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Theoretical Characterization of the Rotational Motion of NH_4^+ in Water Clusters

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Abstract: The rotational mechanism of the NH_4^+ ion in water is analyzed by using both semiempirical (AM1) and ab initio (6-31G* SCF level) methods. AM1 predicts rapid rotation at any degree of first solvent shell hydration from $n = 1$–6. These results are considered artifactual since AM1 favors ion–water structures of a type not found in ab initio calculations and in what experimental work is available. The ab initio calculations predict ease of rotation only if the first shell solvation number is at least five. The ab initio multiple hydrogen bonding mechanism is close to that proposed by Perrin and Gipe based on the Monte Carlo studies of Jorgensen and Gao.

A. Introduction

A theoretical rationalization of the recent experimental observation[1-3] that NH_4^+ ions are nearly freely rotating in liquid water is not obvious. The observed near rigid behavior of NH_4^+ ions in some environments or near free rotation in others[3-5] are easy to rationalize based on simple electrostatic models in which the N–H units of NH_4^+ are either loosely or strongly bound to various sites. Water is intuitively thought to be in the latter class which should result in slow rotational relaxation times. Ab initio[6,7] and semiempirical[8,9] studies of $NH_4^+(H_2O)_n$ clusters have not dealt with this problem. Due to the use of different pairwise potential forms for the NH_4^+–water interaction, the three Monte Carlo studies[10-12] are not in mutual agreement as to the composition of the first solvation shell ($n = 4$–8). Therefore, there is uncertainty as to what dynamic information has been obtained[10] from these studies.

Perrin and Gipe[3] proposed a multiple hydrogen bonding rotational mechanism based on the most recent Monte Carlo study of Jorgensen and Gao.[12] Our extension of this type of analysis is shown schematically in Figure 1 where we present two simplified mechanisms, (i) and (ii). The first mechanism, (i), uses as n = 4 first solvation shell for NH_4^+ in which, on rotation, three of the four NH units are changing from being singly, A, to doubly (bifurcated) hydrogen bonded, B. This involves a C_3 axis rotation of NH_4^+ in a field of three nearly fixed water molecules. This and similar mechanisms imply that all the waters in the first solvation shell are relatively immobilized by complexation with additional external water molecules.

Although no published estimate of the energy difference between configurations A and B has been made, the following analysis provides a guess. DZP or larger basis set[13,14] ab initio SCF or correlationally corrected hydration energies (Table I) for NH_4^+–OH_2 predict that the single donor–single acceptor linear H-bonded structure I (Figure 2) is approximately 3–5 kcal/mol more stable than the bi- and trifurcated transition-state structures, II and III. If the 3 kcal/mol energy difference between the singly H-bonded and bifurcated configurations is nearly additive and largely unchanged in an aqueous environment, a barrier of the order of 9 kcal/mol can be estimated for the A-to-B rotation. Even if nonadditivity and solvation reduce this estimate by several kcal/mol, the A-to-B energy difference would fall into the 6–7 kcal/mol range. This would be much too large to explain the NMR data[1,3] from which a barrier in the order of 1–2 kcal/mol is estimated. Therefore, this analysis provides no support for a type (i) mechanism. A second mechanism,[3] (ii), uses an n = 5 first solvation shell as found in the most recent Monte Carlo study.[12] Mechanism (ii) can be viewed as the rotation of the three NH units in a field of four nearly fixed water molecules. This involves the passage from configuration C-to-D (Figure 1). Configuration C involves a doubly hydrated NH structure, $NH-(OH_2)_2$, of a type not yet computed in the literature. Therefore, an approximate C-to-D energy difference cannot be estimated. Even though such configurations are obtained in Monte Carlo calculations,[12] they are produced by using pairwise potentials having unknown accuracy with regard to modeling small clusters. It is known that Monte Carlo modeled[15] protonated water cluster (n = 1–9) stepwise hydration energies do not compare well with the experimental values in the small cluster range (2–4). However, it is uncertain whether the accurate modeling of small clusters is a prerequisite for modeling liquid systems.

Table I. Basis Set Dependence of the SCF Hydration Energies of NH_4^+–H_2O

structure	hydration energies (kcal/mol)				
basis set	3-21G*[a]	4-31G[b]	6-31G*[c]	6-311G**[d]	TZP,2d[e,f]
linear H-bonded	27.6	27.3	21.5	21.4	18.5[e]
bifurcated	21.8	21.8	18.3	18.2	15.4[e]
trifurcated		20.4	17.1		14.5[e]

[a] This work. [b] Reference 34. [c] This work, see also ref 12. [d] 6-311G** SCF energies: H_2O −76.04701 au; $NH_4(+)$ = −56.55877, linear $NH_4(+)-OH_2$, −132.63992; bifurcated, −132.63484. [e] Reference 13, these value are 21.4, 17.1, and 17.0, respectively, at the correlated level. [f] Reference 14 gives MP4/6-31+G(2d,2p) stabilities at 20.3, 16.7, and 15.6, respectively.

The experimental composition of the first aqueous solvation shell of NH_4^+ is unclear. Experimental[16] stepwise hydration energies of water with $NH_4^+(H_2O)_n$ clusters monotonically de-

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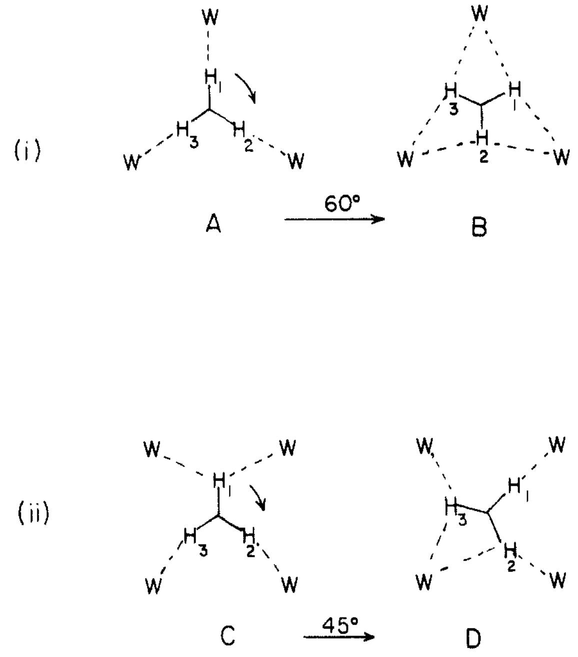

Figure 1. (i) Idealized rotation of NH_4^+ in the tetrahedral complex $NH_4^+(H_2O)_4$. Structure A has four linear H-bonds with water (W). In structure B, three of the four H-bonds assume bifurcated complexations with the three water molecules shown. (ii) Idealized rotation of NH_4^+ in the complex $NH_4^+(H_2O)_5$. One unshown water molecule remains in a linear H-bonded configuration with an NH unit. Four other water (W) molecules are kept at the corners of a coplanar square below the plane of the rotating NH_3 units. The rotation of the NH_4^+ by 45° generates a change from configuration C to D, see Figure 6, structure XVIII for another representation.

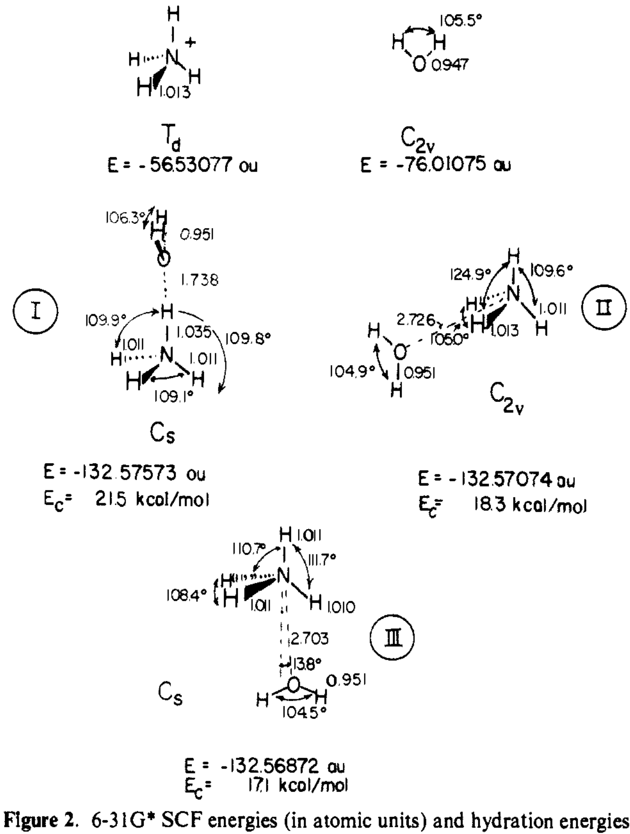

Figure 2. 6-31G* SCF energies (in atomic units) and hydration energies, E_c, (kcal/mol) for the NH_4^+–H_2O complexes. Structure I has a single H-bond configuration and represents the global minimum. All the atoms in the substructure N–H—OH_2 of I are in the same plane (see text). Structures II and III are transition states and are refered to as having bi- and trifurcated configurations. The order of stabilities of I, II, and III are as previously found at the SCF and correlationally corrected levels (see Table 1).

Table II. Comparison of Computed and Observed Hydration Energies of $NH_4^+(H_2O)_n$

structure $NH_4^+(H_2O)_n$ n =	method: AM1[a] stepwise (total)	method: 6-31G* stepwise (total)	exptl (kcal/mol) stepwise (total)
1	15.3	21.5	20.6[d]
2	14.1 (29.4)	18.2 (39.7)[b,c]	16.1 (36.7)[e]
3	12.0 (41.4)	15.6 (55.3)[b,c]	13.1 (49.8)[e]
4	11.1 (52.5)	13.6 (68.9)[b,c]	11.5 (61.3)[e]
5	10.6 (63.1)[e]	10.8 (79.7)[c]	10.1 (71.5)[e]
6	11.0 (74.1)[c]		9.1 (80.6)[e]

[a] Reference 9. [b] Reference 6 and 7. [c] This work, total AM1 heats of formation at $n = 5$ and 6 were −208.7 and −279.0 kcal/mol, respectively, optimized without any geometry restraints; all vibrational frequencies were positive. Calculations were repeated for $n = 1$–4 and were the same as previously published in ref 9. [d] Reference 16. [e] Average of ref 16, 22, and 23.

crease with increasing values of n. There is no experimentally obvious n value for the first solvation shell of water about an NH_4^+ ion based on either the enthalpy or entropy information available from the cluster studies. Each of the Monte Carlo studies cites experimental work which supports different n values for the first solvation shell of NH_4^+. The ab initio cluster computations of Deakyne[7] show that for $n = 2$–4 water-to-water binding has stepwise hydration energies only a few kcal/mol lower than N–H specific site binding. These computations indicate that the energy differences between the $n = 5$ clusters, $NH_4^+(H_2O)_4(H_2O)$ and $NH_4^+(H_2O)_5$, will probably not be large. The goal of the study presented here is to attempt to clarify some of the uncertainties expressed above. We will interpret the NH_4^+ rotation mechanism by using supermolecule calculations at both the ab initio and semiempirical levels. Our eventual conclusion will be that a type (ii) multiple H-bonding mechanism[3] does rationalize the rotational freedom of NH_4^+ in water.

B. Technical Details

Computations were performed with use of Gould 9050, Gould PN1, and SUN3 minicomputers at a University of Paris VI and a VP200 at CIRCE, Orsay, France. The semiempirical computations were performed with a vectoralized 3.00 version of MOPAC (QCPE 455), as modified by B. Duguay, University of Bordeaux. We thank M. Duguay and the computing staffs at both Paris and Orsay for their help. All calculations presented here had near zero gradients (10^{-3}–10^{-4} mdyne or mdyne Å rad^{-1}) for all coordinates. However, second derivative values were not completely checked for in the larger clusters. In the case of the $n = 1$–4, 6-31G* structures already reported in the literature,[6,7] our complexation energies, E_c, were identical.

C. Results and Discussion

1. General Comments. On the basis of a number of recent benchmark level computations[7,14,18–20] of ion–molecule systems, accurate ab initio estimates of the $NH_4^+(H_2O)_n$ hydration enthalpies would require larger basis sets than employed here. However, in the case of similar types of cationic monohydrates, the uncorrected 6-31G* complexation energies[18–20] are 1–2 kcal/mol too high but approach both the experimental hydration enthalpies and the MP4/large basis set hydration energies. Therefore, we concluded that full state of the art treatment of the polyhydrates, with an application of various correction procedures (correlation energy, thermodynamic correction, and basis set superposition error) could not be justified on a cost effectiveness basis. Moreover, the previous theoretical work (e.g., ref 13 and 14) indicates that a more advanced treatment would not significantly change the energy differences for cluster configurations having the *same* number of water molecules. It must also be stressed that experimental stepwise ion–molecule hydration en-

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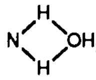
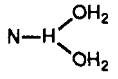
ergies are under continual refinement and in the best cases only accurate to about 1 kcal/mol.[21] In the case of NH_4^+ the $n = 1$ stepwise hydration enthalpy, originally[22] estimated at 17.3 kcal/mol, was next revised to 19.9,[23] with the most recent value given as 20.6.[16] The difference between 17.3 and 20.6 kcal/mol is argumentatively more than the anticipated experimental error. We have opted to use the 20.6 kcal/mol value as the most accurate one in our analysis here. However, we have used the average of the reported measurements for all the other stepwise hydration energies shown in Table II. The cumulative experimental error in estimating the total hydration enthalpies shown in Table II is probably of the order of several kcal/mol at $n = 5$, the total being 72 kcal/mol. On the basis of previous studies[7,14] we had anticipated that 6-31G* hydration energies would be too high by 1–2 kcal/mol per water unit. Therefore, our 6-31G* computed total hydration energy for $n = 5$, 80 kcal/mol (Table II), was anticipated to be between 5 and 10 kcal/mol too high, which is in fact what was observed. With regard to the AM1[24] semiempirical method employed here, hydrogen-bonded complexes[24,25] and related ion–molecule systems related to our study here, $NH_4^+(H_2O)_n$, $n = 1$–4,[9] and $NH_2(CH_2)_mNH_3^+(H_2O)_n$, $m = 2$–4, $n = 1$–4,[26] have been previously treated. Recent work[27-29] reports a number of examples where various degrees of inadequacies are encountered with use of AM1. However, we have found[29,30] errors in one of these papers.[27] In the case of small cationic monohydrates, the AM1 hydration enthalpies are in error by about 5 kcal/mol.[30] Since semiempirical methods will be exploited in modeling large systems, it will be necessary to continually test their advantages and limitations.

2. Semiempirical Analysis. Table II lists the AM1 stepwise and total binding enthalpies of $NH_4^+(OH_2)_n$ clusters. Our $n = 1$–4 results are in agreement with the previous AM1 work.[9] The results of the previous AM1 work[9] of Galera et al. were not compared against recent theoretical[7] and experimental[14] work. Their original evaluation[9] of the AM1 method is revised in a more recent work.[31] Table II shows that the AM1 total hydration enthalpies for $NH_4^+(H_2O)_n$ are in error in the range of 5 kcal/mol ($n = 1$) to about 9 kcal/mol ($n = 4$–5). However, there is no error in the case of the stepwise AM1 hydration enthalpies of the larger clusters. Considering the time and cost advantages of using AM1, this method can be used for initial hydration energy modeling studies of cationic systems (e.g., ref 26). In other studies we have found that the anionic hydation energies are somewhat more accurately computed than the cations. However, with regard to the rotational mechanism studied here, AM1 has serious problems. The AM1 structures of NH_4^+–water complexes[9,31] are in conflict with all the ab initio results reported elsewhere[6,7,14] and here. AM1 predicts that the bifurcated structure II is more stable than both the trifurcated structure III (one negative force constant) and the linear H-bonded structure I (two negative force constants) by 0.8 and 1.1 kcal/mol, respectively. This is in conflict with the ab initio calculations shown in Table I. For the larger clusters, AM1 consistently favors bifurcated components as previously found in the case of $n = 4$[9] and for $n = 5,6$ structure reported here. These types of bifurcated configurations



are not of a type



usually found in experimentally determined structures.[32] Moreover, in the case of NH_4^+ complexes single H-bonded structures, N–H—X, are the primary features (e.g., see ref 4 and 32) and, in some cases, trifurcated association, secondary features.[33] We know of no experimental case for ammonium ion type systems having bifurcated structures of the type found with use of AM1. Even so, the AM1 rotational activation energies of the NH_4^+ ion in a field of five or six water molecules, held rigid at their globally optimized geometries, were only 1.5 kcal/mol. At the $n = 3$ level a mechanism (i) (Figure 1) type optimized rotational pathway was computed, and an activation energy of 2.0 kcal/mol was found. We conclude that at any level of $n = 1$–6 that AM1 predicts low barriers for a rotational mechanism. This results from the fact that AM1 computes essentially isotropic NH_4^+ ion–water interactions.

With regard to other aspects of predicted AM1 structures, in the $n = 6$ cluster all water molecules are part of the first solvation shell having N–O distances in the 2.75–2.80 Å region. Nonfully optimized calculations at the $n = 7$ and 8 showed some nonequivalency of the water molecules (N–O ranging between 2.76 and 3.03). In these latter cases, all water molecules were still in what can be defined as the first solvation shell (i.e., N–O < 3.0).[10-12] However, one test calculation on $n = 5$, with the fifth water molecule attached externally to another first shell water, showed a stepwise solvation enthalpy of 8.9 kcal/mol. This value approaches AM1 stepwise solvation energies (see Table II) for $n = 6$. Although we did not investigate this issue further, we conclude that AM1 predicts a first solvation shell in the range of six to eight water molecules. We especially note that the AM1 computed atomic charges for NH_4^+ on the N and H atoms are −0.09 and +0.27, respectively. These values are much different than the 6-31G* Mulliken charges (−0.95 and +0.49, respectively) or the 6-31G* derived effective potential charges used in one Monte Carlo study (−0.40 and +0.35, respectively)[12] which gave an average first shell solvation number of five. The AM1 charges appear qualitatively near those used in one Monte Carlo study[10] (0.0 and +0.25, respectively) where a first shell solvation number of eight and a rapid rotation rate were computed. Therefore, AM1 appears to qualitatively reproduce the results of this latter study. However, because Mulliken charges are highly basis set dependent one cannot be confident with ab initio semiempirical charge comparisons, and one must rely on the computed energetic behavior of this system. On the basis of the following ab initio study and the above cited experimental information, we conclude that the AM1 results are sufficiently artifactual so as not to contribute to our understanding of the rotational mechanism of this particular system.

3. Ab Initio Analysis. (i) Energetic Analysis. $NH_4^+(H_2O)$. As discussed above with regard to Table I, all levels of ab initio theory predict the linear H-bonded structure I to be more stable than the bi- and trifurcated structures II and III (Figure 1). The preference for the linear H-bonded structure is mainly due to electrostatics,[34] and correlation does not change this order of

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(30) The previously reported (ref 26) and our own AM1 hydration enthalpies (kcal/mol) for the following structures are, respectively, as follows: $CH_3OH_2^+$, 17.5, 21.2; $(CH_3)_2OH^+$, 6.9, 16.2; $CH_3NH_3^+$, 13.5, 14.5; $(CH_3)_2NH_2^+$, 12.6, 13.5; NH_4^+, 14.6, 15.3. Examination of the literature (ref 21) shows that our revised values are lower than the experimental ones by an average of 5 kcal/mol. AM1 errors seem to become smaller as the systems become larger. The good agreement obtained in the case of the enthalpies of hydration of $NH_2(CH_2)_mNH_3^+$ (ref 26) may be due to the size effect. In a number of anion hydrates we found the binding energies were generally computed to within 1 kcal/mol of the experimental values.

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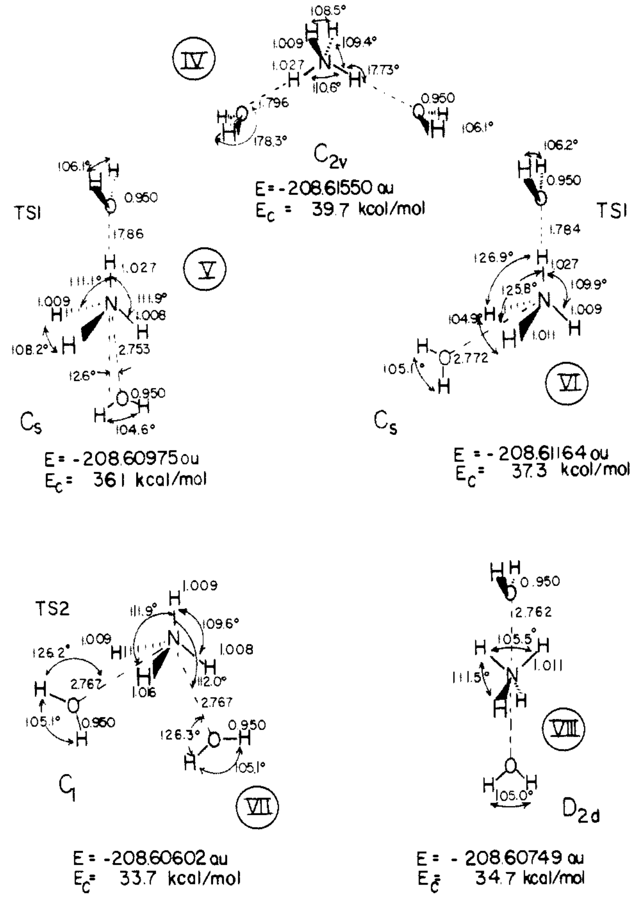


Figure 3. 6-31G* SCF hydration energies for various $NH_4^+(H_2O)_2$ structures. Structure IV has already been reported in ref 6 and 7. All other structures have lower binding energies and represent first- (TS1) or second-order (TS2) transitions states. The types of water bonding in these structures are as follows: IV, two linear H-bonded waters; V, one linear H-bonded water and one trifurcated bonded water; VI, one linear H-bonded water and one bifurcated bonded water; VII and VIII, each have two bifurcated bonded waters.

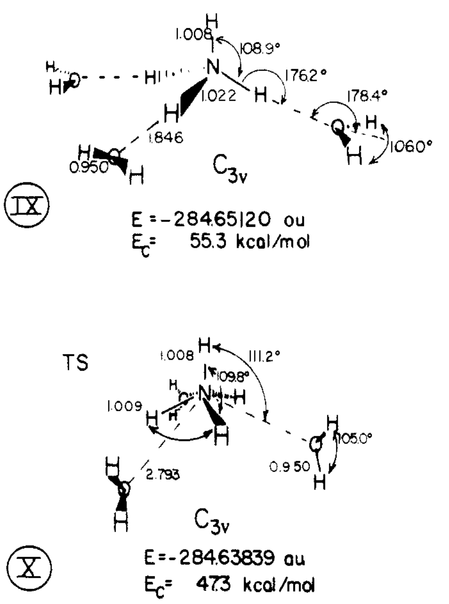


Figure 4. 6-31G* SCF hydration energies for $NH_4^+(H_2O)_3$ structures. The energy difference between structures IX and X represents the first test of mechanism (i), Figure 1 (see text). Structure IX has already been reported in ref 6 and 7. The types of water bonding in these structures are as follows: IX, three linear H-bonded waters; and X, three bifurcated bonded waters.

stability.[13,14] The primary structural features in $NH_4^+(H_2O)_n$ clusters are the NH–O bond distances combined with some directional orientation of the water dipoles toward the H-atom of the N–H moiety. Other structural features are secondary. For example, we found that the rotational barrier for a water molecule about the N–O axis of I is much less than 0.1 kcal/mol (i.e., water is a free rotor in I). Bending the N–H—O linkage by 15° while maintaining the water dipole pointed at the H atom produces a configuration only 0.4 kcal/mol less stable. Therefore, although the N–H—O linkage prefers linearity it does not insist, and bond angles departing by 15–20° from 180°, as found in condensed media,[32,33] are easily rationalized. Pyramidalization of the attached water in I by 15° produced a species only 0.2 kcal/mol less stable. We also found that geometry optimizations in the clusters up to $n = 4$ using frozen NH, OH bond distances and HNH, HOH bond angles give energies which are not significantly improved (<1 kcal/mol) on full optimization. This situation changes slightly at $n = 5$ since water–water interactions start playing a conformational role.

$NH_4^+(H_2O)_2$. A total of five, $n = 2$, structures are shown in Figure 3. As found in previous work,[6,7] the doubly linear H-bonded structure IV is the most stable of those examined. The mixed singly H-bonded, singly trifurcated and bifurcated structures (transition states), V and VI, are less stable than IV by 3.7 and 2.5 kcal/mol, respectively. The doubly bifurcated structures (second-order transition states), VII and VIII, are less stable than IV, by 5–6 kcal/mol. Therefore, the destabilization found for II and III with respect to I, of 3.2 and 4.4 kcal/mol, are not fully additive in the case of structures V–VIII. If they were, structures V–VIII would be less stable than IV by an additional 0.5, 0.7, 0.3, and 1.4 kcal/mol, respectively.

$NH_4^+(H_2O)_3$. For this value of n, a first test can be made of type (i) mechanism (Figure 1). As shown in Figure 4, the energy difference between structure IX (having three linear H-bonded waters) and structure X (having three bifurcated waters) is 8 kcal/mol. On the basis of the I–II energy difference, additivity would have predicted that structure X is 9.6 kcal/mol less stable than IX. Therefore, the nonadditivity factor is 1.6 kcal/mol. The 8 kcal/mol energy difference excludes a type (i) mechanism.

$NH_4^+(H_2O)_4$. As seen in Figure 5, the four-linear H-bonded structure XI is computed to be the most stable structure investigated. At this structural level, all the N–H sites are complexed. As discussed in the above $n = 3$ case, the type (i) mechanism can also be examined looking at the energy differences between XI and XII. This value, 7 kcal/mol, is marginally lower than the 8 kcal found above for the energy difference between IX and X. Structures which are all bifurcated (XIII) and all trifurcated (XIV) are even more unstable with respect to XI than XII. It should now be pointed out that AM1 predicts a structure close to XIII as the global minimum. The 7 kcal/mol energy difference between XI and XII still shows that the rotational mechanism of the NH_4^+ in water cannot be rationalized at the $n = 4$ level of ab initio treatment.

$NH_4^+(H_2O)_5$. The first item to stress in this series of computations is that this cluster has 54 deg of freedom. Technical and financial restrictions required that geometry optimizations be carried out with some frozen geometrical elements. In order to reduce the congestion of numbers in Figure 6, additional geometrical information is presented in the caption. At this point in our study we were interested in the relative energies of various configurations to see if any structures were within several kcal/mol of the local minimum. On the basis of our work (Figure 6) and calculations unreported here we believe that structures XV and XVI are local mimima. Structures of the type XVII and XVIII may not be minima with regard to asymmetric angular displacements of the waters. However, even if structure types XVII and XVIII are not minima this does not affect our argumentation given below.

Of the $n = 5$ structures investigated, the most stable is XV in which the fifth water molecule is complexed to another water molecule; i.e., structure XV is a water bound to the XI shell and will be written as $NH_4^+(H_2O)_4(H_2O)$. Therefore, of the structures computed, this level of ab initio theory predicts that NH_4^+ has

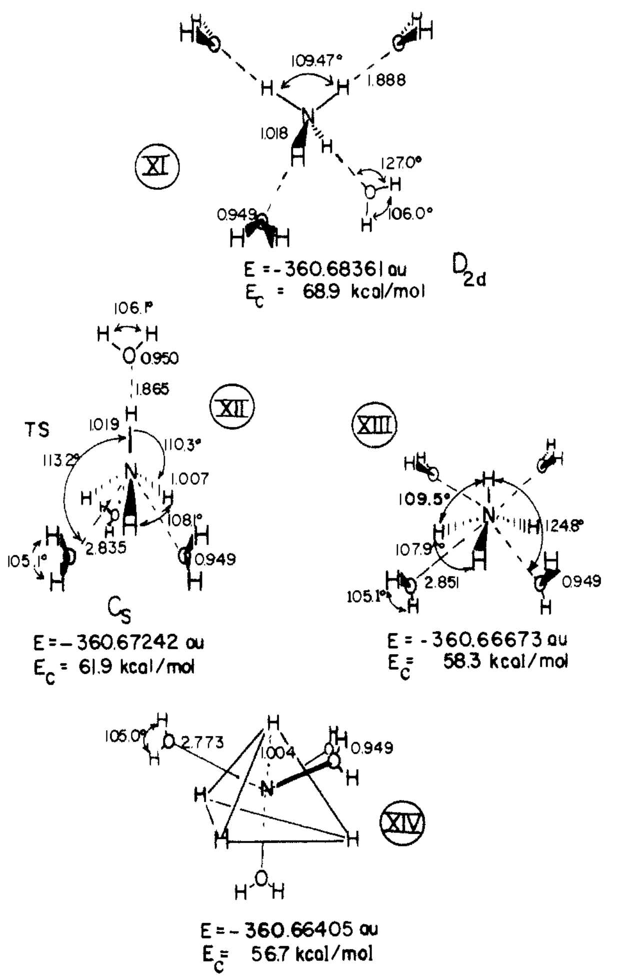


Figure 5. 6-31G* SCF hydration energies for $NH_4^+(H_2O)_4$ structures. Structure XI has already been reported in ref 6 and 7. The energy difference between structures XI and XII is an additional test of mechanism (i), Figure 1 (see text). Structure XIII is close to the structure computed with use of AM1. The types of water bonding in these structures are as follows: XI, four linear H-bonded waters; XII, three bifurcated bonded waters and one linear H-bonded water; XIII, four bifurcated bonded waters; and XIV, four trifurcated bonded waters.

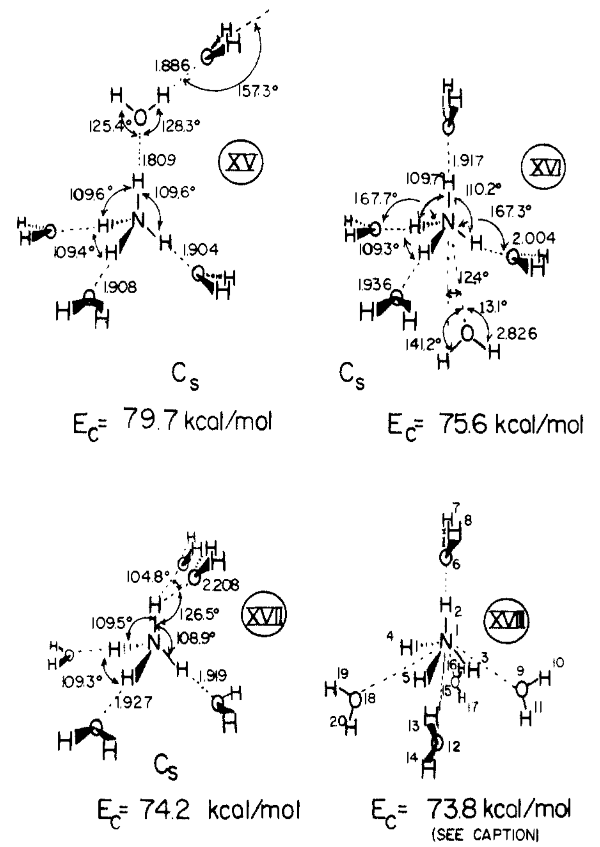
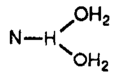


Figure 6. 6-31-G* SCF hydration energies for $NH_4^+(H_2O)_5$ structures. SCF energies of XV, XVI, and XVII are, respectively, −436.71152 au (optimization in 23 of 54 coordinates), −436.705071 (33 coordinates), and −436.702712 (17 coordinates). All of the optimized parameters are not shown in the figure. For XV, 3(NH) = 1.017, NH = 1.023, OH(all) = 0.948–0.949, 3∠HOH = 106.0, external H_2O, 106.2. For XVI, NH = 1.0133–1.0155, OH(all) = 0.948–0.949, 4∠HOH = 106.0. For XVII, NH = 1.012–1.016, OH(all) = 0.949, 3∠HOH = 106.0, 2∠HOH = 105.6. For XVIII, a total of four computations were done with the four water molecules fixed at 0, 90, 180, and 270 deg vis-ā-vis the plane of the paper. Simulation of mechanism (ii), Figure 1, was simulated by optimizing in 29 coordinates the rotation of the H_3 in NH_4^+ as a single unit in a field of four water molecules. This is shown as structure XVIII in which at a four fixed rotation angle the following energies were obtained: 0°, (E = −436.70218 au), 15° (−436.70217), 30° (−436.70217), 45° (−436.70217). For the 0° calculation, NH_2 = 1.016, NH_3 = 1.016, $NH_{4,5}$ = 1.011, NO_6 = 2.935, NO_9 = 2.934, $NO_{12,15}$ = 2.920, NO_{18} = 2.900, OH(all) = 0.949, $\angle HO_{6,9}H$ = 106.0, $\angle HO_{12,15}H$ = 105.6, $\angle HO_{18}H$ = 105.2, $\angle H_2N_1H_3$ = 108.5, $\angle H_2N_1H_{4,5}$ = 109.8, $\angle H_3N_1O_6$ = 108.2, $\angle H_2N_1O_9$ = 105.9, $\angle H_2N_1O_{12,15}$ = 108.3, $\angle H_2N_1O_{18}$ = 108.0. At the other rotational points the NO distances remain in the region of 2.90–2.93, the $\angle H_2N_1O$ varying between 106 and 109. Two calculations at fixed NO(all) = 2.931, NH(all) = 1.016, OH(all) = 0.949, ∠HOH(all) = 106.0, and all other bond angles being tetrahedral (109.47) gave an energy of −436.70196 at both 0° and 45° rotation or an E_c of 73.7 kcal/mol. The types of water bonding in these structures are as follows: XV, four linear H-bonded waters plus one external nearly linear H-bonded water; XVI, four nearly linear H-bonded waters plus one internal nearly trifurcated water; XVII, three linear H-bonded waters, two bifurcated waters attached to the same N–H unit. The XVIII series represents one linear H-bonded water and four waters having bonding types shown in Figure 1, structures C and D. These bonding types are essentially two linear H-bonded and one bifurcated waters (C) and one linear H-bonded and three bifurcated waters (D).

an $n = 4$ first solvation shell. Structure XVI has a complete $n = 5$ coordination, $NH_4^+(H_2O)_5$, with all N–O distances at less than the 3.0 Å radius constituting the first solvation shell.[10-12] This is also true for structure types XVII and XVIII. Structure XVI is 4 kcal/mol less stable than XV.

Structure XVI consists of one trifurcated water and four singly H-bonded waters. This structure is only marginally more stable than the one bifurcated and three singly H-bonded structure, XVII. Structure XVI shows some departure from an N–H—O linearity, 167–168°. However, an optimization imposing N–H—O linearity on XVI gave an E_c value of 74.7 kcal/mol, about 1 kcal/mol less stable than that subsequently found for XVI. Likewise, in the case of XVII, imposing pseudo-C_{3v} symmetry for the three singly bonded waters, and planarity on the



$$N{-}H{<}^{OH_2}_{OH_2}$$

bifurcated structure yielded a structure, 73.8 kcal/mol, only 0.4 kcal/mol less stable than XVII. These structures and others associated with type XVIII discussed below indicate that a large number of configurations of $NH_4^+(H_2O)_5$ lie within 2 kcal/mol of what we found to be the local minimum, XVI. That structures like XVI and XVII should be a local minima for the five-coordinated species falls into the logic of ab initio computations obtained here and by previous workers. These calculations show that when water is added to NH_4^+, the four N–H sites are first complexed. Addition of further waters (n = 5–8) should occur progressively at the four faces of the tetrahedron[10,33] (trifurcated complexation) or complexation (bifurcated) at each N–H unit. A mixture of bi- and trifurcated complexation could also occur. This secondary solvation will produce a probable limit of eight in the first shell solvation number. However, our calculations actually show that at $n = 5$ secondary solvation preferably occurs at the external water sites in the clusters. However, we will argue below that this does not occur at the super cluster or liquid water level where these external sites are already complexed.

With regard to simulating the type (ii) mechanism, a series of computations was carried out with respect to structure class XVIII. In this case structures C (0° rotation, compare Figure 1 (ii) with Figure 6, XVIII. In this case structures C (0° rotation, compare Figure (ii) with Figure 6, XVIII and captions) and D (45°) were computed, with geometry optimization in 29 deg of freedom. Intermediate rotations of 15° and 30° were also computed. All four computations gave the same hydration energy, 73.8 kcal/mol. Two additional computations (see caption of Figure 6) were performed by using fixed molecular parameters, and hydration energies of 73.7 kcal/mol were obtained. This shows that extensive optimizations of the XVIII system are unnecessary if the fixed molecular parameters are carefully selected. The XVIII series of computations showed that there was no barrier to rotation of the NH_4^+ group in a field of four water molecules and that these species are within 2 kcal/mol of the XVI species. The conclusion is that as long as the three N–H units have sufficient access to four well-positioned water molecules, ease of rotation of the NH_4^+ unit is assured. Therefore, of all the computations preformed in our study, the XVIII series gives the best explanation of the rotational mechanism.

(ii) The Proposed Rotational Mechanism. The major conclusion to be drawn from the above series of ab initio computations is that one cannot explain the NH_4^+ rotational mechanism at less than the $n = 5$ level. At the $n = 5$ level certain types of multiple H-bonded structures can occur (e.g., structure types C and D in Figure 1) which cannot occur at less than 5. These structures arise only in a situation in which the number of water molecules exceeds the number of N–H units. We make no claims as to $n = 5$ being the unique first solvation shell situation to assure rotation since no computations were carried out at larger n values. Therefore, our following projection to a full solvation model is speculative.

In analyzing the structure of NH_4^+ in liquid water we will only consider two general types of solvated species, $(NH_4^+(H_2O)_4)_s$ and $(NH_4^+(H_2O)_5)_s$. These correspond to solvated XI and XVI. It is important to stress that *fully* solvated XV and solvated XI are the *same* structures. Therefore, exploitation of the stepwise hydration solvation energy of XV is both unnecessary and deceptive.

The super cluster isomerization (1) conceptually results from the breaking of one water–water hydrogen bond in the solvent

$$(NH_4^+(H_2O)_4)_s = (NH_4^+(H_2O)_5)_s \qquad (1)$$

and inserting this partially bound water into the $(NH_4^+(H_2O)_4)_s$ species to produce $(NH_4^+(H_2O)_5)_s$. The water insertion energy (2) process can be estimated from the difference in the E_c values for XI and XVI (Figures 5 and 6).

$$\underset{\text{XI}}{NH_4^+(H_2O)_4} + H_2O = \underset{\text{XVI}}{NH_4^+(H_2O)_5} \qquad E = -6.7 \text{ kcal/mol} \qquad (2)$$

The energy for breaking one hydrogen bond in water can be estimated in several ways. At the 6-31G* level, the SCF dimerization energy of water is −5.6 kcal/mol.[35] The water–water dimerization energy is also in the range used in most Monte Carlo calculations.[36] These models yield reasonable estimates of the vaporization enthalpy of water, ca. 10 kcal/mol.[37] However, the actual experimental dimerization enthalpy of water is −3.7 kcal/mol.[38] Assuming liquid water has about three H-bonds per unit, this yields an average of about 3.3 kcal/mol per H-bond. By using a range of values from −3 to −6 kcal/mol and the insertion energy (2) of −6.7 kcal/mol an estimate of between −1 and −4 kcal/mol is obtained for reaction 1. This would indicate that a hydration number of five is more favored than four in liquid water. This analysis especially indicates that the computed cluster hydration number of four is deceptive with regard to what occurs in a much larger cluster. Finally, an identical analysis for solvated species XVII and XVIII shows they are still within 2 kcal/mol of solvated XVI. Therefore, a rationalization of the rotational mechanism in liquid water has been achieved.

With regard to the Monte Carlo calculation of Jorgensen and Gao,[12] they predict an average solvation number of about five and a primary interaction energy for this species (1.24 waters per NH unit) of −67 kcal/mol. This number should be roughly compared to an average of our structures XVI–XVIII, i.e., about −75 kcal/mol. However, we have also argued that a better level of ab initio treatment would reduce this latter energy by between 5 and 10 kcal/mol. Although this favorable comparison is probably fortuitious, it does indicate that the Jorgensen and Gao Monte Carlo modeling[12] is reasonable.

Caveat and Conclusion. The reader is warned that the above ab initio based quantitative argumentation is speculative. The qualitative results are easier to accept. The ease of rotation of species XVIII demonstrates that once NH_4^+ has a number of water molecules greater than four in the first solvation shell ease of rotation occurs. Major structural differences occur between ab initio and AM1 methods. AM1 does not place a lower limit on the minimum number of first shell water molecules necessary for ease of rotation. Finally, in spite of the use of pairwise potentials, we view our results as not qualitatively different than those obtained in the most recently[12] published Monte Carlo calculation. We are currently investigating dynamic modeling of this system based on parameterizations capable of reproducing the cluster computations reported here.

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