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Ab Initio study**

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Citation: *The Journal of Chemical Physics* **121**, 3108 (2004); doi: 10.1063/1.1772353

View online: <http://dx.doi.org/10.1063/1.1772353>

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Insights into the structures, energetics, and vibrations of aqua-rubidium(I) complexes: *Ab Initio* study

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(Received 10 May 2004; accepted 20 May 2004)

We have carried out *ab initio* and density functional theory calculations of hydrated rubidium cations. The calculations involve a detailed evaluation of the structures, thermodynamic properties, and IR spectra of several plausible conformers of $\text{Rb}^+(\text{H}_2\text{O})_{n=1-8}$ clusters. An extensive search was made to find out the most stable conformers. Since the water-water interactions are important in hydrated Rb^+ complexes, we investigated the vibrational frequency shifts of the OH stretching modes depending on the number of water molecules and the presence/absence of outer-shell water molecules. The predicted harmonic and anharmonic vibrational frequencies of the aqua- Rb^+ clusters reflect the H-bonding signature, and would be used in experimental identification of the hydrated structures of Rb^+ cation. © 2004 American Institute of Physics.

[DOI: 10.1063/1.1772353]

I. INTRODUCTION

An ultimate understanding of the nature of ions in solutions is one of the most challenging aspects of contemporary solution chemistry and biochemistry.¹ This understanding is very useful in designing novel ionophores/receptors.² In this connection, a large number of theoretical and experimental studies have been carried out to study the solvation phenomenon of ions in the condensed and gas phases.³⁻¹⁴ It is well known that while the anion hydration tends to favor surface states,¹⁵⁻¹⁷ the cation hydration prefers internal states.¹⁸⁻²⁴ The behavior of gase-phase aqueous clusters can provide insights into the formation of hydrogen bonds and chemical reactions in aqueous solvents. Recently, many vibrational predissociation studies of the hydrated ion complexes have been reported. Such spectra contain the fingerprints of many different conformers which exist in the cluster beam; therefore the quantum chemical calculations are very helpful to interpret vibrational predissociation spectra. On the contrary, the vibrational predissociation spectrum facilitates to find out the missing conformers in the theoretical investigations.

In this paper, we report the structures, energetics, and spectra of $\text{Rb}^+(\text{H}_2\text{O})_{n=1-8}$, with special attention being focused on their trend as the cluster size increases. It should be mentioned that several competing and cooperative interactions contribute to the properties of solvated cations. In these cation-water clusters, the structures would result from a competition between hydrogen bonding and ionic interactions. To distinguish different conformers, we represent each cluster as “ $n_1+n_2(S)$ ” where the ion has n_1 and n_2 water molecules in the primary and secondary hydration shells, respectively, with the structural symmetry S in parentheses. If n_2 is con-

sidered between the primary and secondary hydration shells, it is denoted as n_2h , where “ h ” indicates “half.” It is clear that the increase of the cluster size beyond $n=6$ would result in multim minima problems associated with the increasing number of isoenergetic or quasiisoenergetic local minima on the potential energy surface.

II. CALCULATION METHODS

Throughout the present work, oxygen and hydrogen atoms were treated with correlation consistent all-electron basis sets, aug-*cc-pVDZ* and aug-*cc-pVTZ* (which will be abbreviated as *aVDZ* and *aVTZ*, respectively). Since the *aVDZ/aVTZ* basis set is not available for Rb, a Stuttgart RSC 1997 basis set was used. The Stuttgart RSC 1997 basis set employs relativistic core potentials (ECP) and an extended valence basis set. We carried out geometry optimizations using the density functional theory employing Becke's three parameters with Lee-Yang-Parr functionals (B3LYP) and Møller-Plesset second order perturbation theory (MP2) approach. For a few small clusters, coupled cluster calculations with single, double, and perturbative triples correction [CCSD(T)] were also carried out. All calculations were performed with the GAUSSIAN 03 suite of programs.²⁵ The harmonic and anharmonic vibrational frequencies, zero point energies (ZPEs), and thermodynamic quantities were evaluated on the optimized geometries at both B3LYP and MP2 levels. While all clusters $n=1-8$ were calculated with the *aVDZ* basis set, *aVTZ* basis set was employed for the selected low-lying energy clusters up to $n=4$. Rubidium possesses substantial polarizability, and the Stuttgart ECP basis set is unable to reproduce it correctly; therefore we added one diffuse *d* function with exponent 0.24. In the present work, we report binding energies without basis set superposition error (BSSE) correction.²⁶ It is well known that binding energies without BSSE correction are usually overesti-

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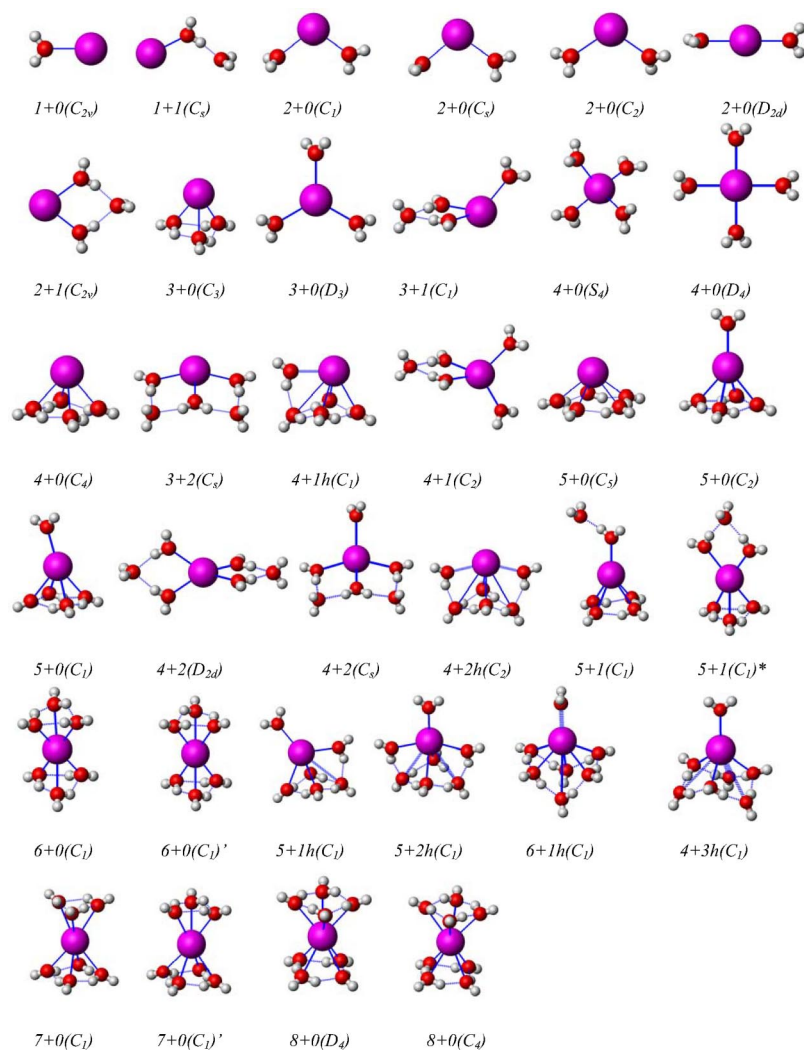


FIG. 1. MP2/*a*VDZ optimized structures of $\text{Rb}^+(\text{H}_2\text{O})_{1-8}$ clusters.

mated, whereas BSSE corrected binding energies tend to be underestimated.^{24,27} While there are many discussions about the substantial role of BSSE when calculating the absolute value of binding energy, the effect on relative stability of clusters is not so critical because of its consistency. Del Bene,²⁸ and Katz *et al.*,²⁹ and Markham *et al.* have also reported BSSE uncorrected values. In this work, the BSSE correction underestimates the binding energies, because the *a*VDZ basis set is still not close to the complete basis set. Even the BSSE-uncorrected binding energies for the *a*VDZ basis set are slightly underestimated.

Entropy depends mainly on the intermonomeric vibrational modes which were transformed from the rotational and translational motions of monomers upon complexation. Although free energy change at 298 K and 1 atm (ΔG_r) is sensitive to the anharmonicity of low frequencies, the contributions from the first- and second-order anharmonicities in Morse-type potentials tend to cancel partially. Thus, entropies based on harmonic approximation tend to be in good agreement with experimental values. However, when frequencies are very low, there could be significant deviations. In particular, the overestimated entropy corresponding to the very low frequencies (in particular $<10 \text{ cm}^{-1}$ at 298 K and 1 atm) can cause serious errors in free energy. The entropy

corresponding to the imaginary frequencies can also make errors in free energy. Thus, in our investigations, we replaced these erroneous vibrational entropies by the smallest value of the rotational entropy of a water monomer. On the other hand, the enthalpy change at 298 K and 1 atm (ΔH_r) is not sensitive to the anharmonicity of low frequencies, and so the harmonic approximation gives very reasonable values near to the true values.

III. RESULTS AND DISCUSSIONS

The MP2/*a*VDZ optimized structures of the various $\text{Rb}^+(\text{H}_2\text{O})_{n=1-8}$ complexes are shown in Fig. 1. Table I contains the MP2/*a*VDZ[B3LYP/*a*VDZ] interaction energies (ZPE-uncorrected ΔE_e and ZPE-corrected ΔE_0) for the hydrated Rb^+ clusters at 0 K and the free binding energies (ΔG_r) and enthalpies (ΔH_r) at 298 K and 1 atm. Some geometric parameters of the selected $\text{Rb}^+(\text{H}_2\text{O})_{n=1-8}$ clusters are listed in Table II. Table III shows the successive and total interaction energies of the low-lying energy conformers. In Table IV, binding enthalpies and free energies for the selected low-lying energy conformers are reported. We present the MP2/*a*VDZ[MP2/*a*VTZ] predicted -OH stretching vibrational spectra for $\text{Rb}^+(\text{H}_2\text{O})_{n=1-8}$ clusters in Fig. 2

TABLE I. MP2/aVDZ(B3LYP/aVDZ) interaction energies and thermodynamic quantities at 298 K and 1 atm.^a

| N | Structure | #HB | #if ^b | $-\Delta E_e$ | $-\Delta E_0$ | $-\Delta H_r$ | $-\Delta G_r$ |
|---|-----------------------|------|------------------|---------------|---------------|---------------|---------------|
| 1 | 1+0(C _{2v}) | 0 | 0(0) | 15.8(14.7) | 14.6(13.5) | 15.2(14.2) | 9.3(8.3) |
| 2 | 1+1(C _s) | 1 | 0(0) | 28.6(27.0) | 25.1(23.6) | 26.4(24.8) | 13.1(11.5) |
| | 2+0(C ₁) | 0 | 0(1) | 29.9(27.8) | 27.5(25.4) | 28.0(26.4) | 17.8(15.5) |
| | 2+0(C _s) | 0 | 0(1) | 29.9(27.8) | 27.5(25.4) | 28.0(26.4) | 17.4(15.0) |
| | 2+0(C ₂) | 0 | 1(0) | 29.9(27.8) | 27.5(25.3) | 28.6(25.8) | 17.2(15.3) |
| | 2+0(D _{2d}) | 0 | 2(3) | 29.6(27.7) | 27.3(25.4) | 28.9(27.5) | 14.9(12.9) |
| 3 | 2+1(C _{2v}) | 2 | 0(0) | 45.6(41.8) | 39.6(36.0) | 41.5(37.8) | 18.0(14.5) |
| | 3+0(D ₃) | 0 | 1(1) | 42.6(39.4) | 39.1(35.9) | 39.9(36.7) | 21.7(19.0) |
| | 3+0(C ₃) | 3 | 0(0) | 45.1(39.5) | 39.1(33.6) | 41.1(35.5) | 17.0(11.8) |
| 4 | 3+1(C ₁) | 2 | 0(0) | 57.4(52.7) | 50.5(45.8) | 52.0(47.3) | 24.7(18.9) |
| | 4+0(C ₄) | 4 | 0(0) | 60.1(53.1) | 51.3(44.4) | 54.3(47.3) | 19.9(13.1) |
| | 4+0(S ₄) | 0 | 3(0) | 53.8(49.7) | 49.3(45.0) | 51.0(45.0) | 25.0(22.0) |
| | 4+0(D ₄) | 0 | 2(1) | 53.3(48.9) | 48.7(44.2) | 49.8(44.8) | 27.0(19.6) |
| 5 | 3+2(C _s) | 2, 2 | 0(0) | 70.8(64.2) | 60.8(54.5) | 63.3(56.9) | 23.5(17.6) |
| | 4+1h(C ₁) | 4, 1 | 0(0) | 73.8(65.7) | 62.8(54.6) | 66.3(58.1) | 23.5(15.5) |
| | 4+1(C ₂) | 2 | 0(0) | 68.0(62.3) | 60.2(54.5) | 61.3(55.6) | 28.6(21.6) |
| | 5+0(C ₂) | 4 | 0(0) | 71.9(64.2) | 62.0(54.3) | 64.6(57.0) | 27.0(17.7) |
| | 5+0(C ₁) | 4 | 0(1) | 71.9(57.9) | 62.0(52.2) | 64.6(52.5) | 27.0(21.5) |
| | 5+0(C ₃) | 5 | 0(0) | 71.5(63.7) | 60.9(53.1) | 64.2(56.4) | 21.4(14.4) |
| 6 | 4+2h(C ₂) | 4, 2 | 0(0) | 87.2(82.8) | 73.8(64.2) | 77.8(68.3) | 25.6(16.3) |
| | 4+2(D _{2d}) | 2, 2 | 1(0) | 81.9(74.6) | 70.7(63.6) | 73.7(65.9) | 26.2(19.2) |
| | 4+2(C _s) | 2, 2 | 1(1) | 80.7(73.1) | 69.9(62.6) | 72.5(65.1) | 27.3(20.5) |
| | 5+1h(C ₁) | 4, 1 | 0(0) | 85.1(73.5) | 72.9(62.4) | 76.1(64.9) | 28.4(20.6) |
| | 5+1(C ₁) | 4, 1 | 0(0) | 82.8(74.6) | 70.7(62.7) | 73.9(65.8) | 28.2(19.7) |
| | 5+1(C ₁)* | 3, 2 | 0(0) | 82.4(73.4) | 70.6(61.8) | 73.5(64.6) | 27.7(18.5) |
| | 6+0(C ₁) | 3, 3 | 0(0) | 82.8(72.2) | 70.6(59.9) | 73.8(63.1) | 26.5(15.9) |
| | 6+0(C ₁)' | 3, 3 | 0(1) | 82.8(72.2) | 70.6(60.0) | 73.8(63.8) | 26.5(14.5) |
| 7 | 4+3h(C ₁) | 6 | 0(1) | 94.6(86.0) | 80.0(71.5) | 83.8(76.0) | 29.0(18.5) |
| | 5+2h(C ₁) | 4, 2 | 0(0) | 97.5(86.9) | 83.0(72.6) | 86.8(76.3) | 29.9(19.4) |
| | 6+1h(C ₁) | 6 | 1(2) | 97.9(85.8) | 82.8(71.7) | 87.5(76.5) | 27.6(19.0) |
| | 7+0(C ₁) | 4, 3 | 0(1) | 96.9(85.0) | 81.9(70.1) | 86.1(74.8) | 28.3(15.6) |
| | 7+0(C ₁)' | 4, 3 | 0(0) | 96.9(86.0) | 81.9(70.0) | 86.1(74.2) | 28.4(15.6) |
| 8 | 8+0(C ₄) | 4, 4 | 0(0) | 110.7(97.5) | 93.2(80.3) | 98.2(85.2) | 29.1(17.1) |
| | 8+0(D ₄) | 4, 4 | 0(0) | 110.7(97.5) | 93.2(80.3) | 98.2(85.1) | 28.2(16.9) |

^aEnergies are in kcal/mol. #HB describes the number of hydrogen bonds for each structure. ΔG_r are corrected by rotational entropy (0.879 kcal/mol) for the imaginary frequencies, and ΔG_r for the chiral structures are further corrected by $-RT \ln 2$, where R is the gas constant. The uncertain values are given in italics. The free energies for clusters having a large number of low frequencies would be underestimated, and so not reliable for $n > 5$.

^b#if denotes the number of imaginary frequencies.

and the details are reported in Table V. The harmonic, scaled harmonic and anharmonic vibrational frequencies for the -OH stretching modes are shown in Table VI.

The MP2/aVTZ hydrogen bond lengths are slightly shorter in comparison to MP2/aVDZ (by ~ 0.2 Å), as shown in Table II. Consequently, the binding energy at the MP2/aVDZ level is smaller than that of MP2/aVTZ. However, both MP2/aVDZ and MP2/aVTZ thermodynamic quantities are consistent, in good agreement with the experimental values (Tables III and IV). However, the B3LYP/aVDZ results are not consistent with the MP2/aVDZ and MP2/aVTZ values in that the former favors smaller coordination numbers than the latter cases. This should be correlated with the fact that the predicted B3LYP binding energies are underestimated compared with the experimental values. Since MP2/aVDZ results are considered to be reliable and are available for all the structures ($n=1-8$) investigated here, we discuss the results obtained at the MP2/aVDZ level, unless otherwise specified. Formerly, Feller and co-workers^{24,30} investigated the cluster stability of alkali-

metal ions in term of the binding enthalpy. However, the lowest binding enthalpy cluster is not always consistent with the lowest binding free energy cluster. Thus, we will consider the stability of Rb⁺-water clusters in several aspects like binding energies, zero-point energies, and free energies.

A. Structures and thermodynamic quantities

1. Low-lying energy structures of Rb⁺(H₂O)_{n=1-4}

The most stable structure of Rb⁺(H₂O) has C_{2v} symmetry as in the case of other alkali metal ion-water complexes. The MP2/aVDZ[MP2/aVTZ] optimized interatomic distance $r(\text{Rb}^+\cdots\text{O})$ is 2.795 Å [2.772 Å]. Feller and co-workers^{24,27} have already done similar calculations for Rb⁺(H₂O) with core valence and extra diffuse basis functions. The purpose of this study is to extend previous research into more detailed structural and energetical analysis of the hydrated rubidium cation complexes comprising up to eight water molecules.

TABLE II. MP2/aVDZ[MP2/aVTZ] geometric parameters of $\text{Rb}^+(\text{H}_2\text{O})_{n=1-8}$ clusters.^a

| N | Structure | $r(\text{Rb}^+\cdots\text{O})$ | $r(\text{O}\cdots\text{H}_n)$ | $\langle(\text{ORbO})_m\rangle$ |
|---|-----------------|--------------------------------|-------------------------------|---------------------------------|
| 1 | 1+0(C_{2v}) | 2.795 [2.772] | | |
| 2 | 1+1(C_s) | 2.721 4.586 [2.701 4.586] | 1.775 [1.766] | |
| | 2+0(C_1) | 2.813–2.822 [2.784–2.790] | | 104.4[104.4] |
| | 2+0(C_s) | 2.814–2.821 [2.785–2.791] | | 105.8[105.8] |
| 3 | 2+1(C_{2v}) | 2.776 4.554 [2.750 4.523] | 1.926 [1.922] | 74.0[74.4] |
| | 3+0(C_3) | 2.899 [2.857] | 2.140 [2.124] | 58.2[58.9] |
| | 3+0(D_3) | 2.849 [2.812] | | 120.0[120.0] |
| 4 | 3+1(C_1) | 2.804–2.860 [2.770–2.813] | 1.937 [1.933] | 73.5[73.9] |
| | | 4.593 [4.555] | | |
| | 4+0(C_4) | 2.964 [2.911] | 1.907 [1.903] | 55.3[56.2] |
| 5 | 3+2(C_s) | 2.773–2.822 4.642 | 1.937, 1.993 | 72.3 |
| | 4+1h(C_1) | 2.785–3.017 3.921 | 1.840–1.943 | 44.6 |
| | 4+1(C_2) | 2.834–2.882 4.626 | 1.943 | 73.1 |
| | 5+0(C_2) | 2.870–3.006 | 1.873–1.876 | 54.3 |
| | 5+0(C_1) | 2.868–3.013 | 1.871–1.877 | 54.2 |
| | 5+0(C_5) | 3.017 | 1.850 | 54.0 |
| 6 | 4+2h(C_2) | 2.810–3.052 3.971 | 1.842 1.928 | 43.7 |
| | 4+2(D_{2d}) | 2.849 4.641 | 1.951 | 73.0 |
| | 4+2(C_s) | 2.811–2.907 4.686 | 1.947 2.000 | 71.6 |
| | 5+1(C_1) | 2.800–3.029 4.734 | 1.812 1.860–1.863 | 53.8 |
| | 5+1(C_1)* | 2.837–3.017 4.636 | 1.946 2.016–2.025 | 54.9 |
| | 5+1h(C_1) | 2.810–3.067 3.947 | 1.829–1.938 | 44.2 |
| | 6+0(C_1) | 2.989–2.990 | 2.038–2.040 | 55.5 |
| | 6+0(C_1)' | 2.990–2.991 | 2.037–2.040 | 55.5 |
| 7 | 4+3h(C_1) | 2.874–2.942 3.907–3.924 | 1.713–1.836 | 43.0 |
| | 5+2h(C_1) | 2.836–3.110 4.006 | 1.822–1.843 1.920 | 43.0 |
| | 6+1h(C_1) | 2.885–3.099 4.087 | 1.826–1.958 | 42.5 |
| | 7+0(C_1) | 2.997–3.052 | 1.847–2.028 | 53.2 |
| 8 | 8+0(C_4) | 3.059 | 1.842 1.843 | 53.0 |
| | 8+0(D_4) | 3.059 | 1.843 | 53.0 |

^aDistances are in angstrom; angles are in degree. " $\langle(\text{ORbO})_m\rangle$ " means the minimum value among the ORbO angles.

In the case of $\text{Rb}^+(\text{H}_2\text{O})_2$, 2+0(C_1), and 2+0(C_s) conformers are more stable than 1+1(C_s). Conformers, 2+0(C_1), 2+0(C_s), 2+0(C_2), and 2+0(D_{2d}) are practically isoenergetic with respect to ΔE_0 , because the potential energy surface at this region is almost flat. Although the linear 2+0(D_{2d}) conformer was the most stable structure in the case of $\text{K}^+(\text{H}_2\text{O})_2$, in the case of $\text{Rb}^+(\text{H}_2\text{O})_2$ it is a saddle point structure. At room temperature, conformers 2+0(C_1), 2+0(C_s), and 2+0(C_2) are all practically isoenergetic in terms of ΔG_r , and so these structures are interconvertible. This indicates that the water molecules would be easily rotated at room temperature; then the free energy contributions from the two lowest frequencies (16 and 18 cm^{-1}) would be replaced by the free energy contributions by the rotational modes of a water molecule. In this way, the MP2/aVTZ calculations give the realistic values for ΔH_r and ΔG_r , close to the experimental values.

In the case of $n=3$, 2+1(C_{2v}) is the most stable structure in ΔE_e , while in ΔE_0 2+1(C_{2v}), 3+0(D_3), and 3+0(C_3) conformers are almost isoenergetic. The 3+0(D_3) cluster is the most stable in terms of free energy.

In the case of $n=4$, 4+0(C_4) is the most stable conformer in terms of ΔE_0 . On the other hand, conformer 4+0(D_4) has the lowest free energy. 3+1(C_1) is 0.8–0.9 kcal/mol higher in ΔE_0 than 4+0(C_4).

TABLE III. MP2 and CCSD(T) successive and total interaction energies of the lowest energy conformers at 0 K for $n=1-8$.^a

| n | Structure | $-\Delta E_e$ | $-\Delta E_0$ | $-\Delta E_0^s$ |
|----------------------------|-----------------|---------------|---------------|-----------------|
| MP2/aVDZ[MP2/aVTZ] | | | | |
| 1 | 1+0(C_{2v}) | 15.8[16.8] | 14.6[15.5] | 14.6[15.5] |
| 2 | 1+1(C_s) | 28.6[29.8] | 25.1[26.3] | |
| | 2+0(C_1) | 29.9[32.0] | 27.5[29.3] | 12.9[13.8] |
| | 2+0(C_s) | 29.9[31.9] | 27.5[29.3] | |
| 3 | 2+1(C_{2v}) | 45.6[47.4] | 39.6[41.5] | 12.1[12.2] |
| | 3+0(C_3) | 45.1[47.4] | 39.1[41.2] | |
| | 3+0(D_3) | 42.6[45.6] | 39.1[41.6] | |
| 4 | 3+1(C_1) | 57.4[60.2] | 50.5[53.2] | |
| | 4+0(C_4) | 60.1[62.9] | 51.3[54.1] | 11.7[12.6] |
| 5 | 4+1h(C_1) | 73.8 | 62.8 | 11.5 |
| | 5+0(C_2) | 71.9 | 62.0 | |
| 6 | 4+2h(C_2) | 87.2 | 73.8 | 10.0 |
| | 5+1h(C_1) | 85.1 | 72.9 | |
| 7 | 5+2h(C_1) | 97.5 | 83.0 | 9.2 |
| | 6+1h(C_1) | 97.9 | 82.8 | |
| 8 | 8+0(C_4) | 110.7 | 93.2 | 9.8 |
| | 8+0(D_4) | 110.7 | 93.2 | |
| CCSD(T)/aVDZ[CCSD(T)/aVTZ] | | | | |
| 1 | 1+0(C_{2v}) | 15.7[16.9] | 14.4[15.5] | 14.4[15.5] |
| 2 | 1+1(C_s) | 28.5 | 24.8 | |
| | 2+0(C_1) | 29.8 | 27.3 | 12.9 |
| | 2+0(C_s) | 29.8 | 27.3 | |
| 3 | 2+1(C_{2v}) | 45.4 | 39.4 | 12.1 |
| | 3+0(D_3) | 42.4 | 38.9 | |

^aEnergies are in kilocalorie/mole. ΔE_0^s is the successive ZPE-corrected interaction energy at 0 K. $\Delta E_0^s(n)=[\Delta E_0(n)-\Delta E_0(n-1)]$.

TABLE IV. Binding enthalpies and free energies for the most stable clusters in either ΔE_0 or ΔG_r for $n=1-6$.^a

| $-\Delta H_r(-\Delta G_r)$ | B3LYP [<i>a</i> VDZ] | MP2 [<i>a</i> VDZ] | MP2 [<i>a</i> VTZ] | CCSD(T) [<i>a</i> VDZ] | CCSD(T) [<i>a</i> VTZ] | Exp. |
|----------------------------|--------------------------|--------------------------|--------------------------|----------------------------|----------------------------|------------|
| 1+0(C_{2v}) | 14.2(8.3) | 15.2(9.3) | 16.2(10.2) | 15.1(9.1) | 16.2(10.2) | 15.9(9.6) |
| 2+0(C_1) | 26.4(15.1) ₋₁ | 28.0(17.8) | 29.9(17.0) ^b | 28.3(16.1) | | 29.5(16.6) |
| 2+0(C_s) | 26.4(15.0) ₋₁ | 28.0(17.4) | 29.9(16.5) | 28.9(14.8) | | |
| 1+1(C_s) | 24.8(11.5) | 26.4(13.1) | 27.5(14.3) | 26.0(13.0) | | |
| 3+0(D_3) | 36.7(19.0) ₋₁ | 39.9(21.7) ₋₁ | 42.1(22.6) ^c | | | 41.7(21.6) |
| 2+1(C_{2v}) | 37.8(14.5) | 41.5(18.0) | 43.3(19.8) | | | |
| 3+0(C_3) | 35.5(11.8) | 41.1(17.0) | 43.3(19.6) | | | |
| 4+0(D_4) | 44.8(19.6) | 49.8(27.0) ₋₂ | 53.4(26.5) ₋₂ | | | 52.9(25.4) |
| 3+1(C_1) | 47.3(18.9) | 52.0(24.7) | 54.8(25.0) ^c | | | |
| 4+0(C_4) | 47.3(13.1) | 54.3(19.9) | 57.1(22.2) | | | |
| 4+1(C_2) | 55.6(21.6) | 61.3(28.6) | | | | 63.4(28.2) |
| 5+0(C_2) | 57.0(17.7) | 64.6(27.0) | | | | |
| 4+1h(C_1) | 58.1(15.5) | 66.3(23.5) | | | | |
| 3+2(C_s) | 56.9(17.6) | 63.3(23.5) | | | | |
| 5+0(C_5) | 56.4(14.4) | 64.2(21.4) | | | | |
| 5+1h(C_1) | 64.9(20.6) | 76.1(28.4) | | | | |
| 5+1(C_1) | 65.8(19.7) | 73.9(28.2) | | | | |
| 4+2(D_{2d}) | 65.9(19.2) | 73.7(26.2) ₋₁ | | | | |
| 4+2h(C_2) | 68.3(16.3) | 77.8(25.6) | | | | |

^aThe binding free energies ($-\Delta G_r$) are given in parentheses. The negative value in subscripts indicates the number of imaginary frequencies, for which the vibrational entropy was replaced by the rotational entropy. The experimental values are taken from Ref. 5b. The free energies would not be reliable for $n \geq 5$.

^bThe vibrational entropy contributions by the two lowest frequency modes (16 and 18 cm^{-1}) are replaced by the rotational entropy contributions by each water molecule.

^cThe frequencies less than 10 cm^{-1} have also been replaced by the rotational entropy of a water molecule.

2. Low-lying energy structures of $\text{Rb}^+(\text{H}_2\text{O})_{n=5-8}$

In the case of $\text{Rb}^+(\text{H}_2\text{O})_5$ clusters, we investigated six different complexes. At the MP2/*a*VDZ level, 4+1h(C_1) is

the most stable conformer in ΔE_0 , while 4+1(C_2) conformer is the most stable in ΔG_r . The conformer 4+1h(C_1) consists of a cyclic water tetramer and one water molecule (located between the first and second hydration

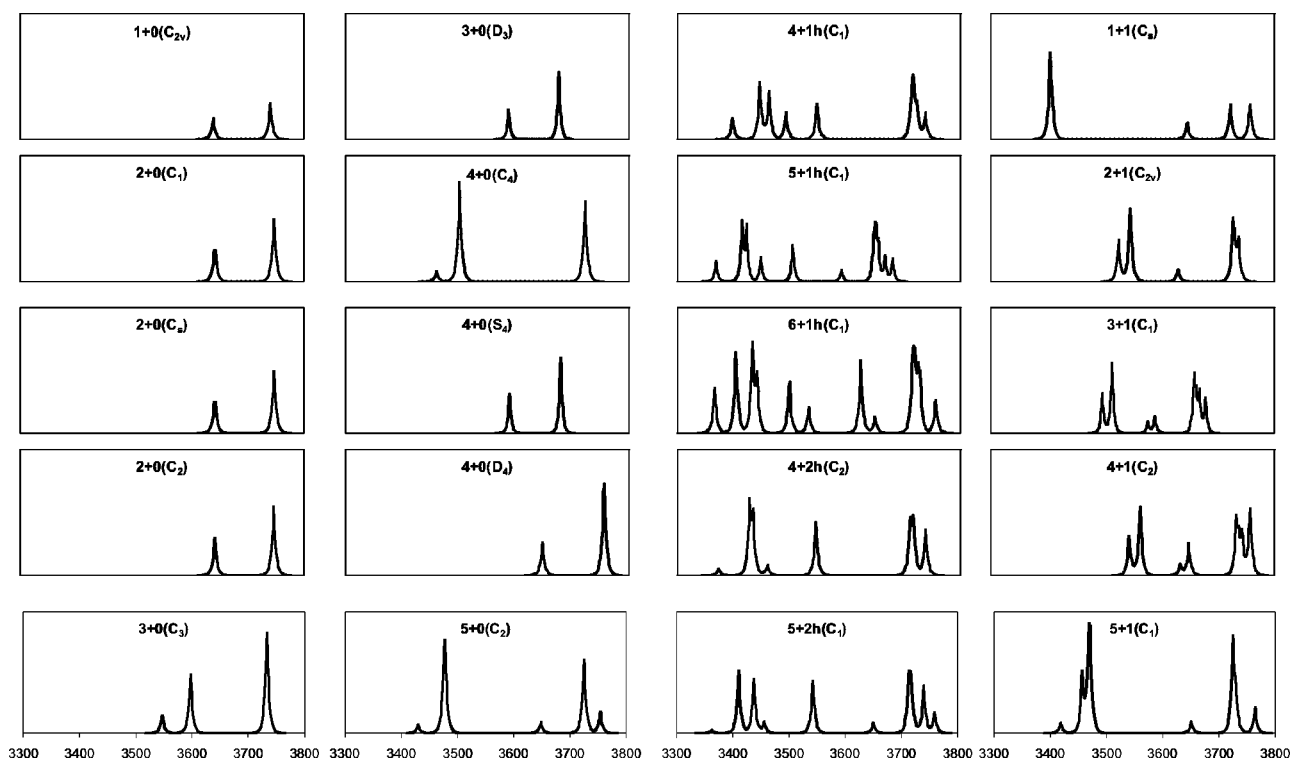


FIG. 2. MP2/*a*VDZ predicted IR spectra of the exponentially scaled -OH stretching frequencies. The IR intensities (I_r) for the scaled frequencies are plotted in terms of $(I_r \exp\{-|\nu - \nu_i|/\Delta\nu\})^{1/2}$ where $\Delta\nu=1 \text{ cm}^{-1}$.

TABLE V. MP2/aVDZ scaled frequencies ν_i (cm^{-1}) and the IR intensities in subscripts (10 km/mol).^a

| α VDZ | ν_3 | ν_1 |
|-----------------|---|---|
| 1+0(C_{2v}) | 3741 ₁₃ | 3640 ₄ |
| 1+1(C_s) | 3757 ₁₂ 3722 ₁₂ | 3646 ₃ 3405 ₇₄ |
| 2+0(C_1) | 3748 ₁₂ 3747 ₁₂ | 3644 ₄ 3642 ₄ |
| 2+0(C_s) | 3748 ₁₂ 3747 ₁₂ | 3644 ₄ 3642 ₄ |
| 2+0(C_2) | 3747 ₉ 3747 ₁₅ | 3643 ₂ 3643 ₅ |
| 2+1(C_{2v}) | 3737 ₁₃ 3730 ₅ 3727 ₂₆ | 3630 ₁ 3547 ₅₃ 3525 ₁₇ |
| 3+0(C_3) | 3734 ₁ 3733 ₂₅ (e) | 3597 ₉ (e) 3574 ₄ |
| 3+0(D_3) | 3751 ₁₀ (e) 3751 ₁₅ | 3646 ₀ 3645 ₅ (e) |
| 4+0(C_4) | 3724 ₂ 3722 ₃₂ (e) 3721 ₀ | 3522 ₀ 3501 ₅₆ (e) 3460 ₂ |
| 4+0(D_4) | 3756 ₀ 3756 ₁₂ (e) 3756 ₁₈ | 3648 ₀ 3647 ₀ 3647 ₁₁ (e) |
| 4+0(S_4) | 3755 ₁₅ 3755 ₀ 3755 ₁₅ (e) | 3647 ₀ 3647 ₄ (e) 3647 ₄ |
| 3+1(C_1) | 3754 ₁₁ 3741 ₁₃ 3734 ₅ 3730 ₂₅ | 3647 ₃ 3632 ₁ 3556 ₅₀ 3536 ₁₆ |
| 3+2(C_3) | 3745 ₂₄ 3745 ₀ 3734 ₅ 3734 ₂₁ 3674 ₅₀ | 3635 ₂ 3631 ₁₃ 3566 ₃₀ 3542 ₀ 3541 ₄₃ |
| 4+1h(C_1) | 3738 ₁₅ 3723 ₁₅ 3717 ₁₄ 3716 ₂₂ 3713 ₁₀ | 3547 ₂₉ 3492 ₁₆ 3462 ₅₀ 3446 ₇₀ 3398 ₁₀ |
| 4+1(C_2) | 3757 ₉ 3757 ₁₂ 3743 ₁₃ 3737 ₆ 3733 ₂₃ | 3649 ₂ 3649 ₄ 3634 ₁ 3563 ₄₇ 3544 ₁₅ |
| 5+0(C_3) | 3723 ₁ 3721 ₃₈ (e) 3719 ₀ (e) | 3495 ₀ (e) 3463 ₁₀₀ (e) 3422 ₂ |
| 5+0(C_2) | 3754 ₁₁ 3727 ₂ 3725 ₂₆ 3725 ₂₉ 3723 ₀ | 3648 ₃ 3501 ₀ 3478 ₆₆ 3477 ₆₇ 3430 ₂ |
| 4+2h(C_2) | 3739 ₁₇ 3738 ₁₃ 3717 ₁₇ 3716 ₁₅ 3711 ₂₇ 3711 ₃ | 3545 ₅₇ 3543 ₁ 3459 ₃ 3434 ₆₁ 3428 ₁₀₀ 3373 ₁ |
| 4+2(D_{2d}) | 3745 ₁₃ (e) 3739 ₁₂ 3739 ₀ 3735 ₂₃ (e) | 3635 ₂ (e) 3568 ₀ 3567 ₉₁ 3550 ₁₅ (e) |
| 4+2(C_2) | 3759 ₁₁ 3748 ₂₄ 3748 ₀ 3737 ₅ 3737 ₂₀ 3680 ₅₀ | 3650 ₂ 3637 ₂ 3634 ₁₀ 3572 ₂₈ 3548 ₀ 3548 ₄₂ |
| 5+1(C_1) | 3764 ₁₁ 3730 ₁₂ 3727 ₃ 3725 ₂₈ 3725 ₂₇ 3724 ₀ | 3651 ₂ 3494 ₀ 3471 ₇₂ 3469 ₇₅ 3457 ₅₆ 3419 ₂ |
| 5+1(C_1)* | 3764 ₁₁ 3730 ₁₂ 3727 ₃ 3726 ₂₈ 3726 ₂₇ 3724 ₀ | 3650 ₂ 3494 ₀ 3470 ₇₂ 3469 ₇₅ 3457 ₅₆ 3420 ₂ |
| 5+1h(C_1) | 3756 ₁₁ 3740 ₁₄ 3725 ₁₄ 3721 ₁₅ 3719 ₁₈ 3716 ₁₂ | 3648 ₃ 3545 ₃₀ 3477 ₁₃ 3447 ₁₃ 3437 ₇₃ 3382 ₉ |
| 6+0(C_1) | 3736 ₀ 3736 ₃ 3735 ₄₁ 3735 ₄₂ 3734 ₂ 3734 ₃ | 3572 ₃₂ 3572 ₃₀ 3571 ₃ 3571 ₂ 3540 ₀ 3540 ₅ |
| 5+2h(C_1) | 3759 ₁₀ 3740 ₁₅ 3740 ₁₂ 3718 ₁₂ 3717 ₁₄ 3714 ₂₆ 3713 ₄ | 3650 ₃ 3543 ₆₀ 3541 ₀ 3456 ₃ 3438 ₇₂ 3411 ₉₅ 3363 ₀ |
| 6+1h(C_1) | 3756 ₁₁ 3728 ₁₄ 3725 ₁₄ 3719 ₁₆ 3717 ₁₃ 3715 ₁₂ 3649 ₃ | 3624 ₅₃ 3532 ₇ 3498 ₂₇ 3441 ₂₆ 3433 ₇₁ 3404 ₆₇ 3366 ₂₁ |
| 7+0(C_1) | 3735 ₂ 3734 ₂₃ 3734 ₂₃ 3728 ₃ 3726 ₂₆ 3726 ₂₆ 3725 ₀ | 3569 ₁₈ 3568 ₁₈ 3536 ₂ 3484 ₀ 3459 ₇₄ 3459 ₇₄ 3406 ₂ |
| 8+0(D_4) | 3731 ₀ 3730 ₆ 3729 ₅₃ (e) 3729 ₀ (e) 3729 ₀ 3728 ₀ | 3481 ₀ 3480 ₀ 3457 ₁₅₀ (e) 3453 ₀ (e) 3401 ₀ 3401 ₀ |
| α VTZ | ν_3 | ν_1 |
| 1+0(C_{2v}) | 3748 ₁₄ | 3656 ₅ |
| 1+1(C_s) | 3765 ₁₃ 3731 ₁₂ | 3661 ₃ 3412 ₇₈ |
| 2+0(C_1) | 3754 ₁₃ 3752 ₁₃ | 3659 ₄ 3657 ₅ |
| 2+1(C_{2v}) | 3745 ₁₄ 3739 ₅ 3736 ₂₇ | 3646 ₁ 3559 ₅₇ 3537 ₁₈ |
| 3+0(D_3) | 3756 ₁₃ (e) 3756 ₁₂ | 3660 ₀ 3659 ₆ (e) |
| 3+0(C_3) | 3736 ₁ 3735 ₂₆ (e) | 3608 ₁₀ (e) 3584 ₁₈ |
| 3+1(C_1) | 3762 ₁₂ 3748 ₁₄ 3742 ₅ 3739 ₂₆ | 3664 ₄ 3648 ₁ 3569 ₅₃ 3549 ₁₆ |
| 4+0(C_4) | 3730 ₂ 3728 ₃₃ (e) 3726 ₀ | 3536 ₁ 3514 ₅₈ (e) 3471 ₂ |
| 4+0(D_4) | 3762 ₀ 3762 ₁₃ (e) 3762 ₂₀ | 3663 ₀ 3663 ₇ (e) 3663 ₀ |

^aThe scaling factor $\alpha = 10^{-5}$ was used. "(e)" denotes the doubly degenerate vibrational mode.

shells) which forms a partial hydrogen bond with the tetramer. 5+0(C_2) and 5+0(C_1) conformers have almost the same binding energy and the same thermodynamic quantities, but they are slightly less stable in ΔE_0 than 4+1h(C_1), and slightly less stable in ΔG_r than 4+1(C_2).

In the case of $\text{Rb}^+(\text{H}_2\text{O})_6$, the number of possible conformers is greater in comparison to smaller clusters, because of a large number of possible arrangements among six water molecules. 4+2h(C_2) conformer is the most stable in ΔE_0 . 4+2h(C_2) has four water molecules in the first hydration shell and two water molecules denoted as half-coordinated. Four hydrogen bonds make a cyclic ring and the remaining two hydrogen bonds are connected in facing the apex of the square cyclic ring (cyclic ring is made of two water molecules in the first hydration shell and the other two are between the first and second hydration shells). In terms of ΔG_r , 5+1h(C_1) is the most stable conformer. This struc-

ture is related to the structure of 4+1h(C_1) by adding one nonhydrogen bonded water molecule in the opposite direction of the five hydrogen bonded molecules.

As the number of water molecules increases, the computing time significantly increases in comparison to smaller clusters. Therefore, we investigated only a few conformers for $\text{Rb}^+(\text{H}_2\text{O})_{7,8}$.

In the case of $\text{Rb}^+(\text{H}_2\text{O})_7$, 5+2h(C_1), and 6+1h(C_1) are the most stable conformers in terms of ΔE_0 among five different structures. 5+2h(C_1) is made by adding one water molecule to the 4+2h(C_2) conformer.

In the case of $n=8$, two conformers have been investigated [8+0(C_4) and 8+0(D_4)] because of the reasons mentioned above. 8+0(C_4) and 8+0(D_4) have almost the same stability in terms of ΔE_0 , ΔH_r , and ΔG_r . Their structures differ only in the helicity of the hydrogen bonds of the two tetramers.

TABLE VI. MP2/*a*VDZ harmonic (ω_h), scaled (ω_s), and anharmonic (ω_a) vibrational -OH stretching frequencies (cm^{-1}) for selected $\text{Rb}^+(\text{H}_2\text{O})_{n=1,3}$ clusters, and MP2/*a*VTZ, CCSD(T)/*a*VDZ and CCSD(T)/*a*VTZ harmonic (ω_h) frequencies for $\text{Rb}^+(\text{H}_2\text{O})_{1-2}$ clusters.

| MP2/ <i>a</i> VDZ | | ν_3 | ν_1 |
|------------------------|------------|----------------|----------------|
| 1+0(C_{2v}) | ω_h | 3890 | 3780 |
| | ω_s | 3741 | 3640 |
| | ω_a | 3692 | 3595 |
| 1+1(C_s) | ω_h | 3907 3869 | 3787 3527 |
| | ω_s | 3757 3722 | 3646 3405 |
| | ω_a | 3713 3674 | 3605 3343 |
| 2+0(C_1) | ω_h | 3897 3896 | 3785 3783 |
| | ω_s | 3748 3747 | 3644 3642 |
| | ω_a | 3701 3703 | 3602 3604 |
| 2+0(C_s) | ω_h | 3898 3896 | 3785 3783 |
| | ω_s | 3749 3747 | 3644 3642 |
| | ω_a | 3702 3702 | 3603 3604 |
| 2+1(C_{2v}) | ω_h | 3886 3878 3874 | 3770 3680 3657 |
| | ω_s | 3737 3730 3727 | 3630 3547 3525 |
| | ω_a | 3688 3684 3679 | 3584 3499 3482 |
| 3+0(C_3) | ω_h | 3882 3881(e) | 3734(e) 3710 |
| | ω_s | 3734 3733(e) | 3597(e) 3574 |
| | ω_a | 3685 3688(e) | 3559(e) 3542 |
| MP2/ <i>a</i> VTZ | | | |
| 1+0(C_{2v}) | ω_h | 3898 | 3797 |
| 2+0(C_1) | ω_h | 3904 3902 | 3801 3800 |
| CCSD(T)/ <i>a</i> VDZ | | | |
| 1+0(C_{2v}) | ω_h | 3871 | 3777 |
| 2+0(C_1) | ω_h | 3878 3877 | 3781 3780 |
| CCSD(T)/ <i>a</i> VTZ | | | |
| 1+0(C_{2v}) | ω_h | 3879 | 3794 |

3. Thermodynamic quantities of $\text{Rb}^+(\text{H}_2\text{O})_{n=1-8}$

The most stable structures for $n=1-8$ in ΔE_0 are 1+0(C_{2v}), 2+0(C_1)/2+0(C_s)/2+0(C_2), 3+0(D_3)/2+1(C_{2v})/3+0(C_3), 4+0(C_4), 4+1(C_1), 4+2(C_2), 5+2(C_2)/6+1(C_1), and 8+0(C_4)/8+0(D_4). The most stable structures for $n=1-6$ in ΔG_r (room temperature, 1 atm) are 1+0(C_{2v}), 2+0(C_1)/2+0(C_s)/2+0(C_2), 3+0(D_3), 4+0(D_4), 4+1(C_2), and 5+1(C_1)/5+1(C_1). The MP2/*a*VDZ free energies for $n=1-5$ [1+0(C_{2v}), 2+0(C_1), 3+0(D_3), 4+0(D_4), 4+1(C_2)] are -9.3, -17.8, -21.7, -27.0, and -28.6 kcal/mol in good agreement with Kebarle's experimental free energies (-9.6, -16.6, -21.6, -25.4, and -28.2 kcal/mol), and these MP2/*a*VDZ enthal-

pies are -15.2, -28.0, -39.9, -49.8, and -61.3 kcal/mol, which seem to be in good agreement with Kebarle's experimental enthalpies (-15.9, -29.5, -41.7, -52.9, and -63.4 kcal/mol). At the MP2/*a*VTZ level, the free energies for $n=1-4$ (after few very low frequency modes, if any, were replaced by water rotational modes) are -10.2, -17.0, -22.6, and -26.5 kcal/mol, and the corresponding enthalpies are -16.2, -29.9, -42.1, and -53.4 kcal/mol, which are in much better agreement with the experimental values than the MP2/*a*VDZ results. The CCSD(T) results are very close to the corresponding MP2 values (Table IV).

B. Vibrational frequencies

Most of the experimental data on vibrational frequencies are based on the observations of the -OH stretching modes. Theoretical prediction of vibrational frequencies and intensities of the -OH stretching modes is very useful for identifying the structures of unknown molecular clusters in experiments.³¹ In the small neutral water clusters, the frequency redshifts for hydrogen bonds with the water type of *daa*, *da*, *dda*, and *aa* (where *d*, *a*, *dd*, and *aa* indicate proton-donor, proton-acceptor, double-donor, and doubly-acceptor, respectively) are roughly around ~600, ~400, ~200, and ~100 cm^{-1} , respectively. Such spectral analysis have provided vital tools to identify molecular structures. The MP2 vibrational frequencies of -OH stretch mode are often slightly less redshifted in comparison with the B3LYP values. The IR spectra differentiate various types of hydrogen bonding of water molecules, while similar shifted peaks appear with similar hydration structures. The analysis of the frequency shifts in the -OH stretching mode reveals the presence of larger shifts resulting from the presence of hydrogen bonds. However, the analysis of larger clusters is rendered more complicated by the possibility of several different conformers coexisting. We report scaled -OH stretching IR vibrational spectra of hydrated rubidium cation complexes in Fig. 2 and the details are shown in Table V. Furthermore, Fig. 3 contains scaled -OH stretching IR vibrational spectra calculated at both MP2/*a*VDZ and MP2/*a*VTZ levels. In *ab initio* calculations, high vibrational frequencies tend to be overestimated, while lower frequencies do not show such a trend. Therefore to generate more realistic value, we employed exponentially scaled frequencies:³² $\nu_i^s = \nu_i e^{-a\nu_i}$ where ν_i^s and ν_i are scaled and unscaled frequencies with

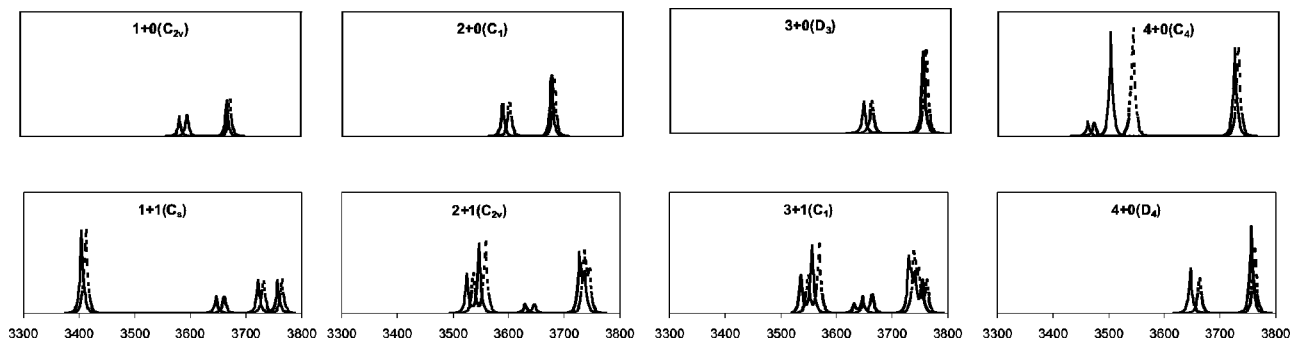


FIG. 3. MP2/*a*VDZ (MP2/*a*VTZ) predicted ν_{sym} and ν_{asym} -OH stretching modes for $\text{Rb}^+(\text{H}_2\text{O})_{n=1,4}$ which are drawn using solid and dashed lines, respectively.

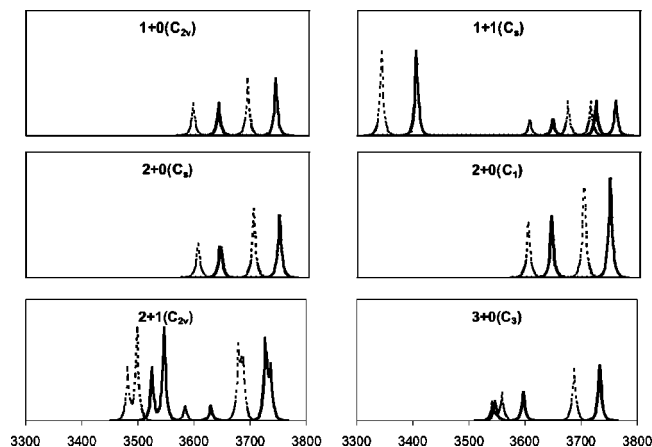


FIG. 4. MP2/aVDZ-predicted harmonic and anharmonic IR spectra of -OH stretching frequencies, which are drawn using solid and dashed lines, respectively.

respect to the vibrational mode i . The exponent α ($\alpha = 10^{-5}$) which is a single parameter was chosen so that water harmonic frequencies may best fit the experimental raw frequencies which include anharmonicity. Consequently, lower frequencies were slightly less scaled down. We also calculated anharmonic vibrational frequencies for selected $\text{Rb}^+(\text{H}_2\text{O})_{1-3}$ clusters (Fig. 4, Table VI). While harmonic vibrational frequencies tend to be overestimated unless scaled, anharmonic vibrational frequencies seem to be slightly underestimated.

IV. CONCLUDING REMARKS

The structure, energetics, and spectra of $\text{Rb}^+(\text{H}_2\text{O})_n$ ($n = 1-8$) have been studied. The hydrated Rb^+ conformers have more diverse structures in comparison with smaller alkali metal ion-water clusters. This is because of the weaker water-cation interaction, larger polarizability of the ion, and stronger water-water interactions. Therefore, we examined various conformers which were not studied in the case of smaller alkali-metal complexes. The rubidium cation-water clusters for $n=1-4$ show remarkably different structures compared to our previous studies on smaller alkali cation-water complexes. In the case of dihydrated smaller alkali metal-water clusters, the $2+0(\text{D}_{2d})$ conformer is the most stable in ΔE_0 . On the other hand, for $\text{Rb}^+(\text{H}_2\text{O})_2$ clusters $2+0(\text{C}_1)/2+0(\text{C}_s)/2+0(\text{C}_2)$ conformers are practically isoenergetic in ΔE_0 , and $2+0(\text{D}_{2d})$ is slightly less stable. In the case of $\text{Rb}^+(\text{H}_2\text{O})_3$ complexes $2+1(\text{C}_{2v})$ conformer is the most stable in ΔE_0 , while for smaller alkali metal-water clusters $3+0(\text{D}_3)$ structure is the most stable. For $\text{Rb}^+(\text{H}_2\text{O})_4$ complexes, the $4+0(\text{C}_4)$ conformer is the most stable in ΔE_0 . For smaller alkali metal ions $4+0(\text{S}_4)$ (Li^+, Na^+) and $3+1(\text{C}_2)$ (K^+) conformers are the most stable in ΔE_0 . In the case of smaller cations the contribution of dispersion energies is almost negligible. However, the contribution of dispersion energies to the total interaction energy gradually increases as the size of the alkali metal changes from Li^+ to Rb^+ . The role of electron corre-

lation in describing the interactions of the larger cations can readily be noted from increase in the magnitude of dispersion energies. It is also illustrative to examine the nature of binding of the second water molecule to the alkali metal ion-water monomer complex. Important differences emerge in the magnitude of the individual interaction energy components. Although the electrostatic, induction, and repulsive exchange decrease, one can observe a small increase in the magnitude of the dispersion energy for larger metal ions. We believe that the conformational preference is due to the enhanced electrostatic and dispersion energies. The magnitude of -OH redshifts increase with the size of the alkali-metal ion. This is very much unlike the interactions of solvated anions, wherein the more strongly bound anions induce much larger red shifts. The significantly larger redshifts observed in clusters containing the larger cations can also be attributed to the formation of water-water hydrogen bonds. One can readily note that the vibrational spectra give a lot of insight into the structure of the cation-water cluster. Thus, though an intermolecular water-water hydrogen bond appears in clusters ($n>4$) for Li^+ , Na^+ , and K^+ , it emerges much sooner for Rb^+ . Finally, our predicted thermodynamic quantities are found to be in good agreement with Kebarle's experimental results.

ACKNOWLEDGMENTS

This work was supported by the Creative Research Initiative Project of Korea Institute of Science and Technology Evaluation and Planning. Partial support was also obtained from the Brain Korea 21 program of the Korean Ministry of Education.

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