14 eV, respectively. Although the Fuke group[16] and Castleman et al.[10−13] observed very weak peaks of unprotonated ammonia

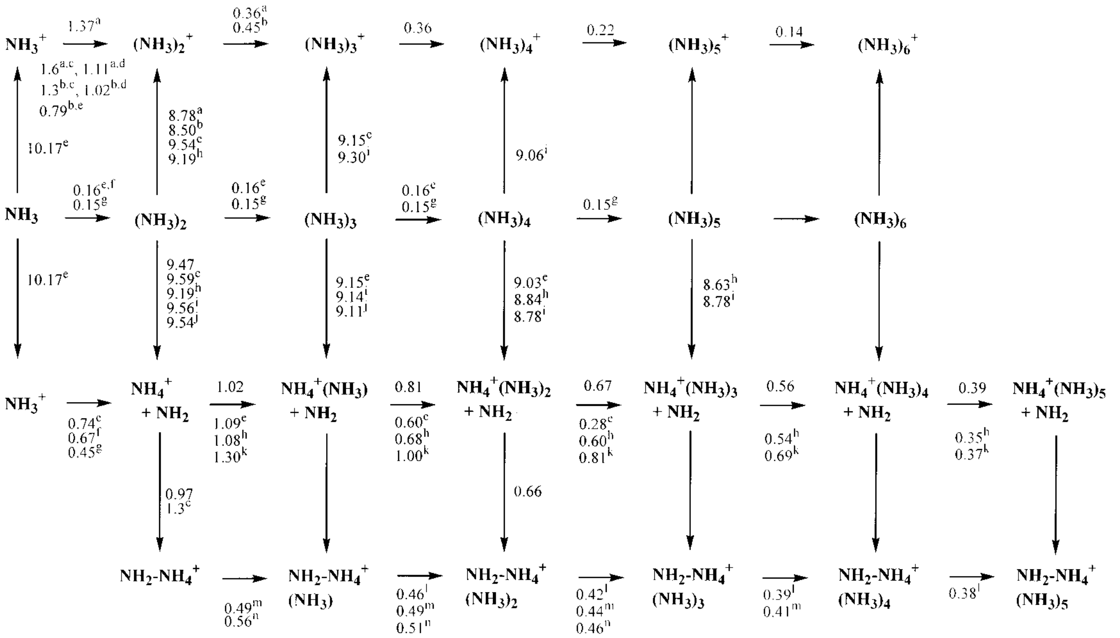


Figure 4. Schematic diagram for the binding energies (eV) ammonia cluster cations at the MP2/6-31+G** level.

cluster except for $n = 2$, the binding energies are relatively large. With increasing cluster cation size, the interaction becomes weaker. As a result, the binding energies decrease in step.

In protonated cluster cations, the binding energies decrease with size. In the protonated tetramer cation, Ceyer et al.[5] observed a binding energy of 0.28 eV. This value is smaller than the others. In protonated hexamer cation, since the cationic character of the NH_4^+ core cation is transmitted to the terminal hydrogen, the growth of the cluster at the second shell is easily combined without the loss of cationic character. That is, although the sixth monomer is located at the second shell, the binding energy decreases at a regular rate. Our binding energy of the unprotonated dimer and protonated cluster cations is in good agreement with other theoretical[17−25,31−37] or experimental[1−16,26−29,37−47] results. In proton-transferred cluster cations, the binding energies also decrease with size. In the core cation, since the $NH_4^+\cdots NH_2$ core is optimized from $NH_3\cdots NH_3^+$), the binding energy is assessed from the separated molecules of NH_4^+ and NH_2. In proton-transferred cations, the decreasing ratio of the binding energy is smaller than those of the others. As a result, the binding energy of the proton-transferred heptamer is as large as that of the protonated hexamer cation. In the same n, the decreasing ratio of the binding energy for protonated cations is larger than those of the unprotonated and proton-transferred cations. That is, the interaction strengths of the protonated complexes are stronger than those of unprotonated and proton-transferred cations. At the first solvation shell, the protonated ammonia cluster complexes are more stable than those of the others.

A schematic diagram for the dissociation reaction of unprotonated heptamer cation $[(NH_3^+)(NH_3)_6$ (**I**) into protonated tetramer cation $NH_4^+(NH_3)_3$ and $NH_2(NH_3)_2$ is represented in Figure 5. In the figure, the potential energy of proton-transferred heptamer $(NH_4^+{-}NH_2)(NH_3)_5$ (**III**) is more stable than that of unprotonated heptamer **I**. The relative energy gap between the proton-transferred **III** and unprotonated heptamer **I** is 0.29 eV at the MP2 level. Meanwhile, in the dissociation reaction, the proton transfer has a potential energy barrier of 0.41 eV. In the dissociation of unprotonated tetramer cation $(NH_3^+)(NH_3)_3$ into protonated trimer cation $NH_4^+(NH_3)_2$ and NH_2, the potential energy of proton transferred tetramer $(NH_4^+{-}NH_2)(NH_3)_2$ is more stable than that of unprotonated tetramer $(NH_3^+)(NH_3)_3$. The relative energy gap between the proton-transferred and unprotonated tetramer is 0.25 eV at the MP2 level.

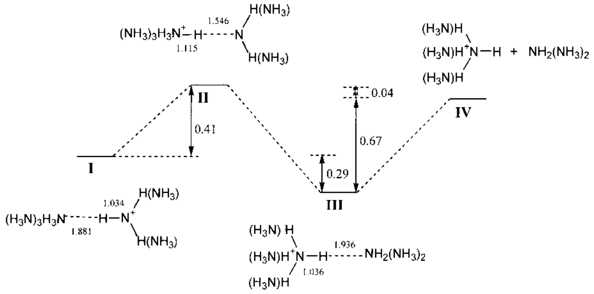


Figure 5. Schematic diagram for the dissociation of unprotonated ammonia heptamer cation $(NH_3)_7^+$ into $NH_4^+(NH_3)_3 + NH_2(NH_3)_2$. Units of relative energies and internuclear distances are electronvolt and angstrom, respectively.

In the photodissociation of unprotonated pentamer and hexamer cations into protonated cations, the Nishi group[6,9] used the photodissociation mechanism of the unprotonated dimer cation as a model. Because of the structural stability of $NH_4^+(NH_3)_4$, the unstable $(NH_3)_6^+$ cation easily dissociates into $NH_4^+(NH_3)_4 + NH_2$. $(NH_3)_5^+$, transforms into a proton-transferred structure, $(NH_3)_3H_3N^+\cdots HNH_2$, which is bonded between a positively charged nitrogen and a hydrogen of the fifth monomer. The above reactions, however, may not occur by the proton-transfer mechanism. If the proton-transfer takes place, a nitrogen of the central NH_4^+ ion should be a dication charge. In the dimer case, the proton-transfer process holds true. But in the other cluster cations $[(NH_3)_n^+$ $(n \geq 3)]$, any geometrical structures formed by the proton transfer and NH_2 dissociation cannot be optimized in our calculation.

Conclusions

We optimized the geometrical structures of unprotonated $(NH_3)_n^+$ $(n = 1{-}6)]$, protonated $NH_4^+(NH_3)_{n-1}$ $(n = 1{-}6)$, and proton-transferred $(NH_4^+{-}NH_2)(NH_3)_{n-2}$ $(n = 3{-}7)$ ammonia cluster cations and evaluated the harmonic vibrational frequencies. In ammonia cluster cations, the NH_3^+, NH_4^+, and $NH_4^+{-}NH_2$ cations are located at a central core of the cation complexes.

The cation complexes are formed by the charge−dipole interaction between a core ion and the neutral ammonia molecules. Except for the hydrogen-bonded type of unprotonated dimer cation, any geometrical structures formed by the proton- and charge-transfer reactions cannot be optimized. In the hydrogen-bonded dimer cation, the proton-transfer reaction takes place from a unprotonated dimer cation $NH_3-NH_3^+$) to a core $NH_4^+-NH_2$) of a proton-transferred cation. In the head-to-head type of unprotonated dimer cations, a positively charged nitrogen atom of NH_3^+ directly interacts with a lone pair orbital of NH_3. At the HF level, a nonsymmetric structure with C_s symmetry is optimized to be stable, while, at the MP2 level, a totally symmetric structure with D_{3d} is optimized. In unprotonated trimer cation, there are two types of isomers formed by the hydrogen-bonded or head-to-head interactions. In two isomers, the hydrogen-bonded complex is more stable. In unprotonated pentamer and hexamer, a central NH_3^+ hydrogen-bonds with the ammonia monomers and simultaneously faces to the other NH_3 through the head-to-head interaction in a complex. On the other hand, the unprotonated tetramer cations have only the hydrogen-bonded interaction. In the calculated infrared absorption bands for unprotonated ammonia cluster cations, the characteristic peaks of the hydrogen-bonded clusters appear near 2500 cm^{-1}. With increasing n, the peaks are shifted from 2306 to 2780 cm^{-1}.

In protonated and proton-transferred ammonia cluster cations, the cation complexes have only the interaction of the hydrogen-bonded type. In protonated ammonia cations, there are no isomers in a complex, while, in proton-transferred ammonia cluster cations, three types of isomers are optimized at the MP2 level. And in protonated and proton-transferred cations, the first shell is completed with the pentamer and heptamer configurations, respectively. In the protonated and proton-transferred cations, the peaks of the stretching mode of the core having the hydrogen bonds red-shift from 2030 to 2780 cm^{-1} with increasing n. In protonated hexamer cation having a ammonia monomer at the second ammonia solvation shell, three characteristic peaks are found.

In ammonia cluster cations formed from the charge−dipole interaction, the interaction becomes weaker with increasing cluster cation size. The bond lengths R_{NN} between two nitrogen atoms and the distances $R_{N\cdots H}$ of the hydrogen-bond increase regularly. And the binding energies also decrease in step. In unprotonated hexamer cation, the binding energy is 0.14 eV. In protonated hexamer and proton-transferred heptamer cations, the binding energies are 0.39 and 0.38 eV, respectively. In the same n, the binding energy of the protonated ammonia cation is larger than those of unprotonated and proton-transferred cations. For the dissociation of unprotonated heptamer $(NH_3)_7^+$ into protonated tetramers $NH_4^+(NH_3)_3$ and $NH_2(NH_3)_2$, the energy barrier between unprotonated and protonated heptamer is 0.41 eV. The proton-transferred heptamer is the more stable one.

Acknowledgment. The author thanks Professor Sun and Professor Iwata for the invaluable help.

References and Notes

(1) Lifshitz, C.; Louage, F. *J. Phys. Chem.* **1989**, *93*, 5633.

(2) Stephan, K.; Futrell, J. H.; Peterson, K. I.; Castleman, A. W., Jr.; Wager, H. E.; Djuric, N.; Mark, T. D. *Int. J. Mass Spectrom. Ion Phys.* **1982**, *44*, 167.

(3) Buck, U.; Lauenstein, Ch. *J. Chem. Phys.* **1990**, *92*, 4250.

(4) Gellene, G. I.; Porter, R. F. *J. Phys. Chem.* **1984**, *88*, 6680.

(5) Ceyer, S. T.; Tiedemann, P. W.; Mahan, B. H.; Lee, Y. T. *J. Chem. Phys.* **1979**, *70*, 14.

(6) Shinohara, H.; Nishi, N.; Washida, N. *J. Chem. Phys.* **1985**, *83*, 1939.

(7) Kaiser, E; de Vries, J.; Steger, H.; Menzel, C.; Kamke, W.; Hertel, I. V. *Z. Phys. D* **1991**, *20*, 193.

(8) Kamke, W.; Herrman, R.; Wang, Z.; Hertel, I. V. *Z. Phys. D* **1988**, *10*, 491.

(9) Shinohara, H.; Nishi, N. *Chem. Phys. Lett.* **1987**, *141*, 292.

(10) Castleman, A. W., Jr.; Tzeng, W. B.; Wei, S.; Morgan, S. *J. Chem. Soc. Faraday Trans.* **1990**, *86*, 2417.

(11) Wei, S.; Purnell, J.; Buzza, S. A.; Stanley, R. J.; Castleman, A. W., Jr. *J. Chem. Phys.* **1992**, *97*, 9480.

(12) Wei, S.; Purnell, J.; Buzza, S. A.; Castleman, A. W., Jr. *J. Chem. Phys.* **1993**, *99*, 755.

(13) Purnell, J.; Wei, S.; Buzza, S. A.; Castleman, A. W., Jr. *J. Phys. Chem.* **1993**, *97*, 12530.

(14) Misaizu, F.; Houston, P. L.; Nishi, N; Shinohara, H.; Kondow, T.; Kinoshita, M. *J. Chem. Phys.* **1993**, *98*, 336; *J. Phys. Chem.* **1989**, *93*, 7041.

(15) Buzza, S. A.; Wei, S.; Purnell, J.; Castleman, A. W., Jr. *J. Chem. Phys.* **1995**, *102*, 4832.

(16) Fuke, K.; Takasu, R. *Bull. Chem. Soc. Jpn.* **1995**, *68*, 3309.

(17) Ben Amor, N.; Maynau, D.; Spiegelmann, F. *J. Chem. Phys.* **1996**, *104*, 4049.

(18) Tachibana, A.; Kawauchi, S.; Kurosaki, Y.; Yoshida, N.; Ogihara, T.; Yamabe, T. *Chem. Phys.* **1994**, *182*, 185; *J. Phys. Chem.* **1991**, *95*, 9647.

(19) Gill, P. M. W.; Radom, L. *J. Am. Chem. Soc.* **1988**, *110*, 4931.

(20) Bouma, W. J.; Radom, L. *J. Am. Chem. Soc.* **1985**, *107*, 345.

(21) Tomoda, S.; Kimura, K. *Chem. Phys. Lett.* **1985**, *121*, 159.

(22) Tomoda, S. *Chem. Phys.* **1986**, *110*, 431.

(23) Tachikawa, H.; Tomoda, S. *Chem. Phys.* **1994**, *182*, 185.

(24) Cao, H. Z.; Evleth, E. M.; Kassab, E. *J. Chem. Phys.* **1984**, *81*, 1512.

(25) Park, J. K.; Iwata, S. *J. Phys. Chem.* **1997**, *101*, 3613.

(26) Buck, U.; Meyer, H.; Nelson, D., Jr.; Fraser, G.; Klemperer, W. *J. Chem. Phys.* **1988**, *88*, 3028.

(27) Posey, L. A.; Guettler, R. D.; Kirchner, N. J.; Zare, R. N. *J. Chem. Phys.* **1994**, *101*, 3772.

(28) Ganghi, N.; Wyatt, J. L.; Symons, M. C. R. *J. Chem. Soc., Chem. Commun.* **1986**, 1424.

(29) Tomoda, S.; Suzuki, S.; Koyano, I. *J. Chem. Phys.* **1988**, *89*, 7268.

(30) Frish, M. J.; Trucks, G. W.; Head-Gordon, M. H.; Gill, P. M. W.; Wong, M. W.; Foresman, J. B.; Johnson, B. G.; Schlegel, H. B.; Robb, M. A.; Replogle, E. S.; Gomperts, R.; Andres, J. L.; Raghavachari, K.; Binkley, J. S.; Gonzalez, C.; Martin, R. L.; Fox, D. J.; Defrees, D. J.; Baker, J.; Stewart, J. J. P.; Pople, J. A. *Gaussian 94*; Gaussian, Inc.: Pittsburgh, PA, 1995.

(31) Kassab, E.; Evleth, E. M. *J. Am. Chem. Soc.* **1987**, *109*, 1653.

(32) Park, J. K. *J. Chem. Phys.* **1997**, *107*, 6795.

(33) Hirao, K.; Fujikawa, T.; Konishi, H.; Yamabe, S. *Chem. Phys. Lett.* **1984**, *104*, 184.

(34) Pullman, A.; Armbruster, A. M. *Chem. Phys. Lett.* **1975**, *36*, 558.

(35) Meot-Ner(Mautner), M.; Speller, C. V. *J. Phys. Chem.* **1986**, *90*, 6616.

(36) Deakyne, C. A. *J. Phys. Chem.* **1986**, *90*, 6625.

(37) Scheiner, S.; Harding, L. B. *J. Am. Chem. Soc.* **1981**, *103*, 2169.

(38) Price, J. M.; Crofton, M. W.; Lee, Y. T. *J. Phys. Chem.* **1991**, *95*, 2182.

(39) Schwarz, H. A. *J. Chem. Phys.* **1980**, *72*, 284.

(40) Ichihashi, M.; Yamabe, J.; Murai, K.; Nonose, S.; Hirao, K.; Kondow, T. In *Structures and Dynamics of Clusters*; Kondow, T., Kaya, K., Terasaki, A., Eds.; Universal Academy Press: Tokyo, 1995; Vol. 16, pp 389−395.

(41) Robin, M. B. *Higher Excited States of Polyatomic Molecules*; Academic Press: New York, 1974; Vol. I, pp 208−229.

(42) Fuke, K.; Takasu, R.; Misaizu, F. *Chem. Phys. Lett.* **1994**, *229*, 597.

(43) Herzberg, G. *Molecular Spectra and Molecular Structure, Vol. II. Infrared and Raman Spectra of Polyatomic Molecules*; Van Nostrand: Princeton, NJ, 1968.

(44) Cook, K. D.; Taylor, J. W. *Int. J. Mass Spectrom. Ion Phys.* **1979**, *30*, 345.

(45) Echt, O.; Morgan, S.; Dao, P. D.; Stanley, R. J. ; Castleman, A. W., Jr. *Phys. Chem.* **1984**, *88*, 217.

(46) Keesee, R. G.; Castleman, A. W., Jr. *J. Phys. Chem. Ref. Data* **1986**, *15*, 1011.

(47) Wei, S.; Tzeng, W. B.; Castleman, A. W., Jr. *J. Chem. Phys.* **1990**, *92*, 332; **1990**, *93*, 2506.

(48) Ibers, J. A.; Stevenson, D. P. *J. Chem. Phys.* **1958**, *28*, 929.