

The Importance of Thermodynamic Quantities for the Determination of the Unknown Conformation: *Ab initio* Studies of $K^+(H_2O)_3$

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The structures, the energetics, and the spectra of $K^+(H_2O)_3$ have been studied at HF and MP2 levels with the basis set of triple-zeta plus two sets of polarization functions (TZ2P) for water molecules. Two structures considered are 3+0 (D_3), and 2+1 (C_{2v}). The 2+1 (C_{2v}) has two hydrogen bonds between the primary hydration and the secondary hydration shell water molecules. They have similar binding energy and enthalpy. The most stable conformation of $K^+(H_2O)_3$ is entropy driven as shown in $Na^+(H_2O)_5$ and in $Na^+(H_2O)_6$ cases. The 3+0 (D_3) conformation is the most stable at 298 K and at 1 atm. based on Gibbs free energy changes (ΔG_f). The thermal contributions to the enthalpy and the Gibbs free energy are corrected for the low frequency modes. The corrected ΔG_f is in good agreement with the experimental value. Vibrational frequencies of two conformations are revealed as their characteristics.

Introduction

Accurate study of solvated metal ions is essential in the ultimate understanding of ion solvation, metal-ligand coordination, and biomechanism in metallo-enzymes.¹⁻³ A number of experimental⁴⁻⁸ and theoretical^{9-21a,22b,c,23} studies of ion solvation have been reported. In particular, K^+ ions hydrated by intracellular water are essential to osmotic control in biological systems. There have been several experimental and theoretical studies of the hydration of K^+ cation. Thermal binding energies of $K^+(H_2O)_n$ ($n=1-6$) are available from experiments by Dzidic and Kebabian.⁶ However, information for the conformation could not be obtained from the experiment. Previous theoretical studies have used only the enthalpies to get the conformational informations. Glendenning *et al.*²³ performed *ab initio* calculations on various hydration structures of a number of alkali metals. They showed the conformations 2+1 (C_{2v}), 2+1 (C_s) and 3+0 (D_3) for $K^+(H_2O)_3$. Here, notation " n_1+n_2 (Symmetry)" denotes the cluster structure where the ion has n_1 and n_2 water molecules in the primary and in the secondary hydration shells. They compared the stability of conformation with the binding energies and the binding enthalpies, and suggested that 2+1 (C_{2v}) should be in the global minimum²⁰ with their MP2/pCVDZ/aug-cc-pVDZ dissociation energies and binding enthalpies. It should be noted that the binding enthalpy difference between the conformations 2+1 (C_{2v}) and 3+0 (D_3) for $K^+(H_2O)_3$ is only 1.2 kcal/mol at room temperature.

We have emphasized the importance of entropy contributions in determining the stable conformation and the primary hydration number of the $Na^+(H_2O)_5$ and $Na^+(H_2O)_6$ clusters at room temperature.^{20,21a} Energetically favorable conformations have bridged-type hydrogen bonds between the waters in the primary and in the secondary hydration shells. This conformation has larger zero point energy (ZPE) because of

the hydrogen bond. In Na^+ -water clusters, the conformation 4+1 (C_2) was as stable as the 5+0 (C_s) in $n=5$ and the conformation 4+2 (D_{2d}) was more stable than the 5+1 (C_1) in $n=6$ at low temperature. But the 5+0 (C_s) and the 5+1 (C_1) clusters became more stable than the 4+1 (C_2) and the 4+2 (D_{2d}) at room temperature, owing to the entropy effect. This means that the entropy controls the conformational change, i.e. the outer shell water comes into the inner shell.

We think that this system is the second example of entropy-driven structure in hydrated alkali metal ion system. It is important to find the correct structure in order to give a guide towards the best potential fit for metal-water interactions. Therefore, we investigated the energetics and the thermodynamic quantities of 3+0 and 2+1 conformations of $K^+(H_2O)_3$. The post-Hartree-Fock methods were employed in order to increase the reliability of the results and to evaluate the impact of electron correlation on binding energies, structures, zero point energy (ZPE) and vibrational frequencies. Since these two conformations have different patterns of vibrational frequencies and those are useful informations in the identification of the $K^+(H_2O)_3$ structures in experiments, we also report the vibrational frequencies for each conformation.

Calculation Methods

The Hartree-Fock (HF) and the second-order Møller-Plesset perturbation (MP2) calculations were performed with the GAUSSIAN 94 suite of programs.²⁴ A basis set of triple-zeta plus two sets of polarization functions (TZ2P) was employed for water molecules, as described in the previous reports^{20,21a} of aqua- $Na(I)$ clusters. For the K^+ ion the (14s10p3d)/[8s7p3d] basis set was employed, which was extended from (14s9p)/[8s5p] by Ahlrichs *et al.*²⁵ The coefficients and exponents of the basis set for K^+ cation are listed

Table 1. Exponents and Expansion Coefficients of the Basis Set for K⁺

(14s/8s)		(10p/7p)		(3d)	
exponents	coefficients	exponents	coefficients	exponents	coefficients
182594.27324000	-0.00022775	891.05446872	0.00218429	1.00000000	1.00000000
27369.00498600	-0.00176640	211.01581996	0.01758911		
6229.17379710	-0.00919497	67.67141238	0.08177747	0.25000000	1.00000000
1764.58234860	-0.03745508				
577.05120588	-0.12204454	25.27148810	0.24565632	0.06250000	1.00000000
210.24933364	-0.29898972	10.13895897	0.43398377		
82.61783064	-0.40514697	4.20186272	1.00000000		
33.23318452	-0.29253151				
		1.60294672	1.00000000		
8.10649021	1.00000000	0.61461253	1.00000000		
3.33402588	1.00000000	0.22199301	1.00000000		
0.84554422	1.00000000	0.03837500	1.00000000		
0.32821627	1.00000000				
0.09375000	1.00000000				
0.02643500	1.00000000				

in Table 1. All the geometries were fully optimized at the above levels of theory. The vibrational frequency analysis was done, and these uncorrected values were used to calculate the zero-point energies (ZPE) and thermal quantities. To investigate the electron correlation effect on the binding energies, the MP2 calculations were performed at the HF-optimized geometries (MP2//HF). To prevent an artificial increase in binding energy, BSSEC (basis set superposition error correction) was applied to the binding energies through the counterpoise correction (CP) procedure of Boys and Bernardi.²⁶ However, the CP correction has been criticized both for overestimating and underestimating the "true" magnitude of this phenomenon.²² In particular, we find that the thermal quantities with BSSE correction tend to be seriously underestimated in comparison with the experimental values, while those without BSSE correction are closer to the experimental ones. In some papers aqua-alkali metal²³ and aqua-alkaline earth metal complexes^{30,10} have been reported with the BSSE-uncorrected BEs. Del Bene has also said that in the calculation of proton affinities, the BSSE-uncorrected BEs are in better agreement with experimental values.²⁷ In cases when basis sets employed are reasonably well balanced such as in this study, our point is that binding energies without BSSE correction should be compared with the experimental values.

The thermal quantities are evaluated under ideal gas and rigid rotor-harmonic oscillator approximation. The rotational and the translational contributions to the thermal quantities at 298 K and 1 atm are taken from the classical expressions. When conformation is chiral, it is appropriate that the ΔS_r and the ΔG_r of the chiral conformation are corrected by $R \ln 2$ and $-RT \ln 2$, respectively,²⁸ where R is the gas constant. The vibrational contributions are evaluated with the unscald normal mode frequencies obtained at the same level of theory used to compute the binding energies. In the simplest harmonic oscillator approximations, zero-point vibrational energy (ZPVE) of a molecule is evaluated theoretically from the equation:

$$\text{ZPVE} = 0.5Nhc \sum_i \bar{\nu}_i$$

where $\bar{\nu}_i$ is the i th harmonic vibrational frequency expressed in cm^{-1} (more rigorously called the harmonic vibrational wavenumber) and Nhc is the appropriate energy conversion factor. This expression is not precise since it does not take into account the effects of anharmonicity. Knowledge of vibrational frequencies also plays a vital role in determining the thermal contributions to enthalpy and entropy which can be expressed as

$$H_{\text{vib}}(T) = Nk \sum_i \left[\frac{1}{2} \Theta_{\text{vib}} + \frac{\Theta_{\text{vib}}}{\exp(\Theta_{\text{vib}}/T) - 1} \right], \quad \Theta_{\text{vib}} = hc\bar{\nu}_i/k$$

$$G_{\text{vib}}(T) = -NkT \sum_i \ln Q_{\text{vib}}, \quad Q_{\text{vib}} = \frac{\exp(-hc\bar{\nu}_i/2kT)}{1 - \exp(-hc\bar{\nu}_i/kT)}$$

$$S_{\text{vib}}(T) = \frac{H_{\text{vib}}(T) - G_{\text{vib}}(T)}{T}$$

where N is the Avogadro's number.

Inspection of the above equations indicates that small frequencies contribute more to the thermal contributions to enthalpy, Gibbs free energy, and entropy than larger frequencies. We note also that when the vibrational frequency becomes zero at constant temperature, the absolute values for $G_{\text{vib}}(T)$ and $S_{\text{vib}}(T)$ tend to be infinity, *i.e.*, this approximation may have overestimated the absolute values of $G_{\text{vib}}(T)$ and $S_{\text{vib}}(T)$. In other words, the dominant error in the above approximation may be the failure of the harmonic approximation for low-frequency vibrations which are rotational in nature. In our loosely bound complex system, there are many low vibrational frequencies. In this case, it is often more appropriate to calculate the thermal component associated with these modes using a hindered rotator approximation. In this work, we performed a normal mode analysis to identify the torsional mode among the low vibrational frequencies, and evaluate the reduced moment of inertia as suggested by Pitzer and Gwinn.²⁹ On the basis of the structural

parameters of the equilibrium geometry, the principal moments of inertia ($\times 10^{-38}$ gcm²) are found to be $I_a=3.47$, $I_b=3.47$, and $I_c=6.88$. The reduced moment of inertia for internal rotation was calculated according to the equation:

$$I_r = A_m \left\{ 1 - \sum_{i=1}^3 \frac{A_m \lambda_{mi}^2}{I_i} \right\}$$

where A_m is the moment of inertia of the top about its own symmetry axis, λ_i is the direction cosine of the angle between the top axis and the i th principle axis of the entire molecule, and I_i is the corresponding moment of inertia ($i=a, b, c$). For 3-0 conformation, $A_m=1.92 \times 10^{40}$ gcm² and $I_r=1.91 \times 10^{40}$ gcm². The symmetry number (σ_m) for the top is 2. Corrections for the hindered internal rotation of the three water tops were applied with the approximate hindered rotator partition function of Truhlar,⁵⁰ which is expressed in terms of switching function:

$$Q_m^r = \sqrt{\frac{8\pi^2 I_r kT}{h^2 \sigma_m^2}}$$

$$Q_{hm} = Q_{vib}^{hor} \tan h \left(Q_m^r \frac{Q_{vib}}{T} \right)$$

Under the above partition function, the thermal contributions to enthalpy, entropy, and Gibbs free energy was calculated according to the equations:

$$G_{hm}(T) = -RT \ln Q_{hm}$$

$$H_{hm}(T) = H_{vib}(T) - \frac{Nhc\bar{\nu}Q_m^r}{\sinh(2Q_m^r hc\bar{\nu}/kT)}$$

$$S_{hm}(T) = \frac{H_{hm}(T) - G_{hm}(T)}{T}$$

Results and Discussion

Structures and Energies. 2+1 (C_{2v}) and 3-0 (D_3) structures are shown in Figure 1 and their geometric parameters are listed in Table 2. Table 2 also shows their HF, MP2//HF and MP2 energies. In 2+1 (C_{2v}) conformation, the secondary hydration shell water molecule forms two HBs (hydrogen bonds) of bridged style with two primary hydration shell

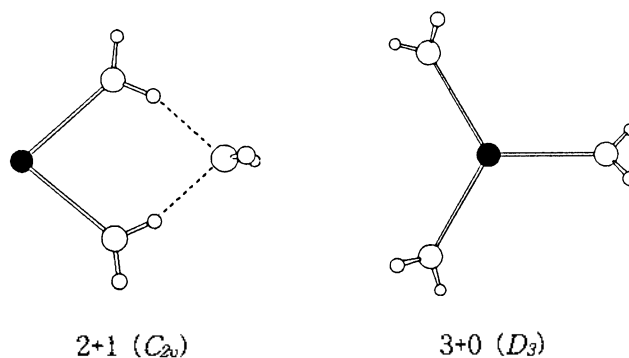


Figure 1. Structures of 2+1 (C_{2v}) and 3+0 (D_3).

water molecules. 3+0 (D_3) is a propeller-like structure. The pyramidal structure of 3+0 (C_3) obtained at HF level by Feller *et al.*^{23a} was not a local minimum at MP2 level. The electron correlation gives a significant effect on the structural parameters (the K-O distance and the HB distance) and the binding energies. For example, electron correlation at the MP2 level shortens the K-O distance by 0.04 Å, and the HB distance by 0.15 Å relative to the HF values, and these structural parameters show that electron correlation effect stabilizes further the 2-1 (C_{2v}) structure with hydrogen bonds. That is, the water-water interaction in HF level is underestimated. When the binding energies are compared for these two conformations, 3+0 (D_3) is slightly more stable in HF energies, but 2+1 (C_{2v}) turns out to be somewhat more stable in MP2 level.

Vibrational Frequencies. Table 3 lists the HF and the MP2/TZ2P-predicted vibrational frequencies, IR intensities, and Raman activities for these two conformers. Theoretically predicted vibrational frequencies and IR intensities of the OH stretching modes have been useful in identifying the unknown conformation in experiments. Therefore, the MP2-predicted OH stretching IR vibrational spectra for 2+1 (C_{2v}) and 3-0 (D_3) are shown in Figure 2. The dotted lines denote the IR spectra for the free water monomer. The details are referred in Tables 3 and 4.

The calculated frequencies may be divided into three regions according to the normal modes. There is no serious difference between HF- and MP2-predicted vibrational frequencies in low- and mid-frequency range. In the low-frequency region, there appear intermonomeric (K⁺ ion and water molecules) coupling motions having very low IR intensities and Raman activities [such as K⁺-water (K-W) stretching and W-K-W bending motions]. The low-lying frequencies

Table 2. HF and MP2/TZ2P Energies and Geometric Parameters of $K^-(H_2O)_3^+$

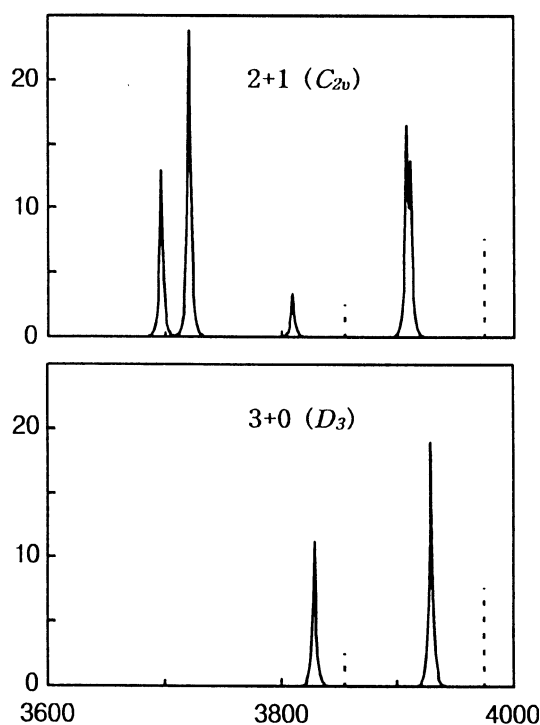
Conformation	Level	Energy	$r(K-O)$	$r(O-H)$	$\angle(H-O-H)$	$r(O \cdots H_n)$
2+1 (C_{2v})	HF	-827.2562	2.666/4.451	0.942 0.948/0.944	106.9/106.2	2.075
	MP2//HF	-828.3342				
	MP2	-828.3372	2.625/4.354	0.960 0.969/0.963	105.4/104.7	1.923
3+0 (D_3)	HF	-827.2585	2.735	0.943	105.7	
	MP2//HF	-828.3332				
	MP2	-828.3354	2.690	0.962	103.9	

^aEnergies are in hartree, distances in Å, and angles in degree. Primary/secondary hydration shell.

Table 3. HF(MP2)/TZ2P Frequencies (cm⁻¹), IR Intensities (km/mol), and Raman Activities (Ram.: Å⁴/amu) for 3-0 (D₃) and 2+1 (C_{2v})^a

Mode	3+0 (D ₃)				Mode	2+1 (C _{2v})			
	Sym.	γ	IR	Ram		Sym.	γ	IR	Ram
γ _s	e	4185 (3929)	130 (106)	40.1	γ _s	b ₁	4178 (3911)	149 (135)	27.3
	a ₂	4185 (3929)	175 (147)	0.0		a ₁	4176 (3911)	52 (40)	69.0
γ _t	a ₁	4104 (3830)	0 (0)	171.6		b ₂	4173 (3908)	314 (263)	6.2
	e	4103 (3829)	86 (63)	16.6	a ₁	4094 (3810)	17 (11)	41.2	
γ _z	a ₁	1787 (1684)	0 (0)	1.9	a ₁	4045 (3721)	458 (570)	167.6	
	e	1786 (1683)	165 (124)	2.4	b ₂	4031 (3697)	70 (168)	19.9	
γ _w	a ₂	366 (340)	644 (477)	0.0	a ₁	1803 (1710)	44 (19)	0.2	
	e	362 (340)	274 (178)	0.5	b ₂	1779 (1678)	78 (58)	2.9	
	e	346 (319)	3 (74)	0.4	a ₁	1771 (1661)	173 (129)	2.5	
	a ₂	331 (308)	22 (108)	0.0	b ₁	637 (692)	370 (249)	0.1	
	a ₁	86 (94)	0 (0)	2.2	a ₂	571 (635)	0 (0)	0.4	
	e	41 (48)	0 (0)	0.5	a ₁	501 (517)	82 (83)	0.0	
					b ₂	475 (485)	459 (401)	0.1	
γ _s ^{K-W}	e	194 (207)	7 (5)	0.0	b ₂	392 (386)	0 (4)	0.4	
γ _s ^{K-W}	a ₁	156 (165)	0 (0)	0.0	b ₁	276 (263)	200 (256)	0.0	
γ _t ^{W-K-W}	e	19 (15)	0 (0)	0.0	a ₂	269 (262)	0 (0)	0.0	
γ _t ^{W-K-W}	a ₂	14 (11)	0 (0)	0.0	a ₂	241 (245)	0 (0)	2.8	
					b ₁	233 (232)	66 (26)	0.4	
					a ₁	221 (240)	5 (2)	0.0	
					b ₂	203 (217)	14 (14)	0.0	
					a ₁	162 (197)	8 (13)	0.0	
					b ₂	114 (144)	0 (0)	0.0	
					a ₁	73 (81)	3 (3)	0.1	
					b ₁	46 (50)	4 (6)	0.0	

γ_w: The intermonomeric water vibrational modes. Subscripts s, t, r, and w of mode frequencies γ mean the following: s=stretch, b=bend, r=rock, and w=wag. The HF/TZ2P frequencies of the water monomer are γ_t=4130, γ_z=1753, and γ_s=4229 cm⁻¹ and MP2 frequencies are γ_t=3855, γ_z=1654, and γ_s=3975 cm⁻¹.

**Figure 2.** MP2-predicted OH Stretching IR Vibrational Spectra for 2+1 (C_{2v}) and 3+0 (D₃).

of 2+1 (C_{2v}) which has somewhat strong IIBs are higher than those of 3+0 (D₃). The lowest HF (MP2) frequencies of 14

Table 4. HF(MP2)/TZ2P Predicted Vibrational Frequency Shifts in the Monomeric Water in the Cluster Relative to the Free Water Monomer, Vibrational Frequencies of the K⁺-water Stretching Modes (γ_s^{K-W}), and the Maximum Frequencies for the Intermonomeric Water Vibrational Modes (γ_w^{max}) (cm⁻¹)

Conformation	Δγ _t	Δγ _z	Δγ _s	γ _s ^{K-W}	γ _w ^{max}
2+1 (C _{2v})	-99 ~ -36 (-158 ~ -45)	1850 (756)	-56 ~ -51 (-67 ~ -64)	221 ~ 203 (240 ~ 217)	637 (692)
3+0 (D ₃)	-27 ~ -26 (-26 ~ -25)	33 ~ 34 (29 ~ 30)	-44 (-46)	194 ~ 156 (207 ~ 165)	366 (340)

(11) cm⁻¹ (a₂) for 3+0 and 46 (50) cm⁻¹ (b₁) for 2+1 correspond to the out-of-plane W-K-W bending modes. The out-of-plane bending mode of 2+1 is the wagging mode of K⁺ cation center and two primary water molecules (γ_w^{W-K-W}). In 2+1 (C_{2v}), γ_t^{W-K-W} (b₂) is for the in-plane rocking mode of two primary water molecules at the center of K⁺ cation against the secondary hydration shell water. γ_b^{W-K-W} ⊥ γ_s^{K-W} (a₁) are for the in-plane bending mode of K⁺ cation and two primary water molecules coupling with the stretching mode of K⁺ cation and the secondary water.

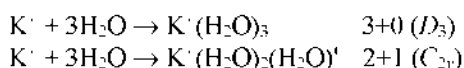
In the mid-frequency region, there are the water wagging and/or rocking motions, which are called the intermonomeric water vibrational motions, which have strong IR intensities but weak Raman activities. Their frequencies are denoted by γ_w. In 2+1 (C_{2v}) which has two bridged-type IIBs, the MP2-predicted vibrational frequencies (γ_w) of the intermonomeric water vibrational motions are increased in

comparison with the HF-predicted vibrational frequencies, owing to the stronger water-water interaction. On the other hand, in 3+0 (D_3) the MP2-predicted γ_w -values are decreased in comparison with the HF-predicted ones. The HF (MP2) maximum frequencies of the intermonomeric water vibrational modes, γ_w^{\max} , are 637 (692) cm^{-1} (b_1 symmetry) for 2+1 (C_{2v}) and 366 (340) cm^{-1} (a_2) for 3+0 (D_3) as shown in Table 3. Especially torsional modes of three water molecules attached to the metal ion appear at 86 (94) (a_1) and 41 (48) cm^{-1} (e) of HF (MP2) frequencies in 3+0 (D_3), while torsional modes appear above 200 cm^{-1} in 2+1 (C_{2v}).

In the high-frequency region the modes are water monomeric vibrations [symmetric stretching (γ_1), asymmetric stretching (γ_3) and bending (γ_2) of H_2O]. Very intense IR intensities appear in all three water monomeric vibrational modes, while strong Raman activities appear only in water monomeric stretching modes (γ_1 and γ_3).

Table 4 lists the vibrational frequency shifts ($\Delta\gamma_1$, $\Delta\gamma_2$ and $\Delta\gamma_3$) of the monomeric water molecules in the aqua- K^+ clusters relative to the intra-water vibrational frequencies (γ_1 , γ_2 , and γ_3) of the water monomer and the vibrational frequencies of the K^+ -water stretching modes ($\gamma_s^{\text{K-W}}$), as well as the maximum frequencies of the intermonomeric water vibrational modes (γ_w^{\max}). The red-shifts of the stretching frequencies (γ_1 and γ_3) of the monomeric water in the clusters and the blue-shifts of the bending frequencies (γ_2) are observed clearly. The largest frequency shift (-158 cm^{-1} for γ_1) appears in MP2 results for 2+1 (C_{2v}) having two HBs. This is one of the characteristics of 2+1 conformation.

Binding Energies and Thermodynamic Quantities. Binding energies and thermodynamic quantities are corresponding to the following reactions.



where $(\text{H}_2\text{O})'$ is the secondary hydration shell water molecule. Table 5 lists the binding energies (ΔE_e , ΔE_e^{B} , and ΔE_θ), the zero-point energy changes (ΔZPE) and thermodynamic quantities (ΔH_r and ΔG_r) of 2+1 (C_{2v}) and 3+0 (D_3). ΔE_e^{B} is the binding energy (ΔE_e) with BSSE correction and ΔE_θ is the sum of ΔE_e and the ZPE change (ΔZPE) for the above reactions.

Clusters containing a metal ion and water molecules may have several conformations. The conformational stability is decided by the interactions between metal and water, or

water and water. Because the water-water interaction is important in these systems, electron correlation effects can not be ignored. 3+0 (D_3) is more stable in HF-BEs (ΔE_e and ΔE_e^{B}), but 2+1 (C_{2v}) is more stable in MP2//HF and MP2-BEs (ΔE_e and ΔE_e^{B}). We have studied the effects of the electron correlation at the HF-predicted geometry. The differences between MP2//HF and HF-predicted binding energies could be considered as the electron correlation effect at HF-geometries, and the differences between MP2//HF and MP2 binding energies could be due to the effect of differences between the HF and MP2 geometries. The electron correlation effect for the binding energy at the HF-SCF predicted geometry shows that in the 2+1 (C_{2v}) the differences of the binding energies ΔE_e (ΔE_e^{B}) are increased by 4.8 (2.8) kcal/mol compared to HF predicted value, while in 3+0 (D_3) those are 2.8 (1.3) kcal/mol. The relative binding energy difference induced by electron correlation for these two conformations is about 2.0 (1.5) kcal/mol. The geometry optimization under the electron correlation effects further stabilizes this 2+1 (C_{2v}) conformation by 0.5 (0.1) kcal/mol. The correlation effect stabilizes the 2+1 (C_{2v}) conformation, by 2.5 (1.6) kcal/mol, more than 3+0 (D_3) conformation. Therefore, this 2+1 (C_{2v}) conformation is more stable and the relative binding energy difference become 0.9 (0.2) kcal/mol. The results from the previous theoretical work with pCVDZ/aug-cc-pVDZ basis sets predicted 1.7 kcal/mol.^{23b}

At 0 K the conformational stability must be decided by the binding energy corrected by zero point energies. As shown in Figure 1 and in the vibrational frequency analysis this 2+1 (C_{2v}) conformation has more tightly bound water molecules. ΔZPE s of 3+0 are smaller than those of 2+1, as shown in Table 5. In the present study of $\text{K}^+(\text{H}_2\text{O})_3$, ΔZPE difference between HF-SCF and MP2 levels is about 0.1 kcal/mol. A striking thing is that ΔZPE at MP2 level has larger value than the value at HF-SCF level in 2+1 (C_{2v}) conformation. We further analyzed the origin of ΔZPE difference for this $\text{K}^+(\text{H}_2\text{O})_3$ system because larger clusters were limited to HF-SCF frequencies. Previous studies have applied the constant scaling method or the exponential scaling method²¹ in order to improve the agreement with experiment and evaluate the thermodynamic quantities including zero-point energy, because HF and MP2 calculations tend to overestimate normal mode frequencies (such as the stretching modes for the water monomer). Since the ΔZPE is the difference in ZPE

Table 5. HF, MP2//HF and MP2/T72P Binding Energies and Thermodynamic Quantities of $\text{K}^+(\text{H}_2\text{O})_3$.^a The thermodynamic quantities are evaluated at 298.15 K and 1 atm

Conformation	HF		MP2//HF		MP2		ΔZPE
	ΔE_e (ΔE_e^{B})		ΔE_e (ΔE_e^{B})	ΔE_θ	ΔE_e (ΔE_e^{B})	ΔE_θ	HF/MP2
2+1 (C_{2v})	-45.3 (-44.2)		-50.1 (-47.0)	-44.2	-50.6 (-47.1)	-44.6	5.9/6.0
3+0 (D_3)	-46.7 (-45.7)		-49.5 (-47.0)	-45.6	-49.5 (-46.9)	-45.7	3.9/3.8
Conformation	MP2//HF		MP2		expt. ^b		
	ΔH_r	ΔG_r	ΔH_r	ΔG_r	ΔH_r	ΔG_r	
2+1 (C_{2v})	-46.5	-23.0	-46.5	-22.9	-47.2	-26.6	
3+0 (D_3)	-46.1	-29.0	-46.1	-29.3			

^aEnergies are in kcal/mol. ^bReference 6.

between the complex system and the isolated monomer systems and the high intramonomeric vibrational frequencies are almost off-set, the ΔZPE depends mainly on the sum of the low lying intermonomeric vibrational frequencies due to the metal-water or the water-water interactions. There are not significant differences in the structures and the energetics between the HF and MP2 calculations for K^+ -water system, thus the HF and MP2 intermonomeric vibrational frequencies do not give a significant difference as previously mentioned in vibrational analysis part. Thus, the zero-point energy difference is insensitive to the changes in the level of theory, too. Such as water clusters and particularly aqua-ion clusters, the ΔZPE is reasonably well described at the HF level.^{21a} In these molecular complex systems the generally used constant scaling approximation is not a good method. Kim *et al.*²¹ applied an exponential scaling factor to their frequencies using the expression $\gamma_i(\text{scaled}) = \gamma_i \exp(-\alpha\gamma_i)$, where α is a constant chosen to give the best agreement between experiment and RHF frequencies for water. Since this scaling method has minimal effects on low frequency modes, this is a better approximation than constant scaling method for the thermodynamic quantity evaluation.

As previously mentioned, the conformational stability was determined by the binding energy corrected by zero point energies at 0 K. The zero point energy difference between these two conformations is about 2.0 kcal/mol regardless of the level of theory, and this value is larger than the binding energy difference (0.9 or 1.7 kcal/mol) of these two complexes. The zero point energy corrected binding energies (ΔE_0) for the 2+1 (C_{2v}) and 3+0 (D_3) are 44.6 and 45.7 kcal/mol, respectively, and the difference is 1.1 kcal/mol. We found that the most stable conformation at 0 K should be 3+0 (D_3) regardless of the level of theory.

ΔE_0 shows that 3+0 conformation is more stable than 2+1. We estimate the thermodynamic functions using the harmonic oscillator-rigid rotator approximation for vibrational-rotational partition functions. As the temperature increases, vibrational enthalpy and entropy are more affected by the low frequencies than by the high ones. The enthalpy contribution is positive, whereas the entropy contribution is negative. The free energy tends to decrease as the temperature increases. Enthalpy predicts that the 2+1 (C_{2v}), which has less low-frequency modes, is more stable by 0.4 kcal/mol, as Feller and coworker's prediction (1.2 kcal/mol).^{23b} If these two conformations have the same entropies, the stability could be determined by binding enthalpy. Since this conformation (with less low-frequencies) is less activated, the vibrational entropy change is also smaller than in the 3+0 (D_3) conformation. The predicted ΔG_r 's for the 2+1 (C_{2v}) and 3+0 (D_3), however, are -22.9 and -29.3 kcal/mol, respectively. Based on Gibbs free energy changes (ΔG_r), conformation 3+0 (D_3) is more stable by 6.4 kcal/mol at 298 K and 1 atm. We note that the entropy effects stabilize this conformation by about 6.8 kcal/mol compared with 2+1 conformation.

In many cases the dominant error in such a treatment may be the failure of the harmonic approximation for one or more low-frequency vibrations that would be treated more appro-

Table 6. The correction of thermodynamic functions for the torsional modes with the hindered rotor approximation at 298.15 K. The reduced moment of inertia for the rotation of water molecule is 1.91×10^{-40} gm², and the symmetry number (σ_n) is 2

	$\bar{\nu}$ (cm ⁻¹)	G (kcal/mol)	H (kcal/mol)	S (cal/molK)
Harmonic Oscillator	48	-0.865	0.595	4.897
Hindered Rotor		-0.608	0.391	3.349
Δ_1		0.257	-0.205	-1.548
Harmonic Oscillator	94	-0.463	0.603	3.574
Hindered Rotor		-0.405	0.515	3.088
Δ_2		0.058	-0.087	-0.486
Total correction		0.572	-0.497	-3.582

priately as hindered internal rotations. Since the harmonic oscillator approximation may overestimate the vibrational thermal contribution to the Gibbs free energy, the predicted ΔG_r has the artificially decreasing value. Three water torsional modes, which have the normal vibrational frequencies (48, 48, and 94 cm⁻¹), are corrected with the hindered rotator partition function (Table 6). The hindered rotor corrected ΔH_r and ΔG_r for the 3+0 (D_3) are -46.6 kcal/mol and -28.7 kcal/mol compared to -46.1 and -29.3 kcal/mol, respectively. These values are closer to the experimentally obtained thermal quantities ($\Delta H_r = -47.2$ kcal/mol and $\Delta G_r = -26.6$ kcal/mol). The correction for the metal-water bending modes and the metal-water stretching modes will decrease the Gibbs free energy change further and increase the enthalpy change, and the difference between the theoretically predicted and experimentally obtained values will be disappeared. However, if we use the BSSE corrected binding energies, the difference increases more and more. These results show that the CP correction overestimates the true magnitude of BSSE in this system.

The added water molecule exists either in the primary hydration shell or hydration one. It is very interesting to study the conditions which determine the location of the molecule. From this study, the enthalpy effect maximizes the number of HBs of the clusters, while the entropy effect increases the coordination number of metal ion as in the previous studies of Na^+ -water clusters.^{20,21a} The competition between enthalpy and entropy effects determines the location. In this and previous studies, the conformations have the similar successive binding energies, which are almost same as the interaction energy obtained from the two hydrogen bonds, but these energies have quite different origins. One is charge-dipole interaction, another is water-water interaction. Our results show that the entropy term prefers the charge-dipole interaction to the water-water interaction. This entropy effect for the hydration shell seems like "inertia effect of the coordination number", and increases the coordination number of the metal ion.

Conclusions

In contrast to previous studies which used only the enthalpies to compare to the conformational stability, this study used the free energies. When conformations are almost isoenergetic in binding energies, the conformational stability should be determined by the Gibbs free energy, not by enthalpy. As we

compare the zero point energy difference in the levels of HF-SCF and MP2, this value is independent of the applied levels of theory. We calculate the thermal contributions to enthalpy and Gibbs free energy under the rigid-rotor and harmonic oscillator approximation. The vibrational thermal quantity evaluation by the generally used constant scaling approximation is not a good approximation. Our MP2/TZ2P calculations predict that the most stable conformation for $K^+(H_2O)_3$ should be 3+0 (D_3) at 0 K and 298.15 K. The predicted Gibbs free energy change is -29.3 kcal/mol under the harmonic oscillator approximation. For the low frequency mode, which is the torsional mode of water molecule, the thermal contributions to the enthalpy and Gibbs free energy are corrected under the hindered rotator approximation. This correction value (-28.7 kcal/mol) is in good agreement with the experimentally obtained value ($\Delta G_f = -26.6$ kcal/mol), while the Gibbs free energy change ($\Delta G_f = -22.9$ kcal/mol) of previously predicted 2+1 (C_{2v}) is far from the experimental value. Thus, it is expected that calculations which are more accurate than the present study would not change our conclusion. The most stable conformation of $K^-(H_2O)_3$ ion is shown to be entropy driven such as $Na^-(H_2O)_5$ and $Na^+(H_2O)_6$ ions. This study also shows that the unknown conformation should be determined by the Gibbs free energy.

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