

# Ab initio Studies of $\text{NH}_4^+(\text{H}_2\text{O})_{1-5}$ and the Influence of Hydrogen-Bonding Nonadditivity on Geometries and Vibrations

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Received: September 24, 1998

Ab initio calculations were performed to investigate the structures, energetics, and vibrations of  $\text{NH}_4^+(\text{H}_2\text{O})_n$  cluster ions at  $n = 0-5$ . Equilibrium geometries of  $\text{NH}_4^+$  and  $\text{NH}_4^+-\text{H}_2\text{O}$  are optimized at the MP2, MP4, CCD, QCISD, and B3LYP levels using the 6-31G\*, 6-31G\*\*, 6-31+G\*, 6-31++G\*\*, 6-311+G\*\*, and 6-311++G\*\* basis sets. The benchmark calculations indicate that using MP2 and B3LYP approaches with the 6-31+G\* basis set is well suited for characterizing large  $\text{NH}_4^+(\text{H}_2\text{O})_n$  clusters. The two approaches correspondingly find the existence of a number of structural isomers at  $n = 2-5$ , of which the isomer with a filled first solvation shell is lowest in energy at  $n = 4$ . The calculations further predict that, at  $n = 5$ , the lowest energy isomer contains a four-membered ring with the second-shell  $\text{H}_2\text{O}$  acting as a double-proton acceptor (AA). The prediction is in good agreement with the observation of jet-cooled  $\text{NH}_4^+(\text{H}_2\text{O})_5$ , where a characteristic hydrogen-bonded-OH stretching absorption at  $\sim 3550 \text{ cm}^{-1}$  is identified for the AA- $\text{H}_2\text{O}$  molecule in the vibrational predissociation spectra (Wang, Y.-S.; Chang, H.-C.; Jiang, J. C.; Lin, S. H.; Lee, Y. T.; Chang, H.-C. *J. Am. Chem. Soc.* **1998**, *102*, 8777). In this study, in addition to energetics, how hydrogen-bonding nonadditivity influences the geometries and vibrations of these clusters is analyzed.

## Introduction

Ion-solvent interactions play an important role in a wide range of chemical and biological systems. The importance is particularly evident in aqueous solutions where the interactions involve hydrogen bonding.<sup>1</sup> To better understand the nature of ion hydration, extensive experimental<sup>2-6</sup> and theoretical<sup>7-19</sup> investigations of cluster ions in the gas phase have been performed over the past few decades. The commonly used experimental techniques are mass spectrometry<sup>2,3</sup> and laser spectroscopy.<sup>4-6</sup> The former provides useful information about the strength of binding between solvent molecules and ion cores whereas the latter reveals structural details. Presently, a large body of thermochemical data about ion hydration exists in the literature;<sup>2,3</sup> however, the number of spectroscopic measurements is limited owing to experimental difficulties.<sup>20</sup> Theoretical calculations offer an alternative approach in increasing our understanding of ion-solvent interactions. Recent advances in ab initio calculations have allowed the structures, binding energies, and vibrational frequencies of molecular clusters to be fairly accurately predicted.<sup>7-19</sup> The calculations not only serve as a useful reference for comparison with experiments but also furnish a complete picture of the structures and dynamics of the clusters of interest.

The density functional theory (DFT) has recently been recognized as a useful method for studying extended systems, such as clusters. The method possesses an attractive feature of being less computationally demanding when including electron correlation in the computation. To date, most of the DFT applications focus on the study of structures, proton affinities, electron affinities, binding energies, isomeric transitions, vi-

brational frequencies, internal rotations, and chemical reactions of neutral molecular systems;<sup>21</sup> only a few applications attempt to elucidate ion-solvent interactions. In this study, we chose to investigate ammonium ion-water clusters, which are abundant in the biosphere.<sup>22</sup> The ammonium ion ( $\text{NH}_4^+$ ), heavily involved in various biological and chemical reactions, is one of the most important ionic species in aqueous solutions. In spite of its importance, our current knowledge of how the ammonium ion interacts with water molecules remains incomplete, and most of the existing work concerns only the interactions within the binary complex  $\text{NH}_4^+-\text{H}_2\text{O}$ .<sup>11</sup> The lack of knowledge of extended systems motivated us to study  $\text{NH}_4^+(\text{H}_2\text{O})_{2-5}$  using DFT-based ab initio calculations. It is found in these clusters that the interaction energies, structures, and vibrational frequencies are strongly influenced by the coupling between hydrogen bonds. The hydrogen bonding nonadditivity, also known as the hydrogen-bond (HB) cooperative effect in many macromolecules, condensed phases, and aqueous solutions,<sup>23-28</sup> is analyzed in detail in the present calculations.

Previous thermochemical measurements<sup>2,3</sup> revealed a smooth decrease in the heat of hydration ( $\Delta H_{n-1,n}$ ) for the clustering,  $\text{NH}_4^+(\text{H}_2\text{O})_{n-1} + \text{H}_2\text{O} \rightarrow \text{NH}_4^+(\text{H}_2\text{O})_n$ , as  $n$  increases from 2 to 6. The absence of an abrupt change between  $\Delta H_{3,4}$  and  $\Delta H_{4,5}$  suggests that structural isomerization can occur at  $n = 4$  when the first hydration is to be filled. This is indeed verified by Wang et al.,<sup>6</sup> who found a number of structural isomers for  $\text{NH}_4^+(\text{H}_2\text{O})_{4-6}$  in a supersonic jet using vibrational predissociation spectroscopy. Interestingly, at  $n = 5$ , the spectra in the hydrogen-bonded-OH stretching region indicate that the most stable isomeric form of  $\text{NH}_4^+(\text{H}_2\text{O})_5$  comprises a symmetric four-membered ring with the fifth water molecule acting as a double-proton acceptor on the second solvation shell. This structure was not previously predicted by Armstrong et al.,<sup>7</sup> who

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calculated the structures and energetics of  $\text{NH}_4^+(\text{H}_2\text{O})_n$  up to  $n = 5$ . In the HF/6-31+G\* calculations, they considered mainly charge–dipole interactions, which are insufficient to account for the complex couplings involved in these clusters.

In this study, we carried out both DFT and conventional ab initio calculations to interpret the spectroscopic observations of  $\text{NH}_4^+(\text{H}_2\text{O})_n$ .<sup>6</sup> We calculated the total interaction energy of the reaction  $\text{NH}_4^+ + n\text{H}_2\text{O} \rightarrow \text{NH}_4^+(\text{H}_2\text{O})_n$  and the stepwise hydration energy of  $\text{NH}_4^+(\text{H}_2\text{O})_{n-1} + \text{H}_2\text{O} \rightarrow \text{NH}_4^+(\text{H}_2\text{O})_n$ . Also explored in the calculations was the dependence of the structures, hydration energies, and vibrational frequency shifts on the number of solvent molecules; how these properties are influenced by the attachment of outer shell solvent molecules was investigated. The predicted spectra, containing information of both vibrational frequencies and absorption intensities, of the OH stretching of the solvent molecules and the NH stretching of the ion core are presented for  $\text{NH}_4^+(\text{H}_2\text{O})_{1-5}$ .

## Methods

The ab initio calculations were performed using the commercial Gaussian 94 package.<sup>29</sup> Equilibrium geometries of the  $\text{NH}_4^+$  and  $\text{NH}_4^+-\text{H}_2\text{O}$  ions were optimized at the MP2, CCD, QCISD, and B3LYP levels using the 6-31G\*, 6-31G\*\*, 6-31+G\*, 6-31++G\*\*, 6-311+G\*\*, and 6-311++G\*\* basis sets as the benchmark calculations. For larger clusters, such as  $\text{NH}_4^+(\text{H}_2\text{O})_{2-5}$ , the geometric parameters were obtained at the MP2 and B3LYP levels using 6-31+G\*. Most of the optimizations were symmetry-unconstrained with the binding energies corrected by zero-point vibrational energy (ZPVE) and basis set superposition errors (BSSE) following the procedures of Boys–Bernardi.<sup>30</sup> The BSSE corrections for the stepwise and the total hydration energies were made as follows:

(1) The stepwise hydration,  $\text{AW}_{n-1} + \text{W} \rightarrow \text{AW}_n$ ,

$$E(\text{BSSE}) = [E(\text{AW}_{n-1})_n - E(\text{AW}_{n-1})] + [E(\text{W}_n) - E(\text{W})]$$

(2) The total hydration,  $\text{A} + n\text{W} \rightarrow \text{AW}_n$ ,

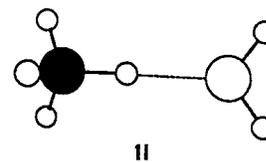
$$E(\text{BSSE}) = [E(\text{A})_n - E(\text{A})] + \sum_{i=1}^n [E(\text{W}_i)_n - E(\text{W}_i)]$$

where  $E(\text{AW}_{n-1})_n$ ,  $E(\text{W}_i)_n$ , and  $E(\text{A})_n$  represent the energies of  $\text{NH}_4^+(\text{H}_2\text{O})_{n-1}$ ,  $(\text{H}_2\text{O})_i$ , and  $\text{NH}_4^+$  calculated using their geometries within the clusters, and  $E(\text{AW}_{n-1})_{n-1}$ ,  $E(\text{W}_i)$ , and  $E(\text{A})$  are the energies of the individual clusters and ions with the basis functions centered on themselves. A complete set of basis functions was employed to describe  $\text{AW}_n$ .

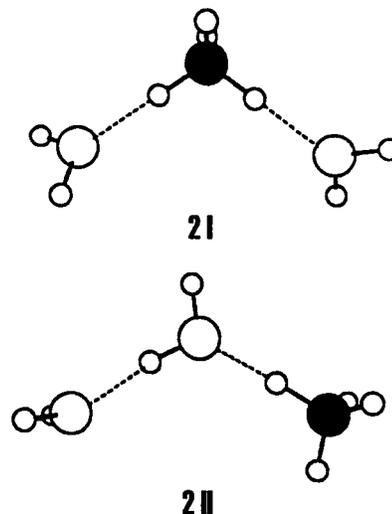
In this presentation, the factors used to scale the calculated frequencies are 0.973 and 0.969 for B3LYP/6-31+G\* and MP2/6-31+G\*, respectively. They were chosen by referring to the experimentally observed free-OH stretching frequencies of two- and three-coordinated  $\text{H}_2\text{O}$  molecules in these clusters.<sup>6a</sup>

## Results and Discussion

To simplify the following discussions, we characterize the water molecules, either in the first (1°) or the second (2°) solvation shell of the  $\text{NH}_4^+$  ion core, according to their hydrogen bonding: single-acceptor (A), single-donor (D), double acceptor (AA), double-donor (DD), single-acceptor-single-donor (AD), single-acceptor-double-donor (ADD), double-acceptor-single-donor (AAD), and double-acceptor-double-donor (AADD).<sup>31</sup> The water molecules are also labeled using parentheses (W1, W2, ..., or Wn) on the basis of their positions. Depending on



**Figure 1.** Ab initio optimized structures of  $\text{NH}_4^+(\text{H}_2\text{O})$ . The N, O, and H atoms are denoted by ●, ○, and ◦, respectively.

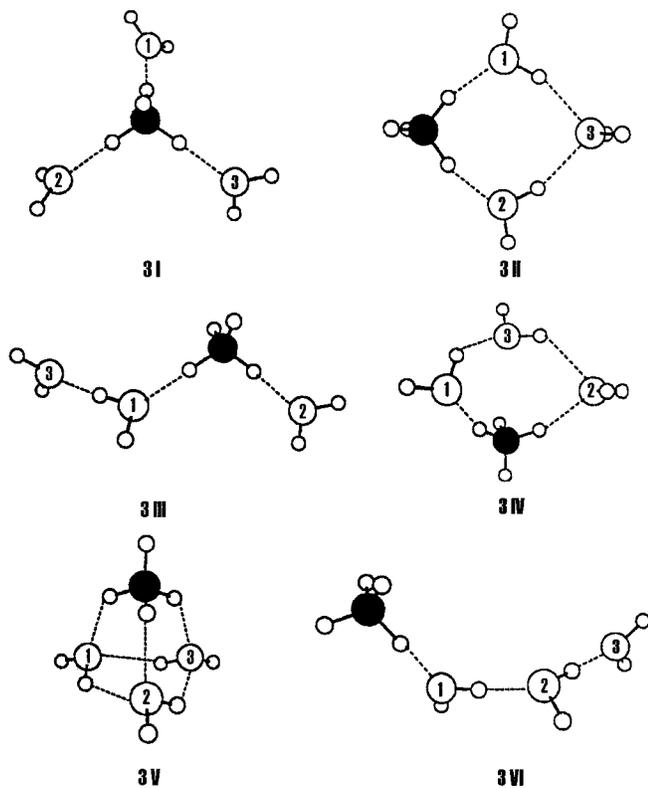


**Figure 2.** Ab initio optimized structures of  $\text{NH}_4^+(\text{H}_2\text{O})_2$ . The N, O, and H atoms are denoted by ●, ○, and ◦, respectively.

how hydrogen bonding is made, the NH and OH groups are prefixed with b or f representing, respectively, hydrogen-bonded or non-hydrogen-bonded (free) states. In comparing the calculated results, both the B3LYP/6-31+G\* and MP2/6-31+G\* values are listed but with the latter given in parentheses.

**A. Geometries and Energetics.** A number of local minima exist in the potential energy surfaces of  $\text{NH}_4^+(\text{H}_2\text{O})_{1-5}$ . Figures 1–5 illustrate some representative structures of these potential minima. Table 1 lists the corresponding energies with and without the BSSE and ZPVE corrections at both the MP2/6-31+G\* and B3LYP/6-31+G\* levels, from which the total and stepwise interaction energies given in Tables 2 and 3 were obtained. Tables 4–6 list the respective geometric parameters of  $\text{NH}_4^+(\text{H}_2\text{O})_{1-3}$ . The salient features of these clusters, presumably formed by successive addition of water molecules to the ammonium ion core, are discussed below.

**A.1.  $\text{NH}_4^+(\text{H}_2\text{O})$ .** Three geometric configurations are found on the interaction hypersurfaces of  $\text{NH}_4^+(\text{H}_2\text{O})$ .<sup>9c</sup> They are (1) direct, (2) bisecting, and (3) axial structures, where the oxygen atom of  $\text{H}_2\text{O}$  approaches the ion core either along the direction of the NH bond, along the bisector of the angle held by the two NH bonds, or along the  $C_{3v}$  symmetry axis of the plane defined by the three hydrogen atoms, respectively. These structures have been scrupulously investigated in previous ab initio calculations.<sup>8,9d,9e</sup> It has been found that the complexation via direct hydrogen bonding yields a structure of the lowest in energy. The structure (with  $C_1$  symmetry) is predominantly determined by charge–dipole interactions. Table 4 lists the geometric parameters of  $\text{NH}_4^+$  and this binary complex, where the  $\text{N}-\text{H}\cdots\text{O}$  hydrogen bond is shown to lie in the plane defined by the  $\text{H}_2\text{O}$  with a bond angle of  $\angle\text{N}-\text{H}\cdots\text{O} \sim 180^\circ$ . Compared to that of  $\text{NH}_4^+$ , the proton-donating  $\text{N}-\text{H}$  bond (denoted as b-NH) is lengthened by  $\sim 0.03 \text{ \AA}$  and the free  $\text{N}-\text{H}$  bonds (denoted as f-NH) are shortened by  $\sim 0.003 \text{ \AA}$ . The predicted

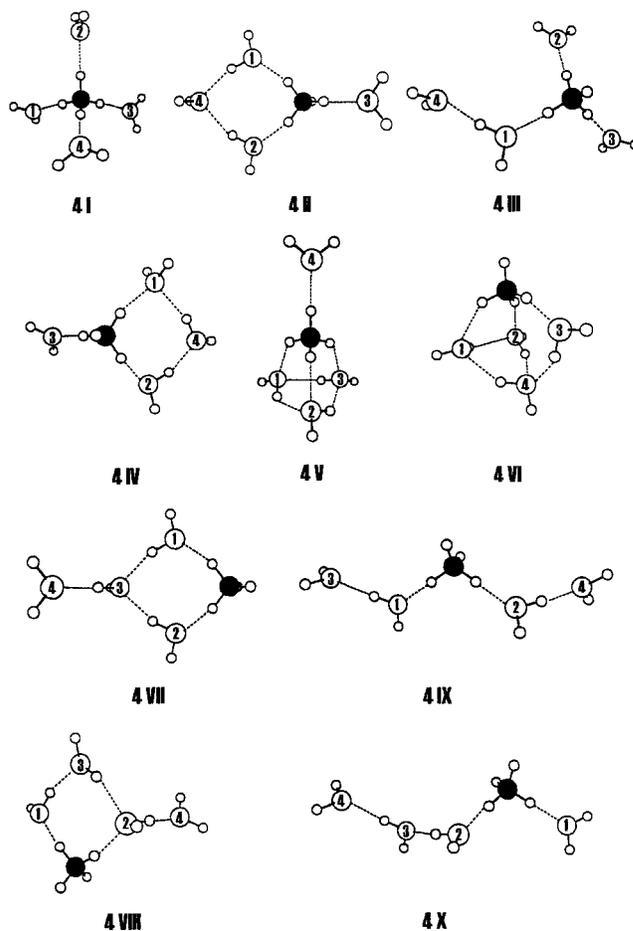


**Figure 3.** Ab initio optimized structures of  $\text{NH}_4^+(\text{H}_2\text{O})_3$ . The N, O, and H atoms are denoted by ●, ○, and ◦, respectively.

$\text{N}\cdots\text{O}$  distance is 2.728 (2.766) Å, which is considerably shorter than the typical separation of  $\sim 4$  Å in neutral van der Waals complexes.

Table 2 compares the binding energies with and without the BSSE and ZPVE corrections of structure **II** at various computational levels. They are performed in an effort to find a reliable and economical method for predicting the properties of larger clusters. The calculated final interaction energy at the higher levels is found to converge at  $-\Delta E_f \sim 17.5$  kcal/mol, a value which is slightly overestimated by MP2 using the 6-31+G\*, 6-31++G\*\*, 6-311+G\*\*, and 6-311++G\*\* basis sets. It appears that the use of basis sets that are more flexible than 6-31+G\* does not substantially improve the accuracy of the MP2 calculations. However, if diffuse functions are not imposed on the heavier atoms, considerable overestimation of the hydration energy can be made by MP2. As for DFT, when using the same basis sets, the B3LYP functional overestimates the interaction energy for more than 1 kcal/mol. Similar to that of MP2, the use of more flexible basis sets only slightly improves the results of this calculation. Comparing the calculated with the measured values shown in Table 2 reveals that the MP2/6-31+G\* method can already provide sufficiently accurate estimates for the interaction energy of  $\text{NH}_4^+$  and  $\text{H}_2\text{O}$ . Unfortunately, application of this method to larger clusters is still impractical at present since extensive disk space is required. The DFT is the alternative. To test the validity of the B3LYP method in elucidating ion–molecule interactions, calculations at both the B3LYP/6-31+G\* and MP2/6-31+G\* levels were performed and compared for clusters with a size of  $n = 2-5$ .

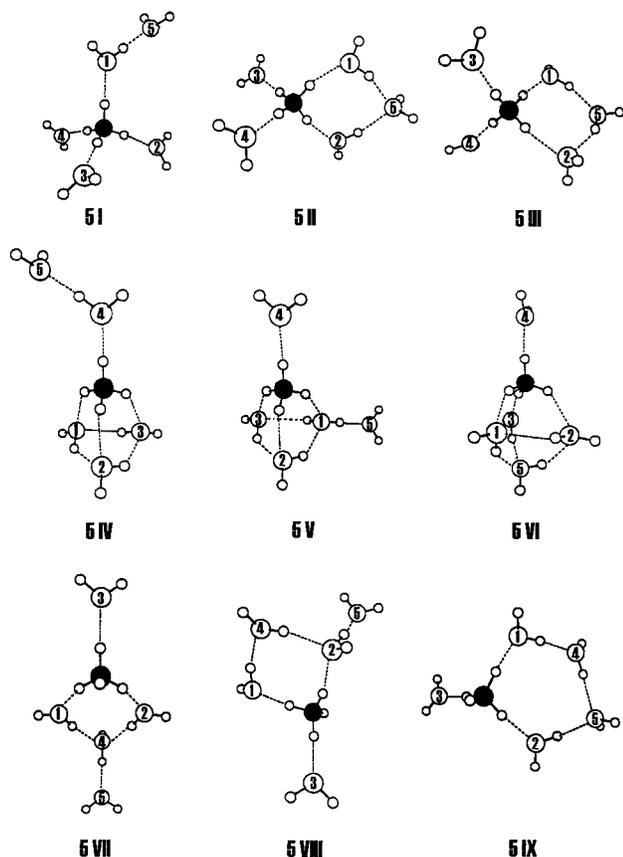
**A.2.  $\text{NH}_4^+(\text{H}_2\text{O})_2$ .** The most energetically favored approach for the second  $\text{H}_2\text{O}$  to  $\text{NH}_4^+(\text{H}_2\text{O})$  is via the formation of an additional  $\text{N}-\text{H}\cdots\text{O}$  hydrogen bond. As illustrated in Figure 2, the optimized geometry of this isomer (**2I**) has a  $C_1$  ( $C_s$ ) symmetry, predicted by B3LYP/6-31+G\* (MP2/6-31+G\*),



**Figure 4.** Ab initio optimized structures of  $\text{NH}_4^+(\text{H}_2\text{O})_4$ . The N, O, and H atoms are denoted by ●, ○, and ◦, respectively.

where the b-NH and the two f-OH bonds involved in each hydrogen bonding lie in the same plane with an angle of  $\angle\text{O}\cdots\text{H}-\text{N} \sim 180^\circ$ . In  $\text{NH}_4^+(\text{H}_2\text{O})_2$ , the second hydrogen bond can also be formed between the two  $\text{H}_2\text{O}$  molecules, giving rise to isomer **2II** which has an energy about 3 kcal/mol higher than that of **2I** (cf. Table 3). Table 5 lists the geometric parameters of these two isomers. In **2I**, the bond length of each b-NH is slightly decreased by  $\sim 0.01$  Å, and the  $\text{N}\cdots\text{O}$  distances are increased by  $\sim 0.05$  Å, compared to those of **1I**. For isomer **2II**, however, the same comparison reveals that it has a bond length increase of more than 0.01 Å in b-NH, and a  $\text{N}\cdots\text{O}$  distance decrease of  $\sim 0.08$  Å. Also noteworthy in **2II** is that the  $\text{O}\cdots\text{O}$  separation of 2.705 (2.746) Å is significantly shorter than the calculated 2.877 (2.906) Å of the neutral water dimer,<sup>32</sup> and the predicted  $\text{N}-\text{H}\cdots\text{O}$  hydrogen bonding energy of 29.19 (27.15) kcal/mol is considerably larger than that of **1I**. Furthermore, the predicted  $\text{O}-\text{H}\cdots\text{O}$  bond strength of 12.66 (11.46) kcal/mol is nearly five-fold larger than 2.79 (2.42) kcal/mol of  $(\text{H}_2\text{O})_2$ .<sup>32</sup> The dramatic increase of the  $\text{N}-\text{H}\cdots\text{O}$  and  $\text{O}-\text{H}\cdots\text{O}$  bonding energies in **2II** indicates that the extent of electron transfer in these two hydrogen bonds is greatly augmented upon complexation.

Comparison of the calculated results between isomers **2I** and **2II** reveals the importance of HB cooperativity in determining the molecular properties of protonated ion–water clusters. In isomer **2I**, the total interaction energy contained by the two  $\text{N}-\text{H}\cdots\text{O}$  hydrogen bonds is 34.73 (32.94) kcal/mol, which is less than twice the  $\text{N}-\text{H}\cdots\text{O}$  bonding energy of **1I** by 3.63 (2.96) kcal/mol. In contrast, the total interaction energy contained by **2II** in the  $\text{N}-\text{H}\cdots\text{O}$  and  $\text{O}-\text{H}\cdots\text{O}$  bonds is 31.73



**Figure 5.** Ab initio optimized structures of  $\text{NH}_4^+(\text{H}_2\text{O})_5$ . The N, O, and H atoms are denoted by  $\bullet$ ,  $\circ$ , and  $\circ$ , respectively.

(29.14) kcal/mol, which is larger than the sum of the interaction energies of  $\text{N}-\text{H}\cdots\text{O}$  in isomer **1I** and  $\text{O}-\text{H}\cdots\text{O}$  in  $(\text{H}_2\text{O})_2$  by 9.76 (8.77) kcal/mol. The increase in interaction energy, together with the elongation of the b-NH bond and the reduction of the  $\text{N}\cdots\text{O}$  and  $\text{O}\cdots\text{O}$  distances, indicates that the  $\text{N}-\text{H}\cdots\text{O}$  and the  $\text{O}-\text{H}\cdots\text{O}$  hydrogen bonds are cooperatively coupled in isomer **2II**. This is opposite to the anticooperative case of **2I**, where the b-NH bonds shorten, the  $\text{N}\cdots\text{O}$  distances increase and the interaction energy is negatively nonadditive when the second  $\text{H}_2\text{O}$  molecule attaches to the ion core. It is now well-known that the HB cooperativity due to concerted charge transfer can greatly enhance the strength of the individual hydrogen bonds involved in the coupling.<sup>33,34</sup> In isomer **2I**, where the  $\text{NH}_4^+$  ion acts as a double proton donor bridging two water molecules, the extent of charge transfer between  $\text{NH}_4^+$  and either  $\text{H}_2\text{O}$  is reduced, resulting in weaker  $\text{N}-\text{H}\cdots\text{O}$  hydrogen bonding compared to that of **1I**. As in isomer **2II**, where the  $1^\circ\text{H}_2\text{O}$  functions both as a proton donor and as a proton acceptor in a linear linkage, the strength of each  $\text{N}-\text{H}\cdots\text{O}$  and  $\text{O}-\text{H}\cdots\text{O}$  hydrogen bond is augmented due to the concerted coupling. Although strongly favored by the HB cooperativity, isomer **2II** remains less stable than **2I** since the  $\text{O}-\text{H}\cdots\text{O}$  hydrogen bonding is much weaker than that of  $\text{N}^+-\text{H}\cdots\text{O}$ .

**A.3.  $\text{NH}_4^+(\text{H}_2\text{O})_3$ .** The  $\text{NH}_4^+(\text{H}_2\text{O})_3$  cluster ion contains a number of energy minima in the interaction potential. Figure 3 depicts the low-energy structures of the isomers with geometric parameters listed in Table 6. Among these isomers, one of the lowest in energy is **3I**, in which  $\text{NH}_4^+$  forms three hydrogen bonds with three geometrically equivalent  $\text{H}_2\text{O}$  molecules. The  $\text{NH}_4^+$  ion in this cluster behaves like a triple proton donor. The behavior diminishes the extent of charge transfer from the ion core to each solvent molecule, thereby weakening each  $\text{N}-\text{H}\cdots\text{O}$

hydrogen bond. Compared to **2I** and **1I**, this isomer has a shorter b-NH bond length, accompanied by an increased  $\text{N}\cdots\text{O}$  distance. The b-NH and the two f-OH bonds of each hydrogen bonding remain coplanar with an angle of  $\angle\text{N}-\text{H}\cdots\text{O} \sim 180^\circ$ . Notably, the energy of the hydration (**2I** +  $\text{H}_2\text{O} \rightarrow$  **3I**) is  $\sim 13$  kcal/mol, which is smaller than  $\sim 15$  kcal/mole of (**1I** +  $\text{H}_2\text{O} \rightarrow$  **2I**) and  $\sim 19$  kcal/mole of ( $\text{NH}_4^+$  +  $\text{H}_2\text{O} \rightarrow$  **1I**).

Two additional isomers (**3II** and **3III**) are considered for  $\text{NH}_4^+(\text{H}_2\text{O})_3$ . The symmetric, ring-shaped isomer (**3II**) is  $\sim 2$  kcal/mol less stable than **3I** and is the second lowest in energy. In this isomer, the water molecule situated on the second solvation shell ( $2^\circ$ ) acts as a double-proton acceptor (AA), forming two equivalent  $\text{O}-\text{H}\cdots\text{O}$  hydrogen bonds with the two single-acceptor-single-donor (AD)  $\text{H}_2\text{O}$  molecules on the first solvation shell ( $1^\circ$ ). The two b-NH and the four OH bonds all lie in the same plane composed by the four hydrogen bonds involving the two AD- $1^\circ\text{H}_2\text{O}$  molecules. The angle contained by the two N-H bonds is tightened by  $4^\circ$  because of the four-membered ring formation. Owing to the HB cooperativity between  $\text{N}-\text{H}\cdots\text{O}$  and  $\text{O}-\text{H}\cdots\text{O}$ , the b-NH bond length of 1.052 (1.045) Å is slightly longer than that of **2I**, and the  $\text{N}\cdots\text{O}$  distance of 2.732 (2.757) Å is slightly shorter than that of **2I**. As for  $\text{O}\cdots\text{O}$ , the average separation of 2.862 (2.895) Å is significantly larger than the corresponding one in **2II**, a result of anticooperative couplings between the two  $\text{O}-\text{H}\cdots\text{O}$  hydrogen bonds. Although isomer **3II** has one more hydrogen bond than **3I**, it is one bond less in  $\text{N}-\text{H}\cdots\text{O}$  and thus is relatively not favored in energy.

Two data sets concerning the bond length of b-NH and the distance of  $\text{N}\cdots\text{O}$  exist for **3III**, and they are exactly out of phase as compared to those of **2I**. In one set where the  $\text{O}-\text{H}\cdots\text{O}$  hydrogen bond is cooperative with  $\text{N}-\text{H}\cdots\text{O}$ , the b-NH bond is lengthened, and the  $\text{N}\cdots\text{O}$  distance is shortened. This involves bonding of the water dimer (W1 + W3) to the ion core. In another set where the HB anticooperativity persists due to water monomer (W2) attachment, the changes in geometry are similar to that of **1I**  $\rightarrow$  **2I**: the b-NH bond is shortened and the  $\text{N}\cdots\text{O}$  distance is lengthened. The equilibrium geometry of this cluster **3III** is, thus, a result of the delicate balance between these two competitive effects. Note that, while the number of  $\text{O}-\text{H}\cdots\text{O}$  hydrogen bonds in **3III** is lower than that in **3II** by one, they are comparable in terms of stability. This is primarily due to the loss of hydrogen bond directionality, which reduces the bond strength,<sup>31</sup> upon ring formation in **3II**.

In the course of performing calculations, MP2/6-31+G\* collapsed on isomer **3IV**, which consists of an asymmetric four-fold ring. This isomer, however, is predicted to be stable by B3LYP/6-31+G\*. Differing from **3II**, it contains an AA- $1^\circ\text{H}_2\text{O}$ , instead of an AA- $2^\circ\text{H}_2\text{O}$ . The potential well of this isomer is relatively shallow, with a minimum which is  $\sim 5$  kcal/mol higher than that of **3I**. Also due to the difference in hydrogen bonding nonadditivity, two distinct data sets on bond lengths and internuclear distances exist: 1.059, 2.670, and 2.754 Å versus 1.040, 2.892, and 2.915 Å for b-NH,  $\text{N}\cdots\text{O}$ , and  $\text{O}\cdots\text{O}$ , respectively. In this isomer, the  $1^\circ\text{H}_2\text{O}$  (W2) no longer lies in the same plane with b-NH, indicating that the interaction between the b-NH dipole and the electron lone pair of O is the dominant intermolecular force in this case. Interestingly, while the number of hydrogen bonds is the same and the degree of losing hydrogen bond directionality is similar between **3II** and **3IV**, the latter is 3.5 kcal/mol less stable because the dipole-electron lone pair interaction is much weaker than the charge-dipole interaction.

TABLE 1: Energies (hartree) of  $\text{NH}_4^+(\text{H}_2\text{O})_n$  at  $n = 0-5$ .

structures	B3LYP/6-31+G*			MP2/6-31+G*		
	$E$	$E_{\text{zpve}}^a$	$E_t^b$	$E$	$E_{\text{zpve}}^a$	$E_t^b$
H <sub>2</sub> O	-76.422 572 3	-76.401 476		-76.209 776 6	-76.188 532	
NH <sub>4</sub> <sup>+</sup>	-56.894 586 0	-56.844 686		-56.701 165 8	-56.650 671	
<b>1I</b>	-133.352 458 5	-133.278 527	-133.276 722	-132.946 353 6	-132.871 481	-132.867 802
<b>2I</b>	-209.804 435 4	-209.706 472	-209.702 984	-209.186 574 3	-209.087 339	-209.080 231
<b>2II</b>	-209.800 504 0	-209.702 219	-209.698 188	-209.181 898 6	-209.082 203	-209.074 181
<b>3I</b>	-286.252 050 9	-286.130 387	-286.125 246	-285.422 959 5	-285.299 643	-285.289 203
<b>3II</b>	-286.253 116 9	-286.128 585	-286.122 197	-285.424 225 9	-285.298 283	-285.285 572
<b>3III</b>	-286.250 003 8	-286.127 600	-286.121 991	-285.420 033 7	-285.296 031	-285.284 798
<b>3IV</b>	-286.247 112 2	-286.122 482	-286.116 586			
<b>3V</b>	-286.246 591 7	-286.121 390	-286.115 792	-285.420 415 0	-285.293 729	-285.282 082
<b>3VI</b>	-286.243 593 7	-286.121 060	-286.114 821	-285.412 694 6	-285.288 559	-285.276 405
<b>4I</b>	-362.695 994 2	-362.550 927	-362.544 061	-361.656 046 4	-361.509 075	-361.495 229
<b>4II</b>	-362.698 969 4	-362.550 921	-362.542 889	-361.659 012 6	-361.509 250	-361.493 268
<b>4III</b>	-362.695 425 0	-362.549 232	-362.542 027	-361.654 423 9	-361.506 464	-361.492 069
<b>4IV</b>	-362.693 964 0	-362.545 536	-362.537 453			
<b>4V</b>	-362.694 190 7	-362.544 672	-362.537 344	-361.656 535 8	-361.505 651	-361.490 465
<b>4VI</b>	-362.696 274 0	-362.545 473	-362.537 078	-361.657 783 6	-361.505 729	-361.488 835
<b>4VII</b>	-362.698 317 9	-362.549 749	-362.540 965	-361.657 447 6	-361.506 999	-361.489 666
<b>4VIII</b>	-362.693 752 4	-362.544 424	-362.535 642			
<b>4IX</b>	-362.694 402 2	-362.547 613	-362.539 906	-361.652 491 5	-361.503 810	-361.488 558
<b>4X</b>	-362.691 920 3	-362.545 146	-362.537 392	-361.649 873 5	-361.501 323	-361.486 038
<b>5I</b>	-439.137 873 6	-438.968 206	-438.959 377	-437.886 160 4	-437.714 516	-437.696 787
<b>5II</b>	-439.141 645 0	-438.970 072	-438.960 490	-437.890 872 4	-437.717 469	-437.698 155
<b>5III</b>	-439.137 830 8	-438.965 797	-438.955 978	-437.886 413 5	-437.712 830	-437.693 601
<b>5IV</b>	-439.137 663 0	-438.963 593	-438.954 162	-437.888 017 0	-437.712 267	-437.693 021
<b>5V</b>				-437.887 725 1	-437.712 639	-437.693 215
<b>5VI</b>	-439.141 692 5	-438.967 112	-438.957 066	-437.892 072 4	-437.716 076	-437.695 632
<b>5VII</b>	-439.143 181 2	-438.971 085	-438.960 788	-437.891 356 4	-437.717 105	-437.696 588
<b>5VIII</b>	-439.139 580 5	-438.966 234	-438.955 872			
<b>5IX</b>	-439.141 002 3	-438.968 150	-438.957 704	-437.889 067 6	-437.714 588	-437.694 145

<sup>a</sup> With ZPVE corrections. <sup>b</sup> With both ZPVE and BSSE corrections.

TABLE 2: First Hydration Energies (kcal/mol) of  $\text{NH}_4^+$ 

methods	$-\Delta E$	$-\Delta E_{\text{cp}}$	$-\Delta E_{\text{zpve}}$	$-\Delta E_t$
B3LYP/6-31G*	25.31	24.11	23.71	22.51
B3LYP/6-31+G*	22.15	21.02	20.31	19.18
B3LYP/6-31G**	25.64	24.30	24.17	22.77
B3LYP/6-31+G*	22.11	21.15	20.30	19.34
B3LYP/6-31+G**	22.02	21.20	20.15	19.33
B3LYP/6-311++G**	22.01	21.17	20.13	19.29
MP2/6-31G*	24.21	22.63	22.41	20.83
MP2/6-31+G*	22.22	19.91	20.25	17.95
MP2/6-31G**	24.21	22.49	22.54	20.83
MP2/6-31++G**	21.74	19.75	19.88	17.88
MP2/6-311+G**	21.61	19.74	19.80	17.93
MP2/6-311++G**	21.61	19.71	19.81	17.91
MP4/6-311++G** <sup>(D)</sup> <sup>a,b</sup>	21.15	19.31	19.35	17.51
MP4/6-311++G** <sup>(SD)</sup> <sup>a,b</sup>	20.96	19.18	19.16	17.38
MP4/6-311++G** <sup>(SDQ)</sup> <sup>a,b</sup>	21.00	19.17	19.20	17.37
MP4/6-311++G** <sup>(SDTQ)</sup> <sup>a,b</sup>	21.34	19.34	19.54	17.54
CCD/6-311++G** <sup>b</sup>	20.92	19.31	19.12	17.51
QCISD/6-311++G** <sup>b</sup>	20.95	20.62	19.15	17.82
exptl		19.9, <sup>c</sup> 17.2, <sup>d</sup> 17.3 <sup>e</sup>		

<sup>a</sup> Of the MP2/6-311++G\*\* geometries. <sup>b</sup> ZPVE corrections made based upon the MP2/6-311++G\*\* geometries. <sup>c</sup> Reference 3. <sup>d</sup> Reference 2b. <sup>e</sup> Reference 3. <sup>f</sup> Reference 2b. <sup>g</sup> Reference 2a.

Isomer **3V** is formed by attaching a cyclic water trimer to the ammonium ion core via three N-H $\cdots$ O hydrogen bonds. The size of the water trimer is slightly expanded with an average O $\cdots$ O distance of 2.87 (2.87) Å and an average angle of  $\angle\text{O-H}\cdots\text{O} \sim 125.2^\circ$  (124.5°), compared to the corresponding values of 2.771 Å and 149.1° for isolated cyclic (H<sub>2</sub>O)<sub>3</sub>.<sup>32</sup> In order to form this isomer, the linearity of the three N-H $\cdots$ O hydrogen bonds must be reduced to  $\angle\text{N-H}\cdots\text{O} \sim 134^\circ$  (133°). Although isomer **3V** possesses three N-H $\cdots$ O and three O-H $\cdots$ O hydrogen bonds, it is higher in energy than **3I** by 5.93 (4.47)

kcal/mol because of the loss of hydrogen bond directionality in both N-H $\cdots$ O and O-H $\cdots$ O.

Calculations of the linear isomer **3VI** were conducted to explore the long-range influence of the ion core. Owing to the increased HB cooperativity, the b-NH bond is further lengthened and the N-H $\cdots$ O bond is shortened. Compared to that of **2II**, the interoxygen separation in **3VI** is shorter by 0.071 (0.067) Å for O<sub>1</sub> $\cdots$ O<sub>2</sub>. This means that adding one more H<sub>2</sub>O to the end of the water chain strengthens the hydrogen bonding between 1°H<sub>2</sub>O and 2°H<sub>2</sub>O. The O<sub>2</sub>-H $\cdots$ O<sub>3</sub> bond, however, is relatively weaker because the 3°H<sub>2</sub>O molecule is situated further away from the ion core. The predicted hydration energy of (**2II** + H<sub>2</sub>O  $\rightarrow$  **3VI**) is 9.69 (8.88) kcal/mol, which is substantially larger than that in neutral water clusters, suggesting that the ion core continues to influence the bonding of the 3°-H<sub>2</sub>O molecule. It is interesting to note that the interaction energy of O<sub>1</sub>-H $\cdots$ O<sub>2</sub> in this linear chainlike isomer is surprisingly large, 19.62 (17.99) kcal/mol, which signifies the important role the HB cooperative effect plays in hydrogen-bonded systems.

**A.4. NH<sub>4</sub><sup>+</sup>(H<sub>2</sub>O)<sub>4</sub>.** Isomer **4I** presents itself as the most stable structure of NH<sub>4</sub><sup>+</sup>(H<sub>2</sub>O)<sub>4</sub>; it contains an ion core with a complete solvation shell. Other isomers of comparable stability can also be found in Table 3, where **4I**, **4II**, and **4III** are within 2 kcal/mol of each other in energy. Previous vibrational predissociation spectroscopy of NH<sub>4</sub><sup>+</sup>(H<sub>2</sub>O)<sub>4</sub> reveals three isomers in a supersonic jet, and they were identified as **4I**, **4II**, and **4III** based upon their characteristic vibrational signatures.<sup>6b</sup> Systematic investigations of the temperature-dependent spectra indicate that the isomers are stable in the order of **4I** > **4II** > **4III**. This experimental observation is in good agreement with the calculated energies listed in Table 3. Note that, for these three isomers, the respective stepwise hydration energies of (**3I** + H<sub>2</sub>O  $\rightarrow$  **4I**), (**3I** + H<sub>2</sub>O  $\rightarrow$  **4II**) and (**3I** + H<sub>2</sub>O  $\rightarrow$  **4III**) are all

**TABLE 3: Total and Stepwise Hydration Energies<sup>a</sup> kcal/mol of  $[\text{NH}_4^+ + n\text{H}_2\text{O} \rightarrow \text{NH}_4^+(\text{H}_2\text{O})_n]$  and  $[\text{NH}_4^+(\text{H}_2\text{O})_{n-1} + \text{H}_2\text{O} \rightarrow \text{NH}_4^+(\text{H}_2\text{O})_n]$  Estimated by B3LYP/6-31+G\* and MP2/6-31+G\***

$\text{NH}_4^+(\text{H}_2\text{O})_n$	B3LYP/6-31+G*		MP2/6-31+G*	
	$-\Delta E_n$	$-\Delta E_{n-1,n}^b$	$-\Delta E_n$	$-\Delta E_{n-1,n}^b$
<b>1I</b>	19.18		17.95	
<b>2I</b>	34.73	15.52 ( <b>1I</b> )	32.94	14.88 ( <b>1I</b> )
<b>2II</b>	31.73	12.66 ( <b>1I</b> )	29.14	11.46 ( <b>1I</b> )
<b>3I</b>	47.77	13.02 ( <b>2I</b> )	45.77	12.65 ( <b>2I</b> )
<b>3II</b>	45.86	11.05 ( <b>2I</b> )	43.49	10.45 ( <b>2I</b> )
<b>3III</b>	45.73	11.10 ( <b>2I</b> ), 13.94 ( <b>2II</b> )	43.01	10.25 ( <b>2I</b> ), 13.66 ( <b>2II</b> )
<b>3IV</b>	42.34	7.58 ( <b>2I</b> )		
<b>3V</b>	41.84		41.30	
<b>3VI</b>	41.23	9.69 ( <b>2II</b> )	37.74	8.88 ( <b>2II</b> )
<b>4I</b>	58.65	10.81 ( <b>3I</b> )	56.74	10.76 ( <b>3I</b> )
<b>4II</b>	57.92	10.07 ( <b>3I</b> ), 11.98 ( <b>3II</b> )	55.51	9.62 ( <b>3I</b> ), 11.81 ( <b>3II</b> )
<b>4III</b>	57.38	9.69 ( <b>3I</b> ), 11.56 ( <b>3III</b> )	54.76	9.12 ( <b>3I</b> ), 11.51 ( <b>3III</b> )
<b>4IV</b>	54.51	12.44 ( <b>3IV</b> )		
<b>4V</b>	54.44	12.63 ( <b>3V</b> )	53.75	12.38 ( <b>3V</b> )
<b>4VI</b>	54.27		52.73	
<b>4VII</b>	56.71	11.12 ( <b>3II</b> )	53.25	10.21 ( <b>3II</b> )
<b>4VIII</b>	53.37	11.57 ( <b>3IV</b> )		
<b>4IX</b>	56.04	10.46 ( <b>3III</b> )	52.55	9.70 ( <b>3III</b> )
<b>4X</b>	54.46	8.73 ( <b>3III</b> )	50.97	8.24 ( <b>3III</b> )
<b>5I</b>	67.34	8.76 ( <b>4I</b> ), 9.89 ( <b>4III</b> )	64.92	8.29 ( <b>4I</b> ), 9.91 ( <b>4III</b> )
<b>5II</b>	68.04	9.22 ( <b>4I</b> ), 10.04 ( <b>4II</b> )	65.78	9.03 ( <b>4I</b> ), 10.00 ( <b>4II</b> )
<b>5III</b>	65.20	6.53 ( <b>4I</b> ), 10.66 ( <b>4IV</b> )	62.92	6.09 ( <b>4I</b> )
<b>5IV</b>	64.06	9.73 ( <b>4V</b> )	62.56	8.99 ( <b>4V</b> )
<b>5V</b>			62.68	9.11 ( <b>4V</b> )
<b>5VI</b>	65.86	11.59 ( <b>4VI</b> )	64.20	11.37 ( <b>4VI</b> )
<b>5VII</b>	68.18	10.51 ( <b>4II</b> ), 11.37 ( <b>4VII</b> )	64.80	9.70 ( <b>4II</b> ), 11.28 ( <b>4VII</b> )
<b>5VIII</b>	65.18	10.87 ( <b>4VI</b> ), 7.85 ( <b>4III</b> ), 11.27 ( <b>4X</b> )		
<b>5IX</b>	66.26	8.99 ( <b>4III</b> )	63.26	8.59 ( <b>4III</b> )

<sup>a</sup> With BSSE and ZPVE corrections. <sup>b</sup> Notations in parentheses denoting the isomers of  $\text{NH}_4^+(\text{H}_2\text{O})_{n-1}$ .

**TABLE 4: Geometric Parameters of  $\text{NH}_4^+$  and  $\text{NH}_4^+(\text{H}_2\text{O})^a$** 

structures	B3LYP/6-31+G*	MP2/6-31+G*
$\text{NH}_4^+$	$d(\text{NH}) = 1.0293$ , $\angle\text{HNH} = 109.47$	$d(\text{NH}) = 1.0287$ , $\angle\text{HNH} = 109.47$
<b>1I</b>	$d(\text{NH}) = 1.0625$ , $1.0264$ ; $D(\text{NO}) = 2.7284$ ; $\angle\text{HNH} = 109.99$ , $109.87$ , $109.97$ ; $109.09$ , $109.06$ , $108.83$ ; $\angle\text{NHO} = 179.64$	$d(\text{NH}) = 1.0529$ , $1.0261$ ; $D(\text{NO}) = 2.7660$ ; $\angle\text{HNH} = 109.95$ , $109.86$ , $109.92$ ; $109.07$ , $109.15$ , $108.87$ ; $\angle\text{NHO} = 179.75$

<sup>a</sup> The bond lengths are in unit of angstroms and angles in degrees.

**TABLE 5: Geometric Parameters of  $\text{NH}_4^+(\text{H}_2\text{O})_2^a$** 

structures	B3LYP/6-31+G*	MP2/6-31+G*
<b>2I</b>	$d(\text{NH}) = 1.050$ , $1.025$ ; $D(\text{NO}) = 2.785$ , $2.784$ ; $\angle\text{HNH} = 110.57$ ; $\angle\text{NHO} = 179.01$ , $179.02$	$d(\text{NH}) = 1.043$ , $1.025$ ; $D(\text{NO}) = 2.814$ ; $\angle\text{HNH} = 110.28$ ; $\angle\text{NHO} = 179.62$
<b>2II</b>	$d(\text{NH}) = 1.082$ , $1.025$ ; $D(\text{NO}) = 2.646$ ; $D(\text{OO}) = 2.705$ ; $\angle\text{NHO} = 178.21$ ; $\angle\text{OHO} = 173.47$	$d(\text{NH}) = 1.066$ , $1.024$ ; $D(\text{NO}) = 2.686$ ; $D(\text{OO}) = 2.746$ ; $\angle\text{NHO} = 177.91$ ; $\angle\text{OHO} = 173.79$

<sup>a</sup> The bond lengths are in unit of angstroms and angles in degrees.

slightly smaller than those of (**2I** +  $\text{H}_2\text{O}$  → **3I**), (**2I** +  $\text{H}_2\text{O}$  → **3II**), and (**2I** +  $\text{H}_2\text{O}$  → **3III**). This property reflects that both the charge delocalization of the ion core and the HB anticooperativity are reinforced by the additional N–H···O formation. Other than this, the general features of these three isomers closely resemble those of **3I**, **3II**, and **3III**.

Isomers **4IV**, **4V**, and **4VI** are similar in energies but are ~4 kcal/mol less stable than **4I**, according to B3LYP/6-31+G\*. The calculation for the ring-shaped isomer **4IV** collapsed when MP2/6-31+G\* was used. Similar to **3V**, isomer **4V** contains a cyclic water trimer but with a complete solvation shell. Owing to the distortion of the hydrogen bonds in the ring, it is considerably higher in energy than **4I**. For isomer **4VI**, the intermolecular interaction is complicated by the presence of roughly three independent units: a water monomer, a water trimer, and an ammonium ion core. A single O–H···O hydrogen bond bridges the water monomer and the trimer, which are linked to the

ammonium ion by one and two N–H···O hydrogen bonds, respectively.

Two channels are available for the fourth  $\text{H}_2\text{O}$  to approach isomer **3II**. This approach can proceed through either linking to the f-NH of  $\text{NH}_4^+$  or the 2° $\text{H}_2\text{O}$  of **3II**. The former leads to the formation of isomer **4II** and the latter to that of **4VII**. Energetics calculations of these two species reveal that the 3° $\text{H}_2\text{O}$  in **4VII** maintains a fairly strong bonding with the 2° $\text{H}_2\text{O}$  molecule; hence, the hydration energy [11.12 (10.21) kcal/mol] of (**3II** +  $\text{H}_2\text{O}$  → **4VII**) is comparable to that [11.98 (11.81) kcal/mol] of (**3II** +  $\text{H}_2\text{O}$  → **4II**).

Upon attaching one more  $\text{H}_2\text{O}$  to **3III**, three isomers (**4III**, **4IX**, and **4X**) can be produced, and their geometries depend on how hydrogen bonds are formed. The species **4III**, which is considerably lower in energy than the other two, has been previously observed by means of vibrational predissociation spectroscopy in a supersonic jet.<sup>6b</sup> The symmetric chainlike

**TABLE 6: Geometric Parameters of  $\text{NH}_4^+(\text{H}_2\text{O})_3^a$** 

structures	B3LYP/6-31+G*	MP2/6-31+G*
<b>3I</b>	$d(\text{NH}_{1,2,3}) = 1.043$ , $d(\text{NH}) = 1.023$ ; $D(\text{NO}) = 2.832$ ; $\angle\text{NHO} = 179.25, 179.23, 179.23$	$d(\text{NH}_{1,2,3}) = 1.038$ , $d(\text{NH}) = 1.023$ ; $D(\text{NO}) = 2.855$ ; $\angle\text{NHO} = 179.27, 179.26, 179.32$
<b>3II</b>	$d(\text{NH}_{1,2}) = 1.052$ , $d(\text{NH}) = 1.023$ ; $D(\text{NO}_{1,2}) = 2.732$ ; $D(\text{O}_1\text{O}_3) = 2.861$ , $D(\text{O}_2\text{O}_3) = 2.862$ ; $\angle\text{NHO}_1 = 162.08$ , $\angle\text{NHO}_2 = 162.06$ ; $\angle\text{O}_1\text{HO}_3 = 159.83$ , $\angle\text{O}_2\text{HO}_3 = 159.85$ ; $\angle\text{H}_1\text{NH}_2 = 105.90$	$d(\text{NH}_{1,2}) = 1.045$ , $d(\text{NH}) = 1.023$ ; $D(\text{NO}_{1,2}) = 2.757$ ; $D(\text{O}_1\text{O}_3) = 2.890$ , $D(\text{O}_2\text{O}_3) = 2.899$ ; $\angle\text{NHO}_1 = 161.04$ , $\angle\text{NHO}_2 = 161.05$ ; $\angle\text{O}_1\text{HO}_3 = 161.07$ , $\angle\text{O}_2\text{HO}_3 = 161.06$ ; $\angle\text{H}_1\text{NH}_2 = 105.97$
<b>3III</b>	$d(\text{NH}_1) = 1.063$ , $d(\text{NH}_2) = 1.046$ , $d(\text{NH}) = 1.024$ ; $D(\text{NO}_1) = 2.707$ , $D(\text{NO}_2) = 2.805$ ; $D(\text{O}_1\text{O}_2) = 2.733$ ; $\angle\text{NH}_1\text{O}_1 = 178.01$ , $\angle\text{NH}_2\text{O}_2 = 178.70$ ; $\angle\text{O}_1\text{HO}_3 = 174.26$ ; $\angle\text{H}_1\text{NH}_2 = 110.72$	$d(\text{NH}_1) = 1.053$ , $d(\text{NH}_2) = 1.041$ , $d(\text{NH}) = 1.024$ ; $D(\text{NO}_1) = 2.739$ , $D(\text{NO}_2) = 2.830$ ; $D(\text{O}_1\text{O}_2) = 2.769$ ; $\angle\text{NH}_1\text{O}_1 = 177.66$ , $\angle\text{NH}_2\text{O}_2 = 179.06$ ; $\angle\text{O}_1\text{HO}_3 = 174.46$ ; $\angle\text{H}_1\text{NH}_2 = 110.68$
<b>3IV</b>	$d(\text{NH}_1) = 1.059$ , $d(\text{NH}_2) = 1.040$ , $d(\text{NH}) = 1.024$ ; $D(\text{NO}_1) = 2.670$ , $D(\text{NO}_2) = 2.892$ ; $D(\text{O}_1\text{O}_3) = 2.754$ , $D(\text{O}_2\text{O}_3) = 2.915$ ; $\angle\text{NH}_1\text{O}_1 = 160.13$ , $\angle\text{NH}_2\text{O}_2 = 162.24$ ; $\angle\text{O}_1\text{HO}_3 = 134.74$ , $\angle\text{O}_3\text{HO}_2 = 134.86$ ; $\angle\text{H}_1\text{NH}_2 = 107.20$	
<b>3V</b>	$d(\text{NH}_1) = 1.037$ , $d(\text{NH}_2) = 1.037$ , $d(\text{NH}_3) = 1.036$ , $d(\text{NH}) = 1.022$ ; $D(\text{NO}_1) = 2.772$ , $D(\text{NO}_2) = 2.774$ , $D(\text{NO}_3) = 2.775$ ; $D(\text{O}_1\text{O}_2) = 2.876$ , $D(\text{O}_2\text{O}_3) = 2.871$ , $D(\text{O}_3\text{O}_1) = 2.868$ ; $\angle\text{NH}_1\text{O}_1 = 134.72$ , $\angle\text{NH}_2\text{O}_2 = 134.32$ , $\angle\text{NH}_3\text{O}_3 = 133.20$ ; $\angle\text{O}_2\text{HO}_2 = 124.89$ , $\angle\text{O}_2\text{HO}_3 = 125.37$ , $\angle\text{O}_3\text{HO}_1 = 125.32$ ; $\angle\text{H}_1\text{NH}_2 = 105.73$ , $\angle\text{H}_2\text{NH}_3 = 105.84$ , $\angle\text{H}_3\text{NH}_1 = 105.79$	$d(\text{NH}_1) = 1.034$ , $d(\text{NH}_2) = 1.034$ , $d(\text{NH}_3) = 1.034$ , $d(\text{NH}) = 1.023$ ; $D(\text{NO}_1) = 2.788$ , $D(\text{NO}_2) = 2.789$ , $D(\text{NO}_3) = 2.790$ ; $D(\text{O}_1\text{O}_2) = 2.870$ , $D(\text{O}_2\text{O}_3) = 2.875$ , $D(\text{O}_3\text{O}_1) = 2.871$ ; $\angle\text{NH}_1\text{O}_1 = 133.32$ , $\angle\text{NH}_2\text{O}_2 = 133.41$ , $\angle\text{NH}_3\text{O}_3 = 133.36$ ; $\angle\text{O}_1\text{HO}_2 = 124.59$ , $\angle\text{O}_2\text{HO}_3 = 124.61$ , $\angle\text{O}_3\text{HO}_1 = 124.41$ ; $\angle\text{H}_1\text{NH}_2 = 106.23$ , $\angle\text{H}_2\text{NH}_3 = 106.24$ , $\angle\text{H}_3\text{NH}_1 = 106.23$
<b>3VI</b>	$d(\text{NH}_1) = 1.095$ , $d(\text{NH}) = 1.025$ ; $D(\text{NO}_1) = 2.612$ ; $D(\text{O}_1\text{O}_2) = 2.634$ , $D(\text{O}_2\text{O}_3) = 2.760$ ; $\angle\text{NH}_1\text{O}_1 = 175.02$ ; $\angle\text{O}_1\text{HO}_2 = 170.99$ , $\angle\text{O}_2\text{HO}_3 = 178.35$	$d(\text{NH}_1) = 1.072$ , $d(\text{NH}) = 1.025$ ; $D(\text{NO}_1) = 2.656$ ; $D(\text{O}_1\text{O}_2) = 2.679$ , $D(\text{O}_2\text{O}_3) = 2.797$ ; $\angle\text{NH}_1\text{O}_1 = 175.18$ ; $\angle\text{O}_1\text{HO}_2 = 169.65$ , $\angle\text{O}_2\text{HO}_3 = 179.43$

<sup>a</sup> The bond lengths are in unit of angstroms and angles in degrees. The numbering of the H atoms on  $\text{NH}_4^+$  follows that of  $\text{H}_2\text{O}$  hydrogen bonded to them.

isomer **4IX**, with the ion core situated in the middle, is more stable than its analog, **4X**, by 1.58 (1.58) kcal/mol. In **4X**, a  $3^\circ\text{H}_2\text{O}$  can also be found. Although this species is the second least stable isomer of all  $\text{NH}_4^+(\text{H}_2\text{O})_4$  presently considered, it maintains a relatively high bonding energy of 8.40 (8.24) kcal/mol for the  $3^\circ\text{H}_2\text{O}$  molecule.

Isomer **4VIII** is the highest in energy of all the species illustrated in Figure 4. This isomer, similar to **3IV** and **4IV** in that it contains an  $\text{AA}-1^\circ\text{H}_2\text{O}$ , was not favored by the MP2/6-31+G\* calculations. This occurs because the approach of the fourth  $\text{H}_2\text{O}$  to **3IV** can effectively open the ring, producing isomers **4IX** and **4X**. While isomer **4VIII** has the same number of  $\text{N}-\text{H}\cdots\text{O}$  and  $\text{O}-\text{H}\cdots\text{O}$  hydrogen bonds as **4VII**, the difference in arrangement of the water molecules results in a large deviation in stability between them.

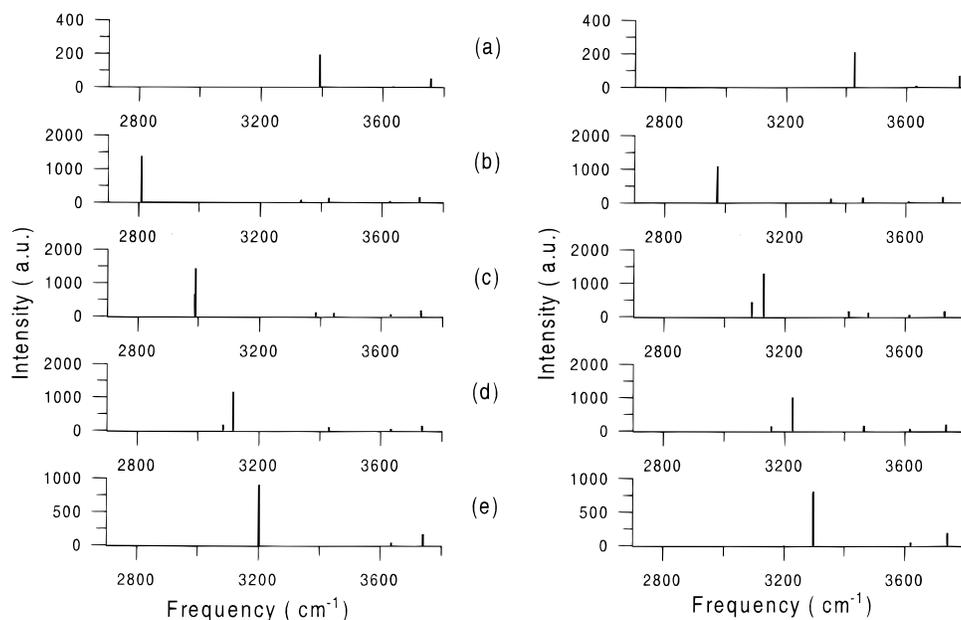
**A.5.  $\text{NH}_4^+(\text{H}_2\text{O})_5$ .** Figure 5 illustrates the isomeric structures of  $\text{NH}_4^+(\text{H}_2\text{O})_5$  predicted by the present calculations. Isomers **5I**–**5VI** have a complete solvation shell whereas the solvation in **5VII**–**5IX** is incomplete with one dangling NH bond exposed. As previously noted, the  $\text{O}-\text{H}\cdots\text{O}$  hydrogen bonds which produce the outer shell are no longer coplanar with the  $\text{H}_2\text{O}$  molecules in these isomers. The formation of these hydrogen bonds is, thus, predominantly governed by the interaction of  $\text{H}_2\text{O}$  dipoles with the oxygen electron lone pairs of the solvent molecules. Formed by attaching the fifth  $\text{H}_2\text{O}$  to **4I**, isomers **5I**, **5II**, and **5III** have been previously identified by vibrational predissociation spectroscopy of  $\text{NH}_4^+(\text{H}_2\text{O})_5$  in a supersonic jet.<sup>6</sup> From systematic temperature dependence measurements, isomer **5II** is found to be the most abundant form of the clusters at low temperatures. The present calculations predict that the ring-closed isomer with an  $\text{AA}-2^\circ\text{H}_2\text{O}$  is 0.70 (0.86) kcal/mol lower in energy than the ring-opened one, consistent with the observations. The finding that isomer **5I** is less stable than **5II**, which is reversed in stability compared to its analogs (**3I**, **3II**) and (**4I**, **4II**), is interesting.

The intriguing ring closing process, **5I**  $\rightarrow$  **5II**, is expected to occur rapidly, since it requires only bond rotation to establish the  $\text{O}-\text{H}\cdots\text{O}$  connection. This process, however, is not favored

by entropy effects at higher cluster temperatures. To better understand the isomeric transition, we calculated the transition state of **4I**  $\rightarrow$  **4II** at the B3LYP/6-31G\* level. This transition, instead of **5I**  $\rightarrow$  **5II**, was chosen to minimize the computational time but still obtain meaningful physical insight into the ring-closing process. It is found that the isomeric transition **4I**  $\rightarrow$  **4II** has a barrier height of less than 1 kcal/mol. The transition state has a geometry similar to that of the ring-open form, but with one of the two OH bonds of the  $2^\circ\text{H}_2\text{O}$  pointing toward the electron lone pairs of  $1^\circ\text{H}_2\text{O}$  after bond reorientation. In this exothermic process, the instability arising due to hydrogen bond distortion in **4II** is compensated by the interaction energy increase due to the additional  $\text{O}-\text{H}\cdots\text{O}$  hydrogen bond formation. The energy involved in this ring formation smoothly decreases from 11.05 (10.45) kcal/mol of (**2I** +  $\text{H}_2\text{O}$   $\rightarrow$  **3II**) to 9.22 (9.03) kcal/mol of (**4I** +  $\text{H}_2\text{O}$   $\rightarrow$  **5II**), indicating that the hydrogen bonding of  $\text{H}_2\text{O}$  with  $\text{NH}_4^+$  not only can alter the strength of the individual  $\text{N}-\text{H}\cdots\text{O}$  bonds but also can influence the interaction between the  $1^\circ\text{H}_2\text{O}$  and  $2^\circ\text{H}_2\text{O}$  molecules.

The other ring-shaped isomer **5III**, which contains an  $\text{AA}-1^\circ\text{H}_2\text{O}$ , is not energetically favored and has an interaction energy about 2 kcal/mol less than that of **5I**. The stepwise hydration energy of (**4IV** +  $\text{H}_2\text{O}$   $\rightarrow$  **5III**), which originates from the formation of the fourth  $\text{N}-\text{H}\cdots\text{O}$  hydrogen bond, is  $-\Delta E_{n-1,n} = 10.66$  kcal/mol. The value is smaller than 10.81 (10.76) kcal/mol of (**3I** +  $\text{H}_2\text{O}$   $\rightarrow$  **4I**), but is significantly larger than 10.04 (10.00) kcal/mol of (**4II** +  $\text{H}_2\text{O}$   $\rightarrow$  **5II**), meaning that the  $\text{N}-\text{H}\cdots\text{O}$  bonding is sensitive to how the  $\text{H}_2\text{O}$  molecules are arranged in the first and the second solvation shells.

The ion core charge delocalization effect intensifies as the solvation number increases from  $n = 1$  to  $n = 5$ . This has been evident from earlier calculations that the individual  $\text{N}-\text{H}\cdots\text{O}$  hydrogen bond gradually weakens as water molecules successively attach to the ion core. Such a charge delocalization creates a unique situation that the bonding between  $\text{NH}_4^+$  and  $1^\circ\text{H}_2\text{O}$  is comparable in strength to that between solvent water molecules at  $n = 4$ . Owing to this effect, isomer **5VII** having a dangling NH bond can be one of the lowest energy structures



**Figure 6.** Vibrational stick spectra of (a) free  $\text{NH}_4^+$  and free  $\text{H}_2\text{O}$ , and the lowest energy isomers of (b)  $\text{NH}_4^+(\text{H}_2\text{O})$ , (c)  $\text{NH}_4^+(\text{H}_2\text{O})_2$ , (d)  $\text{NH}_4^+(\text{H}_2\text{O})_3$ , and (e)  $\text{NH}_4^+(\text{H}_2\text{O})_4$  predicted by B3LYP/6-31+G\* (left) and MP2/6-31+G\* (right).

of  $\text{NH}_4^+(\text{H}_2\text{O})_5$ . Interestingly, this isomer contains three types of water molecules: A– $\text{H}_2\text{O}$  (W3 and W5), AD– $\text{H}_2\text{O}$  (W1 and W2), and AAD– $\text{H}_2\text{O}$  (W4); it can serve as a model molecule for understanding how the frequency red shifts of free-OH stretching vibrations depend on the  $\text{H}_2\text{O}$  coordination. It is also noteworthy that isomer **5VII** is most probably produced by the hydration of **4II** or **4VII**, but not with **4I** as the precursor. This kinetics consideration has been previously employed to explain why this species was not observed in a supersonic expansion,<sup>6b</sup> although it is one of the lowest energy isomers. The similar competition of solvation between 1° $\text{H}_2\text{O}$  and 2° $\text{H}_2\text{O}$  also exists when isomer **5VIII** is formed.

The predominant isomeric forms of  $\text{NH}_4^+(\text{H}_2\text{O})_5$  depicted in Figure 5 have a structure analogous to that of  $\text{NH}_4^+(\text{H}_2\text{O})_{3,4}$ . They can be produced either by covering the dangling N–H bond with  $\text{H}_2\text{O}$  or by attacking the AA– $\text{H}_2\text{O}$  molecule of its analogs at  $n = 3$  and 4. There are other ways of growing larger water clusters as well. Isomers **5IV** and **5V**, for example, are formed by hydrogen bonding  $\text{H}_2\text{O}$  to the water monomer and to the cyclic water trimer of **4V**, respectively. These two species, however, are relatively unstable. The MP2/6-31+G\* calculations predict that they are comparable in energy,  $\sim 3$  kcal/mol higher than that of **5II**, but B3LYP/6-31+G\* collapsed during the structural optimization of **5V**. Interestingly, the isomers (**3IV**, **4IV**, **4VIII**, **5VIII**) containing an AA–1° $\text{H}_2\text{O}$  molecule and free NH bonds are never found by MP2/6-31+G\*.

This work also considered isomer **5IX**, which owns a five-membered ring. The five-membered ring structure is somewhat similar to that found in the neutral water pentamer.<sup>35</sup> While this species is  $\sim 1$  kcal/mol more stable than **5III**, evidence for it was not found in the measurements.<sup>6b</sup>

**B. Vibrational Spectra.** Vibrational predissociation spectra of  $\text{NH}_4^+(\text{H}_2\text{O})_n$  revealed that more than one stable isomer could be synthesized by a free-jet expansion at  $n \geq 4$ .<sup>6</sup> Particularly at  $n = 5$ , a dramatic isomeric transition of **5I**  $\rightarrow$  **5II** was observed at a temperature near 150 K.<sup>6b,c</sup> The observations strongly suggest that  $\text{NH}_4^+(\text{H}_2\text{O})_5$  can serve as a benchmark system for studying hydrogen bond rearrangement dynamics in cluster ions.<sup>36</sup> To assist the interpretation of the experimentally observed spectra and to perceive the spectral changes as a function of

cluster sizes and structures, the predicted vibrational features in the NH and OH stretching regions are plotted in Figure 6 for  $\text{NH}_4^+(\text{H}_2\text{O})_{1-4}$  and are listed in Table 7 for  $\text{NH}_4^+(\text{H}_2\text{O})_5$ . Since in these clusters, the structural isomerization is most dramatic in  $\text{NH}_4^+(\text{H}_2\text{O})_5$ ,<sup>6</sup> the following discussion concerning the spectral features and their isomeric dependence will primarily focus on the clusters with  $n = 5$ . A similar rationale can be applied in discussing  $\text{NH}_4^+(\text{H}_2\text{O})_{1-4}$  and larger clusters when necessary.

**B.1.  $\text{NH}_4^+(\text{H}_2\text{O})_{1-4}$ .** Figure 6 illustrates the calculated spectra of free  $\text{H}_2\text{O}$ ,  $\text{NH}_4^+$ , and  $\text{NH}_4^+(\text{H}_2\text{O})_n$  at  $n = 1-4$  where all the water molecules are hydrogen-bonded to the ion core. Both the MP2/6-31+G\* and B3LYP/6-31+G\* calculations indicate that the frequency shift of the b-NH stretching is substantially larger than that of the f-NH. The red shifts, however, decrease smoothly with  $n$ , an indication of N–H $\cdots$ O bond weakening as  $n$  increases. Notably, such a decrease in red shifts correlates well with the previously discussed changes in b-NH bond lengths, N–H $\cdots$ O distances, and the N–H $\cdots$ O hydrogen bonding energies at  $n = 1-4$ . All these changes lead to the same conclusion that, as the number of N–H $\cdots$ O bonds increases, both the charge delocalization and the HB anticooperative effect intensify.

The frequency shifting of f-NH and f-OH stretches lies in the same direction of b-NHs as  $n$  increases, although they are much smaller in magnitude. For f-OH, the resonances are located at nearly the same frequencies, i.e.  $\sim 3630$  and  $\sim 3730$   $\text{cm}^{-1}$  for the symmetric and asymmetric stretches of A–1° $\text{H}_2\text{O}$  in isomers **1I**–**4I**, respectively. Shown in Figure 6 is the smooth frequency increase of the symmetric stretching from 3627 (3610)  $\text{cm}^{-1}$  of **1I** to 3636 (3619)  $\text{cm}^{-1}$  of **4I**. The frequencies of the asymmetric stretching also increase with a similar measure, from 3723 (3721)  $\text{cm}^{-1}$  to 3739 (3740)  $\text{cm}^{-1}$  for isomers **1I**–**4I**. These frequencies essentially shift toward 3635.7 (3632.7) and 3756.9 (3774.1)  $\text{cm}^{-1}$  of free  $\text{H}_2\text{O}$  at a large  $n$ .<sup>32</sup> This blue shifting derives naturally from charge delocalization of the ion core upon solvation.

**B.2.  $\text{NH}_4^+(\text{H}_2\text{O})_5$ .** Upon formation of the second solvation shell, the  $\text{NH}_4^+(\text{H}_2\text{O})_5$  spectra in the OH stretching region dramatically change. New features emerge at 3300–3600  $\text{cm}^{-1}$

**TABLE 7: Frequencies ( $\text{cm}^{-1}$ ) and Absorption Intensities ( $\text{km/mol}$ ) of NH and OH Stretches of  $\text{NH}_4^+(\text{H}_2\text{O})_5^a$** 

species	B3LYP/6-31+G*		MP2/6-31+G*		assignments	
	scaled frequency	intensity	scaled frequency	intensity		
<b>5I</b>	3064.9	844.6	3158.7	438.7	bonded-NH (1)	
	3179.3	441.1	3256.5	671.2	bonded-NH (2,3,4)	
	3225.4	810.0	3316.7	729.2	bonded-NH (4,2)	
	3226.9	804.0	3317.6	733.0	bonded-NH (3,2)	
	3412.4	668.8	3464.6	542.2	bonded-OH (1)	
	3637.1	37.9	3620.1	35.9	symmetric free-OH (4)	
	3637.1	38.0	3620.5	37.5	symmetric free-OH (3)	
	3637.5	10.8	3620.7	20.1	symmetric free-OH (2)	
	3637.9	19.5	3623.8	24.5	symmetric free-OH (5)	
	3714.1	108.4	3710.7	148.1	two-coordinated free-OH (1)	
	3741.2	105.1	3742.3	131.2	asymmetric free-OH (3)	
	3741.3	110.7	3742.8	124.1	asymmetric free-OH (4)	
	3741.7	136.1	3743.2	151.2	asymmetric free-OH (2)	
	3744.5	117.4	3748.6	134.2	asymmetric free-OH (5)	
	<b>5II</b>	3141.2	113.9	3200.1	36.5	bonded-NH (1,2)
		3170.7	529.6	3271.8	470.3	bonded-NH (1,2)
		3213.9	1064.9	3306.4	1002.8	bonded-NH (3,4)
3228.2		822.9	3318.2	745.4	bonded-NH (3,4)	
3507.6		250.6	3531.3	175.4	bonded-OH (1,2)	
3528.7		483.8	3545.9	438.8	bonded-OH (1,2)	
3618.5		14.5	3600.2	3.6	symmetric free-OH (5)	
3637.4		38.7	3620.6	42.6	symmetric free-OH (3)	
3637.7		16.5	3620.7	19.1	symmetric free-OH (4)	
3717.3		127.8	3715.5	144.7	asymmetric free-OH (5)	
3718.9		254.8	3717.6	318.1	two-coordinated free-OH (1,2)	
3722.2		41.4	3722.3	67.7	two-coordinated free-OH (1,2)	
3741.4		158.3	3742.6	178.8	asymmetric free-OH (3)	
3741.5		83.4	3742.6	99.0	asymmetric free-OH (4)	
<b>5III</b>		2949.7	986.8	3099.9	629.7	bonded-NH (1)
		3165.1	378.5	3239.5	450.2	bonded-NH (3,4)
		3208.6	913.1	3301.6	823.2	bonded-NH (3,4)
	3288.2	390.1	3355.8	453.3	bonded-NH (2)	
	3371.3	744.8	3453.4	541.1	bonded-OH (1)	
	3555.6	251.2	3574.1	201.4	bonded-OH (5)	
	3614.4	21.7	3597.2	6.7	symmetric free-OH (2)	
	3634.9	37.5	3617.8	42.2	symmetric free-OH (4)	
	3635.4	23.0	3618.3	25.2	symmetric free-OH (3)	
	3712.4	122.8	3710.9	140.6	asymmetric free-OH (2)	
	3715.8	113.9	3717.7	164.3	two-coordinated free-OH (1)	
	3722.0	164.5	3730.2	205.3	two-coordinated free-OH (5)	
	3737.6	77.1	3738.6	59.4	asymmetric free-OH (3)	
	3738.2	168.6	3739.1	223.0	asymmetric free-OH (4)	
	<b>5IV</b>	2952.0	1364.9	3084.7	955.9	bonded-NH (4)
		3274.1	438.1	3318.6	521.1	bonded-NH (1,3)
		3325.0	167.5	3389.6	184.2	bonded-NH (1,2,3)
3341.0		145.0	3391.6	174.4	bonded-NH (1,2,3)	
3379.5		731.3	3441.7	588.9	bonded-OH (4)	
3501.5		28.0	3520.7	34.1	bonded-OH (1,2,3)	
3532.0		256.1	3549.8	168.4	bonded-OH (1,2,3)	
3536.5		234.4	3550.0	167.1	bonded-OH (1,2,3)	
3637.8		25.6	3624.4	27.4	symmetric free-OH (5)	
3708.2		202.1	3703.7	232.1	three-coordinated free-OH (1,2,3)	
3708.7		209.1	3703.9	230.7	three-coordinated free-OH (1,2,3)	
3710.4		22.2	3704.3	52.1	three-coordinated free-OH (1,2,3)	
3711.9		123.1	3706.6	170.3	two-coordinated free-OH (4)	
<b>5V</b>		3743.6	120.1	3748.4	137.2	asymmetric free-OH (5)
				3202.7	77.7	bonded-NH (4)
				3287.4	871.2	bonded-NH (1)
				3327.8	516.1	bonded-NH (3)
			3401.6	182.6	bonded-NH (2)	
			3431.6	707.3	bonded-OH (1) <sup>b</sup>	
			3500.0	58.0	bonded-OH (2)	
			3539.4	175.1	bonded-OH (3)	
			3618.0	36.0	symmetric free-OH (4)	
			3625.9	58.2	symmetric free-OH (5)	
			3639.5	218.1	bonded-OH (1) <sup>b</sup>	
			3702.7	182.2	three-coordinated free-OH (2)	
			3707.2	158.1	three-coordinated free-OH (3)	
			3737.1	147.7	asymmetric free-OH (4)	
			3749.9	138.5	asymmetric free-OH (5)	

TABLE 7: (Continued)

species	B3LYP/6-31+G*		MP2/6-31+G*		assignments	
	scaled frequency	intensity	scaled frequency	intensity		
<b>5VI</b>	3066.8	568.8	3158.4	305.8	bonded-NH (3)	
	3160.1	746.9	3247.8	711.8	bonded-NH (4)	
	3255.3	509.2	3323.8	586.9	bonded-NH (1)	
	3330.0	205.2	3389.2	219.5	bonded-NH (2)	
	3451.3	118.9	3482.7	103.3	bonded-OH (5)	
	3471.9	416.5	3503.7	309.1	bonded-OH (1)	
	3508.8	371.3	3534.9	277.8	bonded-OH (3)	
	3540.4	174.6	3549.5	137.2	bonded-OH (2)	
	3635.6	32.4	3618.3	35.3	symmetric free-OH (4)	
	3698.3	155.5	3693.1	195.4	three-coordinated free-OH (5)	
	3702.3	186.8	3696.0	198.8	three-coordinated free-OH (1)	
	3705.4	92.1	3699.5	147.4	three-coordinated free-OH (2)	
	3727.6	144.5	3725.0	184.5	two-coordinated free-OH (3)	
	3737.3	131.6	3737.8	146.8	asymmetric free-OH (4)	
	<b>5VII</b>	3045.3	661.0	3136.9	414.3	bonded-NH (1,2)
		3052.7	697.8	3169.3	573.5	bonded-NH (1,2)
		3165.4	1051.0	3258.1	1101.5	bonded-NH (3)
3339.4		1157.1	3395.5	976.9	bonded-OH (4)	
3403.7		493.6	3447.7	388.2	bonded-OH (1,2)	
3441.5		155.6	3476.5	188.7	free-NH	
3452.7		350.1	3489.5	282.3	bonded-OH (1,2)	
3636.8		31.5	3619.8	35.0	symmetric free-OH (3)	
3641.8		28.0	3626.3	31.4	symmetric free-OH (5)	
3684.7		104.4	3678.5	140.0	three-coordinated free-OH (1)	
3719.7		234.1	3714.6	294.9	two-coordinated free-OH (1,2)	
3722.2		22.0	3718.0	36.3	two-coordinated free-OH (1,2)	
3739.4		128.3	3739.8	146.2	asymmetric free-OH (3)	
3747.0		130.1	3749.2	145.6	asymmetric free-OH (5)	
<b>5VIII</b>		2851.0	1155.6			bonded-NH (1)
		3110.0	308.1			bonded-NH (2)
		3148.0	1233.1			bonded-NH (3)
	3309.4	929.5			bonded-OH (2)	
	3331.0	636.4			bonded-OH (1)	
	3439.7	106.0			free-NH	
	3504.8	334.1			bonded-OH (4)	
	3634.8	41.6			symmetric free-OH (3)	
	3635.3	23.0			symmetric free-OH (5)	
	3685.9	103.9			three-coordinated free-OH (2)	
	3712.5	115.2			two-coordinated free-OH (1)	
	3713.7	145.5			two-coordinated free-OH (4)	
	3737.3	122.4			asymmetric free-OH (3)	
	3739.2	135.2			asymmetric free-OH (5)	
	<b>5IX</b>	2898.6	1196.3	3076.5	808.4	bonded-NH (1)
		3089.7	601.6	3193.5	532.0	bonded-NH (2)
		3164.6	959.2	3270.2	963.5	bonded-NH (3)
3338.6		848.4	3442.1	665.9	bonded-OH (1)	
3438.8		96.3	3488.6	124.3	free-NH	
3486.3		509.3	3532.8	385.7	bonded-OH (2)	
3533.8		330.5	3570.9	284.2	bonded-OH (4)	
3615.4		17.0	3614.2	4.4	symmetric free-OH (5)	
3636.3		30.6	3635.1	34.1	symmetric free-OH (3)	
3708.1		112.9	3725.3	231.1	two-coordinated free-OH (1)	
3711.9		194.2	3729.0	69.5	two-coordinated free-OH (2)	
3713.6		127.4	3729.1	227.5	asymmetric free-OH (5)	
3718.3		94.3	3741.0	158.1	two-coordinated free-OH (4)	
3739.4		128.6	3756.5	147.2	asymmetric free-OH (3)	

<sup>a</sup> The numbering of the b-NH groups on  $\text{NH}_4^+$  follows that of  $\text{H}_2\text{O}$  attached to them. <sup>b</sup> This  $\text{H}_2\text{O}$  molecule acts as a double proton donor and a double acceptor.

for hydrogen-bonded-OH stretches. Table 7 lists the calculated frequencies of the NH and OH stretches of the  $\text{NH}_4^+(\text{H}_2\text{O})_5$  isomers. Identification of these isomers is possible based upon their characteristic stretching frequencies of f-NH, b-NH, f-OH, and b-OH.

**B.2.1. Free-NH Stretching.** Among all the  $\text{NH}_4^+(\text{H}_2\text{O})_5$  isomers illustrated in Figure 5, only **5VII**, **5VIII**, and **5IX** possess a f-NH bond. The vibrational frequency of this NH stretch is 3442 (3477), 3440 and 3439 (3489)  $\text{cm}^{-1}$  for isomers

**5VII**, **5VIII** and **5IX**, respectively. Since isomer **5VIII** contains an  $\text{AA}-1^\circ\text{H}_2\text{O}$  while the other two have  $\text{AA}-2^\circ\text{H}_2\text{O}$ , the minute differences between these three frequencies indicates that the free NH stretching is quite insensitive to how water molecules are arranged in the first and the second solvation shells.

**B.2.2. Bonded-NH Stretching.** Figure 6e displays the spectrum of isomer **4I** containing a complete hydration shell. The spectrum shows a single asymmetric b-NH stretching absorption,

which is triply degenerate, at 3201 (3296)  $\text{cm}^{-1}$ . Adding the fifth  $\text{H}_2\text{O}$  to this isomer lifts up the degeneracy, giving rise to four distinct absorptions in the spectra. For isomers **5I–5IX**, the frequencies of these symmetry-broken b-NH stretches can be either shifted to the blue or to the red of 3201 (3296)  $\text{cm}^{-1}$ , depending on how hydrogen-bonding nonadditivity operates. Both B3LYP/6-31+G\* and MP2/6-31+G\* predict a similar propensity of frequency shifts for the b-NH stretches, although their absolute frequencies differ.

The  $\text{N–H}\cdots\text{O}_1$  hydrogen bond in isomer **5I** is cooperatively coupled with  $\text{O}_1\text{–H}\cdots\text{O}_5$ . This cooperative coupling causes the b-NH stretching of  $\text{N–H}\cdots\text{O}_1$  to resonate at a frequency about 150  $\text{cm}^{-1}$  lower than others. For the symmetric, ring-shaped isomer **5II**, the perturbations from  $2^\circ\text{H}_2\text{O}$  result in a cooperative motion of b-NH with the b-OH of  $1^\circ\text{H}_2\text{O}$ . This degree of cooperativity, however, is less than that of **5I** because the perturbing  $\text{AA–}2^\circ\text{H}_2\text{O}$  is equally shared by two  $1^\circ\text{H}_2\text{O}$  molecules. It gives rise to an additional 50  $\text{cm}^{-1}$  red shift in these two b-NH stretches, as compared to the other two b-NH bonds without ring formation. In **5III**, the perturbation from  $2^\circ\text{H}_2\text{O}$  is slightly more complicated. In addition to the cooperative motion between  $\text{N–H}\cdots\text{O}_1$  and  $\text{O}_1\text{–H}\cdots\text{O}_5$ , the  $\text{O}_5\text{–H}\cdots\text{O}_2$  hydrogen bond is also coupled in. The stretching frequency of the b-NH linked to the  $1^\circ\text{H}_2\text{O}$  (W1) is, therefore, further red shifted to 2950 (3100)  $\text{cm}^{-1}$ , which can be compared with the corresponding frequency of 3065 (3159)  $\text{cm}^{-1}$  for **5I**. In the same isomer, the  $\text{N–H}\cdots\text{O}_2$  and  $\text{O}_5\text{–H}\cdots\text{O}_2$  hydrogen bonds are anticooperative, thus yielding a stretching frequency of 3288 (3356)  $\text{cm}^{-1}$  for this N–H group. The arguments based upon HB cooperativity and anticooperativity can be similarly applied to account for the frequency shifts of NH stretching of other isomers.

**B.2.3. Free-OH Stretching.** Our previous ab initio calculations<sup>31</sup> demonstrated that the f-OH vibrations of  $\text{H}_2\text{O}$  in water clusters and on ice surfaces depend sensitively on the number of coordination. The f-OH stretching frequencies of 2- and 3-coordinated  $\text{H}_2\text{O}$  can differ up to 30  $\text{cm}^{-1}$ . In Table 7, one finds the f-OH stretching frequencies of **5IV**, **5VI**, **5VII**, and **5VIII**, which possess three types of water molecules:  $\text{A–H}_2\text{O}$ ,  $\text{AD–H}_2\text{O}$  (or two-coordinated  $\text{H}_2\text{O}$ ), and  $\text{AAD–H}_2\text{O}$  (or three-coordinated  $\text{H}_2\text{O}$ ). Their vibrations can be described in terms of symmetric and asymmetric f-OH stretching of  $\text{A–H}_2\text{O}$ , 2-coordinated f-OH stretching of  $\text{AD–H}_2\text{O}$ , and 3-coordinated f-OH stretching of  $\text{AAD–H}_2\text{O}$ . More importantly, they are distinct in frequencies. The present calculations predict that the asymmetric f-OH stretching of  $1^\circ\text{H}_2\text{O}$  (W3) in **5VII** resonates at 3739 (3740)  $\text{cm}^{-1}$ , which is significantly lower than 3747 (3749)  $\text{cm}^{-1}$  of  $3^\circ\text{H}_2\text{O}$  (W5). The similar difference can be found for the symmetric stretches. Note that, aside from  $\text{A–H}_2\text{O}$ , the  $\text{AA–H}_2\text{O}$  in isomers **5II** and **5III** can also display both symmetric and asymmetric stretches. These two vibrational modes, however, have frequencies about 20  $\text{cm}^{-1}$  red shifted from those of  $\text{A–H}_2\text{O}$  because of double hydrogen-bond formation.

The f-OH stretching frequency of 2-coordinated  $\text{H}_2\text{O}$  is lower than that of the asymmetric stretch of  $\text{A–H}_2\text{O}$  by  $\sim 15$   $\text{cm}^{-1}$ . This stretch has been previously found in a variety of neutral and protonated water-containing clusters.<sup>6a,31</sup> Depending on how hydrogen bonding is accomplished in  $\text{NH}_4^+(\text{H}_2\text{O})_5$ , the frequencies can spread over the range of 3712 (3707)–3728 (3725)  $\text{cm}^{-1}$ . As for the f-OH stretching of three-coordinated  $\text{H}_2\text{O}$ , the frequencies of **5VII** and **5VIII** are predicted to be located at 3685 (3679) and 3686  $\text{cm}^{-1}$ , respectively. They can be compared with the similar stretches of **5IV** and **5VI** that are  $\sim 20$   $\text{cm}^{-1}$

higher in frequency because of larger hydrogen bond distortion involved in these clusters. Although **5VII** is one of the lowest in energy, the three-coordinated f-OH stretching of this isomer has not yet been previously identified in experiments.<sup>6b</sup> Notably, the three-coordinated f-OH stretching absorption, typically situated at  $\sim 3685$   $\text{cm}^{-1}$ , is well separated from that of the two-coordinated f-OH. Both of them, furthermore, differ in frequency than the symmetric and asymmetric free-OH stretches of  $\text{A–H}_2\text{O}$  and  $\text{AA–H}_2\text{O}$ . The distinct vibrational pattern suggests that infrared spectroscopy of f-OH stretches can be used as a sensitive probe for the location of the water molecule, either on  $1^\circ$ ,  $2^\circ$ , or  $3^\circ$ , as well as the number of coordination of each water molecule in the clusters.<sup>6a,31</sup>

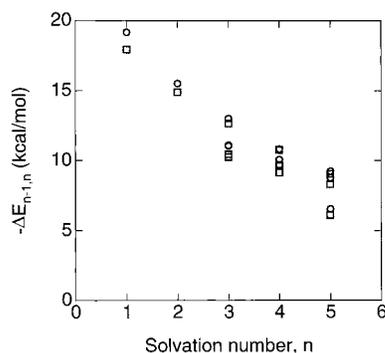
**B.2.4. Bonded-OH Stretching.** Vibrational predissociation spectroscopic measurements<sup>6</sup> establish that isomers **5I** and **5II** are the two most abundant forms of  $\text{NH}_4^+(\text{H}_2\text{O})_5$  synthesized in a free-jet expansion. The ring-open isomer **5I** contains one single bonded-OH whereas the ring-closed **5II** has two; hence, one and two absorptions are expected to be observed in the b-OH stretching region, respectively. Of these two isomers, the frequencies of the latter are higher owing to the anticooperative nature of the interactions between the two  $\text{O–H}\cdots\text{O}$  hydrogen bonds in **5II**. The predicted b-OH stretching frequencies of **5II** are 3508 (3531) and 3529 (3546)  $\text{cm}^{-1}$ , compared to the single frequency of 3412 (3465)  $\text{cm}^{-1}$  for isomer **5I**. Interestingly, the presence of the high-frequency doublet has indeed been confirmed by the vibrational predissociation spectroscopy of isomer **5II**, which displays the symmetric and asymmetric b-OH stretches of the two coupled  $\text{AD–}1^\circ\text{H}_2\text{O}$  molecules at 3551 and 3562  $\text{cm}^{-1}$ , respectively.<sup>6b</sup> It should be noted that the similar b-OH absorptions also exist for isomer **4II**, which contains an identical four-membered ring. The calculated stretching frequencies of them are 3496 (3521) and 3519 (3537)  $\text{cm}^{-1}$ , also lower than 3553  $\text{cm}^{-1}$  observed experimentally.<sup>6b</sup> It is likely that the underestimation of these frequencies in the calculations, particularly in B3LYP/6-31+G\*, is a result of improper choice of the scaling factors which, determined by referring to f-OH stretches, are too small for b-OH stretches. Nevertheless, both the observations and the calculations correspondingly suggest that the absorption bands centering at  $\sim 3550$   $\text{cm}^{-1}$  are the fingerprints of a symmetric four-membered ring involving an  $\text{AA–}2^\circ\text{H}_2\text{O}$  in protonated amine–water clusters.<sup>6c</sup>

In addition to **5II**, isomer **5III** also contains two coupled b-OH stretches. Compared to that of **5I**, the b-OH stretching of  $\text{O}_1\text{–H}\cdots\text{O}_5$  ( $\text{O}_5\text{–H}\cdots\text{O}_2$ ) is lower (higher) in frequency owing to hydrogen bonding nonadditivity. The absorptions of these two stretches are situated at 3371 (3453) and 3556 (3574)  $\text{cm}^{-1}$ , respectively. Notably, this isomer is one of the two possible candidates responsible for the experimentally observed absorption at 3376  $\text{cm}^{-1}$ .<sup>6b</sup> The other candidate is isomer **5VII** which has a 3-coordinated f-OH and three b-OH stretches. Due to the additional hydrogen bond formation between  $\text{AA–}2^\circ\text{H}_2\text{O}$  and  $\text{A–}3^\circ\text{H}_2\text{O}$ , the frequencies of both  $\text{O}_1\text{–H}\cdots\text{O}_4$  and  $\text{O}_2\text{–H}\cdots\text{O}_4$  are  $\sim 100$   $\text{cm}^{-1}$  red shifted from those of **5II**. This bonding also gives rise to the third bonded-OH absorption at 3339 (3396)  $\text{cm}^{-1}$  for the  $2^\circ\text{H}_2\text{O}$  molecule, which now plays a role as an AAD.

Finally, three bonded-OH stretching absorptions can be found in **5IX**. The isomer has a water dimer and a monomer linked by an  $\text{AA–}2^\circ\text{H}_2\text{O}$ . As expected, the b-OH stretching frequency of the  $1^\circ\text{H}_2\text{O}$  (W1) involving the water dimer is lower than that involving the monomeric  $1^\circ\text{H}_2\text{O}$  (W2). The b-OH stretching of the  $2^\circ\text{H}_2\text{O}$  (W4) molecule has the highest frequency, 3534

**TABLE 8: Hydration Energies,  $\Delta H_n$  and  $\Delta G_n$  (kcal/mol), of  $\text{NH}_4^+ + n\text{H}_2\text{O} \rightarrow \text{NH}_4^+(\text{H}_2\text{O})_n$  at 298.15 K**

species	B3LYP/6-31+G*		MP2/6-31+G*		exptl	
	$-\Delta H_n$	$-\Delta G_n$	$-\Delta H_n$	$-\Delta G_n$	$-\Delta H_n^{\circ}$	$-\Delta G_n^{\circ}$
<b>1I</b>	19.77	12.70	18.50	14.68	17.3, <sup>a</sup> 19.9 <sup>b</sup>	11.4, <sup>a</sup> 13.0 <sup>b</sup>
<b>2I</b>	35.67	21.07	33.85	21.04	32.0, <sup>a</sup> 32.3 <sup>b</sup>	19.6, <sup>a</sup> 20.5 <sup>b</sup>
<b>2II</b>	32.96	17.60	30.36	16.55		
<b>3I</b>	48.72	27.06	46.81	26.20	45.4, <sup>a</sup> 44.5 <sup>b</sup>	25.5, <sup>a</sup> 26.4 <sup>b</sup>
<b>3II</b>	48.09	21.32	45.70	20.83		
<b>3III</b>	47.14	24.63	44.42	23.36		
<b>3IV</b>	44.56	18.38				
<b>3V</b>	44.17	17.54	43.73	17.99		
<b>3VI</b>	42.97	19.60	39.32	17.96		
<b>4I</b>	59.44	31.44	57.68	30.44	57.6, <sup>a</sup> 55.3 <sup>b</sup>	29.6, <sup>a</sup> 30.3 <sup>b</sup>
<b>4II</b>	60.05	27.23	57.68	26.31		
<b>4III</b>	58.78	29.12	55.91	28.23		
<b>4IV</b>	56.94	23.41				
<b>4V</b>	57.08	22.63	56.36	24.25		
<b>4VI</b>	57.56	20.63	55.94	20.60		
<b>4VII</b>	59.18	25.64	55.77	19.33		
<b>4VIII</b>	56.29	21.80				
<b>4IX</b>	57.87	27.70	54.40	25.88		
<b>4X</b>	56.33	26.12	52.75	24.14		
<b>5I</b>	68.62	32.07	66.24	31.34	67.3, <sup>a</sup> 65.9 <sup>b</sup>	32.6, <sup>a</sup> 32.9 <sup>b</sup>
<b>5II</b>	70.06	30.43	67.82	30.05		
<b>5III</b>	67.52	27.38	65.11	27.27		
<b>5IV</b>	67.20	24.76	65.67	25.14		
<b>5V</b>			65.43	25.42		
<b>5VI</b>	69.21	25.10	67.42	25.51		
<b>5VII</b>	70.55	30.75	67.23	28.48		
<b>5VIII</b>	68.12	26.21				
<b>5IX</b>	68.97	27.52	65.82	26.53		

<sup>a</sup> Reference 2a. <sup>b</sup> Reference 3.**Figure 7.** Calculated stepwise hydration energies ( $\Delta E_{n-1,n}$ ) of the lowest energy isomers of  $\text{NH}_4^+(\text{H}_2\text{O})_{1-5}$  using B3LYP/6-31+G\* (○) and MP2/6-31+G\* (□).

(3571)  $\text{cm}^{-1}$ , of the three since it experiences HB anticooperativity and is situated furthest away from the ion core.

**C. Thermodynamics.** Table 8 compares the experimentally measured and the ab initio calculated  $-\Delta H_n$  and  $-\Delta G_n$  of the reaction  $\text{NH}_4^+ + n\text{H}_2\text{O} \rightarrow \text{NH}_4^+(\text{H}_2\text{O})_n$ . Detailed comparison between them reveals that B3LYP/6-31+G\* often yields larger values, whereas MP2/6-31+G\* yields values in better agreement with the measurements. At  $n = 1$ , the variation in experimental measurements is large, up to 2.6 kcal/mol. The predicted MP2/6-31+G\* value falls within this uncertainty range, but B3LYP/6-31+G\* significantly overestimates the interaction energy. As for clusters of  $n = 2-5$ , the MP2/6-31+G\* calculations for the lowest energy isomers agree well with the measurements, which have an experimental uncertainty of less than 1 kcal/mol; however, the B3LYP/6-31+G\* values remain slightly overestimated. Figure 7 illustrates the evolution of the hydration energies predicted by B3LYP/6-31+G\* and MP2/6-31+G\* as a function of  $n$ . Noticeably, the difference in prediction between these two methods for the lowest energy isomers gradually

diminishes as  $n$  increases. The estimated  $\Delta E_{n-1,n}$  agrees with each other within 0.5 kcal/mol at  $n = 5$ , indicating that the B3LYP/6-31+G\* approach is appropriate for predicting the stepwise hydration energies of clusters at a larger  $n$ .

Table 8 also displays the dramatic dependence of the Gibbs hydration energies on the isomeric forms of each cluster at room temperature. For the model system  $\text{NH}_4^+(\text{H}_2\text{O})_5$ , the calculated energy is scattered over a wide range from  $\Delta G_n = -24.76$  ( $-25.14$ ) to  $-32.07$  ( $-31.34$ ) kcal/mol. The degree of scattering is substantially larger in  $-\Delta G_n$  than in  $-\Delta H_n$  for all the clusters considered in Table 8. This finding is not unexpected since the entropy term involved in  $-\Delta G_n$  is sensitive to the temperatures as well as to the structures of the isomers. At room temperature, both the B3LYP/6-31+G\* and MP2/6-31+G\* calculations predict that isomer **5I**, with a ring-opened form, is lowest in Gibbs free energy. The ring-closed form is energetically favored only when the cluster is cooled off to a temperature below 160 K. Remarkably, this prediction agrees excellently well with the recent report of Wang et al.,<sup>6b,c</sup> who observed a distinct isomeric transition of **5I**  $\rightarrow$  **5II** for  $\text{NH}_4^+(\text{H}_2\text{O})_5$  with an internal temperature of  $\sim 150$  K. Since the structures of the clusters shown in Table 8 remain unknown in the hydration energy measurements,<sup>2,3</sup> the experimentally determined  $\Delta H_n$  and  $\Delta G_n$  should be considered as isomerically averaged values.

## Conclusions

Both the B3LYP/6-31+G\* and MP2/6-31+G\* methods have been applied to investigate the geometries, energies and vibrations of  $\text{NH}_4^+(\text{H}_2\text{O})_n$  and its structural isomers at  $n = 1-5$ . Results indicate that charge-dipole interactions dominate the hydration of  $\text{NH}_4^+$  in the first solvation shell whereas the arrangement of water molecules in the second hydration shell is predominantly determined by the interactions between  $1^\circ\text{H}_2\text{O}$  dipoles and the O electron lone pairs of  $2^\circ\text{H}_2\text{O}$ . There is no abrupt change in  $\Delta H_{n-1,n}$  at  $n = 4$  and 5 as the stepwise hydration energies ( $\Delta H_{n-1,n}$ ) decrease monotonically with  $n$ . The prediction is in line with previous thermochemical measurements<sup>2,3</sup> and the recent spectroscopic identification of structural isomers at  $n \geq 4$  by Wang et al.<sup>6</sup> The emergence of structural isomers at  $n = 4$  can be attributed to the fact that the strength of the interaction between the ion core and the solvent molecules is comparable to that between solvent molecules as the second hydration shell starts to form.

Dependence of the OH stretching frequency shifts on the solvation number in  $\text{NH}_4^+(\text{H}_2\text{O})_n$  has been scrupulously investigated in this study. The results indicate that the free-OH stretches, in addition to bonded-OH stretches, contain such useful structural information that A-H<sub>2</sub>O, AD-H<sub>2</sub>O, AA-H<sub>2</sub>O, and AAD-H<sub>2</sub>O can be identified on the basis of their characteristic free-OH stretching frequencies. While much structural information is expected to be extracted from b-NH stretches, unfortunately, the experimentally observed spectra are congested in this region,<sup>6b</sup> disallowing unambiguous spectral assignments.

The present calculations reveal that the geometries, interaction energies and vibrational frequencies of the clusters are strongly influenced by the hydrogen bond cooperative effect. The cooperative interactions, with the bridging molecule acting both as a proton donor and as an acceptor, can greatly enhance the strength of the involved hydrogen bonds. This enhancement, lengthening the b-NH (b-OH) bonds but shortening the N-H $\cdots$ O (O-H $\cdots$ O) distances, results in a larger frequency red shift in the b-NH (b-OH) stretches, as compared to the noncooperative case. On the contrary, in anticooperative systems where

the bridging molecule acts as a double proton donor or as a double acceptor, the b-NH (b-OH) bond lengths are substantially decreased, and the N-H...O (O-H...O) distances are, accordingly, increased.

We conclude from systematic comparisons of the present calculations that MP2/6-31+G\* is a better method than B3LYP/6-31+G\* in predicting the interaction energy of  $\text{NH}_4^+$  and  $\text{H}_2\text{O}$ . It yields results in close agreement with the measurements whereas the B3LYP/6-31+G\* calculations tend to overestimate the interaction energies. The MP2 method, however, is disadvantageous in that it requires more disk space when calculating the vibrational frequencies of larger clusters. The B3LYP/6-31+G\* can be an alternative in this case since the DFT-predicted interaction energies agree well with those of MP2/6-31+G\* at a larger  $n$ . The DFT approach, as pointed out by other authors, can indeed provide a reliable and computationally less demanding method for investigating intramolecular<sup>37</sup> and intermolecular hydrogen bonding in molecules and clusters.<sup>38</sup> The present study has demonstrated that this approach can also be applied to enhance our understanding of ion-molecule interactions in cluster ions generated in the gas phase.

**Acknowledgment.** The authors thank the Academia Sinica and the National Science Council (Contract NSC 87-2113-M-001-027-CT and NSC 87-2113-M-001-036) of Taiwan, Republic of China, for financial support. We also thank Dr. A. M. Mebel for useful discussions.

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