



Theoretical study of the microscopic solvation of alkali and alkaline-earth monohydroxides in $(\text{H}_2\text{O})_m$ ($m \leq 3$) clusters



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ABSTRACT

A density functional *m*PW1PW91 study of the most stable conformers of $\text{MOH}(\text{H}_2\text{O})_{0-3}$ clusters ($M = \text{alkali or alkaline-earth atom}$) was performed, along with quantum chemistry CCSD(T,Full) calculations for $M = \text{Li and Be}$. The resulting binding energies for hydration, atom-charge and valence-electron distributions allow for a rationalization of the opposite trends in the cluster-size dependence of adiabatic/vertical ionization energies for the alkali and the alkaline-earth monohydroxides. The closed- and open-shell natures of the latter, respectively, determines their behavior during initial steps of their hydration processes, whereas the ionic/covalent character of their $M\text{—OH}$ bonds plays a minor role except for BeOH .

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1. Introduction

Theoretical study of the initial steps of the hydration process for alkaline-earth monohydroxides offers a unique opportunity to describe the interactions between open-shell species and water molecules in terms of electrostatic and inductive contributions [1,2]. Whereas electrostatic interactions are to be expected for all of these systems owing to the ionic character of the $M\text{—OH}$ bonds [3], inductive effects are predicted to contribute to some extent as a result of delocalization of the MOH unpaired electron distribution over the surrounding water molecules. This situation contrasts with that found for the closed-shell $\text{MOH}(\text{H}_2\text{O})_m$ ($M = \text{Li, Na, K, Rb, Cs}$) [4–8] and $\text{MOH}^+(\text{H}_2\text{O})_m$ ($M = \text{Mg, Ca}$) [9,10] ($m \leq 8$) systems, where electrostatic contributions appear to dominate the interactions of MOH/MOH^+ with water molecules. The latter is supported by the finding for hydrated alkali monohydroxides of fully dissociated conformations, as characterized by a tricoordination of the OH^- moieties with water molecules along with a hydration number for the series of isovalent M^+ moieties, which depends chiefly on their charge-to-radius ratio. In the case of $\text{NaOH}(\text{H}_2\text{O})_m$ clusters, spatial charge polarization of the hydrated, fully dissociated Na^+ and OH^- moieties was also shown to develop at $m = 5$.

In this Letter, we extend a previous study reporting ab initio calculations on the hydration of BaOH in $(\text{H}_2\text{O})_{1-3}$ clusters [2], to encompass the lighter MOH ($M \equiv \text{Be, Mg, Ca, Sr}$) species. Theoretical adiabatic and vertical ionization energies (IE's), binding energies for MOH hydration, and atom-charge and valence-electron distributions for the most stable isomers of such clusters were calculated at the *m*PW1PW91 density-functional theory level. Further calculations were performed on the related systems for alkali monohydroxides, and the results were compared with available data as well as with those for the alkaline-earth monohydroxides to allow for an assessment of the nature and energetics of the corresponding hydration structures, and the role of the MOH valence electrons in their hydration process.

2. Theoretical methods

Following Cabanillas-Vidosa et al. [2,11], the optimum structures and harmonic vibrational frequencies for the most stable isomers of the various $\text{MOH}^x(\text{H}_2\text{O})_m$ clusters ($M = \text{Li, Na, K, Rb, Cs, Be, Mg, Ca, Sr, Ba}$; $x = 0$ for neutrals, $x = +1$ for cations; $m = 0-3$) were computed by the *m*PW1PW91 method of the density functional theory (DFT) [12] using the GAUSSIAN 09 suite of programs [13]. The 6-311++G(d,p) basis sets were used to describe the O and the H atoms in all of the cases except $\text{LiOH}^x(\text{H}_2\text{O})_m$ clusters, for which the AUG-cc-pVTZ basis sets were preferred. For the Be and Li atoms, 6-311++G(d,p) and AUG-cc-pVTZ were also the basis

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sets of preference, respectively, whereas the SDD quasirelativistic effective core potentials (ECP) and their accompanying valence basis sets, as defined in the GAUSSIAN 09 package, were employed to describe the remaining metal atoms. The structures of *mPW1PW91* optimizations were further used to carry out single-point energy calculations at the high correlated coupled cluster singles and doubles excitations approach, including a perturbational estimate of the triples [CCSD(T,Full)] [14,15] in the cases of $M = \text{Li}$ and Be .

Vertical ionization energies (IE_v 's) were computed as the difference in total electronic energies, including zero-point vibrational energy (ZPE) corrections, between the cationic and the neutral clusters, both computed at the optimized structures of the neutral species. Adiabatic ionization energies (IE_a 's) were instead referenced to the optimized geometries of both the cationic and the neutral clusters.

To assess the stability of the alkali/alkaline-earth monohydroxide-water clusters, total binding energies for the hydration processes: $\text{MOH}^x + m \text{H}_2\text{O} \rightarrow \text{MOH}^x(\text{H}_2\text{O})_m$, were estimated as:

$$\Delta E = E[\text{MOH}^x(\text{H}_2\text{O})_m] - E[\text{MOH}^x] - mE[\text{H}_2\text{O}]$$

where $E[\text{MOH}^x(\text{H}_2\text{O})_m]$, $E[\text{MOH}^x]$, and $E[\text{H}_2\text{O}]$ denote the total electronic energies, including ZPE corrections of the relevant species.

3. Results and discussion

Figure 1 shows the molecular structures and the binding energies of the lowest-lying energy conformers of the various hydrated alkaline-earth monohydroxides in the neutral state. Here the notations “*mUwy*”, “*mPwy*”, and “*mDwy*” have been used to describe the relevant conformers of the $\text{MOH}^x(\text{H}_2\text{O})_{1-3}$ clusters, where m is the total number of water molecules, *U/P/D* indicates the undissociated/partially dissociated/dissociated state of $M\text{—OH}$, respectively, and w and y are the hydration numbers of the M and OH moieties [2,4–7]. In the case of $\text{BeOH}(\text{H}_2\text{O})_m$ clusters, the preference for 6-311++G(d,p) over the SDD ECP/valence basis set combination to treat the Be atom relies on the finding for the bare BeOH radical of different equilibrium geometries, i.e., bent (bond angle of 144.1°) and linear, respectively, the former being characterized by a ZPE of 350 meV, which is higher than the barrier to linearity (11 meV) (see Supporting Information). This is consistent with earlier predictions of quasilinearity for ground-state BeOH, as arising from high-level electronic structure calculations [16–18] and recently confirmed by a joint experimental and theoretical study on the spectroscopy of the BeOH $2^2A' - 1^2A'$ electronic transition [19]. It should be mentioned that the use of the SDD ECP on Be leads to most stable $\text{BeOH}(\text{H}_2\text{O})_{1-3}$ conformers, which do not differ from those of Figure 1. For the Mg-containing species, though, the use of the 6-311++G(d,p) basis set on the Mg atom results in no significant differences with the most stable $\text{MgOH}(\text{H}_2\text{O})_{0-3}$ conformers that are shown in Figure 1, which determined the preference for the SDD ECP/valence basis set combinations to treat the metal atoms heavier than Be.

The binding energies for the most stable conformers of $\text{BeOH}(\text{H}_2\text{O})_{1-3}$ were computed at both the *mPW1PW91* and the CCSD(T,Full) levels, and the results are listed in Table 1 along with the corresponding values for IE_a/IE_v (the ΔE 's values for $\text{BeOH}^+(\text{H}_2\text{O})_{1-3}$ are included in Table 1; see also Table S1 of the Supporting Information for a list of the ZPE-corrected total energies of the relevant species). An inspection suggests that both levels of theory reproduce satisfactorily the relevant energetics, especially the systematic increase of ΔE and the decrease of the IE_a and IE_v values with increasing size of the cluster. As noted below, such considerations can be extended to the overall energetics of the $\text{LiOH}(\text{H}_2\text{O})_{0-3}$

Table 1

Binding energies ΔE (in kcal mol⁻¹) for the lowest-lying energy conformers of $\text{BeOH}^x(\text{H}_2\text{O})_m$ ($x=0$ for neutrals, $x=+1$ for cations; $m=1-3$) clusters, and IE_a/IE_v values (in eV) in the case of $x=0/m=0-3$, as computed at the *mPW1PW91* and the CCSD(T,Full) levels.

Species	Theory	ΔE	IE_a	IE_v
BeOH	<i>mPW1PW91</i>	n/a	8.36	8.53
	CCSD(T,Full)	n/a	8.20	8.34
$\text{BeOH}(\text{H}_2\text{O})_1$	<i>mPW1PW91</i>	-14.2	5.58	6.51
	CCSD(T,Full)	-14.8	5.38	6.30
$\text{BeOH}(\text{H}_2\text{O})_2$	<i>mPW1PW91</i>	-32.3	4.56	4.97
	CCSD(T,Full)	-33.2	4.31	4.67
$\text{BeOH}(\text{H}_2\text{O})_3$	<i>mPW1PW91</i>	-44.8	4.05	4.66
	CCSD(T,Full)	-49.5	3.82	4.38
$\text{BeOH}^+(\text{H}_2\text{O})_1$	<i>mPW1PW91</i>	-78.3	-	-
	CCSD(T,Full)	-79.7	-	-
$\text{BeOH}^+(\text{H}_2\text{O})_2$	<i>mPW1PW91</i>	-119.8	-	-
	CCSD(T,Full)	-122.7	-	-
$\text{BeOH}^+(\text{H}_2\text{O})_3$	<i>mPW1PW91</i>	-144.3	-	-
	CCSD(T,Full)	-150.5	-	-

clusters and, altogether, the results account for the choice of the *mPW1PW91* method to treat all of the relevant systems.

It is apparent from Figure 1 that the behaviors of the magnesium, calcium, and strontium monohydroxides, with respect to the initial steps of the hydration process are similar to that of the barium monohydroxide [2]: The solvation by up to three water molecules leads to most stable hydration structures, which are characterized by a concurrent, increasing coordination of both the M and the OH moieties of the MOH cores by the water molecules. This is accompanied by increases in the number of H-bonding interactions within such $\text{MOH}(\text{H}_2\text{O})_m$ clusters upon sequential addition of water molecules. Such similarities might be explained considering that bonding in the relevant, bare MOH radicals is predominantly of $M^+\text{—OH}^-$ character, as revealed by the atom-charge distributions that derive from natural population analysis (Figure 1), which in turn determines that electrostatic interactions play a significant role in binding the solvent molecules to both M^+ and OH^- moieties. Inductive effects also contribute to bind these open-shell clusters, as revealed by the general finding that the corresponding unpaired electron density distributions do not effectively delocalize over such small water clusters [see Figure S1 of the Supporting Information for the results of additional calculations on the electron density distributions of the singly occupied molecular orbitals (SOMO's) for the $\text{MOH}(\text{H}_2\text{O})_{0-3}$ clusters ($M = \text{Mg}, \text{Ca}, \text{Sr}, \text{and Ba}$)]. Instead, these distributions remain chiefly polarized away from the electron clouds on the oxygen atoms of both the water molecules and the OH^- moieties, which reinforces conclusions made in the case of hydrated barium monohydroxides [2] that the OH^- ions exert a major influence on the M^+ counterions.

The nature of the most stable hydration structures for $\text{BeOH}(\text{H}_2\text{O})_m$ clusters differs from that of the remaining alkaline-earth monohydroxides. In the former, only the Be moieties of the BeOH cores are increasingly hydrated upon sequential addition of water molecules (Figure 1), which is arguably dictated by the sizable covalent character of the Be—OH bond in bare BeOH [16–18]. The latter is revealed here by an effective charge on Be of +0.7 (Figure 1), which decreases to +0.6 upon complexation with the first water molecule. At this stage, the lack of a strong polarization in both Be and OH moieties as $\text{Be}^+(\text{OH})^-$, conceivably prevents their concurrent hydration, which appears supported by the absence of H-bonding interactions within the $\text{BeOH}(\text{H}_2\text{O})_1$ cluster. Instead, the addition of the second and third water molecules increases the charges on Be to +(1.0–1.1), as the unpaired electrons of the $\text{BeOH}(\text{H}_2\text{O})_{2,3}$ clusters significantly delocalize over the surrounding solvent molecules (Figure 2), which locate preferentially on the opposite side of the Be atom from the OH moiety. Despite the Be charge changes >40% in going from bare to tri-hydrated BeOH, the

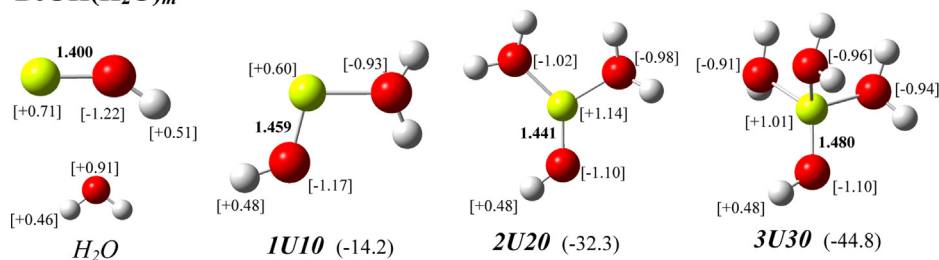
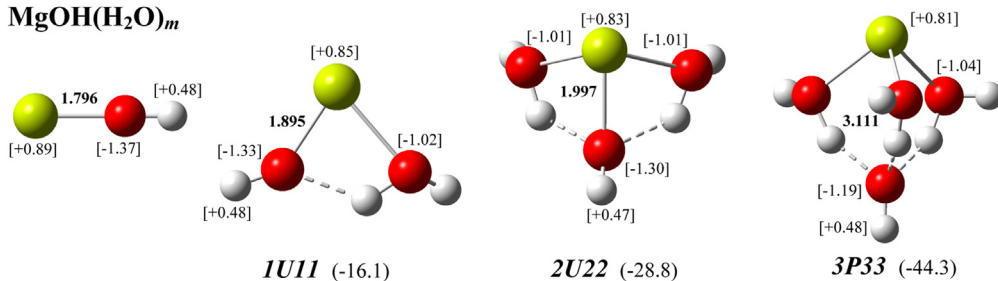
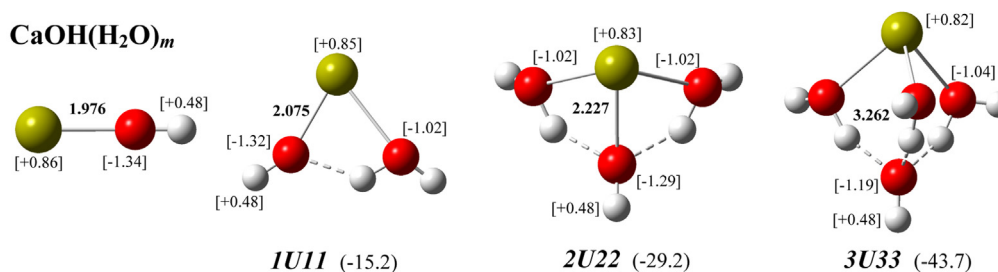
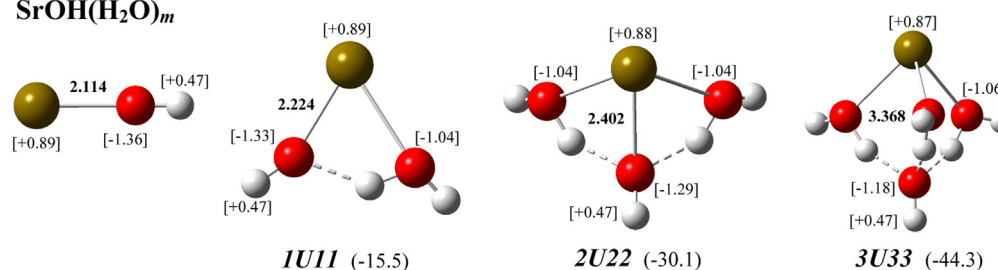
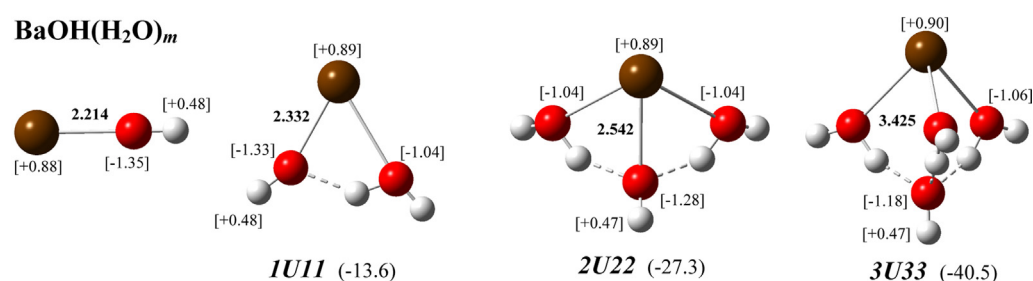
BeOH(H₂O)_m**MgOH(H₂O)_m****CaOH(H₂O)_m****SrOH(H₂O)_m****BaOH(H₂O)_m**

Figure 1. Optimized structures for the lowest-lying energy conformers of neutral MOH(H₂O)_m (M⁺ = Be, Mg, Ca, Sr, Ba; m = 0–3) clusters, as calculated at the mPW1PW91 level. Derived binding energies (in kcal mol⁻¹) are given under each structure. The M–OH bond lengths (in angstroms) and the atom-charge distributions, resulting from natural population analysis are indicated in boldface and in brackets, respectively.

corresponding, relatively small changes in effective charge for the OH moiety, in Be–OH bond distance, and in Be–O–H bond angle (of 15%, 6%, and 14%, respectively) show up that these most stable BeOH(H₂O)_{1–3} conformations are effectively undissociated. Alike the BeOH(H₂O)₁ cluster, H-bonding interactions are not developed

within BeOH(H₂O)_{2,3} probably because of the involvement of the oxygen and hydrogen atoms of the water molecules in the coordination of the Be moieties and delocalization of the unpaired electron, respectively. Such findings indicate that the hydration process in BeOH(H₂O)_{1–3} clusters is dominated by inductive

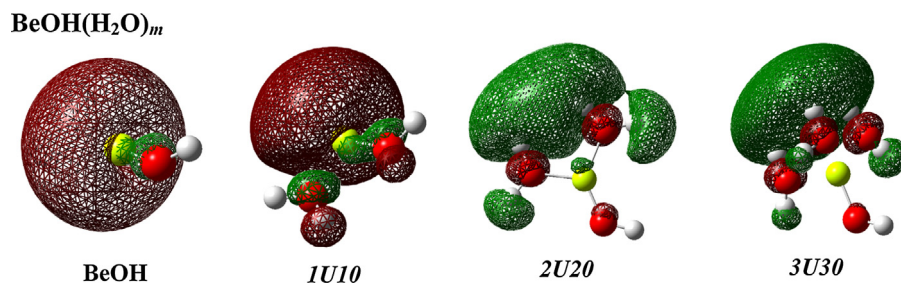


Figure 2. Electronic density distribution of the SOMO's in the lowest-lying energy conformers of neutral $\text{BeOH}(\text{H}_2\text{O})_{0-3}$ clusters. The iso-density surfaces correspond to 0.03 \AA^{-3} .

interactions between the (undissociated) BeOH cores and the solvating water molecules.

Despite the distinct hydration behavior in small water clusters for BeOH, as compared to the remaining alkaline-earth monohydroxides, it is found in all cases that the theoretical IE's for the $\text{MOH}(\text{H}_2\text{O})_m$ clusters generally decrease with m (see Figure 3 and Table S2 of the Supporting Information). The latter is consistent with the findings of a previous photoionization study on $\text{BaOH}(\text{H}_2\text{O})_{1-3}$ clusters [2], and supports the rationalization that the ionization process in the relevant $\text{MOH}(\text{H}_2\text{O})_m$ systems corresponds essentially to removal of their unpaired electrons located primarily on the M moieties of the MOH cores. This is expected to be true for alkaline-earth monohydroxides heavier than BeOH owing to the ionic character of their M–OH bonds. To a lesser extent, the latter seems still valid in the case of neutral $\text{BeOH}(\text{H}_2\text{O})_{0,1}$ clusters:

Be charges of 0.71 and 0.60 electrons are found for $m=0$ and 1, respectively, as compared to 1.64 and 1.39 for the corresponding ionic species (cf. Figure 1 and Figure S2 of the Supporting Information), which shows that most of the electron is lost from the electron density distribution on Be, along with a minor contribution from the OH group as well as from the water molecule. The situation is different for $\text{BeOH}(\text{H}_2\text{O})_{2,3}$ (cf. the effective charges on the Be and the OH moieties of the both neutral and ionic clusters), as the unpaired electron density distribution is mostly delocalized in a large vacant space around the water molecules. Because of the role that the water molecules play in coordinating the Be moieties while solvating the unpaired electrons of the neutral clusters for $m=2$ and 3, the hydration of the latter is not expected to be as effective as for the corresponding ions, thereby leading to a decrease in the ionization energies of $\text{BeOH}(\text{H}_2\text{O})_{2,3}$ with increasing cluster size.

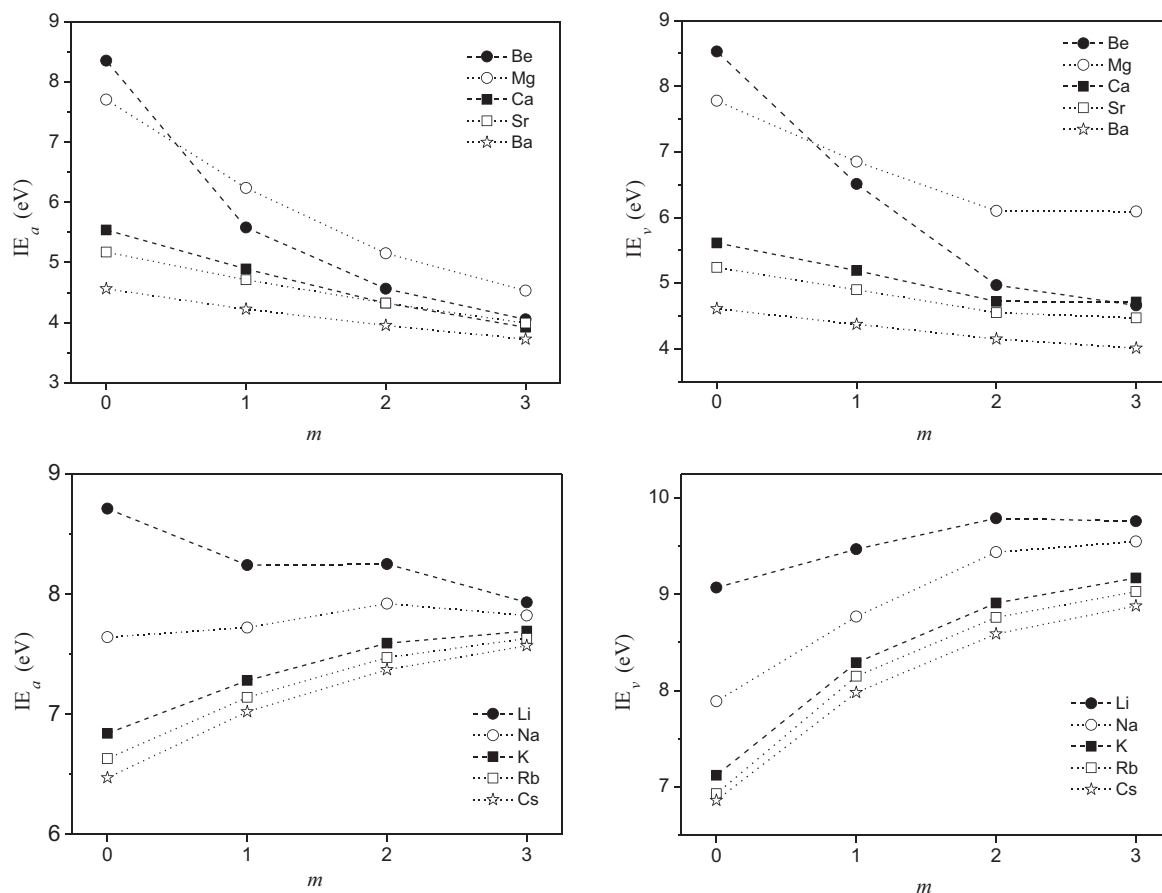


Figure 3. Theoretical IE's for the lowest-lying energy conformers of neutral $\text{MOH}(\text{H}_2\text{O})_m$ ($m=0-3$) clusters as a function of m , as computed at the $m\text{PW1PW91}$ level. The identity of the M atom for the various solvated alkali and alkaline-earth monohydroxides is indicated in the plots. Left column: adiabatic ionization energies (IE_a 's); right column: vertical ionization energies (IE_v 's).

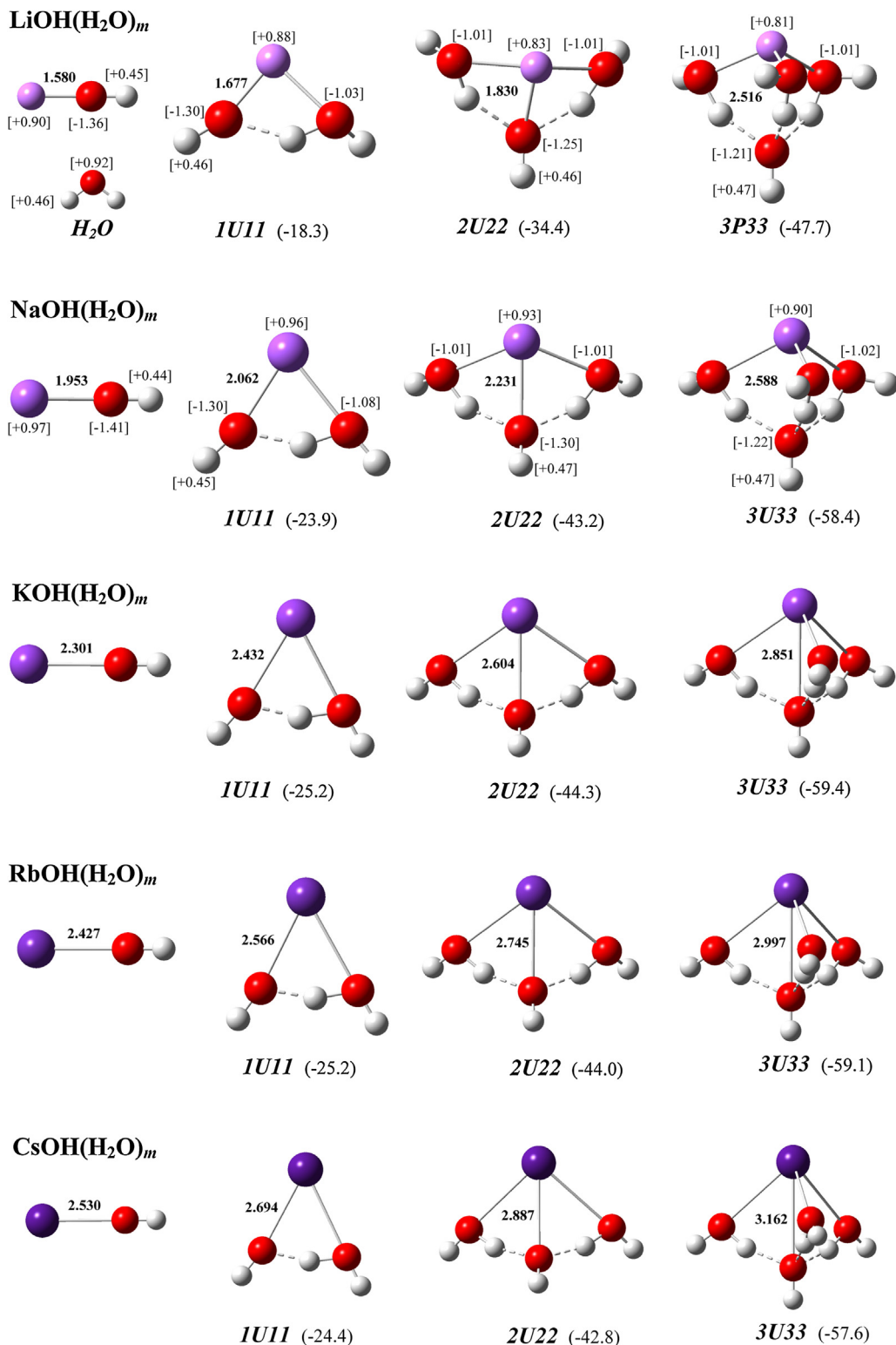


Figure 4. Optimized structures for the lowest-lying energy conformers of neutral MOH(H₂O)_m (M⁺Li, Na, K, Rb, Cs; m=0–3) clusters, as calculated at the *m*PW1PW91 level. Binding energies (in kcal mol⁻¹) calculated at the *m*PW1PW91 level are given under each structure. The M–OH bond lengths (in angstroms) and the atom-charge distributions, resulting from natural population analysis at the DFT level are indicated in boldface and in brackets, respectively.

Figure 4 shows the structures for the lowest-lying energy conformers of the various hydrated alkali monohydroxides in the neutral state, as obtained in the case of Li-containing species using the AUG-cc-pVTZ basis sets for all of the atoms, and in the case of Na-, K-, Rb-, and Cs-containing species using the 6-311++G(d,p) basis sets for the O and H atoms along with the SDD ECP's for metal

atoms. The use of distinct basis sets for LiOH(H₂O)_m clusters is based on the agreement between the present *m*PW1PW91/AUG-cc-pVTZ results and previous predictions of the geometry and quasilinearity for ground-state LiOH⁺, resulting from CCSD(T) calculations combined with large basis sets [20]. Here the bare, ground-state LiOH⁺ radical is found at the *m*PW1PW91/AUG-cc-pVTZ level to have a

bent equilibrium geometry (bond angle of 148.5°) with a ZPE of 276 meV, which is higher than the barrier to linearity, of 6 meV [the energy barrier is 5 meV at the CCSD(T,Full) level]. The use of either the SDD ECP/valence basis set or the 6-311++G(d,p) basis set on Li leads to the same types of most stable $\text{LiOH}(\text{H}_2\text{O})_{0-3}$ conformers as those of Figure 4, but instead results in equilibrium geometries for LiOH^+ that are linear and bent, respectively, the latter featuring a bond angle of 173.5° (see Supporting Information), which deviates from those in the range of $145\text{--}150^\circ$ resulting from the previous higher-level theoretical study [20].

The size dependence of the theoretical IE's for the $\text{MOH}(\text{H}_2\text{O})_{1-3}$ ($M = \text{Li, Na, K, Rb, Cs}$) clusters shows up that the energetics of the corresponding hydration processes are dominated by electrostatic interactions between MOH/MOH^+ species and water molecules. In agreement with the MP2 calculations by Kim and co-workers [4–7], it is found here at the *mpPW1PW91* level that the vertical IE's for the most stable cluster isomers increase with the number of water molecules (see Figure 3 and Table S2 of the Supporting Information). The results are consistent with a previous rationalization [2] that the ionization process in these closed-shell clusters corresponds to removal of one of the electrons located chiefly on the OH^- moieties of the MOH cores, i.e., $[\text{M}^+\text{OH}^-(\text{H}_2\text{O})_m] + \text{IE} \rightarrow [\text{M}^+\text{OH}(\text{H}_2\text{O})_m]^+ + e^-$. Because of charge–charge interactions between the M^+ and $\text{OH}^-(\text{H}_2\text{O})_m$ cores in the neutral clusters, which are absent in their ionic states, the latter are less stabilized than the former with increasing cluster size, thereby resulting in an increase in IE_v 's with m .

The above rationalization seems valid in the case of the corresponding adiabatic IE's, which are generally found here to increase with m , except for hydrated LiOH species (Figure 3). The atom-charge distributions on the lowest-lying $\text{MOH}^+(\text{H}_2\text{O})_m$ conformers of the two lightest alkali monohydroxides, LiOH and NaOH (cf. Figure 4 and Figure S3 of the Supporting Information), support the idea of electron removal from OH^- . Notwithstanding, the rationalization of the opposite IE_a vs. m behavior for hydrated LiOH likely requires the consideration of a different, more delicate balance between the electrostatic contributions to its hydration. The relatively high charge-to-radius ratio of the Li^+ cation, as compared to the remaining alkali ions, is expected to result in relatively strong charge–dipole interactions with the surrounding water molecules, and for neutral clusters, also in stronger charge–charge interactions between their Li^+ and OH^- moieties. The former effect apparently leads to a stronger stabilization of the ionic cluster states than that for the neutral states, which results in larger binding energies for hydration of LiOH^+ than that for LiOH (Table S3 of the Supporting Information), and in a decrease of the IE_a 's for $\text{LiOH}(\text{H}_2\text{O})_m$ with increasing cluster size. This is conceivable considering the structures of the $\text{LiOH}^+(\text{H}_2\text{O})_{1-3}$ clusters (Figure S3 of the Supporting Information), where the direct coordination of water molecules to Li^+ is expected to maximize the relevant charge–dipole interactions, as compared to the $\text{LiOH}(\text{H}_2\text{O})_{1-3}$ clusters (Figure 4) where concurrent coordination of their Li^+ and OH^- moieties by water molecules results in a reduced strength of charge–dipole interactions, as well as in inefficient charge–charge interactions.

4. Conclusions

The theoretical investigation by the DFT/*mpPW1PW91* method of the lowest-lying energy conformers for the smallest hydrated alkaline-earth monohydroxides consistently reveals that both electrostatic and inductive interactions between their MOH cores and the water molecules are major contributions to the initial steps of the corresponding hydration processes. Electrostatic interactions are important because of the significant $\text{M}^+(\text{OH}^-)$ ionic character of the relevant MOH radicals in all of the clusters except $\text{BeOH}(\text{H}_2\text{O})_{0-3}$, whereas inductive effects play a role in avoiding

for the corresponding unpaired electron density distributions to effectively delocalize over the entire clusters. The latter is particularly true for $\text{BeOH}(\text{H}_2\text{O})_{0-3}$ clusters, where the sizable covalent character of the Be–OH bond results in a polarization of solvent molecules on the opposite side of the Be atom from the OH^- moiety in order to delocalize the unpaired electron density distribution. The computed binding energies for MOH hydration, adiabatic and vertical IE's, and atom-charge and valence-electron distributions for the most stable $\text{MOH}(\text{H}_2\text{O})_{0-3}$ isomers ($M = \text{Be, Mg, Ca, Sr, Ba}$) are all compatible with this picture. Similar results have been obtained for the lowest-lying energy conformers of the $\text{MOH}^{0/+}(\text{H}_2\text{O})_{0-3}$ clusters ($M = \text{Li, Na, K, Rb, Cs}$), and the predictions reinforces suggestions made previously that electrostatic contributions dominate the interactions between the alkali monohydroxides and the surrounding water molecules within such small cluster sizes. Additional, more accurate computations at the post-Hartree-Fock/CCSD(T,Full) level of ΔE and IE_a/IE_v for $\text{MOH}(\text{H}_2\text{O})_{1-3}$ ($M = \text{Li, Be}$) clusters, are consistent with predictions made using the DFT/*mpPW1PW91* approach.

The present results show up the significant role that the unpaired electrons on the alkaline-earth monohydroxides play in the initial steps of their hydration processes, as compared to the case for closed-shell alkali monohydroxides, which ultimately account for the opposite trends that are generally found in the cluster size dependence of the theoretical IE_v/IE_a for both series of systems. The latter predictions will hopefully stimulate future experiments through the laser photoionization technique, to study the stepwise hydration behavior of all of the relevant species.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:10.1016/j.cplett.2014.12.008.

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