

Ab initio study of hydrated potassium halides $KX(H_2O)_1-6$ ($X = F, Cl, Br, I$)

Adriana C. Olleta, Han Myoung Lee, and Kwang S. Kim

Citation: *The Journal of Chemical Physics* **126**, 144311 (2007); doi: 10.1063/1.2715565

View online: <http://dx.doi.org/10.1063/1.2715565>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/jcp/126/14?ver=pdfcov>

Published by the AIP Publishing

Articles you may be interested in

Interaction-induced dipoles of hydrogen molecules colliding with helium atoms: A new ab initio dipole surface for high-temperature applications

J. Chem. Phys. **136**, 044320 (2012); 10.1063/1.3676406

Input vector optimization of feed-forward neural networks for fitting ab initio potential-energy databases

J. Chem. Phys. **132**, 204103 (2010); 10.1063/1.3431624

Ab initio study of hydrated sodium halides $NaX(H_2O)_1-6$ ($X = F, Cl, Br, \text{ and } I$)

J. Chem. Phys. **124**, 024321 (2006); 10.1063/1.2147283

Interaction of lead atom with atmospheric hydroxyl radical. An ab initio and density functional theory study of the resulting complexes PbOH and HPbO

J. Chem. Phys. **121**, 7207 (2004); 10.1063/1.1784431

Structure and vibrational spectra of $H + (H_2O)_8$: Is the excess proton in a symmetrical hydrogen bond?

J. Chem. Phys. **113**, 5321 (2000); 10.1063/1.1288918

How can you **REACH 100%**
of researchers at the Top 100
Physical Sciences Universities? (TIMES HIGHER EDUCATION RANKINGS, 2014)

With *The Journal of Chemical Physics*.

AIP | The Journal of
Chemical Physics

THERE'S POWER IN NUMBERS. Reach the world with AIP Publishing.



Ab initio study of hydrated potassium halides $KX(H_2O)_{1-6}$ ($X=F, Cl, Br, I$)Adriana C. Olleta, Han Myoung Lee, and Kwang S. Kim^{a)}*Center for Superfunctional Materials, Department of Chemistry, Pohang University of Science and Technology, San 31, Hyojadong, Namgu, Pohang 790-784, Korea*

(Received 6 November 2006; accepted 15 February 2007; published online 13 April 2007)

The ionic dissociation of salts was examined with a theoretical study of KX ($X=F, Cl, Br, I$) hydrated by up to six water molecules $KX(H_2O)_n$ ($n=1-6$). Calculations were done using the density functional theory and second order Møller-Plesset (MP2) perturbational theory. To provide more conclusive results, single point energy calculations using the coupled cluster theory with single, double, and perturbative triple excitations were performed on the MP2 optimized geometries. The dissociation feature of the salts was examined in terms of K–X bond lengths and K–X stretch frequencies. In general, the successive incorporation of water molecules to the cluster lengthens the K–X distance, and consequently the corresponding frequency decreases. Near 0 K, the KX salt ion pairs can be partly separated by more than five water molecules. The pentahydrated KX salt is partly dissociated, though these partly dissociated structures are almost isoenergetic to the undissociated ones for KF/KCl . For the hexahydrated complexes, KF is undissociated, KCl/KBr is partly dissociated, and KI is dissociated (though this dissociated structure is nearly isoenergetic to a partly dissociated one). On the other hand, at room temperature, the penta- and hexahydrated undissociated structures which have less hydrogen bonds are likely to be more stable than the partly dissociated ones because of the entropy effect. Therefore, the dissociation at room temperature could take place for higher clusters than the hexahydrated ones. © 2007 American Institute of Physics. [DOI: 10.1063/1.2715565]

I. INTRODUCTION

The study of dissociation of a salt in water essentially involves the separation of the associated ions that constitute the salt. Despite its apparent simplicity, it is difficult to describe at the molecular level the mechanism whereby a salt dissociates in water due to its experimental difficulty.^{1–4} The mechanism governing the salt dissociation is highly relevant to diverse biological, environmental, and atmospheric chemical processes^{5,6} as well as recognition by ionophores.⁷

Ab initio calculations on the dissociation of alkali halides in water clusters have scarcely been studied to date.^{8–15} This prompted us to undertake a theoretical study to clarify the characteristics of the processes. Most theoretical studies performed in this field have focused on the characterization of hydrated ions. Halide ions^{16–20} and alkali metal cations^{21–26} hydrated by water clusters have been thoroughly studied both theoretically and experimentally. In this regard, detailed *ab initio* studies of the dissociation phenomena of metal halides by water clusters are particularly interesting.^{8–10} However, the dissociation of potassium halides by water clusters, despite its importance in biological, environmental, and atmospheric chemical processes, has been the subject of much less study.⁵

One way of approaching the structure and properties of aqueous solution of salts involves using a quantum chemical method to examine clusters of a salt formed by water molecules. Salt dissociation involves a cooperative process between salt and water molecules. As water molecules are suc-

cessively incorporated, the cation-anion distance in the salt increases gradually, resulting in an ion pair separated structure.

To accurately predict the relative stability of dissociated and undissociated forms, it is essential to use reliable computational methods to incorporate the electron correlation by employing reasonably large basis sets including diffuse functions. In this regard, we performed high-level *ab initio* calculations as well as density functional theory calculations on potassium-halide clusters hydrated by up to six water molecules [$KX(H_2O)_{n=1-6}$, where $X=F, Cl, Br$, and I].

II. COMPUTATIONAL METHODS

Firstly, the structures of $KX(H_2O)_{1-6}$ water clusters were investigated by using Becke's three parameters with Lee-Yang-Parr functionals²⁷ (B3LYP) with the 6-311++G^{**}(*sp*) basis set. These low-energy conformers were further optimized at the level of second order Møller-Plesset (MP2) perturbational theory with the aug-cc-pVDZ+(2*s*2*p*/2*s*) basis set (abbreviated as aVDZ+). Here, (*sp*) and (2*s*2*p*/2*s*) are highly diffuse basis sets.²⁸ In the case of potassium atom (K), we used the energy adjusted Stuttgart effective core potentials and added a *d* exponent of 0.48 to the valence bases.²⁹ For $X=Br$ and I , we used the diffuse basis set with the effective core potential of Lajohn *et al.*³⁰ For better reliability, single point energy calculations based on the coupled cluster theory with single, double, and perturbative triple excitations [CCSD(T)/aVDZ+] on the MP2/aVDZ+ optimized geometries were performed. Both MP2 and CCSD(T) calculations were carried out with frozen core.³¹

^{a)}Electronic mail: kim@postech.ac.kr

The vibration analysis using the analytical second derivative matrix was carried out to characterize the nature of the stationary points. If an optimized structure, usually with some symmetry constraints, has one or more imaginary frequencies, we further optimized the structure along the imaginary normal modes until we obtained the true local minimum structure where all the frequencies are real.

The interaction energies ($-\Delta E_e$) for hydration of KX are reported with the median value of the energies with and without basis set superposition error (BSSE) correction, while half BSSE is reported like an error bar.²⁸ Zero-point-vibrational energy (ZPE) and thermal energy corrections based on the B3LYP/6-311++G**(*sp*) or MP2/aVDZ+ frequencies were used to obtain the ZPE-corrected binding energies

($-\Delta E_0$) and the binding enthalpy ($-\Delta H_{298\text{ K}}^\circ$) and binding Gibbs free energies ($-\Delta G_{298\text{ K}}^\circ$) at 298 K and 1 atm.

Random phase approximation (RPA) calculations at the B3LYP/6-311++G**(*sp*) level and configuration interactions with single excitations [CI(S)] at the MP2/aVDZ+ level of theory were carried out to obtain charge-transfer-to-solvent (CTTS) energies. The analysis of polarization effects and charge transfer was carried out with charges fitted to the electrostatic potential (ESP charges). ESP charges were calculated by the natural bond orbital (NBO) population analysis.³² All the calculations were carried out with the GAUSSIAN-03 programs.³³

III. RESULTS AND DISCUSSION

A. Energetic properties

Table I shows that the calculated binding energies and frequencies of the salts in isolation are in reasonable agreement with the experimental values, and the variations related to the electron affinity and polarizability of the anions are compared very well with the experimental trend.^{34,35} Compared with the B3LYP results, the MP2/aVDZ+ results appear more consistent with the CCSD(T)/aVDZ+ results. Thus, most of our discussion will be based on the MP2/aVDZ+ structural parameters (geometries and frequencies) and on the CCSD(T)/aVDZ+ energies. At the B3LYP level the polarizability values were underestimated with respect to the experimental ones, whereas at the MP2 level they were overestimated. However, their overall results are consistent.

Figure 1 shows the important low-lying energy structures of $\text{KX}(\text{H}_2\text{O})_{n=1-6}$. The number of water molecules and some letters to distinguish among different structural arrangements are employed to identify the structure of clusters.⁹ Each conformer is denoted as $nRn_p n_p \cdots / m_q m_q \cdots$. Here, n is the number of water molecules, R stands for a ring structure, $\{n_p n_p \cdots\}$ is a set of numbers of heavy atoms (excluding H atoms) present in the rings including both K and X atoms, and $\{m_q m_q \cdots\}$ is a set of numbers of the atoms in the rings where K and X atoms are not present together. $\{n_p n_p \cdots\}$ and $\{m_q m_q \cdots\}$ are given in ascending order. To provide the information of coordination for each structure, (k/l) is used to denote the coordination number for the cation/anion. We also used additional

notations: L for linear shape and “Cube” for cubical shape. In short notation, $nRn_p n_p \cdots / m_q m_q \cdots$ will be simply denoted as $nRn_p n_p \cdots$ except for Fig. 1.

In order to obtain the lowest energy structures, we investigated various hydration structures of $\text{NaX}(\text{H}_2\text{O})_{1-6}$,⁹ which included the hydration structures of salts reported in previous papers,⁸⁻¹⁵ and also considered the hydration structures of alkali metal cations,²¹⁻²⁶ halide anions,²⁰ bases, and acids.¹⁰ We also considered the possible structures based on the topological analysis, as we previously investigated for water clusters and excess electron-containing water clusters.³⁶ This topological analysis was done in consideration of various structures depending on the coordination numbers of the alkali metal cation (M^+) and the halide anion [$\text{cn}(\#_{\text{M}^+}, \#_{\text{X}^-})$, where $\#_{\text{M}^+}$ or $\#_{\text{X}^-}$ was considered to be 2, 3, or 4]. For example, for $n=5$ (pentahydration), $\text{cn}(3,3)$ can have two types of H-bond relay pathways comprised of a set of different numbers of water molecules between M^+ and X^- . Without taking into account the cross-passing H bonds, the two types of paths, $\text{path}(2,2,1)$ and $\text{path}(3,1,1)$, have the shapes of 5R344 and 5R355 in Fig. 1, respectively. By taking into account the cross-passing H bonds, $\text{path}(2,2,1)$ generates 5R3444/34, 5R3444/44, 5R4444/444, etc. (not shown). In this way, we can consider quite many conformers for the clusters. However, in most cases, it is clear that certain conformers do not need to be considered because of their highly strained structures. When generated structures would be considered to be low-lying energy conformers, they were tested for their relative stabilities at the B3LYP/6-31+G* level. In this way, for each hydrated system of KX, more than 100 conformers were investigated for the first screening test, followed by more accurate calculations [B3LYP/6-311++G**(*sp*), MP2/aVDZ+] of ~ 50 low-energy conformers. Then, for the four types of potassium halides, accurate MP2/aVDZ+ calculations with geometry optimization and frequency analysis were carried out on these ~ 200 different conformers. Therefore, it is almost certain that the lowest energy structures reported here would be the global minimum energy structures at the given levels of theory, which we cannot prove though. Furthermore, from our previous study of $\text{NaX}(\text{H}_2\text{O})_{1-6}$ clusters, we have obtained some useful experiences for the structural changes from F to I. As the ionic strengths and ionic radii of halide ions have large influence in the hydration,²⁰ the fluoride ion tends to favor internal-bound states, while the chloride, bromide, and iodide ions have surface-bound states for isolated ionic hydration structures. However, in the binary cation-anion hydration systems, the difference in hydration structure depending on F to I is rather small due to the strong ion-ion interaction. Thus, the hydration structures of potassium-halide salts are similar to those of sodium-halide salts, though there are some differences. Since we reported a number of structures in our previous study of $\text{NaX}(\text{H}_2\text{O})_{1-6}$, we here describe only the important low-lying energy structures of $\text{KX}(\text{H}_2\text{O})_{1-6}$ in Fig. 1.

Table II describes the binding energies evaluated at the B3LYP/6-311++G**(*sp*) and MP2/aVDZ+ levels of theory. The most stable conformers for $\text{KX}(\text{H}_2\text{O})_n$ for $n=6$ ($\text{X}=\text{F}, \text{Cl}, \text{Br}, \text{and I}$) at the B3LYP/6-311++G**(*sp*) level

TABLE I. Calculated and experimental structural parameters for water, potassium, halides, and potassium halides. (Bond lengths (r_e) are in angstrom; angle (\angle) in degree; frequencies (ω) in cm^{-1} ; ionization potential (IP), electron affinity (EA), and dissociation energy (D_0) in eV; and polarizability (α) in \AA^3 . Only OH frequencies [ω_s , ω_a (scaled)] are scaled by a scale factor of 0.96, while other K–X frequencies are not scaled. The data for H_2O and halide atoms are from Ref. 9).

		B3LYP/ 6-311++G** _r [<i>sp</i>]	MP2/ aVDZ+	MP2/ aVTZ+	CCSD(T)/ aVDZ+	CCSD(T)/ aVTZ+	Expt.	Ref.
H_2O	$r(\text{OH})$	0.962	0.966	0.961	0.967	0.962	0.957	34
	$\angle \text{HOH}$	105.0	103.9	104.1	104.0	104.2	104.5	34
	ω_s	3817	3803	3822	3787	3812	3657	35 and 37
	ω_a	3922	3937	3948	3905	3921	3756	35 and 37
	$\omega_s(\text{scaled})$	3664	3651	3669	3635	3660		
	$\omega_a(\text{scaled})$	3765	3780	3790	3749	3764		
K	IP	4.497	4.210	4.210	4.220	4.220	4.34	38
	$\alpha(\text{K})$	52.77	56.65	56.74	43.4	39
	$\alpha(\text{K}^+)$	0.88	0.85	0.86		
F	EA	3.548	3.547	3.596	3.230	3.312	3.401	40
	α	0.35	0.59	0.68	0.557	41
	$\alpha(\text{F}^-)$	2.61	1.79	1.78		
KF	r_e	2.235	2.239	2.223	2.236	2.219	2.171	42
	ω_e	398	403	414	406	418	426	42 and 43
	D_0	4.804	5.047	5.226	4.745	4.920	5.28	44
Cl	EA	3.729	3.554	3.578	3.431	3.506	3.614	45
	α	1.44	2.62	2.86	2.18	41
	$\alpha(\text{Cl}^-)$	3.89	4.94	5.56		
KCl	r_e	2.692	2.739	2.714	2.746	2.719	2.667	46
	ω_e	269	265	274	264	273	281	46 and 47
	D_0	4.265	4.203	4.367	4.058	4.223	4.39	48
Br	EA	3.594	3.315	3.440	3.270	3.270	3.364	49
	α	2.37	4.07	4.07	3.05	39 and 41
	$\alpha(\text{Br}^-)$	5.46	9.04	9.04		
KBr	r_e	2.850	2.903	2.903	2.913	2.913	2.821	49 and 50
	ω_e	212	202	202	200	200	213	46 and 51
	D_0	3.913	3.626	3.690	3.678	3.678	3.96	52 and 53
I	EA	3.279	3.118	3.088	3.071	3.071	3.059	54 and 55
	α	4.97	6.44	6.44	5.35	41 and 56
	$\alpha(\text{I}^-)$	9.36	13.68	13.68		
KI	r_e	3.153	3.142	3.142	3.152	3.152	3.048	49 and 53
	ω_e	170	173	173	172	172	186.5	46
	D_0	3.144	3.262	3.261	3.195	3.195	3.31	56

are 1R3, 2R33, 3R333, 4R334, 5R344, and 6R444, respectively, except for the case of $\text{KI}(\text{H}_2\text{O})_6$ which has the structure of 6R4444. At the MP2/aVDZ+ level, the most stable conformers for $\text{KX}(\text{H}_2\text{O})_{1-4}$ ($\text{X}=\text{F}$, Cl, Br, and I) are 1R3, 2R33, 3R333, and 4R334, which are consistent with the B3LYP results. However, in the case of $\text{KX}(\text{H}_2\text{O})_4$, 4R334 is nearly isoenergetic to 4R344. Furthermore, we note that K-water interactions are anisotropic due to the presence of unoccupied d orbitals in the potassium atom, and this feature appears as the halogen atom increases its polarizability. Thus, though the most stable conformers for $\text{KX}(\text{H}_2\text{O})_5$ for $\text{X}=\text{F}/\text{Cl}$ are 5R344, similar to the case of the NaX -water clusters, those for $\text{X}=\text{Br}/\text{I}$ are 5R355. However, both 5R344 and 5R355 are nearly isoenergetic for $\text{X}=\text{F}/\text{Cl}/\text{Br}$, while for $\text{X}=\text{I}$, 5R355 is nearly isoenergetic to 5R3344. In the case of

$n=6$, the lowest energy structure for $\text{X}=\text{Cl}/\text{Br}$ is 6R445, whereas that for $\text{X}=\text{I}$ is 6R335. Here, 6R4444 is nearly isoenergetic to 6R444 and 6R3345 for $\text{X}=\text{F}$ and $\text{X}=\text{Cl}/\text{I}$, respectively. Table III confirms that the CCSD(T)/aVDZ+ interaction energies are consistent with and very close to the MP2/aVDZ+ interaction energies. Therefore, we facilitate our discussion based on the MP2 results because CCSD(T) values for $n=6$ were not obtained due to the convergence problem.

As water molecules are incorporated, the cluster binding energy increases because of the increased strength of the interactions and the increased number of hydrogen bonds, as shown in Fig. 2(a). However, in Fig. 2(b) the successive binding energy (i.e., energy change resulting from the addition of a new water molecule; $\Delta E_0^n - \Delta E_0^{n+1}$) increases up to

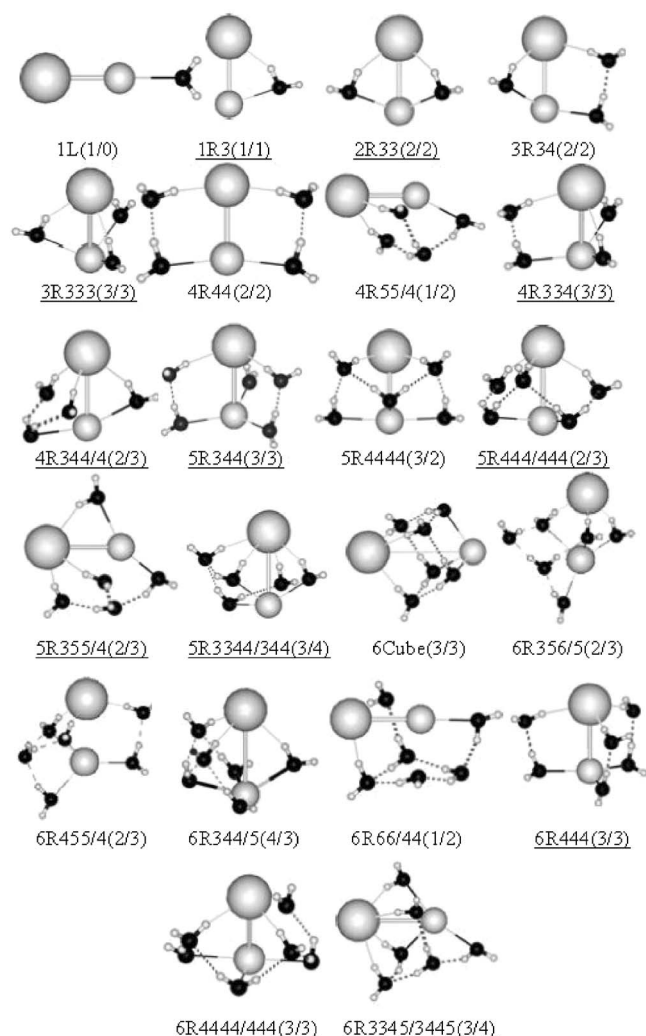


FIG. 1. Various conformers of $KX(H_2O)_{1-6}$ ($X=F/Cl/Br/I$). The important structures are underlined.

four water molecules but is saturated from $n=4$ because the subsequent water molecule starts to build up a second solvation shell. For $n=3$, each ion in 3R333 is tricoordinated by three water molecules. The successive binding energies for the first few water molecules are much larger in $KF(H_2O)_n$ than in $KX(H_2O)_n$ ($X=Cl/Br/I$).

B. Structural properties

Table IV lists the selected structural parameters calculated at the MP2/aVDZ+ level. The four salts ($X=F/Cl/Br/I$) exhibit similar lowest energy structures for $n \leq 4$. In the case of the lowest energy clusters of $KX(H_2O)_{1-3}$, the water molecules play a role in bridging between a cation and an anion. These structures show a water-shared ion pair. The addition of the fourth water molecule starts to build up a second solvation shell as water molecules can no longer coordinate to both ions, and so strong water-water interactions begin to develop. Therefore, not only the coordination number of the halide atom but also the hydrogen bonds between water molecules increase. The

structures of clusters containing five or more water molecules were examined with various conformers that yielded a number of minima on the potential surface.

The ionic radius of fluoride ion is shorter than that of oxygen, and so the K–F distances are shorter than the K–O distances in mono- and dihydrated K–F systems. However, in the trihydrated systems the K–F distances are longer than the K–O distances. The K–O stretching frequencies are in the range of 190–220 cm^{-1} . The hydrated Na^+ and K^+ ions have different coordination numbers, 4 and 4–6, respectively. The K^+ ion is on the transition point from the internal-bound (Li^+ and Na^+) to partly surface-bound (Rb^+ and Cs^+) structure. The hydrated halide anions have the coordination number of 4 within the hexahydrated systems. The hydrated K–X salts have more water-water H bonds than the hydrated Na–X salts.⁹ The water-water H bonding slightly decreases the K–X distances for the tri- to pentahydrated KF and KCl systems. For the hexahydrated KX systems, 6Cube has a completely dissociated structure, but it is much less stable than 6R4444. 6R444 is partly dissociated for $X=Cl/Br/I$, but it is still undissociated for $X=F$. In the case of $X=I$, 6R3345 which is regarded as a dissociated structure is more stable than 6R4444. Here, the terms of (full) dissociation (i.e., solvent separated ion pair), partial dissociation (half-dissociation or partial contact ion pair), and undissociation (i.e., contact ion pair) are based on our previous work of $\text{NaX}(H_2O)_n$, and the brief discussion is given in the footnote in Table IV.

Figure 3 clarifies the above discussion. Figure 3(a) shows the change of K–X bond length with respect to the water cluster size n . For $KF(H_2O)_n$ where $n \leq 3$, the bond length increases, but for $n=4$ and 5 the bond length slightly decreases as the interactions between water molecules begin to develop and the binding energies increase. However, for $n=6$, the bond length increases again. A similar trend is also observed for other hydrated salts (KCl, KBr, and KI), while the bond length for $n=4$ (and 5) is almost constant with respect to the change of the cluster size n . For $n=4/5/6$, the hydrated KX systems have two nearly isoenergetic conformers except for $\text{KBr}(H_2O)_5$. A more appropriate way of comparing the effect of water molecules on the salt geometry is in terms of the relative distance increase from the isolated molecule. The largest increase in K–X distance occurs in KI clusters followed by KCl and KBr clusters. The elongation effect is greater in the clusters of six water molecules. This suggests that the ion pair formed upon the dissociation is more efficiently stabilized in the clusters for $n=6$. The presence of a partial second shell of water molecules between the two ions introduces significant stabilization in the ion pair as their dipole moments oppose that from the formation of the ion pair. In the clusters containing four water molecules, however, the dipole of one water molecule does not directly oppose the dipole established by the ion pair, which results in less efficient stabilization of the ion pair.

In Fig. 3(b), the K–O distance remains constant regardless of the number of water molecules. This reveals that the characteristics of the interaction are similar in all clusters and hence the interaction is governed by the presence of interwater hydrogen bonds and water-halide ion hydrogen bonds.

TABLE II. MP2/aVDZ+(B3LYP/6-311++G**[sp]) interaction energies of $KX(H_2O)_{1-6}$ clusters. [Values in parentheses are the B3LYP/6-311++G**[sp] energies. Energies are in kcal mol⁻¹. $-\Delta E_e = -(\Delta E_e^N + \Delta E_e^B)/2 \pm (BSSE/2)$, where $-\Delta E_e^N$ and $-\Delta E_e^B$ are the binding energies without and with BSSE correction, respectively. Thus, the lower and upper values are $-\Delta E_e^N$ and $-\Delta E_e^B$, respectively. Hydration energies with ZPE correction are denoted by $-\Delta E_0$. ΔH_{298} and ΔG_{298} are the enthalpy change and Gibbs free energy change for hydration at 298 K. $-\Delta G_{298}$ could be underestimated for $n \geq 4$ because of low frequency terms (though the magnitude would not be reliable, the relative stabilities would be useful information). The lowest energies for each cluster type and the structures corresponding to the lowest MP2 ΔE_0 are highlighted in bold characters.]

Conf	$-\Delta E_e$	$-\Delta E_0$	$-\Delta H_{298}$	$-\Delta G_{298}$	Conf	$-\Delta E_e$	$-\Delta E_0$	$-\Delta H_{298}$	$-\Delta G_{298}$
KF(H ₂ O) ₁₋₆					KCl(H ₂ O) ₁₋₆				
1L					1L	(9.2±0.4)	(8.1)		
1R3	22.1±1.3	(22.6±0.5)	20.3	(21.0)	1R3	17.2±1.0	(16.7±0.3)	15.5	(15.0)
2R33	41.0±2.4	(42.4±0.9)	36.9	(38.5)	2R33	33.0±1.9	(32.1±0.7)	29.5	(28.6)
3R34	54.6±3.0	(57.2±1.4)	48.4	(50.9)	3R34	45.4±2.4	(45.0±1.3)	39.6	(39.1)
3R333	57.5±3.5	(58.8±1.4)	51.3	(52.7)	3R333	47.6±2.8	(46.2±1.1)	42.4	(41.0)
4R44	68.0±3.4	(71.6±2.0)	59.5	(62.9)	4R44	57.5±3.1	(57.5±1.9)	49.5	(49.3)
4R344	70.4±4.3	(71.1±2.1)	61.3	(61.8)	4R344	59.4±3.6	(57.1±1.8)	51.4	(48.9)
4R334	70.1±4.1	(72.5±1.9)	61.6	(63.9)	4R334	59.2±3.3	(58.2±1.7)	51.7	(50.6)
					5R4444	71.0±4.3	(68.9±2.6)	60.6	(57.8)
5R444	83.5±5.2	(83.4±2.6)	71.5	(72.0)	5R444	71.9±4.6	(68.7±2.4)	61.4	(58.2)
5R355	83.2±5.2	(84.6±2.7)	71.8	(72.9)	5R355	72.0±4.5	(69.6±2.4)	61.2	(58.9)
5R344	82.4±4.6	(85.6±2.5)	71.8	(74.6)	5R344	71.0±3.3	(70.0±2.3)	61.3	(60.1)
6Cube	94.0±6.2	(95.8±3.4)	78.6	(79.9)	6Cube	81.8±5.8	(80.7±3.3)	67.3	(65.6)
6R455	94.9±5.8	(97.2±3.2)	81.3	(83.2)	6R455	82.0±5.0	(81.0±3.0)	69.5	(67.9)
6R444	94.5±5.3	(98.3±2.9)	81.6	(84.9)	6R444	81.4±4.4	(81.5±3.0)	69.6	(69.2)
6R4444	95.6±5.9	(96.1±3.2)	81.7	(81.7)	6R4444	83.8±5.3	(80.8±3.1)	71.0	(67.1)
					6R3345	83.3±5.5	(80.2±3.1)	70.6	(67.0)
KBr(H ₂ O) ₁₋₆					KI(H ₂ O) ₁₋₆				
1L		(9.4±0.3)	(8.3)		1L	(10.5±0.3)	(10.3)		
1R3	16.8±1.2	(16.2±0.3)	15.0	(14.5)	1R3	16.0±1.2	(16.2±0.3)	14.5	(14.6)
2R33	32.5±2.4	(31.1±0.6)	29.1	(27.9)	2R33	31.0±2.4	(31.0±0.7)	27.8	(27.9)
3R34	44.6±3.1	(43.5±1.1)	39.0	(37.8)	3R34	42.8±3.0	(43.3±1.2)	37.4	(37.8)
3R333	47.0±3.5	(44.8±1.0)	41.9	(40.0)	3R333	44.9±3.5	(44.6±1.0)	40.1	(39.9)
					4R55	55.5±4.4	(54.9±2.1)	47.2	(46.3)
4R44	56.5±3.9	(55.7±1.7)	48.6	(47.7)	4R44	54.4±3.6	(55.1±1.6)	46.3	(47.3)
4R344	58.7±4.4	(55.4±1.6)	50.9	(47.6)	4R344	56.2±4.3	(54.9±2.1)	48.8	(47.4)
4R334	58.4±4.2	(56.5±1.6)	51.1	(49.2)	4R334	56.0±4.1	(56.1±1.5)	49.0	(49.1)
5R344	69.5±4.8	(67.9±2.2)	60.1	(58.1)	5R344	66.8±4.7	(67.2±2.0)	57.7	(57.2)
5R4444	70.3±5.1	(67.1±2.3)	60.0	(56.4)	5R4444	68.2±5.0	(66.8±2.4)	57.4	(55.0)
5R444	71.3±5.4	(67.0±2.2)	60.7	(56.7)	5R3344	68.4±5.5	(66.5±2.2)	58.6	(55.5)
5R355	71.2±5.4	(67.7±2.2)	60.9	(57.4)	5R355	68.7±5.3	(67.4±2.0)	58.8	(56.6)
6R356		(78.6±2.9)		(65.9)	6R344		(78.0±2.7)		(64.1)
6Cube	81.1±6.4	(78.9±3.1)	67.1	(64.1)	6Cube	78.8±6.4	(78.1±2.8)	65.0	(61.8)
6R444	80.3±5.4	(79.0±2.8)	68.8	(66.9)	6R444	77.3±5.2	(77.9±2.7)	66.1	(64.1)
6R66	81.7±6.3	(78.6±3.2)	68.2	(64.6)	6R66	79.6±6.2	(78.3±3.2)	66.3	(62.5)
6R455	81.7±6.0	(78.7±2.8)	69.4	(66.1)	6R455	78.2±5.8	(78.1±2.5)	66.2	(65.2)
6R4444	83.1±6.2	(78.8±2.9)	70.5	(65.4)	6R4444	80.4±6.2	(78.0±2.7)	68.0	(65.6)
6R3345	82.1±6.5	(78.6±2.9)	69.6	(65.8)	6R3345	80.2±6.4	(78.4±2.8)	68.2	(64.0)

Figure 3(c) shows that the $X \cdots H$ distances are almost constant regardless of the cluster size. The main difference in the $X \cdots H$ distance between different salts lies in the electronegativity of the halide involved. Consequently, particularly short $X \cdots H$ distances correspond to the hydrated fluorine salt clusters, which depart clearly from other hydrated halide salt clusters.

We investigated various low-lying energy structures based on topological analysis. The barriers between different conformers would be around 1–2 kcal/mol [for example, for $KCl(H_2O)_4$, the barrier between 4R344 and 4R334 is ~ 1.6 kcal/mol]. Since the interconversion between the vari-

ous conformers would not be significant near 0 K, their IR frequencies would be identifiable at low temperatures. These different conformers provide real frequency wave numbers (not imaginary wave numbers). Therefore, they are local minimum energy structures. These structures can be distinguishable at low temperature gas-phase cluster experiments. However, as the temperature increases, the structures can change due to the entropy effect. At room temperature, based on the free energy ΔG_{298} , the low-energy structures of $KX(H_2O)_{1-6}$ are 1R3, 2R33, 3R333, 4R334, 5R344, and 6R444, as listed in Table II. The minimum free energy structures from monohydrated to tetrahydrated systems are the

TABLE III. CCSD(T)/aVDZ+interaction energies of $KX(H_2O)_{1-5}$. [See the footnote of Table II. The values of nearly isoenergetic lowest energy conformers for **5R355** ($X=F$), **5R344**, **5R355** ($X=Cl$), **5R444** ($X=Br$), and **5R334** ($X=I$) are not reported due to the convergence problem. The CCSD(T) values are consistent with the MP2 values. The lowest energy structures are marked in bold characters. The BSSEs were used with the MP2/aVDZ+ values because the difference between CCSD(T) and MP2 BSSEs is usually very small, and the thermal energies were also used with the MP2 values.]

Conf	$-\Delta E_e$	$-\Delta E_0$	$-\Delta H_{298}$	$-\Delta G_{298}$	Conf	$-\Delta E_e$	$-\Delta E_0$	$-\Delta H_{298}$	$-\Delta G_{298}$
KF(H ₂ O) ₁₋₆					KCl(H ₂ O) ₁₋₆				
1R3	22.0±1.3	20.2	19.4	11.0	1R3	17.0±1.0	15.2	14.2	6.2
2R33	40.9±2.4	36.9	34.3	17.3	2R33	32.6±1.9	29.1	26.6	10.4
3R34	54.5±3.0	48.3	44.2	18.7	3R34	45.0±2.4	39.2	35.0	10.1
3R333	57.6±3.5	51.4	47.1	21.1	3R333	47.1±2.8	41.9	38.0	13.4
4R44	67.9±3.4	59.4	53.7	19.3	4R44	57.0±3.1	49.0	43.2	9.7
4R344	70.7±4.3	61.6	55.4	19.1	4R344	59.1±3.6	51.1	45.4	10.5
4R334	70.2±4.1	61.7	55.8	21.2	4R334	58.7±3.3	51.2	45.6	12.4
5R344	82.6±4.6	72.0	64.3	21.4					
KBr(H ₂ O) ₁₋₆					KI(H ₂ O) ₁₋₆				
1R3	16.5±1.2	14.7	13.6	4.8	1R3	16.0±1.2	14.5	13.5	6.3
2R33	32.2±2.4	28.8	26.5	10.3	2R33	30.9±2.4	27.8	25.5	10.2
3R34	44.4±3.1	38.7	34.6	9.7	3R34	42.8±3.0	37.4	33.3	9.4
3R333	46.8±3.5	41.6	37.8	13.0	3R333	44.9±3.5	40.2	36.5	12.9
4R44	56.2±3.9	48.3	42.5	9.0					
4R344	58.6±4.4	50.8	45.1	10.1	4R344	56.5±4.3	49.1	43.6	9.7
4R334	58.1±4.2	50.8	45.3	12.3	4R334	56.0±4.1	49.0	43.6	11.5
5R355	71.0±5.4	60.7	53.3	9.0	5R355	68.8±5.3	58.9	51.7	8.4

same with the ΔE_0 -based ones. However, penta- and hexahydrated structures at room temperature are different from those near 0 K. Conformers 5R344 and 6R444 which have less H bonds are more stable at the room temperature. Then, the less-dissociated structures are favorable at room temperature than at very low temperatures. Thus, at room temperature the dissociated structures would be seen for higher clusters than the hexahydrated ones. However, more conclusive results would be obtained by using high-level *ab initio* molecular dynamics simulations.

C. Vibration frequencies

The K–X stretching frequencies reflect the bond length elongation arisen from the weakening of the K–X bond as water molecules are added to the system. Thus, the K–X stretching frequencies in Fig. 3(d) reflect the K–X bond lengths in Fig. 3(a), while their trends are opposite with respect to the cluster size n . Table V shows that, for all the four types of salts up to three water molecules, the O–H(X) frequencies decrease as water molecules are added to the cluster. However, with the addition of the fourth water molecule to the system, the frequency is almost constant (with only

slight increase/decrease depending on the structure of isoenergetic conformers), reflecting the stabilization of the system as hydrogen bonds between water molecules begin to develop. With the addition of the fifth water molecule, such behavior of the clusters diverges depending on the halide type of salts and the structure of isoenergetic conformers. The incorporation of the sixth water molecule causes an additional increase in the K–F stretching frequency for the undissociate structure, while it causes a significant decrease in the K–X frequencies ($X=Cl/Br/I$) for partially (or fully) dissociated structures. The latter effect is much more significant for the dissociated structure of $KI(H_2O)_6$.

Figure 4 shows the IR spectra for the scaled MP2/aVDZ+ predicted O–H stretching vibrational frequencies (scale factor: 0.96) of the lowest energy structures. The full MP2/aVDZ+ frequency data (unscaled) and spectra (scaled) for $KX(H_2O)_{1-6}$ ($X=F, Cl, Br, I$) are available in the journal's Electronic Auxiliary Publications Service (EPAPS).⁵⁷ The $KX(H_2O)_{1-6}$ clusters exhibit both the O–H frequencies involving hydrogen bonds (OH_b) and the O–H frequencies not involving hydrogen bonds (OH_n). The OH_b stretching frequencies show a marked decrease with respect

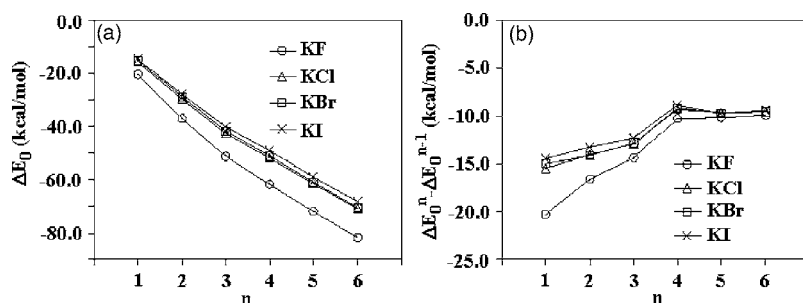


FIG. 2. MP2/aVDZ+ interaction energies (ΔE_0) (a) and successive interaction energy ($\Delta E_n - \Delta E_{n-1}$) (b) of the lowest-energy structures of $KX(H_2O)_{n=1-6}$.

TABLE IV. MP2/aVDZ+structural parameters and K–X and K–O stretch frequencies for $\text{KX}(\text{H}_2\text{O})_{1-6}$. [Hb/co/Hd denotes the number of H bonds/coordination number/dangling hydrogen atoms. Bond lengths, r_{KX} , r_{KO} , and r_{XH} , are in angstroms. r_{KO} and r_{XH} indicate the smallest distances K–O and X–H, respectively. ω_{KX} and ω_{KO} indicate the unscaled K–X and K–O stretching wave numbers in cm^{-1} . “*/**” denotes the half/full dissociation based on both (i) the degree of elongation of r_{KX} (Δr_{KX}) with respect to the pure KX without hydration (i.e., partial dissociation for $0.5 \text{ \AA} < \Delta r_{\text{KX}} < 1.0 \text{ \AA}$ and full dissociation for $\Delta r_{\text{NaX}} > 1.0 \text{ \AA}$) and (ii) the degree of coupling of the KX stretch frequency modes ω_{KX} with other modes (i.e., partial dissociation for $50 \text{ cm}^{-1} < \omega_{\text{KX}} < 100 \text{ cm}^{-1}$ and full dissociation for $\omega_{\text{KX}} < 50 \text{ cm}^{-1}$ for which other modes are more dominating so that this mode may not be considered as the KX stretching mode).]

Conf	Hb/co/Hd	r_{KX}	r_{KO}	r_{XH}	ω_{KX}	ω_{KO}	Conf	Hb/co/Hd	r_{KX}	r_{KO}	r_{XH}	ω_{KX}	ω_{KO}
KF(H ₂ O) _{1–6}							KCl(H ₂ O) _{1–6}						
KF		2.24			403		KCl		2.74			266	
1R3	0/2/1	2.36	2.57	1.48	281	201	1R3	0/2/1	2.84	2.60	2.13	258	192
2R33	0/4/2	2.50	2.60	1.55	163	207	2R33	0/4/2	2.96	2.62	2.16	136	214
3R333	0/6/3	2.68	2.63	1.60	109	196	3R333	0/6/3	3.13	2.64	2.18	*94	203
4R344	2/5/3	2.70	1.58	2.65	128	220	4R344	2/5/3	3.17	2.66	2.13	*79	215
4R334	1/6/4	2.64	2.65	1.56	134	188, 213	4R334	1/6/4	3.10	2.65	2.13	106	211, 223
5R444	4/5/3	2.73	2.74	1.57	126	203	5R444	4/5/3	3.05	2.70	2.06	137	190, 210
5R355*	3/5/4	*2.76	2.65	1.56	*84	212	5R355*	3/5/4	*3.24	2.67	2.10	*72	214
5R344	2/6/5	2.60	2.67	1.57	182	212	5R344	2/6/5	3.08	2.67	2.14	118	210
6Cube**	6/6/3	**4.41	2.66	1.53	**48	229, 244	6Cube**	6/6/3	**5.06	2.65	2.06	**47	221, 229
6R455	4/5/5	2.68	2.67	1.58	143	213	6R455	4/5/5	3.11	2.62	2.18	118	220
6R444	3/6/6	2.58	2.68	1.59	205	208	6R444	3/6/6	3.10	2.67	2.18	132	191
6R4444	5/6/4	*2.74	2.69	1.54	131	208	6R4444*	5/6/4	*3.25	2.70	2.12	*83	188
							6R3345**	4/7/4	*3.46	2.69	2.12	**42	211
KBr(H ₂ O) _{1–6}							KI(H ₂ O) _{1–6}						
KBr		2.90			202		KI		3.14			173	
1R3	0/2/1	3.01	2.60	2.28	155	229	1R3	0/2/1	3.25	2.60	2.55	138	221
2R33	0/4/2	3.13	2.62	2.30	119	211	2R33	0/4/2	3.38	2.62	2.56	104	212, 209
3R333	0/6/3	3.28	2.65	2.33	*89	200	3R333	0/6/3	3.55	2.65	2.58	*75	198, 200
4R344	2/5/3	3.33	2.67	2.28	*73	215	4R344	2/5/3	3.62	2.67	2.52	*62	215
4R334	1/6/4	3.28	2.65	2.27	*94	198, 217	4R334	1/6/4	3.55	2.65	2.54	*80	199, 216
5R344	2/6/5	3.26	2.66	2.29	103	206	5R344	2/6/5	3.52	2.66	2.55	*89	206
5R444*	4/6/3	*3.40	2.72	2.26	*70	202	5R3344**	3/7/3	*3.77	2.68	2.54	**44	211
5R355*	3/5/4	*3.39	2.67	2.25	*65	216	5R355*	3/5/4	*3.69	2.66	2.50	*54	215
6Cube**	6/6/3	**5.16	2.65	2.22	**37	223, 238	6Cube**	6/6/3	**5.54	2.65	2.46	**36	223, 239
6R444	3/6/6	3.24	2.68	2.30	113	208	6R444	3/6/6	3.51	2.67	2.56	*96	207
6R455	4/5/5	3.36	2.66	2.27	*70	212	6R455	4/5/5	3.55	2.66	2.57	*72	210
6R4444*	5/6/4	*3.42	2.71	2.27	*68	189	6R4444*	5/6/4	*3.75	2.71	2.52	*54	190, 196
6R3345*	4/6/4	*3.49	2.68	2.31	*56	205	6R3345**	5/7/4	*3.97	2.69	2.51	**29	209

to those of the isolated water molecule [$\sim 1000\text{--}400 \text{ cm}^{-1}$ in the case of $\text{KF}(\text{H}_2\text{O})_{1-6}$ and $\sim 400 \text{ cm}^{-1}$ for $\text{KX}(\text{H}_2\text{O})_{1-6}$, where $\text{X}=\text{Cl}, \text{Br}, \text{and I}$]. The free OH_n peaks remain constant in both frequency and intensity for all the salt-water clusters. These predicted frequencies would be useful for facilitating the future experiments because such OH stretching frequency shifts have been utilized for structural identification of various hydrated molecular clusters.^{58–61} However, the IR spectra of some mixed structures would be present as the temperature increases, and at room temperature the spectral features of 5R344 and 6R444 could be seen for $n=5$ and 6.

D. Electronic properties

Table VI lists the electronic properties of the $\text{KX}(\text{H}_2\text{O})_{1-6}$ clusters calculated at MP2 and B3LYP levels of theory. The calculated Koopman's (IP_K) and vertical ionization potentials (IP_V) of the $\text{KF}(\text{H}_2\text{O})_{1-6}$ complexes increase up to $n=3$ and become almost constant for $n \geq 3$. On the

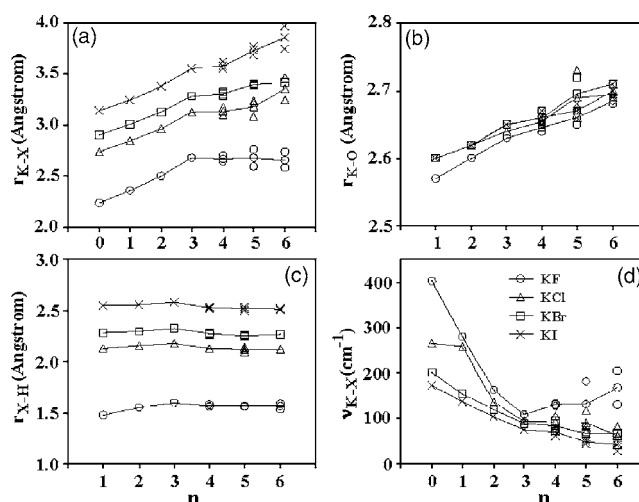


FIG. 3. MP2/aVDZ+ bond distances [(a) $r_{\text{K-X}}$, (b) $r_{\text{K-O}}$, and (c) $r_{\text{X-H}}$ in Å] and (d) K–X stretch frequencies ($\nu_{\text{K-X}}$ in cm^{-1}) for the lowest-energy structures (including the nearly isoenergetic structures) of $\text{KX}(\text{H}_2\text{O})_{n=1-6}$. The lines were drawn based on the lowest energy structures.

TABLE V. MP2/aVDZ+predicted O \cdots H(X) stretching frequencies (ω in cm $^{-1}$; scale factor of 0.96) and intensities (in 10 km/mol) of KX(H $_2$ O) $_{1-6}$.

KF(H $_2$ O) $_{1-6}$				KCl(H $_2$ O) $_{1-6}$			
1R3	2569 ₁₅₃			1R3	3194 ₉₁		
2R33	2848 ₁₈₂	2971 ₅₇		2R33	3259 ₈₆	3290 ₆₈	
3R333	3049 ₁₇₀	3049 ₁₇₀	3178 ₇₁	3R333	3318 ₆₄	3318 ₆₄	3357 ₆₇
4R344	2991 ₁₁₁	3055 ₁₁₈	3189 ₄₅	4R344	3267 ₆₆	3293 ₈₄	3362 ₅₈
4R334	2989 ₁₅₂	3121 ₁₀₅	3214 ₉₅	4R334	3318 ₉₁	3354 ₅₉	3383 ₄₈
5R444	3003 ₁₁₇	3045 ₁₃₄	3169 ₂₂	5R444	3269 ₇₄	3299 ₈₄	3337 ₄₈
5R355	2936 ₁₀₁	3024 ₁₂₉	3197 ₄₉	5R355	3224 ₅₉	3259 ₁₁₁	3370 ₆₀
5R344	3011 ₁₇₂	3091 ₁₀₁	3246 ₅₈	5R344	3339 ₈₃	3354 ₇₅	3406 ₃₇
6R444	3065 ₁₆₄	3066 ₆₄	3197 ₁₆	6R444	3366 ₉₃₁	3366 ₉₃₁	3392 ₂₅
6R4444	2935 ₁₅₆	3056 ₁₀₆	3194 ₂₉	6R4444	3237 ₁₀₀	3285 ₇₃	3354 ₄₈
6R455	3020 ₉₇	3047 ₁₈₂	3176 ₂₆	6R3345	3277 ₅₉	3331 ₇₉	3417 ₄₃
					3513 ₂₆		
KBr(H $_2$ O) $_{1-6}$				KI(H $_2$ O) $_{1-6}$			
1R3	3232 ₉₀			1R3	3299 ₈₄		
2R33	3284 ₇₇	3309 ₇₈		2R33	3335 ₆₆	3352 ₈₃	
3R333	3342 ₆₀	3342 ₆₁	3374 ₇₅	3R333	3376 ₃₅₂	3377 ₃₅₂	3400 ₃₅₄
4R344	3297 ₆₃	3319 ₈₃	3379 ₆₂	4R344	3336 ₅₅	3352 ₈₅	3402 ₆₈
4R334	3339 ₈₉	3371 ₅₈	3395 ₅₅	4R334	3383 ₈₁	3397 ₅₄	3416 ₆₁
5R344	3360 ₉₈	3373 ₆₅	3413 ₃₉	5R344	3399 ₉₂	3409 ₆₂	3433 ₄₂
5R444	3294 ₇₃	3325 ₇₈	3354 ₅₆	5R3344	3364 ₄₈	3379 ₇₈	3436 ₅₁
5R355	3260 ₅₅	3288 ₁₁₅	3386 ₆₂	5R355	3302 ₄₇	3318 ₁₂₃	3410 ₆₅
6R444	3384 ₉₈	3385 ₁₀₁	3406 ₀	6R455	3352 ₂₃	3428 ₆₈	3442 ₂₄
6R4444	3267 ₉₆	3311 ₇₂	3372 ₅₃	6R4444	3310 ₈₇	3347 ₇₀	3389 ₆₃
6R3345	3339 ₉₀	3361 ₄₂	3423 ₆₂	6R3345	3337 ₄₉	3360 ₉₃	3438 ₅₇
	3517 ₁₈						

other hand, the vertical ionization potentials of the KX(H $_2$ O) $_{1-6}$ clusters with X=Cl, Br, and I increase monotonically with n . This increase for $n \geq 4$ becomes rather smaller than that for $n \leq 4$, indicating that the electronic structure around the K atom is weakly affected by the fifth and sixth water molecules after the primary coordination is completed at $n=4$.

Atomic charges for the ion pair derived from a natural population analysis was performed for the most stable structures and are shown in Table VII, where we also report the charges for the first excited state. Figure 5(a) shows the CI(S) polarity change of the K and halide atoms for the tran-

sition from the ground state to the first excited state for the lowest energy structures. The total charge of the ion pair is given as (δq_{CT}) which is associated with the charge transferred from the ion pair to the water molecules. The positive value of charge transfer denotes the case that the salt has positive charge and the water cluster has the same amount of negative charge [Fig. 5(b)]. Figure 5 shows that KF is particularly different from KX (X=Cl/Br/I). KF shows significant CTTS phenomena even for $n=1$, while KX shows significant CTTS phenomena from $n=3$. For $n \geq 4$, water molecules can no longer coordinate to both cation and anion,

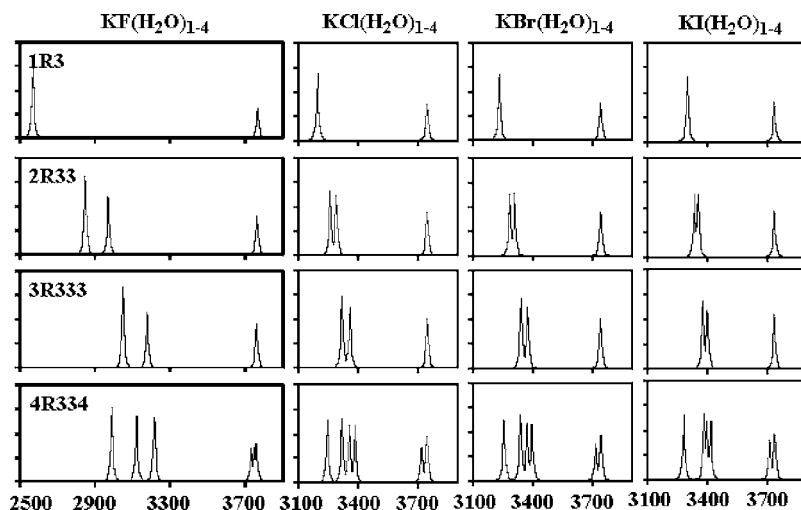
FIG. 4. MP2/aVDZ+IR spectra [scaled harmonic frequencies (ω_s); scale factor=0.96] for the OH stretching modes of the undissociated and dissociated KX(H $_2$ O) $_{1-6}$ clusters.

TABLE VI. Electronic properties of $KX(H_2O)_{1-6}$. [IP_V and μ are vertical IPs (in eV) and dipole moment (in debye) at the MP2/aug-cc-pVDZ+[2s2p/2s] level. E_{CTTS}^{RPA} and $E_{CTTS}^{Cl(S)}$ are charge-transfer-to-solvent energies (in eV) at RPA-B3LYP//6-311++G**[sp] and Cl(S)/aug-cc-pVDZ+[2s2p/2s] levels and their oscillator strengths (f).]

Conf	IP _V	μ	δE ^{RPA} _{CTTS} (f)			δE ^{Cl(S)} _{CTTS} (f)			Conf	IP _V	μ	δE ^{RPA} _{CTTS} (f)			δE ^{Cl(S)} _{CTTS} (f)					
KF(H ₂ O) ₁₋₆							KCl(H ₂ O) ₁₋₆													
KF	9.64	9.54	3.68	0.01	7.31	0.02	KCl	8.51	11.26	3.47	0.01	5.42	0.03							
1R3	11.14	7.36	4.92	0.00	8.43	0.02	1R3	8.83	9.21	4.08	0.01	6.15	0.03							
2R33	11.11	5.33	5.81	0.00	8.74	0.07	2R33	9.14	7.37	4.69	0.01	6.88	0.05							
3R333	11.35	3.69	6.53	0.00	8.84	0.00	3R333	9.51	5.77	5.32	0.03	7.52	0.08							
4R344	11.83	2.96	6.74	0.01	8.93	0.04	4R344	9.76	4.23	5.52	0.03	7.68	0.09							
4R334	11.61	3.24	6.41	0.02	8.88	0.02	4R334	9.63	5.18	5.45	0.03	7.67	0.09							
5R444	11.92	3.44	6.72	0.03	9.05	0.02	5R444	9.78	4.32	5.41	0.02	7.72	0.09							
5R355	11.87	2.43	6.80	0.01	8.93	0.04	5R355	9.68	4.32	5.57	0.02	7.72	0.09							
5R344	11.68	3.01	6.74	0.00	8.91	0.04	5R344	9.73	4.69	5.57	0.02	7.80	0.08							
6R455	11.78	2.27	6.78	0.02	8.98	0.03	6R3345	9.98	3.30	5.65	0.03	7.91	0.08							
6R444	11.36	2.77	6.84	0.05	9.02	0.01	6R444	9.87	4.25	5.69	0.02	7.94	0.06							
6R4444	11.92	3.64	6.72	0.04	9.07	0.03	6R4444	9.90	2.91	5.61	0.03	7.84	0.08							
KBr(H ₂ O) ₁₋₆							KI(H ₂ O) ₁₋₆													
KBr	8.02	11.65	3.16	0.01	4.89	0.03	KI	7.41	12.26	2.49	0.01	4.24	0.03							
1R3	8.27	9.75	5.53	0.04	1R3	7.57	10.58	3.01	0.01	4.80	0.04							
2R33	8.56	8.03	4.27	0.01	6.20	0.07	2R33	7.79	8.99	3.56	0.02	5.39	0.07							
3R333	8.88	6.46	4.84	0.03	6.80	0.10	3R333	8.06	7.55	4.10	0.04	5.94	0.11							
4R344	9.12	4.81	5.02	0.04	6.96	0.11	4R344	8.26	5.81	4.26	0.05	6.07	0.13							
4R334	9.01	5.84	4.99	0.04	6.94	0.12	4R334	8.17	6.87	4.26	0.04	6.07	0.14							
5R344	9.09	5.30	5.10	0.03	7.06	0.10	5R344	8.26	6.29	4.40	0.05	6.20	0.14							
5R444	9.25	3.47	5.04	0.04	7.07	0.09	5R3344	8.41	4.41	4.29	0.05	6.24	0.13							
5R355	9.13	4.98	5.08	0.03	6.99	0.12	5R355	8.26	6.16	4.33	0.06	6.10	0.14							
6R444	9.23	4.81	5.20	0.03	7.19	0.08	6R455	8.32	5.73	4.42	0.04	6.19	0.14							
6R4444	9.25	4.55	5.11	0.04	7.09	0.10	6R4444	8.37	4.22	4.37	0.05	6.18	0.13							
6R3345	9.40	3.22	5.08	0.04	7.20	0.10	6R3345	8.39	4.88	4.39	0.04	6.26	0.13							

and strong water-water interactions start to develop. This leads to a shortening of the K–X bond length and to a consequent decrease on the charge transfer.

IV. CONCLUSION

We studied the ionic dissociation of the KF, KCl, KBr, and KI clusters hydrated by up to six water molecules:

$KX(H_2O)_n$ ($n=1-6$). Calculations were done using B3LYP and MP2 methods in conjunction with the 6-311++G**[sp] and aug-cc-pVDZ+(2s2p/2s) basis sets, respectively. The results provided by both methods were similar up to the addition of four water molecules; however, the MP2 method [which is consistent with the CCSD(T) method in the present systems] predicted different lowest energy conform-

TABLE VII. MP2/aVDZ+charge distribution (NBO) for the ground and first excited states of $KX(H_2O)_{1-6}$.

State	KF(H ₂ O) ₁₋₆		KCl(H ₂ O) ₁₋₆		KBr(H ₂ O) ₁₋₆		KI(H ₂ O) ₁₋₆	
Ground	q_K	q_F	q_K	q_{Cl}	q_K	q_{Br}	q_K	q_I
KF	0.988	−0.988	KCl	0.980	−0.980	KBr	0.975	−0.975
1R3	0.992	−0.889	1R3	0.986	−0.919	1R3	0.982	−0.913
2R33	0.994	−0.846	2R33	0.986	−0.876	2R33	0.983	−0.868
3R333	0.989	−0.817	3R333	0.981	−0.844	3R333	0.979	−0.840
4R334	0.986	−0.823	4R334	0.980	−0.847	4R334	0.977	−0.840
5R344	0.983	−0.826	5R444	0.970	−0.819	5R355	0.967	−0.814
6R4444	0.975	−0.811	6R4444	0.967	−0.824	6R4444	0.965	−0.819
Excited	q_K	q_F	q_K	q_{Cl}	q_K	q_{Br}	q_K	q_I
KF	0.002	−0.088	KCl	0.006	−0.057	KBr	0.007	−0.054
1R3	0.525	−0.730	1R3	0.027	−0.019	1R3	0.029	−0.020
2R33	0.767	−0.853	2R33	0.073	−0.028	2R33	0.072	−0.019
3R333	0.828	−0.875	3R333	0.352	−0.162	3R333	0.346	−0.166
4R334	0.897	−0.871	4R334	0.455	−0.199	4R334	0.453	−0.217
5R344	0.942	−0.870	5R444	0.558	−0.222	5R355	0.557	−0.258
6R4444	0.914	−0.871	6R4444	0.731	−0.295	6R4444	0.711	−0.334
							6R3345	0.748

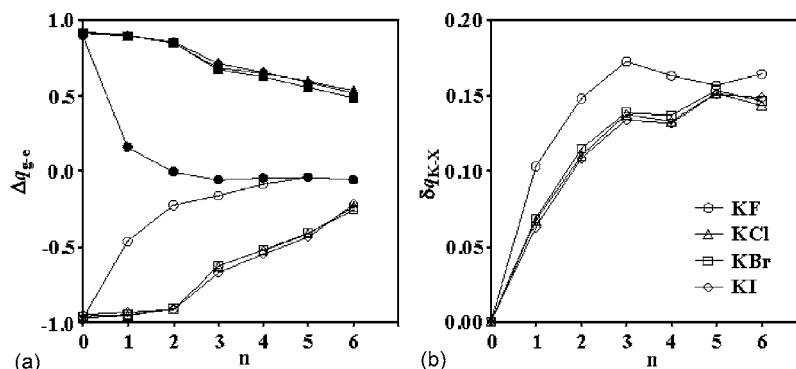


FIG. 5. (a) CI(S)//MP2/aVDZ+ polarity change of the potassium atom (open symbols) and halide atom (filled symbols) for the transition from the ground state to the first excited state for the lowest energy structures of $\text{KX}(\text{H}_2\text{O})_{n=1-6}$ and (b) MP2/aVDZ+ electron transfer ($\delta q_{\text{K}^+ \rightarrow \text{X}^-}$ in electron) from KX to the water cluster: ($\delta q_{\text{KX}} = -\delta q_{\text{water}}$).

ers for $\text{KX}(\text{H}_2\text{O})_{5-6}$ for $\text{X}=\text{Cl}, \text{Br}, \text{and I}$. At very low temperatures (near 0 K), the zwitterionic forms appeared with the addition of five water molecules. For these pentahydrated clusters, the lowest KX structures were partly dissociated, though the partly dissociated KF and KCl structures were nearly isoenergetic to the undissociated ones. In the case of the hexahydrated clusters, partly dissociated structures were observed for KCl/KBr, and a dissociated structure was found for KI. The K–X stretching frequency tended to be much smaller as the degree of dissociation increased. As the temperature increases, the most highly populated structures would change due to the entropy effect. At room temperature, for the penta- and hexahydration based on the free energy ΔG_{298} , undissociated conformers 5R344 and 6R444 which have less H bonds were the most stable. Then, at room temperature the dissociated structures would be seen for higher clusters than the hexahydrated ones.

ACKNOWLEDGMENTS

This work was supported by BK21 and KOSEF(GRL).

- ¹O. Hoff, U. Kahnert, S. Bahr, and V. Kemper, J. Phys. Chem. B **110**, 17115 (2006).
- ²S. C. Park, T. Pradeep, and H. Kang, J. Chem. Phys. **113**, 9373 (2000).
- ³S. Gopalakrishnan, D. Liu, H. C. Allen, M. Kuo, and M. J. Shultz, Chem. Rev. (Washington, D.C.) **106**, 1155 (2006).
- ⁴S. Ghosal, J. C. Hemminger, H. Bluhm, B. S. Mun, E. L. D. Hebenstreit, G. Ketteler, D. F. Ogletree, F. X. Requejo, and M. Salmeron, Science **307**, 563 (2005).
- ⁵K. W. Oum, M. J. Lakin, D. O. De Haan, T. Brauer, and B. J. Finlayson-Pitts, Science **279**, 74 (1998); W. H. Robertson and M. A. Johnson, *ibid.* **298**, 69 (2002).
- ⁶A. H. Tang, G. S. Zhuang, Y. Wang, H. Yuan, and Y. L. Sun, Atmos. Environ. **39**, 3397 (2005).
- ⁷J. M. Mahoney, A. M. Beatty, and B. D. Smith, J. Am. Chem. Soc. **123**, 5847 (2001); J. Yoon, S. K. Kim, N. J. Singh, and K. S. Kim, Chem. Soc. Rev. **35**, 355 (2006); K. Chellappan, N. J. Singh, I.-C. Hwang, J. W. Lee, and K. S. Kim, Angew. Chem., Int. Ed. **44**, 2899 (2005); Angew. Chem. Lett. **419**, 340 (2006); C. C. Pye, Int. J. Quantum Chem. **76**, 62 (2000); C. C. Pye, M. R. Tomney, and T. G. Enright, Can. J. Anal. Sci. Spectrosc. **50**, 254 (2005).
- ⁸S. S. M. C. Godinho, P. C. do Couto, and B. J. C. Cabral, Chem. Phys. Lett. **399**, 200 (2004); J. Chem. Phys. **122**, 044316 (2005); J. Chem. Phys. Lett. **419**, 340 (2006); C. C. Pye, Int. J. Quantum Chem. **76**, 62 (2000); C. C. Pye, M. R. Tomney, and T. G. Enright, Can. J. Anal. Sci. Spectrosc. **50**, 254 (2005).
- ⁹A. C. Olleta, H. M. Lee, and K. S. Kim, J. Chem. Phys. **124**, 024321 (2006).
- ¹⁰N. J. Singh, H.-B. Yi, S. K. Min, M. Park, and K. S. Kim, J. Phys. Chem. B **110**, 3808 (2006); N. J. Singh, A. C. Olleta, A. Kumar, M. Park, H.-B. Yi, I. Bandyopadhyay, H. M. Lee, P. Tarakeshwar, and K. S. Kim, Theor. Chem. Acc. **115**, 127 (2006); J. M. Park, J.-H. Cho, and K. S. Kim, Phys. Rev. B **69**, 233403 (2004).

- ¹¹C. P. Petersen and M. S. Gordon, J. Phys. Chem. A **103**, 4162 (1995).
- ¹²D. E. Woon and T. H. Dunning, J. Am. Chem. Soc. **117**, 1090 (1995).
- ¹³T. Asada and K. Nishimoto, Chem. Phys. Lett. **232**, 518 (1995).
- ¹⁴P. Jungwirth, J. Phys. Chem. A **104**, 145 (2000); P. Jungwirth and D. J. Tobias, J. Phys. Chem. B **106**, 6361 (2002).
- ¹⁵A. L. Sobolewski and W. Domcke, Phys. Chem. Chem. Phys. **7**, 970 (2005).
- ¹⁶M. Arshadi, R. Yamdagni, and P. Kebarle, J. Phys. Chem. **74**, 1475 (1970).
- ¹⁷H. Kistenmacher, H. Popkie, and E. Clementi, J. Chem. Phys. **58**, 5627 (1973).
- ¹⁸L. Perera and M. L. Berkowitz, J. Chem. Phys. **99**, 4236 (1993); **99**, 4222 (1993).
- ¹⁹B. Yates, H. F. Schaefer III, T. J. Lee, and J. E. Rice, J. Am. Chem. Soc. **110**, 6327 (1988); S. S. Xantheas and T. H. J. Dunning, J. Phys. Chem. **98**, 13489 (1994).
- ²⁰D. Majumdar, J. Kim, and K. S. Kim, J. Chem. Phys. **112**, 101 (2000); J. Kim, H. M. Lee, S. B. Suh, D. Majumdar, and K. S. Kim, *ibid.* **113**, 5259 (2000); J. Baik, J. Kim, D. Majumdar, and K. S. Kim, *ibid.* **110**, 9116 (1999); H. M. Lee and K. S. Kim, *ibid.* **114**, 4461 (2001); H. M. Lee, D. Kim, and K. S. Kim, *ibid.* **116**, 5509 (2002).
- ²¹A. T. Blades, P. Jayaweera, M. G. Ikononou, and P. Kebarle, J. Chem. Phys. **92**, 5900 (1990).
- ²²M. T. Rodgers and P. B. Armentrout, J. Phys. Chem. A **101**, 1238 (1997).
- ²³A. J. Stace, Science **294**, 1292 (2001).
- ²⁴D. J. Miller and J. M. Lisy, J. Chem. Phys. **124**, 184301 (2006).
- ²⁵D. Feller, E. D. Glendening, D. E. Woon, and M. W. Feyereisen, J. Chem. Phys. **103**, 3526 (1995).
- ²⁶J. Kim, S. Lee, S. J. Cho, B. J. Mhin, and K. S. Kim, J. Chem. Phys. **102**, 839 (1995); H. M. Lee, J. Kim, S. Lee, B. J. Mhin, and K. S. Kim, *ibid.* **111**, 3995 (1999).
- ²⁷A. D. Becke, J. Chem. Phys. **98**, 5648 (1993); C. Lee, W. Yang, and R. G. Parr, Phys. Rev. B **37**, 785 (1988).
- ²⁸K. S. Kim, P. Tarakeshwar, and J. Y. Lee, Chem. Rev. (Washington, D.C.) **100**, 4145 (2000); J. Kim, J. Y. Lee, K. S. Oh, J. M. Park, S. Lee, and K. S. Kim, Phys. Rev. A **59**, R930 (1999).
- ²⁹A. Nicklass, M. Dolg, H. Stoll, and H. Preuss, J. Chem. Phys. **102**, 8942 (1995).
- ³⁰M. M. Hurley, L. F. Pacios, P. A. Christiansen, R. B. Ross, and W. C. Ermler, J. Chem. Phys. **84**, 6840 (1986); L. A. Lajohn, P. A. Christiansen, R. B. Ross, T. Atashroo, and W. C. Ermler, *ibid.* **87**, 2812 (1987).
- ³¹S. Petrie, J. Phys. Chem. A **102**, 6138 (1998).
- ³²E. D. Glendening, A. E. Reed, J. E. Carpenter, and F. Weinhold, NBO, Version 3.1.
- ³³M. J. Frisch, G. W. Trucks, H. B. Schlegel *et al.*, GAUSSIAN03, Revision A.1, Gaussian, Inc., Pittsburgh, PA, 2003.
- ³⁴W. S. Benedict, N. Gailar, and E. K. Plyer, J. Chem. Phys. **24**, 1139 (1956).

- ³⁵M. Farmik, M. Weimann, and M. A. Suhm, J. Chem. Phys. **118**, 10120 (2003).
- ³⁶S. Lee, J. Kim, S. J. Lee, and K. S. Kim, Phys. Rev. Lett. **79**, 2038 (1997); J. Kim and K. S. Kim, J. Chem. Phys. **109**, 5886 (1998).
- ³⁷T. Shimanouchi, *Tables of Molecular Vibrational Frequencies Consolidated* (National Bureau of Standards, Washington, D.C., 1972), Vol. I, pp. 1–160.
- ³⁸J. E. Huheey, E. A. Keiter, and R. L. Keiter, in *Inorganic Chemistry: Principles of Structure and Reactivity*, 4th ed., edited by J. Piro (HarperCollins College, New York, 1993).
- ³⁹*CRC Handbook of Chemical and Physics*, 68th ed., edited by R. C. Weast, M. J. Astle, and W. H. Beyer (CRC, Boca Raton, FL, 1987).
- ⁴⁰C. Blondel, C. Delsart, and F. Goldfarb, J. Phys. B **34**, L281 (2001).
- ⁴¹M. Atoji, J. Chem. Phys. **25**, 174 (1956).
- ⁴²S. E. Veazey and W. Gordy, Phys. Rev. **A138**, 1303 (1965).
- ⁴³R. F. Barrow and A. D. Caunt, Proc. R. Soc. London, Ser. A **219**, 120 (1953).
- ⁴⁴J. D. D. Martin and J. W. Hepburn, J. Chem. Phys. **109**, 8139 (1998).
- ⁴⁵R. Trainham, G. D. Fletcher, and D. J. Larson, J. Phys. B **20**, L777 (1987).
- ⁴⁶L. Brewer and E. Brackett, Chem. Rev. (Washington, D.C.) **61**, 425 (1961).
- ⁴⁷Z. K. Ismail, R. H. Hauge, and J. L. Margrave, J. Mol. Spectrosc. **54**, 402 (1975).
- ⁴⁸C. Blondel, P. Cacciani, C. Delsart, and R. Trainham, Phys. Rev. A **40**, 3698 (1989).
- ⁴⁹B. P. Fabricand, R. O. Carlson, C. A. Lee, and I. I. Rabi, Phys. Rev. **91**, 1403 (1953).
- ⁵⁰A. Honig, M. Mandel, M. L. Stitch, and C. H. Townes, Phys. Rev. **96**, 629 (1954).
- ⁵¹F. H. de Leeuw, R. van Wachem, and A. Dymanus, J. Chem. Phys. **50**, 1393 (1969).
- ⁵²T.-M. R. Su and S. J. Riley, J. Chem. Phys. **72**, 1614 (1980).
- ⁵³J. R. Rusk and W. Gordy, Phys. Rev. **127**, 817 (1962).
- ⁵⁴D. Hanstorp and M. Gustafsson, J. Phys. B **25**, 1773 (1992).
- ⁵⁵C. R. Webster, I. S. McDermid, and C. T. Rettner, J. Chem. Phys. **78**, 646 (1983).
- ⁵⁶T.-M. R. Su and S. J. J. Riley, J. Chem. Phys. **71**, 3194 (1979).
- ⁵⁷See EPAPS Document No. E-JCPSA6-126-310713 for electronic files that contain the MP2/aVDZ+ results (a) geometries (xyz coordinates in angstrom), (b) unscaled frequencies (cm⁻¹) and IR intensities (km/mol), and (c) graphs of scaled IR spectra of KX(H₂O)₁₋₆ (X=F, Cl, Br, I). This document can be reached via a direct link in the online article's HTML reference section or via the EPAPS homepage (<http://www.aip.org/pubservs/epaps.html>).
- ⁵⁸J. R. R. Verlet, A. E. Bragg, A. Kammrath, O. Cheshnovsky, and D. M. Neumark, Science **307**, 93 (2005).
- ⁵⁹N. J. Singh, M. Park, S. K. Min, S. B. Suh, and K. S. Kim, Angew. Chem., Int. Ed. **45**, 3795 (2006); Angew. Chem. **118**, 3879 (2006); H. M. Lee, S. B. Suh, J. Y. Lee, P. Tarakeshwar, and K. S. Kim, J. Chem. Phys. **112**, 9759 (2000); H. M. Lee, S. B. Suh, P. Tarakeshwar, and K. S. Kim, *ibid.* **122**, 044309 (2005).
- ⁶⁰S. Vaupel, B. Brutschy, P. Tarakeshwar, and K. S. Kim, J. Am. Chem. Soc. **128**, 5416 (2006).
- ⁶¹N. I. Hammer, J.-W. Shin, J. Headrick, E. G. Diken, J. R. Roscioli, G. H. Weddle, and M. A. Johnson, Science **306**, 675 (2004).