***Ab initio* study of the neutral and anionic alkali and alkaline earth hydroxides: Electronic structure and prospects for sympathetic cooling of OH[−]**

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We have performed a systematic *ab initio* study on alkali and alkaline earth hydroxide neutral (MOH) and anionic (MOH[−]) species where M = Li, Na, K, Rb, Cs or Be, Mg, Ca, Sr, Ba. The CCSD(T) method with extended basis sets and Dirac-Fock relativistic effective core potentials for the heavier atoms has been used to study their equilibrium geometries, interaction energies, electron affinities, electric dipole moment, and potential energy surfaces. All neutral and anionic species exhibit a linear shape with the exception of BeOH, BeOH[−], and MgOH[−], for which the equilibrium structure is found to be bent. Our analysis shows that the alkaline earth hydroxide anions are valence-bound whereas the alkali hydroxide anions are dipole bound. In the context of sympathetic cooling of OH[−] by collision with ultracold alkali and alkaline earth atoms, we investigate the 2D MOH[−] potential energy surfaces and the associative detachment reaction $M + OH^- \rightarrow MOH + e^-$, which is the only energetically allowed reactive channel in the cold regime. We discuss the implication for the sympathetic cooling of OH[−] and conclude that Li and K are the best candidates for an ultracold buffer gas. *Published by AIP Publishing.* [<http://dx.doi.org/10.1063/1.4983627>]

I. INTRODUCTION

Anions play an important role in many different fields of chemistry and physics, from the chemistry in Earth's atmosphere¹ to the study of highly correlated systems.^{2,3} In particular, the detection of molecular anions in various astrophysical environments (coma of comets,⁴ interstellar molecular clouds,⁵ and extraterrestrial atmospheres⁶), the recent prospects for laser cooling of atomic⁷ and molecular⁸ anions, and the possibility of using anions for sympathetic cooling of anti-protons⁹ are some of the exciting topics which have broadened interest in the structure and dynamics of molecular anions.

Anionic alkali and alkaline earth hydroxides (MOH[−]) are simple molecular anions, and their study can bring new insights into the molecular structure and bonding properties of anions. Neutral alkali and alkaline earth hydroxides (MOH) have been extensively studied both theoretically^{10–20} and experimentally^{21–35} (see also the reviews of Ellis³⁶ and Gurvich *et al.*³⁷). The interest lies in the general context of molecular structure and the understanding of the M–O bond. The alkali (Li, Na, K, Rb, and Cs) and heavy alkaline earth (Ca, Sr, and Ba) hydroxides are known to exhibit a linear equilibrium geometry while lighter alkaline earth hydroxides are either quasi-linear (MgOH)²² or bent (BeOH).¹⁵ The linear structure is usually explained by the stronger ionic character of the alkali and heavy alkaline earth hydroxides while the more covalent character of the BeOH and MgOH molecules favours a bent structure. Moreover, they all exhibit a low

energy bending degree of freedom, making the compounds floppy. On the other hand, no information exists on their anion counterparts, with the exception of RbOH[−] for which several theoretical studies have been performed in the context of cold chemistry.^{38–41}

One of the contexts in which the MOH[−] anions can play a role is sympathetic cooling of OH[−] by collision with ultracold alkali and alkaline earth atoms. Direct laser cooling methods are routinely used to reach the ultracold regime for neutral and cationic atoms (mostly alkali and alkaline earth) but have so far never been applied to anions although some atomic anions such as La[−] and Os[−] exhibit stable excited electronic states and represent potential candidates for laser cooling.^{7,42} The direct laser cooling of molecules is complicated by the lack of closed transition cycles and requires advanced cooling schemes. It has only been successfully applied to a few diatomic molecules such as SrF,⁴³ CaF,⁴⁴ and YO.⁴⁵ Other approaches such as Sisyphus cooling have been demonstrated for polyatomic molecules.^{46,47} Laser cooling strategies have been proposed for diatomic anions⁸ such as C₂[−] but not yet realized. Sympathetic cooling offers a simpler and more general way to reach the ultracold regime for molecules. The method relies on collisions between cold or ultracold atoms and the target species. Cryogenic helium is widely used as a buffer gas to cool down translational and internal degrees of freedom of various neutral and ionic molecules but the temperature is limited to a few kelvin. Another possibility is to use laser-cooled atoms as a buffer gas, in which case the experimental setup is usually a combination of a cooling scheme such as a magneto-optical trap (MOT) and an ion trap used to confine the target ion. The ability of the ultracold atom to cool the translational and internal degrees of freedom of the target ion will depend

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on the polarizability of the atom, the mass ratio and the shape of the potential energy surface (PES) that characterizes the collision. In addition, chemical reactions such as charge transfer or associative detachment may occur in such environments, leading to a loss of the ion if the kinetic energy release is larger than the trap depth or if the ion loses its electric charge. The hydroxide anion OH^- is one of the simplest and most studied molecular anions. Its behaviour in radio-frequency traps has been extensively studied^{48–50} and photodetachment tomography can be used as a thermometer for the temperature of internal degrees of freedom⁵⁰ which have been well characterized. The OH^- anion therefore seems to be an ideal candidate for the experimental realization of the sympathetic cooling of anions. The cooling of OH^- by ultracold Rb atoms has been studied experimentally,⁵¹ but it was shown that the process is hindered by the associative detachment reaction $\text{Rb} + \text{OH}^- \rightarrow \text{RbOH} + e^-$.

The first objective of the present paper is to investigate the structural properties of the MOH^- anions (where $M = \text{Li, Na, K, Rb, Cs}$ or $\text{Be, Mg, Ca, Sr, Ba}$). We compare these properties to those of the corresponding neutral hydroxides MOH and we also discuss the trends along the alkali and alkaline earth series. The second objective is to investigate the prospects for sympathetic cooling of OH^- on the basis of the 2D MOH^- potential energy surfaces and the $M + \text{OH}^- \rightarrow \text{MOH} + e^-$ associative detachment reaction.

The paper is structured as follows: in Sec. II we describe the computational methods, in Sec. III we investigate the molecular structure and properties of the alkali and alkaline earth anion and neutral hydroxides, and in Sec. IV we discuss the potential energy surfaces, the associative detachment reaction, and the implications for sympathetic cooling.

II. COMPUTATIONAL METHODS

All calculations were performed on the Hydra and Vega clusters of the ULB/VUB computing center using the MOLPRO 2012 package.⁵² The coordinates used to describe the molecular species MOH and MOH^- are represented on Figure 1, with the usual Jacobi coordinates: R_M the distance between M and the center of mass of OH , R_{OH} the distance between O and H , θ the angle between the $\mathbf{R}_M$ and $\mathbf{R}_{\text{OH}}$ vectors, and R_{MO} the distance between the M and O atoms. Accordingly, the geometry for $\theta = 0^\circ$ corresponds to the case where

FIG. 1. Coordinates defining the MOH anionic and neutral systems.

the M-O-H atoms are aligned whereas $\theta = 180^\circ$ corresponds to the O-H-M collinear configuration.

The coupled cluster level of theory with single, double, and perturbative triple excitations (CCSD(T)) as implemented in the MOLPRO program⁵³ was used for all calculations. The electronic structure of the alkali atoms is $[\text{core}](n-1)s^2(n-1)p^6ns^1$ with n corresponding to the highest principal quantum number, while for the alkaline earth atoms the ns orbital is doubly occupied (ns^2). Li and Be are exceptions as they do not have p electrons, their electronic structures are $1s^22s^1$ and $1s^22s^2$, respectively. In the following, we will refer to the $(n-1)s^2(n-1)p^6$ (or $1s^2$ for Li and Be) electrons as outer core electrons (oc) and the ns^1 or ns^2 electron(s) as valence electrons (val). For the lighter atoms, Li, Na, Be, and Mg, the augmented correlation-consistent polarized valence basis set aug-cc-pVnZ (shortened as AVnZ, with $n = \text{Q or 5}$)⁵⁴ was used for valence correlation whereas the aug-cc-pwCVnZ core-correlation consistent basis set (shortened AWCvNz) was used when including the outer core electrons into the correlation treatment. Explicitly treating the outer core electrons allows to account for the outer core-valence correlation. The ECPmMDF Dirac-Fock relativistic effective core potentials (ECPs) were used for the heavier atoms, allowing m core electrons to be implicitly treated: 10 electrons for K and Ca, 28 electrons for Rb and Sr, and 46 electrons for Cs and Ba.⁵⁵ These small core ECPs allow an explicit correlation treatment of the outer core and valence electrons. The corresponding basis sets published alongside the ECPs were used: segmented spdfg functions for Rb, Cs, Sr, and Ba atoms, spdf functions for K, and spd functions for Ca.⁵⁵ For all alkali and alkaline earth atoms, each type of functions has been supplemented by a single even tempered function for which the exponent is determined from the exponents of the last two functions of the previous basis set. AVnZ and AWCvNz basis sets were used for the H and O atoms, respectively. The $1s_{\text{O}}$ orbital was included in the correlation treatment.

III. MOLECULAR PROPERTIES

At linear geometry ($C_{\infty v}$ symmetry), the electronic ground state of the alkali hydroxide anion MOH^- is defined by the $X^2\Sigma^+$ term symbol whereas for the neutral MOH species it is a $X^1\Sigma^+$ state. At bent geometries (C_s symmetry), these states correlate to X^2A' and X^1A' , respectively. For the alkaline earth hydroxides, the ground state at linear geometry is $X^2\Sigma^+$ for the neutral and $X^1\Sigma^+$ for the anion, and X^2A' and X^1A' states at bent geometries, respectively. In C_s point group, the 4 highest molecular orbitals are $1a'^22a'^21a''^23a'$ with the HOMO orbital being unoccupied for neutral alkali hydroxides, singly occupied for neutral alkali earth hydroxides and anionic alkali hydroxides, or doubly occupied for anionic alkaline earth hydroxides. This $3a'$ orbital corresponds mainly to the ns atomic orbital of the M atom while the 3 other molecular orbitals are principally formed by the p atomic orbitals of O. We have performed geometry optimizations for all alkali and alkaline earth neutral and anionic species. The neutral alkali and alkaline earth hydroxides exhibit a linear structure with the exception of BeOH . For the anions, the equilibrium structure is also linear for $M = \text{Li, Na, K, Rb, Cs, Ca, Sr, and Ba}$. For

TABLE I. CCSD(T)/oc optimized R_{MO} and R_{OH} distances (in Å) for the neutral and anion MOH species. The AWCV5Z basis set has been used for O, Be, Li, and Mg, AWCVQZ for Na, and AV5Z basis set for H. See Section II for the basis used for the heavier alkali and alkaline earth atoms. Experimental values are given for the neutral case, when available. All species have a linear equilibrium structure except BeOH, BeOH⁻, and MgOH⁻ for which the calculated equilibrium angle θ is 37°, 66°, and 50°, respectively.

	Anion		Neutral			
	This work		This work		Expt.	
	R_{MO}	R_{OH}	R_{MO}	R_{OH}	R_{MO}	R_{OH}
LiOH	1.623	0.949	1.579	0.948	1.578	0.949 ⁵⁶
NaOH	2.007	0.953	1.938	0.951	1.95 ²⁷	0.941 ⁷²
KOH	2.274	0.955	2.202	0.954	2.196	0.960 ³⁴
RbOH	2.380	0.956	2.303	0.955	2.301	0.957 ³¹
CsOH	2.475	0.957	2.403	0.956	2.391	0.960 ³⁰
BeOH	1.461	0.960	1.395	0.948	...	...
MgOH	1.872	0.956	1.761	0.947	1.767	0.940 ²²
CaOH	2.031	0.951	1.977	0.951	1.975	0.957 ²⁹
SrOH	2.161	0.953	2.105	0.952	2.111	0.922 ³³
BaOH	2.265	0.955	2.212	0.955	2.201	0.923 ²⁶

MgOH⁻ and BeOH⁻, however, it is predicted to be bent. In the case of Mg and Be hydroxides, all three nuclear coordinates variables were optimized, i.e., θ , R_{MO} , and R_{OH} . For all other species, after examining the PES near $\theta = 0^\circ$ and making sure that the equilibrium geometries correspond to the linear case, the angle θ was held fixed at 0° , and R_{MO} and R_{OH} were optimized. The calculated optimized angle for BeOH, BeOH⁻, and MgOH⁻ is 37°, 66°, and 50°, respectively. Our results for the optimized distances are presented in Table I and Figure 2 along with available experimental values for the neutral species. Note that the calculated properties of the M and OH fragment are in excellent agreement with experimental values: discrepancies are 0.03 eV for the ionization potential of M,⁵⁹ and 0.005 eV for the electron affinity of OH⁵⁹ and the alkali atoms.⁶³

FIG. 2. Optimized R_{MO} distance for various alkali and alkaline earth hydroxide anions (lower panel) and neutrals (upper panel). The blue dots correspond to outer core calculations (oc), red dots correspond to valence correlation (val), and green dots are experimental values (see Table I for references). The ACVQZ and AWCVQZ basis sets were used for the Li, Na, Mg, O, and H atoms for val and oc calculations, respectively. See Section II for the basis used for the heavier alkali and alkaline earth atoms.

Figure 2 shows the optimized R_{MO} distance for valence and outer core calculations. As can be seen, the R_{MO} equilibrium distance increases with the size of the alkali or alkaline earth atoms for both the anionic and neutral molecular species. The inclusion of outer core electrons in the correlation treatment gives results in much better agreement with experimental values. In particular, the effect of the outer core correlation increases with the size of the M atoms. This is not surprising since the difference in energy between the valence and outer core orbitals decreases with increasing size of M and, therefore, the magnitude of their interaction increases. This trend is less marked for the alkaline earth hydroxides and a deviation can be observed for CaOH. This can be attributed to the small basis set used for Ca. Indeed, the optimized companion basis set for the ECP10MDF effective core potential used to describe the 3s, 3p, and 4s orbitals of Ca only has [12s, 12p, 10d] functions, smaller than the basis sets used for the other alkali and alkaline earth atoms. The discrepancy is diminished when using the AWCV5Z basis set for O and H (see result in Table I).

In Table I, both the R_{MO} and R_{OH} distances are reported. The equilibrium distances for the anion are slightly larger than those for their neutral counterparts, as expected from the weakening effect of the added electron on the bond strength and the more diffuse electronic density of the anion. The largest difference occurs for Mg hydroxide for which the difference in the R_{MO} distance is 0.11 Å, which is due to the bent structure of MgOH⁻. The optimized R_{OH} distance does not vary as much as the R_{MO} distance for the different species, yet it also increases with the size of the M atom. The R_{OH} optimized values do not agree as well as the R_{MO} distance with experimental results. This can be explained by the strong anharmonic character of the OH bond which leads to a large difference between r_e (the geometry at the minimum of the potential energy surface) and r_0 (averaged over the ground state vibrational wave function), usually derived from experiments. In addition, the very loose bending motion of the MOH species implies that the ground state vibrational wave function spans a large portion of the nuclear configuration space, which delocalizes the H atom. Higgins *et al.*⁵⁶ have reported r_e and r_0 values for various R_{MO} and R_{OH} bonds. The differences are as large as 0.05 Å, which supports our conclusion. All neutral species have been known to be linear with the exception of BeOH for which the predicted bent structure has recently been confirmed by an experimental study¹⁵ supported by *ab initio* calculations. Our geometrical parameters agree well with MRCI + Q results from Ref. 15 ($R_{BeO} = 1.401$ Å, $R_{OH} = 0.944$ Å, and $\theta = 39^\circ$).¹⁵ The bent structure is even reinforced in the anionic case, with an increase of θ by 29°. MgOH, which has a quasi-linear structure (minimum corresponding to a linear structure but with a very flat PES) becomes bent when adding an excess electron. The obtained barrier to linearity is 0.03 eV (242 cm⁻¹) for BeOH, 0.18 eV (1452 cm⁻¹) for BeOH⁻ and 0.04 eV (323 cm⁻¹) for MgOH⁻, values that are below their respective zero-point energy. It is interesting to note that the bent structure of BeOH, BeOH⁻, and MgOH⁻ is already predicted at the HF level of theory.

The linear or bent structures of the different neutral and anionic MOH species can be explained by molecular orbital

considerations. Two molecular orbitals need to be considered: the $3a'$ highest occupied molecular orbital (HOMO) of the anions and the $2a'$ molecular orbital (HOMO-2). We have extracted the Hartree-Fock energy of these two orbitals from MOH⁻ calculations and plotted them as a function of θ . The results are shown in Figure 3 for all investigated species. The energy of the HOMO (top panel), a bonding orbital with mainly ns_M character, decreases with increasing θ for all species, which therefore favours a bent structure. This orbital is unoccupied for the neutral alkali hydroxides, singly occupied for the neutral alkaline earth hydroxides and anionic alkali hydroxides, and doubly occupied for the anionic alkaline earth hydroxides. The influence of this orbital on the bending is stronger in the doubly occupied case. The HOMO-2 (bottom panel) orbital, with major contribution from M and O inplane p atomic orbitals, is doubly occupied in all cases. It strongly favours a bent structure for Be and Mg, slightly favours a bent structure for Ca, Na, and Li, and favours the linear structure for all other species. The HOMO-2 molecular orbital is shown in Figure 4 for BeOH⁻ and CsOH⁻. In the case of CsOH⁻, the molecular orbital exhibits an anti-bonding character for the bent structure, while it is the opposite for BeOH⁻ where the bonding character is enhanced at bent geometries. The change in the nodal structure seen on Figure 4 is due to the mixing with

FIG. 3. Hartree-Fock/AVQZ energies of the HOMO (top panel) and HOMO-2 (bottom panel) molecular orbitals of the MOH⁻ anions as a function of the bending angle θ . Energies given relative to the energy of the respective molecular orbital for $\theta = 0^\circ$.

FIG. 4. HOMO-2 molecular orbital for the linear and bent ($\theta = 45^\circ$) structure of BeOH⁻ (top) and CsOH⁻ (bottom). Red and black lines correspond to the positive and negative signs of the electronic wave function. The figure shows the enhanced electronic density of the Be-O bond for BeOH⁻ at bent geometries whereas for CsOH⁻ the bond exhibits an anti-bonding character.

the p_z orbital that becomes possible when the linear symmetry is broken ($C_{\infty v}$ to C_s point group). The behaviour of both orbitals with respect to θ allows to explain the bent structure of BeOH, the increase of the bent character for BeOH⁻ and MgOH⁻ and more generally the flattening of the anions PES compared to their neutral counterpart, as well as the more rigid structure of the alkali hydroxides in contrast to the alkali earth hydroxides.

The dissociation energies (D_e and D_0) were also calculated and are shown in Figure 5 and Table II. The D_e are obtained by subtracting the energy at dissociation (M + OH⁻

FIG. 5. Dissociation energy for various neutral (upper panel) and anion (lower panel) alkali and alkaline earth hydroxides. The blue dots correspond to outer core calculations (oc), red dots correspond to valence correlation, (val) and green dots are experimental values (see Table II for references). The AVQZ and AWCQZ basis sets were used for the Li, Na, Mg, O, and H atoms for val and oc calculations, respectively. See Section II for the basis used for the heavier alkali and alkaline earth atoms.

TABLE II. D_e CCSD(T)/oc dissociation energies (in eV) and ZPE corrected D_0 values (given in parentheses) for the neutral and anionic MOH species along with experimental values and given error bars for the neutral. The AWCV5Z basis set has been used for O, Be, Li, and Mg, AWCVQZ basis set for Na, and AV5Z basis set for H. See Section II for the basis used for the heavier alkali and alkaline earth atoms.

	Anion		Neutral	
	This work	This work	This work	Expt.
LiOH	2.989(2.895)	4.594(4.475)	4.53[4], ¹⁶ 4.54, ⁵⁸ 4.467 ⁵⁹	
NaOH	2.073(2.011)	3.469(3.388)	3.47[9], ²⁵ 3.548, ⁵⁹ 3.38 ⁵⁸	
KOH	2.074(2.001)	3.599(3.512)	3.721, ⁵⁹ 3.69[9], ²⁵ 3.53 ⁵⁸	
RbOH	2.047(1.978)	3.621(3.610)	3.692, ⁵⁹ 3.77[9], ²⁵ 3.61 ⁵⁸	
CsOH	2.143(2.075)	3.885(3.807)	3.866, ⁵⁹ 3.90[9], ²⁵ 3.95 ⁵⁸	
BeOH	3.668(3.562)	4.692(4.574)	4.94[43] ⁶⁰	
MgOH	2.565(2.500)	3.267(3.187)	3.227[22], ³² 3.59[22] ⁶⁰	
CaOH	3.112(3.023)	4.057(3.947)	4.115[435], ⁶¹ 4.332[342], ⁶¹ 4.23 ⁶⁰	
SrOH	3.157(3.078)	4.148(4.050)	4.00[17], ⁶² 4.31[10], ³⁵ 4.47, ²⁵ 4.249[653] ⁶¹	
BaOH	3.417(3.343)	4.525(4.436)	4.64[17] ⁶²	

for the anion and $M + OH$ for the neutral) from the energy of the molecular species at its equilibrium geometry. All calculations were corrected for the harmonic zero point energy (ZPE) yielding D_0 , obtained at the CCSD(T)/QZ/oc level of theory, and for the basis set superposition error, using the counterpoise method⁵⁷ where the energies of the fragments M or OH are obtained at equilibrium geometry including the full basis set.

The dissociation energies are very close for all alkali hydroxides with the notable exception of LiOH, for which the interaction is much stronger. Similar to the case of Li, the binding energy of the Be hydroxide is significantly larger than that of the other alkaline earth hydroxides, for both the neutral and the anion. This can be explained by the smaller $M-O$ bond and the lack of p orbitals for Li and Be, allowing stronger mixing with the orbitals of OH . The anion's bond strengths are weaker than their neutral counterparts. This is most likely due to the decrease in the electrostatic interaction when adding an excess electron, the partial charge going from M^+-OH^- to $M-OH^-$, as confirmed by a Mulliken population analysis. The alkaline earth hydroxides are predicted to be more stable than the alkali hydroxides both in the neutral and anionic case. This arises from the larger contribution of the $3a'$ HOMO bonding molecular orbital for the alkaline earth hydroxides, which is singly and doubly occupied for the neutral and anion, respectively, while it is unoccupied and singly occupied in the alkali hydroxides case, respectively. Our conclusion on the effect of the correlation of outer core electrons on the intermolecular distance also applies to the interaction energies, i.e., the effect increases with increasing the size of the M atom.

Figure 6 shows the potential energy curves of the different MOH^- anions as a function of the distance R_M for the equilibrium value of θ , i.e., bent for $MgOH^-$ and $BeOH^-$ and linear for all other anions. This figure offers a pictorial view of the major differences between the MOH^- species: the variation in the equilibrium distance and depth of the interaction well.

For all investigated species, the anion is stable (lower in energy than the neutral) at intermediate and large R_{MO} distances, resulting in a positive electron affinity (EA). Table III

FIG. 6. Potential energy curves for the MOH^- anions, where $M = Li, Na, K, Rb, Cs$ and Be, Mg, Ca, Sr, Ba . Curves shown for the equilibrium value of θ (50° for $MgOH^-$, 66° for $BeOH^-$, and 0° for all other anions) with energy relative to the dissociation channel $M + OH^-$. Obtained at the CCSD(T)/oc/AWCVQZ level of theory (see Section II for computational details). The interatomic R_{OH} distance was held fixed at its CCSD(T)/AWCVQZ equilibrium value (0.9643 Å). Solid lines correspond to alkali hydroxides whereas the dashed lines correspond to alkaline earth hydroxides.

shows the CCSD(T)/oc ZPE corrected vertical electron affinities of the alkali and alkaline earth hydroxides. Hartree-Fock values are also presented. No experimental or theoretical values are available for comparison. It should be emphasized that all neutral and anionic species exhibit very large zero point energies (between 0.3 and 0.35 eV, based on harmonic calculations). The ZPE being larger than the difference between the adiabatic and vertical EAs and the ground state vibrational wave function spanning a large fraction of the nuclear coordinates (R_{OH} , R_{MO} , and θ) there will be no difference between the measured vertical and adiabatic EAs. The EA of the hydroxides decreases with increasing size of the M atom. For the alkali, a similar trend occurs in the atomic case,⁶³ which is due to the increase of the screening effect of the nucleus for heavier atoms. The identical trends for the atomic and molecular electron affinities can be explained by the nature of the orbital that binds the excess electron: in the atomic as well as in the molecular case, the bonding orbital corresponds to the ns valence orbital of the alkali atom. The situation is different for the alkaline earth atomic anions where the excess electron is loosely bound to the excited np orbital. This gives rise to small electron affinities (Ca, Sr, and Ba)⁶⁴ or no stable atomic anions (Be and Mg).⁶⁴ In the molecular case, the closed-shell

TABLE III. ZPE corrected CCSD(T)/oc vertical electron affinities (EAs) of the neutral alkali and alkaline earth hydroxides with the AWCV5Z basis set for Li, Be, Mg, and O, AWCVQZ for Na, and AV5Z for H. See Section II for the basis used for the heavier alkali and alkaline earth atoms. The Hartree-Fock values are also presented.

MOH	CC	HF	MOH	CC	HF
LiOH	0.256	0.174	BeOH	0.812	-0.162
NaOH	0.432	0.347	MgOH	1.145	0.272
KOH	0.304	0.220	CaOH	0.881	0.050
RbOH	0.259	0.171	SrOH	0.844	0.056
CsOH	0.181	0.100	BaOH	0.714	0.008

configuration of alkaline earth hydroxide stabilizes the anion for which the excess electron is bound to a $n\sigma$ (or a' in point group C_s) molecular orbital corresponding mainly to the ns valence orbital of the alkaline earth atom, as in the case of alkali hydroxides. LiOH and BeOH do not follow the trend, which is especially remarkable for LiOH since the other alkali hydroxides follow the atomic trend. One possible explanation for the peculiarity of BeOH and LiOH comes from their small size relative to the OH fragment, the small M–O distance, and strong M–O interaction compared to the other MOH^- species. This leads to a larger distortion of the HOMO orbital which alters its atomic ns nature.

Assuming classical dipole-charge interaction, the electron affinities may be linked to the strength of the dipole moment. The latter have been calculated using the finite difference method at the CCSD(T) level of theory. We have carefully checked the convergence of the dipole moment with respect to the electric field's strength. The results are given in Table IV along with available experimental values. While the theoretical values have been obtained at the optimized geometries (see Table I), the measured values are averaged over the ground vibrational wave function. The dipole moment being sensitive to the geometry (in particular the bending motion), this may explain the differences between calculated and experimental values. No evident trend is observed. However, it is clear that the dipole moment of the alkali hydroxides is much larger than those for the alkaline earth hydroxides. For the latter, based on the fact that a dipole moment of 1.625 D is needed to bind an excess electron² and that the binding molecular orbital is a valence orbital (neutral and anionic alkaline hydroxides share a common HOMO), we can conclude that the alkaline hydroxides are valence-bound anions. In addition, Hartree-Fock calculations (see Table III) fail to predict the stability of BeOH^- and barely predict positive EA for all other alkaline earth hydroxide anions. This suggests strong quantum effects and the importance of electron correlation. On the other hand, the alkali hydroxides exhibit very large dipole moments and, unlike the alkaline earth hydroxides, the stability of the anions is already reasonably well predicted at the Hartree-Fock level. Moreover, the molecular orbital that binds the excess electron is the first excited molecular orbital of the neutral. This analysis suggests that the alkali hydroxide anions are dipole bound anions.

Understanding the structure, interaction energies, and stability of neutral and anionic alkali and alkaline earth hydroxides is not straightforward and simple models are not sufficient

to interpret these properties where several effects compete with each other. We believe that the results on the anionic species may bring new insights into the understanding of the alkali and alkaline earth hydroxides.

IV. POTENTIAL ENERGY SURFACES, ASSOCIATIVE DETACHMENT, AND IMPLICATIONS FOR SYMPATHETIC COOLING

The feasibility of sympathetic cooling of OH^- using ultra-cold Rb atoms has been studied by theoretical methods^{38–41} and is currently under experimental investigation using an ion-atom hybrid trap. The first experimental results⁵¹ have shown a loss of OH^- from the trap, which was attributed to the associative detachment (AD) reaction $\text{Rb} + \text{OH}^- \rightarrow \text{RbOH} + e^-$. In a previous work,⁴¹ we have shown that the rate coefficient strongly depends on the position of the crossing between the neutral and anion potential energy surfaces (PESs), which defines the autodetachment region. This crossing occurs in the repulsive part of the PESs at an energy less than 0.5 eV below the $\text{Rb} + \text{OH}^-$ dissociation limit, indicating that the AD reaction is barrierless and can be expected to be efficient even in the cold regime. However, if the crossing point occurred above the dissociation limit instead, a dramatically smaller rate coefficient would be obtained. On the other hand, the rate coefficient has a weak dependence in the temperature (i.e., the collision energy and the rotational distribution of OH^-). The AD reaction limits the prospects of cooling OH^- in collisions with Rb atoms. However, it is worth investigating whether other laser-cooled alkali or alkaline earth atoms offer better prospects. To this purpose, we have extended our previous work⁴¹ by calculating the M– OH^- PES and the AD reaction rate using a simple Langevin model.

The global potential energy surfaces of all studied anion hydroxides were obtained at the CCSD(T)/oc/AWCQZ level of theory. They share a common shape similar to the RbOH^- PES obtained by Gonzales-Sanchez *et al.*,³⁸ with the exception of MgOH^- and BeOH^- for which the minimum corresponds to a bent structure, as previously discussed. Figure 7 shows the global 2D potential energy surface of MgOH^- and NaOH^- . The different PESs differ in the depth of the potential well and the anisotropy.

To estimate the anisotropic character, we have calculated the energy difference between the $\theta = 180^\circ$ (at optimized R_{MO}) structure and the global minimum for each species. This very simple model allows to qualitatively discuss the anisotropy character of the different PESs. Results are shown in Table V. The values are very close with the exception of BeOH^- and LiOH^- . Both Li and Be atoms are more likely to undergo closer encounter with the colliding partner leading to a stronger interaction, which can be either favourable (at $\theta = 0^\circ$ for Li and 66° for Be) or disadvantageous (at $\theta = 180^\circ$).

The potential energy surfaces (PESs) of the neutral and anion cross in the repulsive region. This crossing point defines the autodetachment region where the anion becomes unstable and can spontaneously autodetach and eject an electron. This corresponds to the associative detachment reaction $\text{M} + \text{OH}^- \rightarrow \text{MOH} + e^-$ which is allowed if the anion and neutral surfaces cross below the considered energy range. In

TABLE IV. CCSD(T)/oc dipole moment of the neutral alkali and alkaline earth hydroxides with the AWC5Z basis set for Li, Be, Mg, and O, AWCQZ for Na, and AV5Z for H. See Section II for the basis used for the heavier alkali and alkaline earth atoms. Values given in Debye (D).

MOH	This work	Expt.	MOH	This work	Expt.
LiOH	4.573	4.755 ⁵⁶	BeOH	1.201	...
NaOH	6.716	6.832[9] ⁷¹	MgOH	1.154	...
KOH	7.390	7.415[2] ⁶⁶	CaOH	1.139	1.465[61] ⁶⁵
RbOH	6.585	...	SrOH	1.530	1.900[14] ⁶⁵
CsOH	6.741	7.1[5] ³⁰	BaOH	1.465	...

FIG. 7. Contour plot of the MgOH^- (top panel) and NaOH^- (bottom panel) 2D potential energy surface. Obtained using the CCSD(T)/oc method with all orbitals correlated except the $1s_{\text{Mg}}$ and $1s_{\text{Na}}$ and corrected for the basis set superposition error. The AWCVQZ basis set for Mg, Na, and O and AVQZ basis set for H. The interatomic R_{OH} distance was held fixed at its CCSD(T)/oc/AWCVQZ equilibrium value (0.9643 Å).

this case, it is the collision energy that induces the detachment of the electron but this may also happen when exciting the vibrational states of MOH^- . The AD reaction produces vibrationally excited MOH and the excess energy is carried away by the ejected electron. The height of the crossing point strongly depends on the system. Figure 8 shows the potential energy curves (PECs) at linear geometry in the repulsive region for the alkali and alkaline earth hydroxides, respectively. A trend can be seen for the alkali hydroxides, where the crossing between the anion and neutral PECs occurs lower in energy for heavier alkali atoms. This trend follows the change in electron affinity: the smaller the EA, the lower the crossing. However, the Li hydroxide deviates from the trend and one has to take into

TABLE V. CCSD(T)/oc energy difference between global minimum and $\theta = 180^\circ$ at equilibrium R_{M} distance for the alkali and alkaline earth hydroxide anions. The AWCVQ basis set for Li, Be, Na, Mg, and O and AVQZ for H. See Section II for the basis used for the heavier alkali and alkaline earth atoms.

MOH^-	ΔE (eV)	MOH^-	ΔE (eV)
LiOH^-	2.110	BeOH^-	3.250
NaOH^-	1.420	MgOH^-	2.084
KOH^-	1.236	CaOH^-	2.272
RbOH^-	1.242	SrOH^-	2.200
CsOH^-	1.396	BaOH^-	2.256

FIG. 8. CCSD(T) anion (solid) and neutral (dashed) curves at linear geometry for alkali (top panel) and alkaline earth (bottom panel) hydroxides. The AWCV5Z basis set was used for O, Mg, Li, Na and H, with all electrons correlated except the $1s_{\text{Mg}}$ and $1s_{\text{Na}}$ orbitals. See Section II for the basis used for the heavier alkali and alkaline earth atoms. The crossing point between the curves is indicated by a square. Energy given relative to the dissociation limit $\text{M} + \text{OH}^-$.

account other factors such as the difference between the dissociation energy of the anion and neutral to explain the position of the crossing point. For the alkaline earth hydroxides, the neutral and anion curves are almost parallel and the crossing occurs much higher in energy. This is also the case in the bent case, suggesting that the curve crossing occurs at very high energy in the entire angular space. The larger electron affinity of the alkaline earth hydroxides explains the higher crossing point. These conclusions support the general idea that anions formed from neutrals with higher EA are more stable against the detachment process.

As was shown for Rb hydroxide,^{39,41} the crossing point occurs higher in energy for larger θ values. This is also true for other hydroxides. This can easily be explained by the increase in energy for both anion and neutral hydroxides as a function of θ and by the difference in energy between the neutral and anion PECs. We define $V_c(\theta)$, the height of the crossing point as a function of θ . The rate of the associative detachment reaction $\text{M} + \text{OH}^- \rightarrow \text{MOH} + e^-$ can be obtained from a simple Langevin model which depends upon the height of the crossing point, the collision energy, the Langevin cross section, and the ro-vibrational energy of OH^- .^{39,41} The AD rate constant for OH^- in its vibrational ground state ($v = 0$) can be expressed

as

$$k_{AD}(T) = \sum_{J=0}^{\infty} \left(W(J) \int_0^{\infty} f(\varepsilon) \sigma_L \rho(J, \varepsilon, V_c(\theta)) d\varepsilon \right), \quad (1)$$

where $f(\varepsilon)$ is the Maxwell-Boltzmann distribution, σ_L is the Langevin cross section which depends on the mass and the polarizability of the M atom, ε is the collision energy, and ρ is the accessible angular space (which depends on $V_c(\theta)$ and ε). The $W(J)$ term accounts for the weight of each rotational state assuming a thermal equilibrium distribution, $W(J) = Q_{\text{rot}}^{-1} (2J+1) \exp(-E_J/k_bT)$ where Q_{rot} is the rotational partition function. Figure 9 shows the associative detachment reaction k_{AD} as a function of the height of the crossing point for various temperatures. To obtain the latter, we have used our $V_c(\theta)$ results for RbOH⁻ and varied $V_c(0)$, the value of the crossing height at $\theta = 0^\circ$.⁴¹ By doing so, we assume that the dependence on θ of the $V_c(\theta)$ is the same for all other alkali and alkaline earth atoms. We carefully checked that the deviation from this assumption does not significantly affect our conclusions.

One can see that the rate drops dramatically when $V_c(0)$ is above the dissociation limit. However when the crossing point is below the dissociation limit, the rate is almost constant with respect to temperature. Note that if the crossing height is below 0 for the entire angular space, the rate constant of the AD reaction will be equal to the Langevin rate. As has been pointed out in our previous work on RbOH⁻,⁴¹ the PECs in the repulsive region are very sensitive to the computational method and basis sets used. To make sure that the choice of the method will not affect our conclusion on the AD reaction, we have calculated the height of the crossing point using different basis sets (AVQZ-AWCVQZ, AV5Z-AWCV5Z, AV6Z when possible and ACWVQZ + extended diffuse functions). We also studied the influence of the R_{OH} bond length on the crossing height. Lithium hydroxide is the most sensitive system with the different calculated crossing heights ranging from 0.07 a.u. to 0.13 a.u. However, this only affects slightly the conclusion on the AD reaction at low to room temperature since the rate is already below $10^{-17} \text{ cm}^3 \text{ s}^{-1}$ for a crossing height of 0.03 a.u. at 300 K. The same conclusions were reached for all

other species. Therefore, the sensitivity of the crossing point will only be relevant for crossings near the threshold energy as for rubidium hydroxide, for which the effect of basis sets and ECPs on the crossing height have already been discussed elsewhere.⁴¹ In addition to the position of the crossing point, the AD rate constant also depends on the Langevin cross section, i.e., the mass ratio m_M/m_{OH} and the polarizability of the M atom. The red line on Figure 9 corresponds to k_{AD} obtained using the polarizability and mass of Li. One can see that the difference is only observed for crossing heights below 0 (inset).

Based on the anionic and neutral curve crossings seen on Figure 8 and the behaviour of the AD rate constant as a function of this crossing height (Figure 9), we can conclude that the AD reaction will only be appreciable for Rb and Cs. The obtained values for the rates are $4.2 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ and $1.2 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$ at 300 K for Rb and Cs, respectively. The rate weakly depends on the temperature, decreasing to $3.8 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ and $1.1 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$ at 50 K, respectively. For comparison, the usual Langevin rate⁶⁷ (without taking the dependence on V_c into account) is $4.3 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$ for Rb-OH⁻ and $4.7 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$ for Cs-OH⁻. The relative simplicity of this Langevin-based model may be questioned. However, in rare cases where full quantum calculations can be performed, Langevin-based dynamics show excellent agreement (see Ref. 41 and references therein). It should also be noted that a full quantum rate constant will still strongly depend on the crossing point between the anion and neutral potential energy surfaces.

In the context of the experimental study of sympathetic cooling of OH⁻ with ultracold M atoms, we can make the following conclusions: (i) The only energetically possible reactive process for low to room temperature is the AD reaction. Based on the position of the crossing point between the anion and neutral PES, this reaction should be suppressed for all alkali and alkaline earth atoms except Rb and Cs; (ii) a low m_M/m_{OH} mass ratio is desirable to avoid heating due to micro-motion in radio frequency traps,⁶⁸ hence the use of lighter M atoms should be preferred; (iii) the energy of the laser used in the laser cooling scheme of the atom must be lower than the electron affinity of OH (1.82 eV) to avoid photodetachment of OH⁻, which leads to a loss of ions. The last condition is only fulfilled by K, Rb, and Cs. In the case of the presence of a laser field (e.g. use of a MOT), K seems to be the most suitable candidate. In comparison to Rb, the mass ratio is smaller and the loss of OH⁻ due to the AD reaction will be largely reduced. On the other hand, the relaxation rate should still be as effective as for Rb^{38,40} since both species share similar interaction energies and anisotropy characters. Alternatively, one could also use an optical dipole trap instead of a MOT to confine the atoms.⁶⁹ In this case, the energy of the confining laser is usually lower than the electron affinity of OH,⁷⁰ suggesting the possibility to use the other mentioned alkali and alkaline earth atoms such as lithium. The latter should be the most suited one since the mass ratio is smaller than 1 while the AD rate should be even smaller than for K. The LiOH⁻ PES exhibits a deeper well and a stronger anisotropy than for RbOH⁻. This will affect the elastic and rotational quenching rate constants, and the cooling rates. However, an accurate description of the cooling properties of the Li + OH⁻ system would require

FIG. 9. Rate constant of the associative detachment reaction for Rb (black) and Li (red) as a function of the height of the crossing point between anion and neutral curves at linear geometry. Values for several temperatures are plotted. Energy of the crossing point relative to the $M + \text{OH}^-$ dissociation limit.

quantum-mechanical nuclear dynamics calculations, which are outside the scope of the present paper.

V. CONCLUSION

A systematic *ab initio* study on the neutral and anion alkali and alkaline earth hydroxides has been performed. Equilibrium parameters, interaction energies, electronic dipole moments, electron affinities, and potential energy surfaces have been obtained at the CCSD(T) level of theory. Our results for the neutral species have been compared to experimental values. We found the minimum structure to be linear for all neutral species, with the exception of BeOH, in agreement with the existing literature. To our knowledge, there are no theoretical or experimental studies on the anionic species, and our results constitute the first investigation of the MOH[−] molecular anions. All anions are predicted to be linear with the exception of BeOH[−] and MgOH[−]. An analysis of the molecular orbitals is used to interpret this change in the structure. The M–O distance is larger for the anions than for the neutrals. This implies a weakening of the chemical bond, which is supported by our results on the dissociation energies. The stability of the metal hydroxides has been discussed in terms of dipole moment and molecular orbitals. We conclude that the alkali hydroxides are dipole-bound anions whereas the alkaline earth hydroxides are valence-bound anions with important electron correlation effects. The potential energy surfaces of the alkali and alkaline earth hydroxide anions exhibit similar shape: a flat potential around the minimum structure ($\theta = 66^\circ$ for BeOH[−], 50° for MgOH[−], and 0° for the other MOH[−] species) and a maximum for the M–H–O conformation. The PESs differ in their depth and anisotropy character.

In the context of sympathetic cooling of OH[−] by collisions with ultracold alkali or alkaline earth atoms, we investigated the associative detachment reaction $M + \text{OH}^- \rightarrow \text{MOH} + e^-$, which is the only energetically accessible reaction in the energy range considered here. Based on the calculated crossing point between the neutral MOH and anion MOH[−] PES that defines the autodetachment region, we showed that the AD reaction should only be appreciable for Rb and Cs for which the crossing point occurs below the dissociation energy. The usual scheme for sympathetic cooling is based on laser-cooled atoms in a MOT. Many criteria should be fulfilled in order for the cooling process to be efficient: reactive collisions such as AD should be avoided; the laser energy should be lower than the electron affinity of OH to prevent photodetachment; a low mass ratio should be preferred to avoid heating through coupling with the micromotion in the radio frequency trap; and the elastic cross section should be larger than the inelastic cross section. Based on these considerations, K is the only atom that satisfies all conditions. We note that when using a Paul trap, the m_M/m_{OH} mass ratio should be smaller than 1, but this limitation can be overcome by using a higher multipole trap and/or by confining the buffer gas in the region of the trap where micromotion is limited.⁶⁸

Alternatively, one could use an optical dipole trap to confine the buffer gas, in which case the energy of the laser is below the electron affinity of OH. This prevents the photodetachment and allows a larger choice for the buffer gas. In this

case, all alkali and alkaline earth atoms except Rb and Cs can be used. Li provides the lowest mass ratio and would therefore seem to be the most natural choice.

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