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Hydration Phenomena of Sodium and Potassium Hydroxides by Water Molecules

Anupriya Kumar, Mina Park, Joo Youn Huh, Han Myoung Lee, and Kwang S. Kim*

Center for Superfunctional Materials, Department of Chemistry, Pohang University of Science and Technology, San 31, Hyojadong, Namgu, Pohang 790-784, Korea

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The hydrated structures, dissociation energies, thermodynamic quantities, infrared spectra, and electronic properties of alkali-metal hydroxides (MOH , $\text{M} = \text{Na}$ and K) hydrated by up to six water molecules $[\text{MOH}(\text{H}_2\text{O})_{n=1-6}]$, are investigated by using the density functional theory and Møller–Plesset second-order perturbation theory. Further accurate analysis based on the coupled cluster theory with singles, doubles, and perturbative triples excitations is more consistent with the MP2 results. NaOH shows a peculiar trend in dissociation: it begins to form a partially dissociated structure for $n = 3$, and it dissociates for $n = 4$ and 6 , whereas it is undissociated for $n = 5$. However, for $n = 5$, the dissociated structure is nearly isoenergetic to the undissociated structure. For KOH , it begins to show partial dissociation for $n = 5$, and complete dissociation for $n = 6$.

1. Introduction

Alkali-metal hydroxides are widely used as electrolytes in electrochemical purification in industry and in determination of the metal-ion complexes in biology. Substantial research has been done on the aqueous solvation of various ions,^{1,2} acids,^{3,4} bases,⁵ and salts^{6,7} in water during the past few decades. Here, we are particularly interested in the dissociation of alkali-metal hydroxides. Alkali-metal ions are important species in life. However, their biochemical mechanisms are not well understood. Most of the protein-bound metal ions for functions are bound to at least one water molecule.⁸ Aqueous NaOH (NaOD) catalyses stereospecific epimerization of α -amino acids.⁹ Mostly, the catalytic activity in metal enzymes is due to the deprotonation of a metal ion bound by water molecules to give a hydroxyl group that is still bound to the metal ion after the deprotonation. These hydroxyl groups can act as a nucleophile and attack as a substrate.¹⁰ A similar hydroxide group is obtained by the dissociation of a base in all aqueous alkali-metal hydroxide clusters. Detection of Na^+ and K^+ ions around nucleic acid molecules has been a challenge due to unclear differentiation between water and metal ions.¹¹ Negatively charged phosphates of DNA cause molecules to repel each other. The partially hydrated Na^+ ions electronically interact with the negatively charged phosphates of DNA, allowing the DNA molecules to form helices. Also, the role of the $\text{Na}^+ - \text{K}^+$ pump in muscle activity is well-known. Thus, for mimicking various medicinal and environmental mechanisms, the understanding of mechanistic actions of alkali-metal ions would be highly beneficial. Indeed, the alkali-metal ion recognition by receptors has been an important subject for biosensing.¹²

It is well-known that in contrast to alkali halides the mean activity coefficient of alkali hydroxide solutions of equal concentration decreases in the order $\text{CsOH} > \text{KOH} > \text{NaOH} > \text{LiOH}$. Harned and Owen¹³ proposed that hydroxides undergo local hydrolysis because the polarizing ability of the alkali cations is larger for the smaller ions. In this regard, Davis¹⁴

stated that ion pairs exist in hydrated solutions and the association is electrostatic.

It is a known phenomenon that all alkali-metal hydroxides are deliquescent except LiOH . They have linear structures with low-frequency bending vibrations.^{15–22} However, the experimental investigation is difficult as they have low vapor pressure and are highly reactive.^{20–22} Lown and Thirsk²³ studied the proton-transfer conductance of concentrated aqueous alkali-metal hydroxide solutions at elevated temperatures and pressures and suggested that at high concentrations most of the water molecules are dominated by their proximity to an ion and so cannot participate in the proton-transfer mechanism of conductance by the hydroxyl anion. This mechanism is most disrupted by KOH and least by LiOH due to its greater ionic association. This is well supported by the Raman spectral study of aqueous alkali-metal hydroxides.²⁴

With addition of water molecules to the base, the complex formed becomes energetically more stable with the red shift in the IR frequency due to the increased metal–hydroxide bond length. Thus, the absence of the IR stretching frequency band would indicate that the alkali-metal cation is dissociated, while both remain coordinated to the water molecules. It was found that the aqueous dissociation of CsOH , RbOH , and LiOH requires 4, 5, and 7 water molecules for complete dissociation as a global minimum energy structure, respectively.²⁵ To complete the trend of aqueous dissociation of alkali-metal hydroxides, here we present the detailed study of $\text{MOH}(\text{H}_2\text{O})_{n=1-6}$ ($\text{M} = \text{Na}$ and K) using high-level *ab initio* calculations with large basis sets including diffuse basis functions that would be able to describe the correct dissociation phenomena. Most of the initial geometries were taken from the theoretical studies of hydrated CsOH , RbOH , and LiOH . In the case of penta- and hexahydrated complexes, we carried out new searches for other low-lying energy conformers. The equilibrium geometries were confirmed by evaluating the vibrational frequencies at both DFT and MP2 levels of theory. Here, we particularly discuss the dissociation phenomena of mono- to hexahydrated bases along with these structures, energetics, charge transfers (CT), electronic properties and spectra.

* Corresponding author. Tel: +82-54-279-2110. Fax: +82-54-279-8137. E-mail: kim@postech.ac.kr.

TABLE 1: Geometrical Parameters and Dissociation Energies of NaOH and KOH^a

MOH	parameter	B3LYP 6-311++G**	MP2 aVDZ+	MP2 aVTZ+	CCSD(T) aVDZ+	CCSD(T) aVTZ+	expt	ref
NaOH	$r_{\text{Na}\cdots\text{O}}$	1.96	1.99	1.98	1.99	1.98	1.95	16
	r_{OH}	0.95	0.96	0.96	0.96	0.95		
	$\angle\text{NaOH}$	180.0	180.0	180.0	180.0	180.0		
	D_0	81.0	79.3{81.9}	83.7{83.4}	72.6{75.3}	76.9{76.5}	80.0, 77.9	30, 31
	μ	6.66	7.18{7.03}	7.02{6.89}	7.22{7.04}	7.05{6.91}		
	ω_1	556	538{571}	542{553}	542{578}	547{558}	540, 431	18
	ω_2	3971	3946{3952}	3964{3961}	3928{3936}	3952{3954}		
	$\omega_2(\text{scaled})$	(3812)	(3788)	(3806)	(3771)	(3794)		
KOH	$r_{\text{K}\cdots\text{O}}$	2.25	2.26	2.23	2.26	2.23	2.196	15
	r_{OH}	0.96	0.96	0.96	0.96	0.96		
	$\angle\text{KOH}$	179	178	180.0	180.0	180.0		
	D_0	84.3	82.2	86.6	73.6	79.4	85.1, 81.4	30, 31
	μ	7.79	8.06	7.84	8.05	7.89		
	ω_1	438	436	449	437	452	408	19
	ω_2	3937	3898	3912	3892	3903		
	$\omega_2(\text{scaled})$	(3779)	(3742)	(3755)	(3736)	(3747)		

^a Distances are in Å; angles in degrees; dissociation energy (D_0) in kcal mol⁻¹; dipole moment (μ) in debye. B3LYP uses 6-311++G** for NaOH and KOH. The aVTZ+ basis set denotes aug-cc-pVTZ+(2s2p/2s). In ref 32, the [CCSD(T)/aug-cc-pVTZ]/[CCSD(T)/6-311++G(3df,3pd)] gives the $r_{\text{Na}\cdots\text{O}}$ distance (1.943/1.944 Å), ω_1 (565/591 cm⁻¹) and ω_2 (4008/3952 cm⁻¹), and the $r_{\text{K}\cdots\text{O}}$ distance (2.226/2.223 Å), ω_1 (451/450 cm⁻¹) and ω_2 (3952/3899 cm⁻¹). ω_2 (scaled) is scaled by 0.96 for the O \cdots H stretch mode to obtain the realistic frequencies including anharmonicity. The values for D_0 in braces denotes the cases obtained with freezing only the 1s orbital for Na, and others are the cases obtained with the default frozen core orbital option (1s2s2p for Na).

2. Computational Details

We investigated various dissociated and undissociated structures of clusters MOH(H₂O)_{1–6} including those of LiOH–, RbOH– and CsOH–water clusters.²⁵ Calculations were done at the density functional theory (DFT) level with the Becke's three parameter exchange potential and Lee–Yang–Parr correlation functional (B3LYP)²⁶ and the Møller–Plesset second-order perturbation theory (MP2) level. For B3LYP, the 6-311++G**[sp] basis set was used for Na, O, and H, and energy-adjusted Stuttgart effective core potentials (ECP) were used with d exponents (0.48) added to the K valence basis for K (which will be simply denoted as Stuttgart basis sets).²⁷ For MP2, the cc-pVDZ basis set was employed for Na, and the above Stuttgart basis set was used for K. For oxygen and hydrogen atoms, the aug-cc-pVDZ+diffuse(2s2p/2s) basis set was used.²⁸ This basis set will be denoted simply as aVDZ+. The coupled cluster theory with singles, doubles, and perturbative triples excitations [CCSD(T)] was studied with single point calculations on the optimized MP2 geometries by using the same basis set. For brevity, the basis set of water is simply used to represent the basis set of the complex.²⁹ Thus, calculations carried out at the B3LYP, MP2 and CCSD(T) levels are denoted as B3LYP/6-311++G**, MP2/aVDZ+ and CCSD(T)/aVDZ+, respectively. In the case of MP2/aVDZ+ and CCSD(T)/aVDZ+ calculations, the frozen core orbital option [1s2s2p for Na; 1s2s2p for K employing the ECP; 1s for O] was chosen. When only the 1s orbital is frozen for Na, the binding energy of NaOH is overestimated at the MP2/aVDZ+ level (81.9 kcal/mol), in contrast to the case based on the standard frozen orbitals (1s2s2p) (79.3 kcal/mol) and the experimental value^{30,31} (~80 kcal/mol). Also, when only the 1s orbital is frozen for Na, the binding energy of NaOH at the CCSD(T)/aVTZ+ level (76.5 kcal/mol) is similar to that calculated by using the standard frozen orbitals (1s2s2p) (76.9 kcal/mol). Thus, the standard frozen core orbitals were used in our calculations because most of the calculations were based on MP2/aVDZ+. Detailed calculations on NaOH and KOH can be referred from a series of work by Lee and Wright.³² For the hydration of NaOH/KOH by water molecules, we have reported the zero-point energy (ZPE) uncorrected (ΔE_e) and corrected (ΔE_0) binding energies. The enthalpies (ΔH_{298}) and Gibbs free energies (ΔG_{298}) were obtained using the standard expression

for ideal gases at 298 K and 1 atm. The basis set superposition error (BSSE) corrections cannot equally treat the dissociated and undissociated states, because the binding energy of NaOH/KOH is calculated without BSSE correction. Thus, we did not do BSSE correction. Furthermore, the BSSE-uncorrected binding energy of NaOH/KOH is in good agreement with the experimental value, whereas the BSSE-corrected binding energy is underestimated. For CCSD(T), the ZPE and thermal energy corrections were done by using the MP2/aug-cc-pVDZ+diffuse(2s2p/2s) values. For NaOH and KOH, the MP2 and CCSD(T) calculations using aug-cc-pVTZ+diffuse(2s2p/2s) (to be shortened as aVTZ+) were also performed. The CT energies were obtained by using configuration interaction with singles excitations [CI(S)] on the MP2 geometries ($E^{\text{CI(S)}}_{\text{CT}}$) and by using the random-phase-approximation (RPA) at the B3LYP level of theory ($E^{\text{RPA}}_{\text{CT}}$). Other electronic properties such as vertical and Koopman's ionization potentials (IP), polarizability (α) and dipole-moment (μ) are also reported at the MP2 level of theory. The calculations were carried out using the Gaussian 03 suite of programs.³³ The figures presented here were drawn using Posmol³⁴ and some available graphic packages.

3. Results and Discussion

In Table 1, we have compared the calculated geometrical structures and dissociation energies of NaOH and KOH with the experimental data.^{10–21,35} The B3LYP/MP2/CCSD(T) M–O distances for M = Na and K are 1.96/1.99/1.99 and 2.25/2.26/2.26 Å, respectively, in reasonable agreement with the experimental values (1.95 and 2.20 Å)^{15,16,31} and the previous calculated results.³⁶ The OH⁻ distance is 0.95/0.96/0.96 Å. NaOH has a linear structure (180°), whereas KOH has an almost linear structure (178°). The calculated Na \cdots OH stretching frequency (556/539 cm⁻¹ at B3LYP/MP2) is in excellent agreement with the experimental value (540 cm⁻¹),¹⁸ whereas the calculated K \cdots OH stretching frequency (438/436 cm⁻¹) is slightly overestimated compared with the experimental value (408 cm⁻¹).¹⁹ The predicted dissociation energies (D_0) for NaOH and KOH (79.3 and 82.2 kcal mol⁻¹, respectively) at the MP2/aVDZ+ level are in reasonable agreement with the experimental value (80.0 and 81.4 kcal mol⁻¹, respectively).^{30,31}

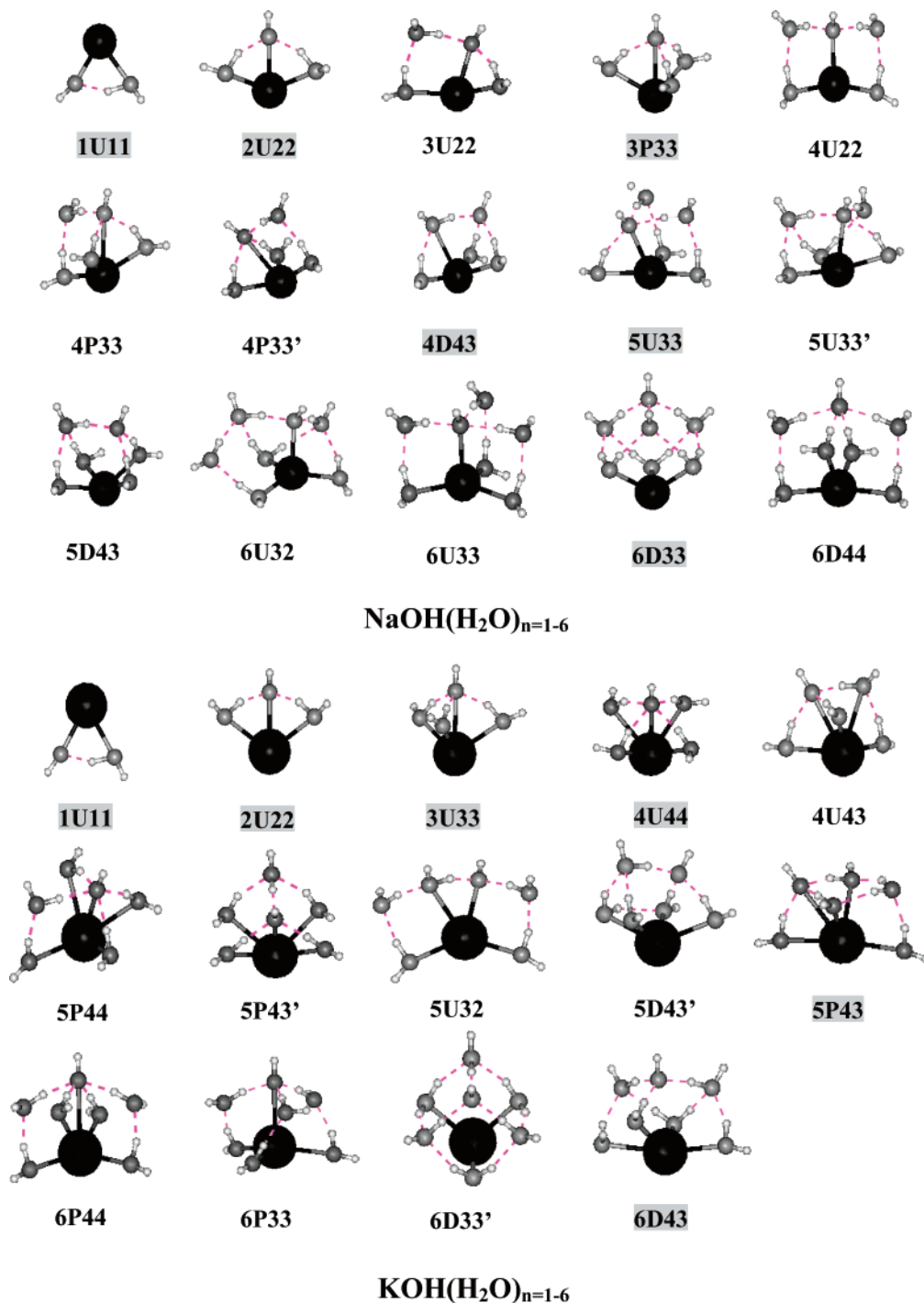


Figure 1. MP2/aVDZ+ low-lying energy conformers of NaOH(H₂O)_{n=1-6} and KOH(H₂O)_{n=1-6}.

We have investigated the dissociation trends and spectroscopic properties of NaOH(H₂O)_{n=1-6} and KOH(H₂O)_{n=1-6} clusters. Figure 1 shows various optimized structures of low-lying energy conformers of hydrated sodium and potassium hydroxides at the MP2/aVDZ+ level. As for the notations of “*nUn₁n₂*”, “*nPn₁n₂*”, and “*nDn₁n₂*”, U/P/D indicates the undissociated/partially dissociated/dissociated state, *n* is the number of water molecules, and *n₁* and *n₂* are the hydration numbers of M⁺ (Na⁺, K⁺) and OH[−], respectively. We mainly focus our attention on the undissociated and dissociated forms of these hydrated clusters by monitoring the M–O distances and the stretching mode of M–OH by successive addition of water molecules to the cluster. Table 2 lists the binding energies of various structures of the NaOH(H₂O)_{n=1-6} clusters (i.e., hydra-

tion energies of NaOH by *n* number of water molecules) at the B3LYP/6-311++G** and MP2/aVDZ+ levels of theory. The corresponding values for the KOH(H₂O)_{n=1-6} clusters are in Table 3. Table 2 (lower part) also lists the BSSE corrected binding energies at both B3LYP/6-311++G** and MP2/aVDZ+ levels of theory on the selected conformers such as 2U11, 2U22, 4P33, 4D43, 4U44, 5U33 and 5D43. It has been observed that the BSSE corrections, due to the unbalanced basis incompleteness that might underestimate the dispersion energies (the dispersion energies of 2U22 and 2U11 for NaOH–(H₂O)₂ are significant, i.e., −11.36 and −7.09 kcal/mol, respectively, at the MP2 level of symmetry adapted perturbation theory³⁷), tend to underestimate the binding energies at the MP2/aVDZ+ level as observed in the study of hydrated alkali-metal ions.²⁹

TABLE 2: Binding Energies of NaOH(H₂O)_{1–6} (Hydration of NaOH by *n* Water Molecules in kcal mol^{–1})^a

<i>n</i>	conf	MP2/aVDZ+				conf	B3LYP/6-311++G**	
		–Δ <i>E</i> _e	–Δ <i>E</i> ₀	–Δ <i>H</i> ₂₉₈	–Δ <i>G</i> ₂₉₈		–Δ <i>E</i> _e	–Δ <i>E</i> ₀
1	1U11	23.24	21.25	22.51	13.53		24.41	22.52
	1U10	11.20	9.95	9.92	4.89		13.63	12.28
2	2U22	43.56	39.27	41.19	23.39		45.91	41.61
	2U11	40.96	36.88	38.95	20.66		42.43	39.17
3	3P33	62.05	55.08	58.02	29.16		63.75	56.83
	3U22	59.84	53.08	55.86	28.36		62.75	56.05
	3U32	57.49	50.56	53.27	25.59		59.21	52.27
4	4P33	75.47	66.35	69.77	33.33	(4D33)	78.03	69.02
	4P33'	75.43	66.37	69.79	33.36	(4D33')	77.34	69.06
	4U22	74.78	65.63	69.09	32.54		74.81	65.94
	4D43	75.39	66.50	69.92	32.96	(4U33)	78.04	68.97
	4U44	74.95	64.62	68.31	29.02		73.79	63.82
5	5U33	88.81	76.96	81.03	34.81		91.29	79.54
	5U33'	88.84	76.55	80.85	33.31	(5D33')	89.70	77.68
	5D43	88.50	76.86	81.12	33.71		89.38	77.60
	5U32	86.28	75.37	79.35	33.78		90.23	79.11
6	6D33	104.48	88.75	94.77	35.01		105.56	89.28
	6U32	101.85	88.01	92.96	36.29		104.36	90.12
	6D44	101.97	87.53	92.38	35.64		101.90	87.30
	6U33	101.57	87.22	91.91	36.43		102.75	88.66

<i>n</i>	conf	MP2/aVDZ + ^b	B3LYP/6-311++G** ^b	<i>n</i>	conf	MP2/aVDZ + ^b	B3LYP/6-311++G** ^b
2	2U22	41.76 ± 1.80	44.48 ± 1.43	4	4P33	71.82 ± 3.65	75.69 ± 2.34
	2U11	39.16 ± 1.80	41.32 ± 1.11		4D43	71.74 ± 3.65	75.71 ± 2.33
5	5U33	84.45 ± 4.36	88.30 ± 2.99	4	4U44	71.15 ± 3.80	71.64 ± 2.15
	5D43	83.86 ± 4.64	86.28 ± 3.10				

^a In the notations of “*nUn₁n₂*”, “*nPn₁n₂*” and “*nDn₁n₂*”, U/P/D indicates the undissociated/partially dissociated/dissociated state, *n* is the number of water molecules, and *n₁* and *n₂* are the hydration numbers of M⁺ (Na⁺, K⁺) and OH[–], respectively. Lowest energy conformers are boldfaced.

^b 50%-BSSE-corrected energy.²⁸ The value after “±” denotes 50%-BSSE: then the upper limit is the full BSSE-corrected value.

TABLE 3: Binding Energies (kcal mol^{–1}) of KOH(H₂O)_{1–6} (Hydration of KOH by *n* Water Molecules in kcal mol^{–1})^a

<i>n</i>	conf	MP2/aVDZ+				conf	B3LYP/6-311++G**	
		–Δ <i>E</i> _e	–Δ <i>E</i> ₀	–Δ <i>H</i> ₂₉₈	–Δ <i>G</i> ₂₉₈		–Δ <i>E</i> _e	–Δ <i>E</i> ₀
1	1U11	23.57	21.75	22.74	15.42		23.36	21.62
2	2U22	44.26	40.03	41.70	24.81		43.87	39.64
3	3U33	61.82	55.46	57.57	31.97		60.69	54.18
	3U22	58.99	52.94	55.20	29.23		59.03	52.61
	3U32	58.74	51.67	54.36	26.39		56.99	49.85
4	4U44	76.01	66.08	69.28	31.76		71.13	61.34
	4U43	75.21	66.52	69.31	33.97	(4U33)	74.19	65.44
	4U42	72.74	64.95	68.13	31.52	(4U22)	73.35	64.65
	4U32	72.26	63.81	66.70	31.66	(4U22')	72.91	64.12
5	5P43'	89.58	77.34	81.52	33.37	(5D33)	84.96	73.22
	5P44	88.59	76.74	80.32	34.41	(5D44)	84.28	72.29
	5U32	84.56	74.13	77.63	33.28	(5U22)	85.72	75.01
	5D43'	88.23	76.90	80.66	34.03		86.06	74.45
	5P43	90.06	78.45	82.32	35.50	(5D43)	86.45	75.57
6	6P44	101.27	87.07	91.27	35.07		97.12	82.61
	6P33	99.43	86.76	90.45	37.31		98.38	85.13
	6D33'	101.77	86.31	91.88	32.27		100.54	84.35
	6U32	98.56					98.09	84.38
	6U44'	100.80	85.89	90.49	33.09	(6D44)	96.30	80.77
	6D43	101.75	87.68	92.21	35.54		99.88	85.22

^a In the notations of “*nUn₁n₂*”, “*nPn₁n₂*” and “*nDn₁n₂*”, U/P/D indicates the undissociated/partially dissociated/dissociated state, *n* is the number of water molecules, and *n₁* and *n₂* are the hydration numbers of M⁺ (Na⁺, K⁺) and OH[–], respectively. Lowest energy conformers are boldfaced.

In the case of hydrated hydroxide anion clusters,⁵ it was found that the MP2 binding energy based on full BSSE correction is underestimated. The BSSE-uncorrected binding energies are similar to the experimental values. Similar observations were made by others.^{8,38} The role of BSSE corrections is important for the binding energies, but the relative stability is not important because of its consistency. For these conformers, the BSSE correction has little effect on the trend of the stability. Therefore, in the present study, we studied the binding energies without BSSE correction. For testing the quality of the basis sets, we have reported higher level calculations at MP2/aVTZ+, CCSD-

(T)/aVDZ+, and CCSD(T)/aVTZ+ levels of theory, as can be referred in Table 1. The calculated binding energies and geometries are consistent and in good agreement with the experimental data. This reflects the appropriateness of the basis sets used. The lowest energy structures of the undissociated and dissociated cases (including nearly isoenergetic structures) for *n* = 1–6 are further investigated at the CCSD(T)/aVDZ+ level of theory (Table 4) to confirm the actual state of conformation.

Previously, we have discussed the criterion for the distinction of the dissociated/undissociated structures of hydrated salts.⁷ Although the distinction cannot be clearly made, we here use

TABLE 4: CCSD(T)/aug-cc-pVDZ+(2s2p/2s) Binding Energies of NaOH (H₂O)_{1–6} and KOH (H₂O)_{1–6}^a

conf	–ΔE _e	–ΔE ₀	–ΔH ₂₉₈	–ΔG ₂₉₈	conf	–ΔE _e	–ΔE ₀	–ΔH ₂₉₈	–ΔG ₂₉₈
NaOH(H ₂ O) _{1–6}					KOH(H ₂ O) _{1–6}				
1U11	23.08	21.09	22.34	13.37	1U11	23.38	21.56	22.55	15.23
2U22	43.33	39.04	40.97	23.17	2U22	44.07	39.83	41.51	24.61
3P33	61.81	54.84	57.78	28.92	3U33	61.67	55.31	57.43	31.82
3U22	59.56	52.79	55.57	28.07					
4U22	71.4	62.25	65.71	29.16					
4P33	75.20	66.08	69.50	33.06	4U44	76.47	66.54	69.74	32.22
4P33'	75.15	66.10	69.51	33.08	4U43	75.02	66.33	69.12	33.78
4D43	75.08	66.19	69.61	32.65	5P43'	89.87	77.62	81.80	33.66
5U33	88.86	77.01	81.08	34.86	5P44	88.97	76.96	80.63	33.99
5U33'	89.05	76.76	81.06	33.52	5D43'	88.28	76.95	80.70	34.07
5D43	88.49	76.86	81.11	33.70	5P43	89.85	78.24	82.11	35.29
					6P33	99.19	86.51	90.19	37.06
6U32	101.68	87.84	92.79	36.12	6P44	101.61	87.41	91.61	35.41
6D33	104.40	88.67	94.68	34.92	6D33'	101.97	86.52	92.08	32.47

^a Zero point energy and thermal energy corrections used the MP2/aug-cc-pVDZ+(2s2p/2s) values.

the previous approach. The partial/full dissociation is based on both the degree of elongation of r_{MOH} (Δr_{MOH}) with respect to the pure MOH without hydration (i.e., partial dissociation for $0.6 \text{ \AA} < \Delta r_{\text{NaX}} < 1.0 \text{ \AA}$, and full dissociation for $\Delta r_{\text{MOH}} > 1.0 \text{ \AA}$) and the degree of coupling of the MOH stretching mode ω_{MOH} with other modes (i.e., partial dissociation for $50 \text{ cm}^{-1} < \omega_{\text{MOH}} < 100 \text{ cm}^{-1}$, and full dissociation for $\omega_{\text{MOH}} < 50 \text{ cm}^{-1}$ for which other modes are more dominating so that this mode may not be considered as the MOH stretching mode).

At the CCSD(T)/MP2/aVDZ+ level, the lowest energy undissociated/partially dissociated/dissociated structures for NaOH(H₂O)_{*n*–1–6} in ΔE_0 are 1U11, 2U22, 3P33, 4D43, 5U33, and 6D33, whereas 5D33 is nearly isoenergetic with 5U33, and 4P33/4P33' are nearly isoenergetic with 4D43. For KOH(H₂O)_{*n*–1–6}, the lowest energy undissociated/partially dissociated/dissociated structures in ΔE_0 are 1U11, 2U22, 3U33, 4U44, 5P43, and 6D43. These results show that the coordination number of 3 is favored for Na⁺ in these small clusters, and that of 4 is favored for K⁺. We note that the undissociated conformers show smaller ZPEs than the dissociated conformers. To compare relative stabilities of the undissociated, partially dissociated and dissociated conformers, their ZPE-corrected binding energies (ΔE_0) are shown in Figure 2 at the CCSD(T)/aVDZ+ level. In the case of NaOH, the partially dissociated structure (3P33) starts to appear for $n = 3$, and the dissociated structures appear for $n = 4$ and 6, whereas for $n = 5$ the undissociated structure is the most stable, though the partially dissociated structure is nearly isoenergetic with the undissociated one. For KOH, the undissociated structures are the most stable for $n = 1–4$, and a partially dissociated/dissociated structure is the most stable for $n = 5/6$.

Between different levels of calculation, the MP2/aVDZ+ results are consistent with the CCSD(T)/aVDZ+ results in the case of NaOH. For KOH, 4U44 is more stable than 4U43 at CCSD(T)/aVDZ+. The B3LYP/aVDZ results show some differences in the energy order from the MP2/aVDZ+ results due to the difference in coordination number for both metal and hydroxide ions. In particular, for NaOH the 4D33, 4D33', 4U33 and 5D33' structures at the B3LYP level are changed to 4P33, 4P33', 4D43 and 5U33' at the MP2 level, respectively, and for KOH the 4U22', 4U22, 4U33, 5D44, 5U22, 5D33, 5D43 and 6D44 structures at the B3LYP level are changed to 4U32, 4U42, 4U43, 5P44, 5P32, 5P43' and 6U44' at the MP2 level, respectively. Nevertheless, both CCSD(T)/aVDZ+ and MP2/aVDZ+ levels of theory (and B3LYP calculations) show that

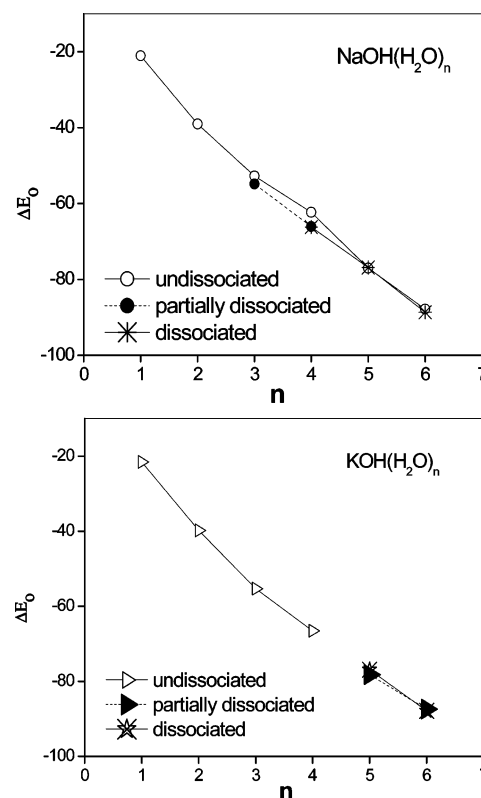


Figure 2. Comparison of the lowest undissociated, partially dissociated and dissociated energies (ΔE_0) of NaOH(H₂O)_{*n*–1–6} and KOH(H₂O)_{*n*–1–6} at the CCSD(T)/aVDZ+ level.

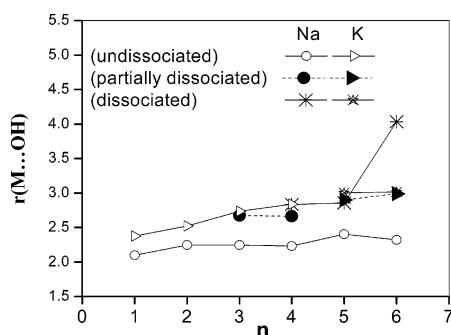
both NaOH and KOH need six water molecules for complete dissociation.

Table 5 lists the conformational characteristics and geometrical parameters (including the rotational constants) of the lowest energy undissociated, partially dissociated and dissociated structures at the MP2/aVDZ+ level. In mono- to hexahydrated undissociated clusters, the coordination number of the metal (M⁺) increases from 2 to 4, whereas it is 3 for most of the clusters containing NaOH and 4 for the clusters containing KOH. Figure 3 shows the change of Na---OH ($r_{\text{Na}---\text{OH}}$) and K---OH ($r_{\text{K}---\text{OH}}$) distances by the addition of water molecules for the undissociated, partially dissociated and dissociated clusters. With successive addition of water molecules, both the number of hydrogen bonds and the coordination number of the metal atom tend to increase. The $r_{\text{Na}---\text{OH}}$ in NaOH(H₂O)_{*n*} for $n = 1–6$ are (2.097, 2.247, 2.674, 2.835, 2.404 and 4.031 Å)

TABLE 5: MP2/aug-cc-pVDZ+(2s2p/2s) Conformational Characteristics and Geometric Parameters [Distances ($r/\text{\AA}$) and Rotational Constants (A, B, C in GHz)] for the Low-Energy Conformers of $\text{MOH}(\text{H}_2\text{O})_{0-6}$ ($M = \text{Na/K}$)^a

	δE_0	HB/coord	$r_{M\cdots OH}$	$r_{M\cdots Ow}$	$r_{HO\cdots Hw}$	$\omega_{M\cdots OH}$	$\omega_{M\cdots Ow}$	A	B	C
NaOH(H ₂ O) ₁₋₆										
NaOH			1.99			539				
1U11	0.00	1/2	2.097	2.296	1.522	483	228	10.81	8.58	4.82
2U22	0.00	2/3	2.247	2.300	1.585	416	286, 256	7.33	3.25	2.61
3U22	2.25	3/3	2.246	2.31	1.531	372	279, 232	3.69	2.02	1.47
3P33	0.00	3/4	2.674*	2.321	1.604	73*	287, 253, 240	2.66	2.66	2.21
4U22	3.94	4/3	2.230	2.321	1.564	352	308, 306	1.88	1.48	1.44
4P33	0.11	4/4	2.640*	2.317	1.582	55*	307, 284, 220	1.94	1.48	1.39
4P33'	0.09	4/4	2.665*	2.315	1.570	42*	302, 290, 225	1.88	1.48	1.44
4D43	0.00	4/4	2.835*	2.335	1.516	none**	300, 278, 232, 102	2.24	1.47	1.37
5U33	0.00	5/4	2.404	2.352	1.595	142	319, 299, 273	1.34	1.21	0.99
5U33'	0.25	6/4	2.434	2.362	1.556	134	286, 261, 244	1.70	1.15	0.96
5D43	0.15	5/4	2.856*	2.364	1.530	none**	261, 252, 233, 222	1.48	1.28	1.13
6U32	0.83	7/4	2.320	2.354	1.471	239	307, 261, 210	1.40	0.78	0.61
6D33	0.00	9/3	4.031**	2.329	1.551	none**	283, 283, 277	0.99	0.99	0.98
KOH(H ₂ O) ₁₋₆										
KOH			2.256			436				
1U11	0.00	1/2	2.376	2.552	1.491	418	210	9.15	5.62	3.48
2U22	0.00	2/3	2.523	2.604	1.568	380	224, 217	4.60	2.98	2.10
3U33	0.00	3/4	2.734	2.626	1.628	105	216, 210, 209	2.10	2.09	1.86
4U44	0.00	4/5	2.838	2.740	1.708	110	196, 180, 180, 110	1.65	1.64	1.32
4U43	0.21	4/5	2.769	2.624	1.551	186	273, 211, 186, 104	1.78	1.29	1.14
5P44	1.28	5/4	2.923*	2.668	1.667	94*	202, 180, 172, 169	1.38	1.03	0.95
5P43'	0.62	5/5	2.917*	2.734	1.593	93*	212, 190, 179, 174	1.30	1.11	0.99
5D43'	1.29	6/4	3.002**	2.655	1.530	none**	206, 198, 176, 127	1.22	1.12	0.98
5P43	0.00	6/5	2.898*	2.632	1.565	81*	221, 217, 163, 148	1.55	0.97	0.84
6P33	1.42	6/4	2.895*	2.695	1.572	96*	186, 185, 152	0.85	0.84	0.72
6P44	0.52	6/5	2.989*	2.688	1.677	95*	198, 168, 168, 162	1.11	0.77	0.72
6D33'	1.41	9/3	4.434**	2.656	1.551	none**	248, 233, 193	0.94	0.80	0.80
6D43	0.00	7/4	3.017**	2.680	1.543	none**	213, 204, 191, 189	1.08	0.81	0.71

^a HB/coord indicates the number of hydrogen bonds/the coordination number of MOH. The coordination numbers of M^+ (Na^+ , K^+) and OH^- are found from notations of “ $n\text{Un}_1n_2$ ”, “ $n\text{Pn}_1n_2$ ” and “ $n\text{Dn}_1n_2$ ”. $r_{\text{HO}\cdots\text{Hw}}$ is the nearest distance from OH^- to H of the neighboring water molecule. Frequencies are not scaled. The relative energy (δE_0) is given at the CCSD(T)/aVDZ+ level. Experimental values of the $r_{M\cdots O}$ distances for NaOH and KOH are 1.95 and 2.196 Å, respectively.^{15,16} CCSD(T)/cc-pVTZ+(2s) gives the $r_{\text{Na}\cdots O}$ distance (1.943/1.944 Å), ω_1 (565/591 cm^{-1}), and the $r_{K\cdots O}$ distance (2.226/2.223 Å), ω_1 (451/450 cm^{-1}). “*/**” denotes the partial/full dissociation based on the degree of elongation of r_{MOH} (Δr_{MOH}) with respect to the pure MOH without hydration (i.e., partial dissociation for $0.6 \text{ \AA} < \Delta r_{\text{NaX}} < 1.0 \text{ \AA}$, full dissociation for $\Delta r_{\text{MOH}} > 1.0 \text{ \AA}$), and based on the degree of coupling of the MOH stretch frequency modes ω_{MOH} with other modes (i.e., partial dissociation for $50 \text{ cm}^{-1} < \omega_{\text{MOH}} < 100 \text{ cm}^{-1}$, full dissociation for $\omega_{\text{MOH}} < 50 \text{ cm}^{-1}$ for which other modes are more dominating so that this mode may not be considered as the MOH stretching mode; ref 7).

**Figure 3.** $M\cdots\text{OH}$ distances of the lowest-energy undissociated, partially dissociated and dissociated conformers (in Å at the MP2/aug-cc-pVDZ+(2s2p/2s) level).

and the $r_{K\cdots OH}$ in $\text{KOH}(\text{H}_2\text{O})_n$ for $n = 1-6$ increases (2.376, 2.523, 2.734, 2.838, 2.898 and 3.017 Å). As $r_{\text{Na}\cdots OH}/r_{K\cdots OH}$ increases, there is a noticeable decrease in $\omega_{\text{Na}\cdots OH}/\omega_{K\cdots OH}$ stretching frequencies. These (unscaled) frequencies for the lowest energy structures of $\text{NaOH}(\text{H}_2\text{O})_{n=1-6}$ are predicted to be 483, 416, 73, none, 142 and none cm^{-1} at the MP2/aVDZ+ level, and those of $\text{KOH}(\text{H}_2\text{O})_{n=1-6}$ are predicted as 418, 380, 105, 110, 81 and none cm^{-1} , which are well correlated with $r_{\text{Na}\cdots OH}$ and $r_{K\cdots OH}$, respectively (Table 5). However, a few of these modes with $\omega_{M\cdots OH} < 100 \text{ cm}^{-1}$ are coupled with $\text{HO}\cdots\text{Ow}$ modes (where w denotes a water molecule). Thus, in the

case of $\text{KOH}(\text{H}_2\text{O})_n$, the cases $n = 1-4$ are undissociated, the case $n = 5$ is partially dissociated, and the case $n = 6$ is dissociated. These low frequencies are unscaled because unscaled low frequencies are often more realistically close to the experimental values without overestimation, in contrast to the OH/NH frequencies that reflect highly anharmonic potential surfaces due to their high frequencies and so require the frequency scaling (scale factor of 0.96). Therefore, often an exponentially scaled approach (with less reduction for low frequencies)³⁹ is used instead of constant scaling for all the frequencies. The $r_{\text{Na}\cdots OH}$ of the partially dissociated and dissociated structures for $n = 3-6$ are 2.674 (3P33), 2.835 (4D43), 2.856 (5D43) and 4.031 Å (6D33), and the $r_{K\cdots OH}$ for $n = 5-6$ are 3.002 (5D43') and 3.017 Å (6D43), respectively. As these $r_{\text{Na}\cdots OH}$ and $r_{K\cdots OH}$ distances are very large compared with the unhydrated $\text{Na/K}\cdots\text{OH}$ distances of 1.99 and 2.26 Å, the $\text{Na/K}\cdots\text{OH}$ stretching modes upon dissociation practically do not appear (except for the highly coupled modes with other water molecules). As seen in Table 5, the coordination number of Na^+/K^+ (regardless of the dissociated and undissociated states) tends to be 3 or 4, and OH^- is also coordinated to 3 or 4 hydrogen atoms of water molecules via hydrogen bonds.

Combined with our previous work, we note that LiOH , NaOH , KOH , RbOH and CsOH can be dissociated as local minimum energy structures by 3, 4, 5, 4 and 3 water molecules

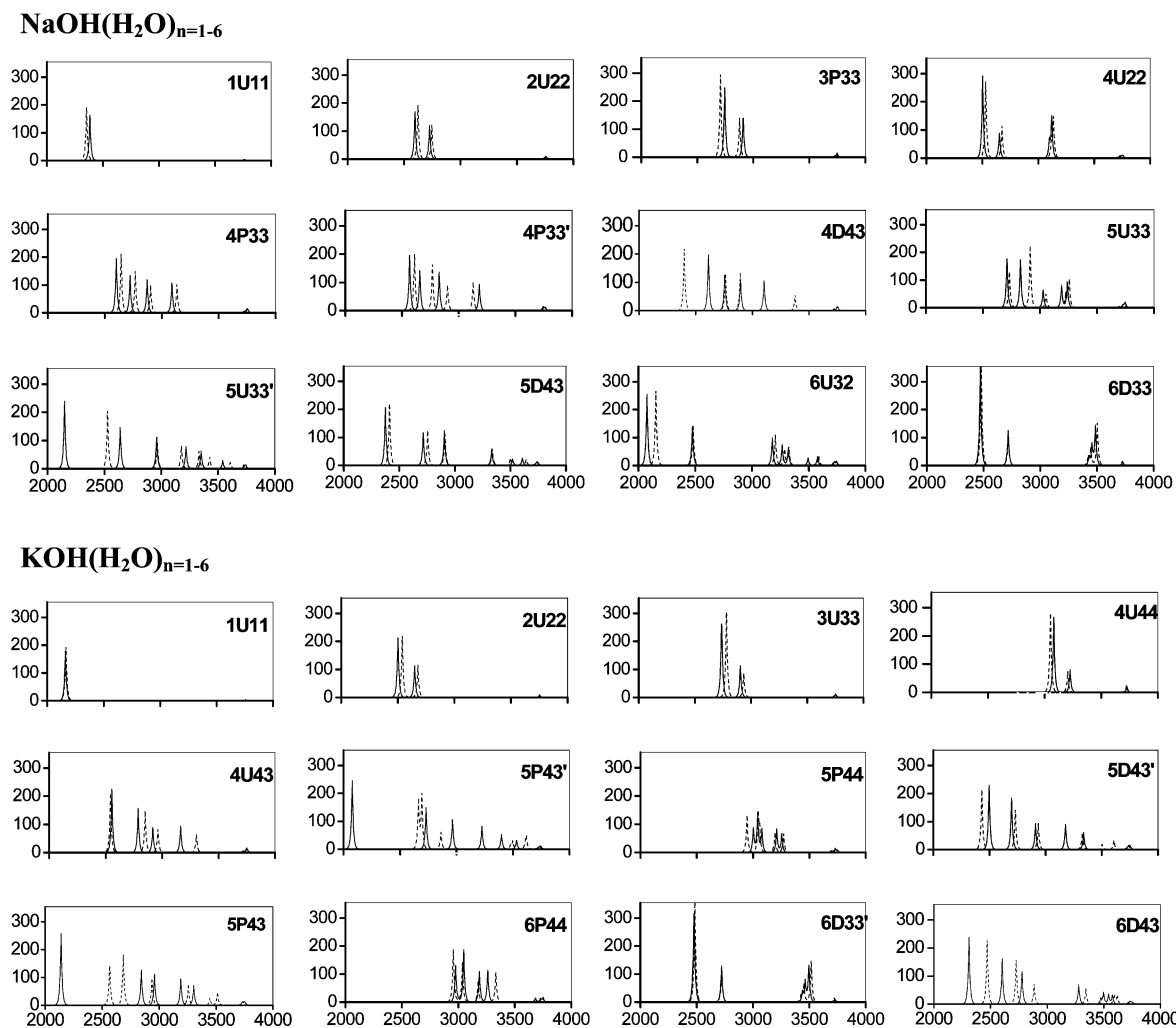


Figure 4. B3LYP/6-311++G** (solid line) and MP2/aVDZ+ (dotted line) IR spectra (intensity in 10 km/mol) for the O–H vibrational frequencies (cm^{-1}) of the lowest undissociated, partially dissociated and dissociated $\text{NaOH}(\text{H}_2\text{O})_{n=1-6}$ and $\text{KOH}(\text{H}_2\text{O})_{n=1-6}$ clusters.

and the global minimum energy structures by 7, 6, 6, 5 and 4 water molecules, respectively. As the OH stretching frequencies are widely used to identify diverse cluster structures,⁴⁰ we report scaled MP2/aVDZ+ (and B3LYP/6-311++G**) vibrational frequencies (ω_s) with the scaling factor of 0.96 for the O...H stretching modes (including OH^-) of the lowest energy dissociated, partially dissociated and undissociated structures (including isoenergetic conformers) in Figure 4 and Table 6. This information would be very useful for future IR experiments to identify the dissociated/partially dissociated/undissociated structures of $\text{Na/KOH}(\text{H}_2\text{O})_{n=1-6}$ with the IR signatures. The scaling factor 0.96 at both B3LYP and MP2 levels of theory was chosen from the comparison of the experimental and calculated average values of asymmetric and symmetric OH stretching frequencies of the water monomer. The OH stretching frequencies of $\text{HO}^-\cdots\text{H}-\text{OH}$ are in general lower than those of $\text{Ow}\cdots\text{H}-\text{OH}$.

Table 7 lists the electronic properties of $\text{Na/KOH}(\text{H}_2\text{O})_{n=1-6}$: ionization potential (IP), dipole moment (μ), polarizability (α), CT energy (δE_{CT}) and HOMO–LUMO energy gap (δE_{gap}). The electron pairs are stabilized by hydration, so IP increases with an increase in the number of water molecules. Polarizability increases with the increase in the cluster size. As the water molecules are polarized toward the metal cation and OH^- , the dipole moment (μ) of MOH decreases with the increasing number of water molecules. The CT energies are related to the

charge-transfer from M^+ or water molecules (in large clusters) to OH^- , and so they are related to δE_{gap} . $\delta E_{\text{CT}}^{\text{RPA}}$ would be slightly underestimated at the RPA-B3LYP level with respect to the experimental values, and $\delta E_{\text{CT}}^{\text{CI(S)}}$ could be overestimated at the [CI(S)] level due to the high-energy HF virtual orbital energies, as noted in the halide ions.⁴¹

To show the charge transfer in the $\text{NaOH}(\text{H}_2\text{O})_{n=1-6}$ and $\text{KOH}(\text{H}_2\text{O})_{n=1-6}$ clusters, we calculated NBO charges at the MP2/aug-cc-pVDZ+(2s2p/2s) level for the lowest energy conformers, listed in Table 8. Analysis of the NBO charge in the CTTS complex shows a partial electron charge transfer from OH^- to water molecules.

4. Conclusion

We have studied the hydration and dissociation phenomena of sodium and potassium hydroxides using B3LYP/6-311++G**, MP2/aVDZ+ and CCSD(T)/aVDZ+. As we go above the first column in the periodic table, more water molecules are required for complete dissociation. We find that the dissociated structures are tri- and tetraordinated for all alkali-metal hydroxides. The hexahydrated NaOH and KOH are dissociated as the global minimum energy structures, and the tetrahydrated NaOH and pentahydrated KOH are dissociated as a local minimum energy structures. Combined with our previous work, LiOH, NaOH, KOH, RbOH and CsOH are dissociated as local minimum energy structures by 3, 4, 5, 4 and 3 water molecules,

TABLE 6: MP2/aug-cc-pVDZ+(2s2p/2s) O···H Stretch Scaled Harmonic Frequencies (cm⁻¹) and Intensities (in 10 km/mol in Subscripts) of NaOH(H₂O)₀₋₆ and KOH(H₂O)₀₋₆ (Scale Factor: 0.96)

NaOH(H ₂ O) ₀₋₆	
NaOH: 3788 ₁	
1U11: 2353 ₁₉₇ , 3750 ₄ , 3772 ₁	
2U22: 2623 ₁₉₇ , 2746 ₁₂₄ , 3745 ₅ , 3747 ₁ , 3765 ₅	
3P33: 2707 ₁₅₁ , 2707 ₁₅₁ , 2877 ₁₄₁ , 3722 ₁ , 3741 ₇ , 3741 ₇ , 3742 ₀	
4U22: 2530 ₂₇₉ , 2675 ₁₁₇ , 3118 ₅₆ , 3135 ₁₄₅ , 3720 ₁ , 3721 ₅ , 3725 ₅ , 3746 ₆ , 3758 ₆	
4P33: 2643 ₂₁₇ , 2767 ₁₅₄ , 2902 ₁₀₀ , 3133 ₁₀₂ , 3708 ₁ , 3718 ₅ , 3745 ₅ , 3746 ₅ , 3751 ₇	
4P33': 2610 ₂₀₉ , 2769 ₁₇₁ , 2901 ₉₅ , 3127 ₁₀₅ , 3705 ₁ , 3722 ₅ , 3744 ₅ , 3748 ₅ , 3748 ₇	
4D43: 2399 ₂₂₁ , 2763 ₁₃₄ , 2894 ₁₃₉ , 3378 ₅₆ , 3720 ₁ , 3721 ₅ , 3741 ₅ , 3745 ₄ , 3751 ₈	
5U33: 2732 ₁₃₅ , 2915 ₂₂₇ , 3053 ₅₀ , 3226 ₅₇ , 3257 ₁₀₂ , 3695 ₁ , 3703 ₆ , 3725 ₅ , 3737 ₇ , 3740 ₅ , 3747 ₆	
5U33': 2528 ₂₀₈ , 2967 ₉₂ , 3178 ₈₅ , 3334 ₆₅ , 3427 ₄₃ , 3607 ₂₃ , 3696 ₁ , 3712 ₆ , 3726 ₄ , 3727 ₈ , 3750 ₇	
5D43: 2411 ₂₂₉ , 2755 ₁₂₆ , 2911 ₁₁₇ , 3337 ₆₀ , 3501 ₂₆ , 3642 ₂₃ , 3700 ₁ , 3727 ₆ , 3731 ₄ , 3738 ₅ , 3743 ₆	
6U32: 2154 ₂₇₈ , 2482 ₁₄₆ , 3206 ₁₁₃ , 3288 ₆₀ , 3325 ₆₈ , 3494 ₂₅ , 3588 ₃₅ , 3713 ₁ , 3721 ₅ , 3723 ₇ , 3728 ₅ , 3745 ₆ , 3749 ₆	
6D33: 2478 ₁₈₇ , 2478 ₁₈₇ , 2717 ₁₁₂ , 3422 ₁₆ , 3422 ₁₆ , 3444 ₆₆ , 3466 ₀ , 3503 ₇₇ , 3503 ₇₇ , 3692 ₁ , 3723 ₇ , 3723 ₇ , 3724 ₁	
KOH(H ₂ O) ₀₋₆	
KOH: 3742 ₀	
1U11: 2166 ₂₀₀ , 3742 ₀ , 3756 ₄	
2U22: 2540 ₂₂₆ , 2678 ₁₁₇ , 3734 ₁ , 3752 ₅ , 3752 ₄	
3U33: 2780 ₁₆₃ , 2782 ₁₆₂ , 2934 ₉₁ , 3713 ₁ , 3749 ₈ , 3749 ₇ , 3750 ₂	
4U44: 3049 ₂ , 3051 ₁₄₇ , 3052 ₁₄₈ , 3204 ₇₄ , 3698 ₁ , 3723 ₁₂ , 3723 ₁₁ , 3724 ₀ , 3725 ₁	
4U43: 2543 ₂₁₅ , 2850 ₁₅₃ , 2963 ₈₆ , 3304 ₆₄ , 3706 ₁ , 3718 ₅ , 3746 ₆ , 3751 ₈ , 3753 ₆	
5P43: 2663 ₁₇₅ , 2693 ₁₉₄ , 2863 ₆₅ , 3481 ₁₈ , 3499 ₂₈ , 3610 ₁₆ , 3618 ₄₂ , 3689 ₁ , 3723 ₆ , 3735 ₇ , 3736 ₄	
5P44: 2946 ₁₃₃ , 3046 ₁₃₂ , 3058 ₆₈ , 3194 ₇₂ , 3271 ₆₈ , 3690 ₄ , 3691 ₄ , 3724 ₇ , 3725 ₆ , 3732 ₅ , 3751 ₈	
5D43': 2432 ₂₂₅ , 2730 ₁₄₆ , 2935 ₉₆ , 3326 ₆₁ , 3503 ₁₉ , 3608 ₃₃ , 3687 ₁ , 3722 ₅ , 3732 ₅ , 3737 ₇ , 3744 ₆	
5P43: 2566 ₁₄₉ , 2686 ₁₉₀ , 2937 ₁₀₀ , 3257 ₇₇ , 3447 ₂₆ , 3513 ₄₇ , 3706 ₁ , 3734 ₁₀ , 3734 ₁ , 3752 ₈ , 3753 ₆	
6P33: 2625 ₂₁₆ , 2630 ₂₁₆ , 2834 ₈₇ , 3356 ₃₉ , 3358 ₄₁ , 3360 ₈₃ , 3693 ₁ , 3726 ₇ , 3727 ₈ , 3728 ₁ , 3753 ₉ , 3753 ₉ , 3754 ₉	
6P44: 2955 ₁₉₆ , 2990 ₄ , 3036 ₁₄₃ , 3176 ₇₉ , 3331 ₂₀ , 3332 ₉₂ , 3682 ₁₃ , 3683 ₁ , 3686 ₁ , 3728 ₁₂ , 3729 ₀ , 3751 ₉ , 3751 ₉	
6D33': 2484 ₁₈₇ , 2485 ₁₈₇ , 2723 ₁₁₁ , 3427 ₁₅ , 3428 ₁₅ , 3451 ₆₈ , 3480 ₀ , 3516 ₇₅ , 3516 ₇₅ , 3691 ₁ , 3721 ₇ , 3721 ₇ , 3722 ₁	
6D43: 2471 ₂₃₃ , 2726 ₁₆₂ , 2885 ₇₃ , 3341 ₅₇ , 3486 ₁₅ , 3502 ₃₁ , 3591 ₃₄ , 3619 ₃₁ , 3677 ₁ , 3721 ₅ , 3723 ₆ , 3736 ₅ , 3752 ₉	

TABLE 7: Electronic Properties of NaOH(H₂O)₀₋₆ and KOH(H₂O)₀₋₆^a

<i>n</i>	conformer	IP _V	IP _K	α	μ	δE ^{RPA} _{CT} (<i>f</i>)	δE ^{CI(S)} _{CT} (<i>f</i>)	δE _{gap}
0	NaOH	8.05	9.03	3.86	7.18			8.80 (3.34)
1	1U11	8.96	10.07	5.46	5.16	3.71 (0.01)	6.18 (0.03)	10.12 (4.56)
2	2U22	9.63	10.68	7.08	3.37	4.82 (0.02)	7.13 (0.05)	11.06 (5.45)
3	3U22	10.12	10.92	8.92	2.89	5.13 (0.02)	7.43 (0.06)	11.48 (5.94)
4	3P33	9.93	11.14	8.82	2.40	5.41 (0.03)	7.66 (0.05)	11.62 (6.17)
	4U22	10.01	11.23	10.71	1.95	4.81 (0.00)	7.75 (0.05)	11.95 (5.90)
	4P33	10.06	11.03	10.66	2.94	5.35 (0.03)	7.43 (0.05)	11.67 (6.29)
	4P33'	10.05	11.31	10.67	2.44	5.57 (0.03)	7.78 (0.06)	11.96 (6.15)
5	4D43	9.97	11.23	10.56	1.96	5.54 (0.03)	7.75 (0.05)	11.95 (6.26)
	5U33	10.20	11.47	12.38	1.44	5.72 (0.04)	7.89 (0.06)	12.22 (6.48)
	5U33'	10.26	11.53	12.35	3.06	5.57 (0.02)	7.80 (0.04)	12.22 (6.31)
	5D43	10.11	11.44	12.41	2.76	5.60 (0.02)	7.73 (0.04)	12.10 (6.26)
6	6U32	10.12	11.32	14.09	0.89	5.67 (0.02)	7.79 (0.06)	12.13 (6.42)
	6D33	10.18	11.53	14.40	0.60	5.72 (0.03)	7.80 (0.04)	12.09 (6.51)
0	KOH	7.65	8.67	4.24	8.06			8.50 (3.28)
1	1U11	8.56	9.75	6.23	5.84	3.69 (0.00)	6.38 (0.04)	9.67 (4.42)
2	2U22	9.43	10.45	8.05	3.92	4.65 (0.01)	7.12 (0.04)	10.44 (5.35)
3	3U33	9.69	10.98	9.84	2.37	5.31 (0.02)	7.55 (0.05)	10.98 (6.01)
4	4U44	10.07	11.44	11.60	2.52	5.68 (0.04)	7.88 (0.06)	11.44 (6.42)
	4U43	9.89	11.16	11.75	1.63	5.51 (0.03)	7.69 (0.05)	11.17 (6.24)
	5P44	10.16	11.53	13.53	2.08	5.95 (0.04)	7.97 (0.06)	11.54 (6.54)
	5P43'	10.21	11.56	13.58	4.00	5.52 (0.02)	7.74 (0.04)	11.56 (6.23)
5	5D43'	10.03	11.38	13.61	2.84	5.58 (0.02)	7.70 (0.04)	11.39 (6.36)
	5P43	10.03	11.33	13.65	1.94	5.57 (0.03)	7.73 (0.04)	11.34 (6.27)
	6P33	10.15	11.48	15.56	0.95	5.82 (0.01)	7.98 (0.05)	11.49 (6.57)
	6P44	10.26	11.65	15.41	1.58	6.06 (0.04)	8.07 (0.06)	11.66 (6.60)
6	6D33'	10.01	11.37	15.49	1.30	5.68 (0.02)	7.75 (0.04)	11.38 (6.37)
	6D43	10.25	11.62	15.50	4.43	5.67 (0.02)	7.76 (0.04)	11.62 (6.43)

^a IP_V and IP_K are vertical and Koopman's IPs (in eV), and μ is the dipole moment (in Debye) at the MP2/aug-cc-pVDZ+(2s2p/2s) level. δE^{RPA}_{CT} (*f*) and δE^{CI(S)}_{CT} (*f*) are CT energies (in eV) with the oscillator strength in parentheses (*f* in au) at the RPA-B3LYP and CI(S) levels. δE_{gap} is the HOMO-LUMO energy gap (eV) at the MP2 level, and the values in parentheses are at the B3LYP level. α is the polarizability (au) at the B3LYP level.

respectively, and the global minimum energy structures by 7, 6, 6, 5 and 4 water molecules, respectively. We hope that this information would facilitate future experiments for the dissociation phenomenon of alkali-metal hydroxides.

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TABLE 8: NBO Charges of NaOH (H₂O)_{1–6} and KOH (H₂O)_{1–6} at MP2/aug-cc-pVDZ+(2s2p/2s)

n	conf	MP2/aVDZ+		n-H ₂ O
		Na	OH	
1	1U11	0.98	−0.87	−0.11
2	2U22	0.97	−0.81	−0.16
3	3P33	0.95	−0.74	−0.21
4	4D43	0.94	−0.72	−0.22
5	5U33	0.93	−0.76	−0.18
6	6D33	0.95	−0.70	−0.24

n	conf	MP2/aVDZ+		n-H ₂ O
		K	OH	
1	1U11	1.00	−0.86	−0.14
2	2U22	0.99	−0.80	−0.19
3	3U33	0.99	−0.75	−0.23
4	4U44	0.98	−0.75	−0.23
5	5P43	0.98	−0.73	−0.25
6	6D43	0.97	−0.72	−0.25

Supporting Information Available: The MP2/aug-ccpVDZ+diffuse(2s2p/2s) optimized structures and xyz coordinates of the lowest energy conformers of NaOH(H₂O)_{n=1–6} and KOH(H₂O)_{n=1–6} are provided. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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