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Theoretical Study of RbOH, CsOH, FrOH, and Their Cations: Geometries, Vibrational Frequencies, and the Ionization Energies

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High-level ab initio calculations, employing a range of theoretical methods up to RCCSD(T), together with effective core potentials and large valence basis sets, have been used to calculate the geometry and harmonic vibrational frequencies of RbOH, CsOH, FrOH, and the corresponding cations. It is concluded that although fairly good agreement with the M−O stretch frequency is obtained, there is likely to have been a misassignment of the bending vibration in previous infrared studies of RbOH and CsOH. Also, despite excellent consistency among the calculated results, there are discrepancies with previously reported equilibrium bond lengths. The adiabatic ionization energies of RbOH, CsOH, and FrOH are reported, together with the dissociation energies of the neutrals and the cations. It is concluded that the cations have a $^2\Pi$ ground state.

I. Introduction

There is interest in the structure and thermodynamics of MOH species, where M is an alkali metal, owing to the use of alkali metal species in nuclear reactors[1] and also their presence in the upper atmosphere.[2] The ionic nature of these species also leads one to expect a low ionization energy, since ionization essentially corresponds to a detachment of an electron from OH^- in the presence of M^+. Recently, we have performed high-level calculations to obtain accurate thermodynamics for MOH, for M = Li,[3] Na,[4] and K.[5] The results on the neutrals have been compared with those of Bauschlicher et al.[6] and others, where generally good agreement has been obtained. In our previous work on the lighter species,[3−5] the calculated adiabatic ionization energies were compared to previous photoelectron results,[7] where it was found that the photoelectron results were slightly too low, which was attributed to the high temperatures (and so internal excitation) of the MOH and/or the presence of other species in the vapor phase.

In the present work, we tackle the heaviest alkali metal hydroxides, which follows from refs 3−5 and also from our work on the heavier alkali metal monoxides.[8] We aim to calculate the equilibrium geometry, vibrational frequencies, and thermodynamics for the neutrals and the cations and consequently to calculate the ionization energies. First, we shall review the data available on the three neutral species. Note that Gurvich et al. have reviewed the data available on RbOH and CsOH in great detail in ref 9, and therefore, only an outline of the previous work will be given herein.

(a) RbOH. For RbOH, except for some weak unassigned infrared bands seen by Spinar and Margrave[10] in the vapor above $RbOH_{(s)}$, the first spectroscopic observation of the RbOH molecule was made using microwave spectroscopy.[11] An essentially linear structure was deduced, but there were anomalies in the observed microwave spectra, since the variation in the rotational constant was nonlinear with increased excitation of the bending mode and the trend was opposite to expectations. Bond lengths of 2.305 Å for Rb−O and 0.965 Å for O−H were obtained from the derived rotational constants. The infrared spectrum of matrix-isolated RbOH was reported by Acquista and Abramowitz.[12] The assigned fundamentals were at 354.4 cm^{-1} for ν_1 and 309.0 cm^{-1} for ν_2. The vibrational and rotational information was reinterpreted in ref 13 employing a new formulation of the vibration−rotation interactions that occur in linear triatomic molecules, and this allowed them to develop a force field, but limited to a harmonic treatment, to yield an Rb−O bond length of 2.301 ± 0.002 Å and an O−H bond length of 0.95 ± 0.01 Å. The application of a semirigid model by Brown et al.[14] yielded an Rb−O bond length of 2.3025 ± 0.0014 Å and an O−H bond length of 0.986 ± 0.011 Å. In 1990, Girichev et al. employed electron diffraction to obtain structural information on the vapors above RbOH,[15] and bond lengths for the monomer and dimer were derived. The Rb−O bond length was found to be 2.50 ± 0.02 Å, slightly longer than that obtained in the microwave studies, but it must be remembered that contributions from a higher vibrational energy level may be present. Nuclear quadrupole coupling constants were reported in ref 16 from further microwave studies. Much more recently, Belyaeva reported an infrared absorption study of RbOH and its dimer in various rare gas matrixes.[17] The identity of the dimer bands was made by reference to the previously reported spectra of the monomers and eliminating these. It should be pointed out that very early studies[18] assumed that RbOH had a linear structure, while later work by Jensen and Padley[19] assumed a bent structure (114°). The conclusions of the later microwave studies described above veer more toward quasilinearity. It is of note, however, that in ref 19 an ω_2 vibrational frequency of 1300 cm^{-1} was estimated—significantly greater than the estimated ω_1 vibrational frequency of 369 cm^{-1}.

RbOH has also been tackled in theoretical studies. Early studies by Nemukhin and Stepanov[20] employing the diatomics-

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in-molecules (DIM) approach with two parametrizations indicated $\omega_1 = 332$ or $335\ \mathrm{cm}^{-1}$ and $\omega_2 = 676$ or $700\ \mathrm{cm}^{-1}$, i.e., the bending frequency being significantly higher than the Rb−O stretch. The atom superposition and electron delocalization (ASED) model of Stiakaki et al.[21] yielded structural and energetic information with an Rb−O bond length of 2.345 Å, while the electrostatic model of Mestdagh and Visticot[22] yielded the dipole moment and the dissociation energy. The only ab initio study appears to be that of Bauschlicher et al.,[6] who fixed the O−H bond distance and derived the Rb−O bond length and the ω_1 vibrational frequency at the SCF and CISD levels of theory, employing a (18s14p11d4f/12s10p5d3f) basis set for Rb. An Rb−O bond length of 2.323 Å and a harmonic frequency for the Rb−O stretch vibration of $378\ \mathrm{cm}^{-1}$ were obtained at the CISD level of theory. No data on the cation appear to be available.

(b) CsOH. Experimental studies on CsOH commenced in 1958 with a failed attempt to observe an infrared absorption from vapor above CsOH.[10] In 1966, a preliminary report of the microwave spectrum by Kuczkowski and Lide[23] was made in which some evidence for an effective linear geometry was presented, together with a determination of the Cs−O bond length. This work was followed up the following year with a fuller report of the microwave spectrum.[24] Again, effective linearity of the molecule was confirmed, but anomalies in the microwave spectra were noted. In the latter work, vibrational energy spacings were estimated as well as some refinement of the bond lengths. The estimated vibrational spacings were $\nu_1 = 400 \pm 80\ \mathrm{cm}^{-1}$ and $\nu_2 \approx 300\ \mathrm{cm}^{-1}$. A follow-up study[25] reported the results of a matrix-isolation infrared study, where ν_1 was determined as $335.6\ \mathrm{cm}^{-1}$ and ν_2 as $306\ \mathrm{cm}^{-1}$. Again, no evidence was found for nonlinearity. Lide and Matsumura,[11] in 1969, employing their reformulation of the vibration−rotation interactions that occur in linear triatomic molecules, refined the Cs−O bond length to 2.391 ± 0.002 Å and the OH bond length to 0.96 ± 0.01 Å. A reanalysis of the rotational and vibrational spectra of CsOH was reported in 1994[14] by Brown et al. in which they used their semirigid bender model. They noted that there was a peculiarity in that the O−H bond length was deduced to be rather long at 0.992 Å, as opposed to the expected 0.96 Å. A Cs−O bond length of 2.393 ± 0.012 Å was deduced. Finally, Kawashima, Suenram, and Hirota[16] reported the results of further microwave experiments from which they determined nuclear quadrupole coupling constants for CsOH. Again, early studies[18] assumed that CsOH had a linear structure, while later work by Jensen and Padley[19] assumed a bent structure (117°), with again the later microwave studies concluding quasilinearity. As with RbOH, the authors of ref 19 deduced an ω_2 vibrational frequency of $1300\ \mathrm{cm}^{-1}$, significantly greater than the estimated ω_1 vibrational frequency of $330\ \mathrm{cm}^{-1}$.

In addition to the experimental studies, theoretical work has been undertaken. There has been an electrostatic model study by Mestdagh and Visticot[22] and an ASED molecular orbital study by Stiakaki et al.[21] Reference 21 reported some structural and energetic properties, with the Cs−O bond length being derived as 2.447 Å. The only ab initio study so far reported is that from Bauschlicher and co-workers.[6] In that work, a (14s9p6d4f/7s7p5d3f) valence basis set for Cs was employed together with an effective core potential (ECP) that was based on averaged Dirac−Fock wave functions. SCF and CISD calculations were employed with a fixed O−H bond length. The Cs−O bond length was derived as 2.419 Å at the CISD level with the ω_1 vibrational frequency calculated as $378\ \mathrm{cm}^{-1}$.

Estimates of the cationic vibrational frequencies have been put forward in the JANAF tables;[26] however, as will be shown below, at least one of these estimates is far removed from our best value.

(c) FrOH. For FrOH, there are no experimental or theoretical data available on either the neutral or the cation, to our knowledge.

II. Theoretical Methods

(a) RbOH/RbOH$^+$. For the neutral $X^1\Sigma^+$ and the cationic $X^2\Pi$ species, the geometries were optimized using two different basis sets based on the LANL2 ECP.[27] We remove the valence functions from the standard LANL2 basis set, leaving just the ECP (which describes the 1s−3d electrons), and added our own valence functions (which describe the 4s4p5s electrons) to form basis sets as follows.

For the LANL2[7s6p3d] basis set, we first obtain a [1s1p] set of contracted functions by performing an RHF calculation on Rb$^+$ with an uncontracted (13s11p) set of even-tempered basis functions with $\zeta_s = 50.0{-}0.0606056$, ratio = 1.75, and $\zeta_p = 20.0{-}0.0742419$, ratio = 1.75. The expansion coefficients were then employed as the contraction coefficients to form the [1s1p] set. This was augmented with the following uncontracted functions:

$$\text{six s},\quad \zeta = 2.2{-}0.0426883,\quad \text{ratio} = 2.2$$

$$\text{five p},\quad \zeta = 1.6{-}0.0683013,\quad \text{ratio} = 2.2$$

$$\text{three d},\quad \zeta = 1.08{-}0.12,\quad \text{ratio} = 3.0$$

With this (19s16p3d/7s6p3d) rubidium basis set, the standard 6-311++G(3d,3p) basis sets were used for O and H. This basis set was used with the (U)MP2, (U)B3LYP, and (U)QCISD methods to obtain the optimized geometry and harmonic vibrational frequencies using Gaussian.[28]

For the LANL2[7s6p3d2f] basis set, the above functions were further augmented with two f functions with $\zeta = 0.5$ and 0.166 666 7. With this (19s16p3d2f/7s6p3d2f) rubidium basis set, the aug-cc-pVTZ basis sets were employed for O and H. This basis set was used with the (U)CCSD(T) method to obtain the optimized geometry and harmonic vibrational frequencies.

Finally, the ECP[10s8p5d4f3g] basis set that has been reported in full in ref 8 was employed in (R)CCSD(T)[29] single-point calculations (using MOLPRO)[30] at the (U)CCSD(T)/LANL2[7s6p3d2f]-optimized geometries to obtain more reliable energetics. The valence basis set is described as (26s18p5d4f3g/10s8p5d4f3g), and the ECP is the ECP28MWB one of Dolg and co-workers.[31,32] In these calculations, the aug-cc-pV5Z basis sets were employed for O and H but with the h functions of O removed. The total number of basis functions in this set of calculations was 299.

(b) CsOH/CsOH$^+$. For the neutral $X^1\Sigma^+$ and the cationic $X^2\Pi$ species, the geometries were optimized using two different basis sets, based on the LANL2 ECP.[27] We remove the valence functions from the standard LANL2 basis set, leaving just the ECP (which describes the 1s−4d electrons), and added our own valence functions (which describe the 5s5p6s electrons) to form basis sets as follows.

For the LANL2[9s8p3d] basis set, we first obtain a [1s1p] set of contracted functions by performing an RHF calculation on Cs$^+$ with an uncontracted (21s19p) set of even-tempered basis functions with $\zeta_s = 45.0{-}0.013533$, ratio = 1.5, and $\zeta_p = 20.0{-}0.013533$, ratio = 1.5. The expansion coefficients were then employed as the contraction coefficients to form the [1s1p]

TABLE 1: Optimized Geometrical Parameters (Å) and Computed Harmonic Vibrational Frequencies of RbOH ($\tilde{X}^1\Sigma^+$)

method[a]	bond lengths (Å)	frequencies[b] (cm^{-1})		
		ω_1 (σ)	ω_2 (π)	ω_3 (σ)
B3LYP/LANL2[7s6p3d];6-311++G(3d,3p)	Rb−O = 2.488; O−H = 0.956	369	277	3902
MP2/LANL2[7s6p3d];6-311++G(3d,3p)	Rb−O = 2.491; O−H = 0.957	368	364	3910
		358	*271*	*2848*
QCISD/LANL2[7s6p3d];6-311++G(3d,3p)	Rb−O = 2.487; O−H = 0.954	371	355	3923
		362	*264*	*2857*
CCSD(T)/LANL2[7s6p3d2f];aug-cc-pVTZ	Rb−O = 2.472; O−H = 0.959	376	361	3881

[a] All correlated calculations had O 1s frozen and Rb 1s2s2p3s3p3d represented by the ECP. [b] The values in italics are for RbOD.

set. This was augmented with the following uncontracted functions:

$$\text{eight s,}\quad \zeta = 2.0-0.015625,\quad \text{ratio} = 2.0$$

$$\text{seven p,}\quad \zeta = 1.5-0.0234375,\quad \text{ratio} = 2.0$$

$$\text{three d,}\quad \zeta = 1.35-0.15,\quad \text{ratio} = 3.0$$

With this (29s26p3d/9s8p3d) cesium basis set, the standard 6-311++G(3d,3p) basis sets were used for O and H. This basis set was used with the (U)MP2, (U)B3LYP, and (U)QCISD methods to obtain the optimized geometry and harmonic vibrational frequencies using Gaussian.

For the LANL2[9s8p3d2f] basis set, the above functions were further augmented with two f functions with $\zeta = 0.45$ and 0.15. With this (29s26p3d2f/9s8p3d2f) cesium basis set, the aug-cc-pVTZ basis sets were employed for O and H. This basis set was used with the (U)CCSD(T) method to obtain the optimized geometry and harmonic vibrational frequencies.

Finally, the ECP[10s8p5d4f3g] basis set that has been reported in full in ref 8 was employed in (R)CCSD(T) single-point calculations (using MOLPRO) at the (U)CCSD(T)/LANL2[9s8p3d2f]-optimized geometries to obtain more reliable energetics. The valence basis set is described as (28s24p5d4f3g/10s8p5d4f3g), and the ECP is the ECP46MWB one of Dolg and co-workers.[31,32] In these calculations the aug-cc-pV5Z basis sets were employed for O and H but with the h functions of O removed. The total number of basis functions in this set of calculations was 299.

(c) FrOH/FrOH$^+$. For the neutral $X^1\Sigma^+$ and the cationic $X^2\Pi$ species, the geometries were optimized using two different basis sets, based on the CRENBL78 ECP.[32,33] We remove the valence functions from the standard CRENBL78 basis set, leaving just the ECP (which describes the 1s−5d electrons), and added our own valence functions (which describe the 6s6p7s electrons) to form basis sets as follows.

For the CRENBL78[9s8p4d] basis set, we first obtain a [1s1p] set of contracted functions by performing an RHF calculation on Fr$^+$ with an uncontracted (19s19p) set of even-tempered basis functions with ζ_s and $\zeta_p = 20.0-0.013533$, ratio = 1.5. The expansion coefficients were then employed as the contraction coefficients to form the [1s1p] set. These were augmented with the following uncontracted functions:

$$\text{eight s,}\quad \zeta = 5.0-0.0200452,\quad \text{ratio} = 2.2$$

$$\text{seven p,}\quad \zeta = 3.0-0.0264597,\quad \text{ratio} = 2.2$$

$$\text{four d,}\quad \zeta = 2.0-0.0466472,\quad \text{ratio} = 3.5$$

With this (27s26p4d/9s8p4d) francium basis set, the standard 6-311++G(3d,3p) basis sets were used for O and H. This basis set was used with the (U)MP2, (U)B3LYP, and (U)QCISD methods to obtain the optimized geometry and harmonic vibrational frequencies using Gaussian.

For the CRENBL78[9s8p4d3f] basis set, the above functions were further augmented with three f functions with $\zeta = 1.8$, 0.4, and 0.088 888 89. With this (27s26p4d3f/9s8p4d3f) francium basis set, the aug-cc-pVTZ basis sets were employed for O and H. This basis set was used with the (U)CCSD(T) method to obtain the optimized geometry and harmonic vibrational frequencies.

Finally, the CRENBL78[11s10p5d4f3g] basis set that has been reported in full in ref 8 was employed in (R)CCSD(T) single-point calculations (using MOLPRO) at the CCSD(T)/CRENBL78[9s8p4d3f]-optimized geometries to obtain more reliable energetics. The valence basis set is described as (29s28p5d4f3g/11s10p5d4f3g). In these calculations, the aug-cc-pV5Z basis sets were employed for O and H but with the h functions of O removed. The total number of basis functions in this set of calculations was 306.

III. Results and Discussion

(a) Geometry and Vibrational Frequencies. *(i) RbOH/RbOH$^+$.* The results presented in Table 1 indicate that the four levels of theory are leading to very similar results. At the highest level of theory, the O−H bond length is calculated to be 0.959 Å, which is very close to that found for LiOH (0.951 Å, ref 3), NaOH (0.954 Å, ref 4), and KOH (0.958 Å, ref 5). The implication is that the OH bond is slightly strengthened in these species compared to the isolated OH$^-$ molecule ($r_e = 0.964$ Å, $\omega = 3680 \pm 37$ cm^{-1}; see refs 34 and 35)—a fact supported by the slightly higher calculated ω_3 frequency, which essentially corresponds to the O−H stretch. The vibrational frequencies are also consistent, although the ω_2 value at the B3LYP level appears a little out of line. The agreement between our best harmonic value of 376 cm^{-1} and the experimental fundamental frequency[12] of 354 cm^{-1} is good. It is interesting to note that at the highest levels of theory the ω_1 and ω_2 frequencies are calculated to be quite close in energy. This is in contrast to the conclusions of the infrared[12] studies, where ω_2 was deduced to be 309.0 cm^{-1}. Some disagreement between the calculations and the assignment of the experimental spectra arose for LiOH,[3] NaOH,[4] and KOH[5] and most likely arises from the presence of dimers (and maybe higher *n*-mers) in the vapor that is trapped in the matrix-isolation studies. (We note in passing that Girichev et al. have commented[15] that the ω_1 vibrational frequency for NaOH obtained from matrix isolation studies is probably in error, a conclusion we reached independently in ref 4.) Attempts to identify the monomer and *n*-mer bands in the experiments were made by recording spectra at different temperatures and the use of isotopic studies, but these studies were not wholly conclusive. In addition, we note that the peak at 354.4 cm^{-1} in ref 12 looks like it may have more than one contribution. Bauschlicher et al.[6] calculated ω_1 from a parabolic fit of energies. Under the assumption that the OH bond length was fixed, they obtained values of 380 cm^{-1} at the SCF level and 398 cm^{-1} at the CISD level, in reasonable agreement with the

TABLE 2: Optimized Geometrical Parameters and Computed Harmonic Vibrational Frequencies of Rb$^+$OH ($\tilde{X}^2\Pi$)

method^a	bond lengths (Å)	frequencies^b (cm^{-1})		
		ω_1 (σ)	ω_2 (π)	ω_3 (σ)
B3LYP/LANL2[7s6p3d];6-311++G(3d,3p)	Rb−O = 2.961; O−H = 0.975	142	160, 342	3701
MP2/LANL2[7s6p3d];6-311++G(3d,3p)	Rb−O = 2.951; O−H = 0.969	145	183, 353	3791
QCISD/LANL2[7s6p3d];6-311++G(3d,3p)	Rb−O = 2.959; O−H = 0.971	143	190, 358	3752
CCSD(T)/LANL2[7s6p3d2f];aug-cc-pVTZ	Rb−O = 2.926; O−H = 0.974	151	174, 338	3724

[a] All correlated calculations had O 1s frozen and Rb 1s2s2p3s3p3d represented by the ECP. All computed $\langle S^2 \rangle \leq 0.760$. [b] See text for discussion of nondegenerate π vibrations.

TABLE 3: Optimized Geometrical Parameters and Computed Harmonic Vibrational Frequencies of CsOH ($\tilde{X}^1\Sigma^+$)

method^a	bond lengths (Å)	frequencies^b (cm^{-1})		
		ω_1 (σ)	ω_2 (π)	ω_3 (σ)
B3LYP/LANL2[9s8p3d];6-311++G(3d,3p)	CsO = 2.658; OH = 0.957	336	327	3887
MP2/LANL2[9s8p3d];6-311++G(3d,3p)	CsO = 2.660; H = 0.958	336	393	3896
		328	*292*	*2838*
QCISD/LANL2[9s8p3d];6-311++G(3d,3p)	CsO = 2.656; H = 0.955	338	383	3908
		330	*284*	*2847*
CCSD(T)/LANL2[9s8p3d2f];aug-cc-pVTZ	CsO = 2.635; H = 0.960	346	388	3864

[a] All correlated calculations had O 1s frozen and Cs 1s2s2p3s3p3d4s4p4d represented by the ECP. [b] The values in italics are for CsOD.

values obtained herein. Both the present study and that reported in ref 6 used large basis sets, although we employed an ECP herein that takes some account of relativistic effects. In addition, the basis sets we employ are more complete for the O and H atoms. We would also expect the CCSD(T) procedure to be more accurate than the CISD approach used in ref 6. Thus, the relatively close agreement of the two studies is pleasing and lends weight to the values obtained.

Three further points are worth noting at this juncture. First, the calculations presented here lead to harmonic values, whereas experiments measure fundamentals. However, it is highly unlikely that the anharmonicity will be large enough to explain the disparity. Second, we note that the energetic proximity of the ω_1 and ω_2 vibrations may lead to an interaction between them. Naturally this cannot occur at linearity, where the symmetries are different, but upon bending, one of the π components will have the same symmetry (a′) as the stretch vibration. To establish the effect of anharmonicity and coupling between ω_1 and ω_2 at nonlinear geometries, a potential energy surface along the Rb−O and bending directions will be required. A detailed analysis of the energy levels will also be required. This is beyond the scope of the present paper. (Note that the high vibrational frequency of the O−H stretch, ω_3, should mean that there will be very little coupling with it.) Finally, matrix isolation studies suffer from the fact that the matrix atoms may interact with the isolated molecules, affecting the observed vibrational frequencies, as noted for example in refs 12 and 13.

We also calculated the vibrational frequencies of RbOD at the MP2 and QCISD levels (see Table 1 and see the same behavior as reported in the microwave study): $\omega_{\mathrm{RbOH}}/\omega_{\mathrm{RbOD}} = 1.03$ for both the present calculated results and experimental Rb−O stretch frequencies; $\omega_{\mathrm{RbOH}}/\omega_{\mathrm{RbOD}} = 1.35$ for both the present calculated results and experimental bending frequencies; the calculated OH/OD stretching ratio is 1.37, close to the expected $\sqrt{2}$ value.

Regarding the molecular parameters, the microwave study[11] reported "r_e" values of 2.305 Å for the Rb−O bond length and 0.965 Å for the O−H bond length. These values were obtained from a derived B_e value. It should be noted that the use of the B_0 value in the derivation of the bond lengths led to an unphysically short O−H bond length of 0.913 Å, suggesting that these results should be treated with some caution. Consideration of the vibration−rotation interactions in RbOH led to a refinement[13] of the geometry, giving values of 2.301 ± 0.002 Å for the Rb−O bond length and 0.95 ± 0.01 Å for the OH bond length. The semirigid model of ref 14 led to values of 2.3025 ± 0.0014 Å for the Rb−O bond length and a somewhat long O−H bond length of 0.986 ± 0.011 Å. It seems clear that there is still some uncertainty in the extraction of bond lengths from the rotational spectra. Although the O−H bond length from ref 13 is in good agreement with the value obtained herein, our Rb−O bond length is somewhat longer. The calculated Rb−O bond length from ref 6 appears to be in better agreement with experiment, with a value of 2.323 Å being obtained at the CISD level of theory. However, the present work is *expected* to give the more reliable values owing to the more complete basis sets employed, the higher level of theory, and the consistency of our results. It is interesting to note the good agreement between the present work and the electron diffraction study,[15] where a value of 2.50 ± 0.02 Å for the Rb−O bond length in RbOH was obtained, but the latter value is thermally averaged.

Table 2 contains the results of the calculations on RbOH$^+$. Again, there is a high degree of consistency in the data obtained. The longer Rb−O bond length is as expected, since ionization of the ionic RbOH molecule is largely a removal of an electron from OH$^-$, and so the interaction in the cation is expected to be charge−dipole rather than charge−charge. The nondegeneracy of the π bending levels is due to three effects: (i) the effect of small spin contamination, since unrestricted wave functions are employed; (ii) symmetry breaking in the wave function upon bending; (iii) the Renner−Teller effect. Further comments will be presented below in subsection b.

(ii) CsOH/CsOH$^+$. As with RbOH, the calculations on CsOH exhibit a good consistency (see Table 3). The Cs−O bond length is again longer than that derived in microwave studies, as with the RbOH results. Comparing with the ab initio results[6] of Bauschlicher et al., we see that their Cs−O bond length of 2.391 Å is slightly shorter than the values obtained herein but was obtained assuming a fixed O−H bond length on 0.9472 Å. Again, very good agreement occurs between the present results and the (thermally averaged) value from the electron diffraction study,[15] with the Cs−O bond length in CsOH being derived as 2.62 ± 0.01 Å therein. Again, we note our large basis sets, high level of theory, and especially the consistency in the calculated results.

TABLE 4: Optimized Geometrical Parameters and Computed Harmonic Vibrational Frequencies of Cs^+OH ($\tilde{X}^2\Pi$)

		frequencies[b] (cm^{-1})		
method[a]	bond lengths (Å)	ω_1 (σ)	ω_2 (π)	ω_3 (σ)
B3LYP/LANL2[9s8p3d];6-311++G(3d,3p)	CsO = 3.210; OH = 0.976	119	177, 320	3699
MP2/LANL2[9s8p3d];6-311++G(3d,3p)	CsO = 3.189; OH = 0.969	125	204, 337	3790
QCISD/LANL2[9s8p3d];6-311++G(3d,3p)	CsO = 3.197; OH = 0.970	124	195, 332	3755
CCSD(T)/LANL2[9s8p3d2f];aug-cc-pVTZ	CsO = 3.152; OH = 0.974	132	184, 314	3721

[a] All correlated calculations had O 1s frozen and Cs 1s2s2p3s3p3d4s4p4d represented by the ECP. All computed $\langle S^2\rangle \leq 0.760$. [b] See text for discussion of nondegenerate π vibrations.

TABLE 5: Optimized Geometrical Parameters and Computed Harmonic Vibrational Frequencies of FrOH ($\tilde{X}^1\Sigma^+$)

		frequencies (cm^{-1})		
method[a]	bond lengths (Å)	ω_1 (σ)	ω_2 (π)	ω_3 (σ)
B3LYP/CRENBL78[9s8p4d];6-311++G(3d,3p)	FrO = 2.500; OH = 0.958	351	313	3878
MP2/CRENBL78[9s8p4d];6-311++G(3d,3p)	FrO = 2.504; OH = 0.959	350	363	3886
QCISD/CRENBL78[9s8p4d];6-311++G(3d,3p)	FrO = 2.500; OH = 0.955	338	383	3908
CCSD(T)/CRENBL78[9s8p4d3f];aug-cc-pVTZ	FrO = 2.466; OH = 0.960	362	362	3865

[a] All correlated calculations had O 1s frozen and Fr 1s2s2p3s3p3d4s4p4d4f5s5p5d represented by the ECP.

TABLE 6: Optimized Geometrical Parameters and Computed Harmonic Vibrational Frequencies of Fr^+OH ($\tilde{X}^2\Pi$)

		frequencies[b] (cm^{-1})		
method[a]	bond lengths (Å)	ω_1 (σ)	ω_2 (π)	ω_3 (σ)
B3LYP/ CRENBL78[9s8p4d];6-311++G(3d,3p)	FrO = 3.173; OH = 0.976	118	156, 311	3697
MP2/ CRENBL78[9s8p4d];6-311++G(3d,3p)	FrO = 3.155; OH = 0.968	125	191, 330	3788
QCISD/ CRENBL78[9s8p4d];6-311++G(3d,3p)	FrO = 3.100; OH = 0.970	124	195, 332	3755
CCSD(T)/ CRENBL78[9s8p4d3f];aug-cc-pVTZ	FrO = 3.105; OH = 0.974	133	180, 313	3716

[a] All correlated calculations had O 1s frozen and Fr 1s2s2p3s3p3d4s4p4d4f5s5p5d represented by the ECP. All computed $\langle S^2\rangle \leq 0.760$. [b] See text for discussion of nondegenerate π vibrations.

With regard to the calculated vibrational frequencies, as with RbOH, some disparity occurs. Here, the π bending vibration is calculated to be higher in frequency than the Cs−O stretch. The unexpected energy ordering, when coupled with the presence of dimers, has almost certainly led to misassignment of the vibrational frequencies of CsOH. Comparing with the ω_1 value obtained by Bauschlicher et al.[6] of 378 cm^{-1} at the CISD level of theory, we see that again the values obtained herein at the highest levels of theory are a little lower. The agreement between the best calculated harmonic value of 346 cm^{-1} herein and the experimental fundamental value of 336 cm^{-1} is very good.

We also calculated the vibrational frequencies of CsOD at the MP2 and QCISD levels (see Table 3) and see the same behavior as reported in the microwave study: $\omega_{CsOH}/\omega_{CsOD} = 1.02$ for both the present calculated results and experimental Cs−O stretch frequencies; $\omega_{CsOH}/\omega_{CsOD} = 1.35$ for both the present calculated results and experimental bending frequencies; the calculated OH/OD stretching ratio is 1.37, close to the expected $\sqrt{2}$ value.

The results for $CsOH^+$ are given in Table 4. Reasonably consistent results are obtained between all levels of theory, and again, the nondegenerate π vibrational frequencies are noted (and will be discussed further in subsection b below). The recent JANAF tables[26] contained estimates of the vibrational frequencies of $CsOH^+$, with $\omega_1 = 300$ cm^{-1}, $\omega_2 = 275$ cm^{-1}, and $\omega_3 = 3600$ cm^{-1}. As may be seen from Table 4, ω_1 in particular seems to have been overestimated in ref 26.

(iii) FrOH/FrOH$^+$. Since there are no data to which to compare, we restrict ourselves to noting that there is good agreement between the four levels of theory for the calculated bond lengths of FrOH and that the calculated OH bond length is fairly close to the experimental value of 0.964 Å for OH^- but is slightly shorter (see the results in Table 5). It is an unexpected result that the calculated Fr−O bond length is shorter than that of the Cs−O one in CsOH. Initially one is tempted to attribute this to the different ECP employed for FrOH compared to RbOH and CsOH; however, for the alkali metal monoxides,[8] where the same ECP was employed, the Fr−O bond length in FrO was longer than the corresponding one in CsO. In addition, we note that the calculated atomic ionization energy for Fr was in excellent agreement with experiment.[8] It is worth noting here that a Mulliken population analysis indicated that for RbOH and CsOH largely ionic character is present, with the charge on the metal being ∼0.95*e* (see Table 7). For FrOH, however, the charge on the francium atom was ∼0.85, from which we infer that there is more covalent character in this species. We are fully aware of the limitations of Mulliken population analysis and therefore examined the molecular wave function. We conclude that covalency does indeed exist and is due to the involvement of the 6p electrons in the bonding. We find that the $n = 6$ shell increases in energy, leading to its being closer to the valence electrons. We found such an interaction in RaF_2,[36] which we concluded was adequate to describe the bent geometry of that species. (Note that Ra^{2+} is isoelectronic with Fr^+.) As we noted in ref 36, this interaction may be thought of in terms of polarization of the inner-valence region.

TABLE 7: Computed Charge of M in MOH and MOH^+, Where M = Rb, Cs, and Fr, Obtained from Mulliken Population Analyses at Different Levels of Calculations

	charge (in units of *e*) of M		
	Rb	Cs	Fr
	MOH		
MP2	0.944	0.951	0.864
QCISD	0.944	0.951	0.865
CCSD(T)	0.973	0.970	0.875
	MOH^+		
MP2	0.978	0.985	0.970
QCISD	0.976	0.985	0.971
CCSD(T)	1.004	0.998	0.994

TABLE 8: Computed AIEs and/or [VIEs] of RbOH at Different Levels of Calculations (Not Corrected for ZPVE)

	AIEs [VIEs] (eV)	
method	$RbOH^+$ ($\tilde{X}^2\Pi$)	$RbOH^+$ ($\tilde{A}^2\Sigma^+$)
B3LYP[a]	6.875	
MP2[a]	6.906	11.146[b]
QCISD[a]	6.563	
CCSD(T)[c]	6.824	
RCCSD[d,e]	6.951 [7.123]	[11.322]
RCCSD(T)[d,e]	7.129 [7.295]	[11.466]

[a] LANL2[7s6p3d];6-311++G(3d,3p). [b] The $\tilde{A}^2\Sigma^+$ state is a saddle point at the optimized linear geometry. [c] LANL2[7s6p3d2f];aug-cc-pVTZ. [d] At the respective CCSD(T)/LANL2[7s6p3d2f];aug-cc-pVTZ optimized geometry. [e] With the ECP28MWB[10s8p5d4f3g] basis set for Rb and the aug-cc-pV5Z(no h) basis for O and H.

TABLE 9: Computed AIEs and/or [VIEs] of CsOH at Different Levels of Calculations (Not Corrected for ZPVE)

	AIEs [VIEs] (eV)	
method	$CsOH^+$ ($\tilde{X}^2\Pi$)	$CsOH^+$ ($\tilde{A}^2\Sigma^+$)
B3LYP[a]	6.654	
MP2[a]	6.698	10.892[b]
QCISD[a]	6.353	
CCSD(T)[c]	6.633	
RCCSD[d,e]	6.911 [7.068]	[11.137]
RCCSD(T)[d,e]	7.092 [7.240]	[11.270]

[a] With the LANL2[9s8p3d];6-311++G(3d,3p) basis sets. [b] The $\tilde{A}^2\Sigma^+$ state is a saddle point at the optimized linear geometry. [c] With the LANL2[9s8p3d2f];aug-cc-pVTZ basis sets. [d] At the respective CCSD(T)/LANL2[9s8p3d2f];aug-cc-pVTZ optimized geometry. [e] With the ECP46MWB[10s8p5d4f3g] basis set for Cs and the aug-cc-pV5Z(no h) basis for O and H.

TABLE 10: Computed AIEs and/or [VIEs] of FrOH at Different Levels of Calculations (Not Corrected for ZPVE)

	AIEs [VIEs] (eV)	
method	$FrOH^+$ ($\tilde{X}^2\Pi$)	$FrOH^+$ ($\tilde{A}^2\Sigma^+$)
B3LYP[a]	7.117	
MP2[a]	7.127	11.006
QCISD[a]	6.755	10.766
CCSD(T)[b]	7.133	10.793
RCCSD[c,d]	7.059 [7.642]	10.827 [11.099]
RCCSD(T)[c,d]	7.255 [7.821]	10.857 [11.202]

[a] With the CRENBL[9s8p4d];6-311++G(3d,3p) basis sets. [b] With the CRENBL[9s8p4d3f];aug-cc-pVTZ basis sets. [c] At the respective CCSD(T)/CRENBL[9s8p4d3f];aug-cc-pVTZ optimized geometry. [d] With the CRENBL[11s10p5d4f3g] basis set for Fr and the aug-cc-pV5Z(no h) basis for O and H. The MOLPRO suite of programs were used.

The results for $FrOH^+$ are given in Table 6. Reasonably consistent results are obtained between all levels of theory, and again, the nondegenerate π vibrational frequencies are noted (and will be discussed further below).

(b) Ionization Energies. As noted in the Theoretical Methods, further single-point calculations were performed in order to obtain accurate ionization energies. Both adiabatic ionization energies (AIEs) and vertical ionization energies (VIEs) were obtained by making use of the appropriate geometries (see Tables 8−10). We have used the basis sets and methods previously for calculating the ionization energies for the monoxide species[8] where the error in the determination of the ionization energies of the alkali metal atoms was ascertained, and we also calculated the error in the calculation of the electron affinity of OH in the previous LiOH−KOH papers.[3−5] We thus estimate that the error in our calculated ionization energies from those effects will be about 0.03 eV.

As may be seen from Tables 8−10, the adiabatic energy for these three species is relatively low, as expected since the ionization is the removal of an electron essentially from OH^- but in the field of the alkali metal cation. Correcting the RCCSD(T) results for the zero-point vibrational energy, we arrive at “best” values for the AIEs of 7.09 eV for RbOH, 7.05 eV for CsOH, and 7.22 eV for FrOH. There are only a few experimental data to which to compare these values. First, Schoonmaker and Porter[37] observed the metal cation from electron impact ionization of the vapor above solid RbOH and CsOH. The appearance potential of these cations was ~10 eV, and so it can be concluded that AIE(RbOH, CsOH) $\leq$ 10 eV, since ionization of the neutral followed by dissociation of the cation had to occur. Emel’yanov et al. studied[38] the vapors above cesium hydroxide and obtained an appearance potential of 7.21 ± 0.14 eV, whereas similar experiments by Gorokhov et al. obtained a value of 7.40 ± 0.15 eV.[39] As may be seen from Table 9, these are in reasonable agreement with, but higher than, our best AIE value of 7.09 ± 0.03 eV. There is a reasonable geometry change upon ionization, and so it may be that the true onset has not been seen in the photoionization efficiency curves in refs 38 and 39. No other data appear to be available.

Since the MOH^+ species have $^2\Pi$ ground states, they will be subject to the Renner−Teller interaction and hence be expected to have two different bending vibrational frequencies corresponding to the $^2A'$ and $^2A''$ components. We previously found[3] that $LiOH^+$ was a quasilinear molecule because there was a calculated distortion from linearity in the r_e structure leading to a bent $^2A''$ component (and a linear $^2A'$ component) but that the barrier to linearity was smaller than the zero-point energy. For $NaOH^+$, again a bent $^2A''$ component was found, but it was almost isoenergetic with the linear structure.[4] For KOH^+, optimizations starting from a bent structure led back to a linear one for both the $^2A'$ and the $^2A''$ states.[5] Lee et al.[40] have described five different cases of the Renner−Teller effect, distinguishing between cases where both components have linear equilibrium geometries and cases where they both have nonlinear minima. Note, though, that methods such as UHF and ROHF do not treat a $^2\Pi$ state correctly, and so the resulting wave function will not necessarily be a correct description of the molecule at linearity because there is an inherent symmetry-breaking in that method (see, for example, ref 41). We have discussed this issue in ref 5 and noted that techniques such as the state-averaged CASSCF, which has been successfully applied to both Jahn−Teller[42] and pseudo Jahn−Teller[43] molecules, are probably required for these species.

We also include in Tables 8−10 some results for the VIE for the $\tilde{A}^2\Sigma^+$ state, as well as those for the $\tilde{X}$ state. Clearly the $^2\Sigma^+$ state is well above the ground state. Note that the linear geometry was calculated to be a saddle point in some cases, and therefore, this state is likely to be a bent $^2A'$ state. The AIE and the VIE are fairly close together for RbOH and CsOH, and both the ground-state neutral and the ground-state cation are linear. Thus, the first photoelectron band may be relatively simple in structure, although some complications may arise from the Renner−Teller effect.

(c) Dissociation Energies and ΔH_f^{298}. *(i) RbOH/$RbOH^+$.* Table 11 gives the dissociation energies for RbOH and $RbOH^+$. In the former case, dissociation energies to both neutral and ionic products are given, with the former being obtained from the latter, making use of the electron affinity (EA) of OH (1.828 eV)[34,35] and the ionization energy of Rb (4.177 eV).[26] In all cases, the full counterpoise correction (CP) was employed in order to account for basis set superposition error, where the optimized geometries were used in each case. Our best value

TABLE 11: Computed D_e (with CP) at RCCSD(T)/ECP28MWB[10s8p5d4f3g];aug-cc-pV5Z(no h) (Frozen O 1s) Level[a]

	D_e (kcal mol^{-1})	
	RCCSD	RCCSD(T)
$RbOH \rightarrow Rb^+ + OH^-$	133.5	133.3
$RbOH \rightarrow Rb + OH$	79.3	79.1
$Rb^+OH \rightarrow Rb^+ + OH$	10.8	10.8

[a] The RCCSD(T) E_{tot} for the ground states of RbOH and its cation at their respective minimum-energy geometries are −99.829 234 9 and −99.567 263 6 E_h.

TABLE 12: Computed D_e (with CP) at RCCSD(T)/ECP28MWB[10s8p5d4f3g];aug-cc-pV5Z(no h) (Frozen O 1s) Level[a]

	D_e (kcal mol^{-1})	
	RCCSD	RCCSD(T)
$CsOH \rightarrow Cs^+ + OH^-$	131.2	131.3
$CsOH \rightarrow Cs + OH$	83.5	83.6
$Cs^+OH \rightarrow Cs^+ + OH$	9.5	9.6

[a] The RCCSD(T) E_{tot} for the ground states of CsOH and its cation at their respective minimum-energy geometries are −95.886 383 9 and −95.625 763 2 E_h.

for D_e(RbOH) is 79 kcal mol^{-1}, which becomes 77 kcal mol^{-1} after correction for ZPVE, and is lower than the recent recommendation by Gurvich et al.[9] of 85 ± 1 kcal mol^{-1}. Note that the latter value was obtained from thermodynamic functions, which allowed the thermochemical quantities measured and/or derived from experiments at elevated temperatures to be corrected to 0 K. This correction involves use of vibrational frequencies and rotational constants, and as noted above, we believe that there is some misassignment of the former quantities in previous work. We also compare with the values obtained by Bauschlicher et al.[6] who obtained a value of 83 ± 2 kcal mol^{-1} at the CISD level of theory that is between our value and the Gurvich et al. recommendation. Stiakaki et al.[21] calculate $D_e = 82$ kcal mol^{-1}, and Mestdagh and Visticot[22] obtain $D_0 = 76$ kcal mol^{-1}, in excellent agreement with the value obtained herein. Our D_0 value may straightforwardly be converted to a ΔH_f^{298} value, yielding ΔH_f^{298}(RbOH) = −50 kcal mol^{-1}, which is less than the value of −57 ± 1 kcal mol^{-1} recommended in ref 9.

The dissociation energy of the cation is calculated to be $D_e = 10.8$ kcal mol^{-1}, which may be corrected for ZPVE to $D_0 = 9.8$ kcal mol^{-1}. This value is relatively small, but as noted above, this is expected owing to the loss of the charge−charge interaction upon ionization. The value is somewhat larger than that for RbO$^+$, 3.6 kcal mol^{-1},[8] owing to the presence of the dipole on OH in the RbOH$^+$ molecule. There appear to be no experimental values to which to compare for the cation.

(ii) CsOH and CsOH$^+$. The calculated dissociation energies for CsOH and CsOH$^+$ are given in Table 12. In all cases, the full counterpoise correction (CP) was employed in order to account for basis set superposition error, where the optimized geometries were used in each case and the EA of OH was used, as for RbOH, with IE(Cs) = 3.894 eV.[26] Our best value for the neutral is 83.6 kcal mol^{-1}, which may be corrected for ZPVE to $D_0 = 82$ kcal mol^{-1}, which may be seen to be lower than the recent recommendation[9] of 88 ± 1 kcal mol^{-1}, as was the case for RbOH. Similar comments apply here as were made for RbOH, since again we conclude herein that there has been misassignment of the vibrational frequencies for CsOH. We also note that Bauschlicher et al.[6] obtained a value of 87 ± 2 kcal mol^{-1}, which is close to the recommendation of Gurvich et al. Stiakaki et al.[21] calculate $D_e = 81$ kcal mol^{-1}, and Mestdagh and Visticot[22] obtain $D_0 = 81$ kcal mol^{-1}. Both of these are in good agreement with the value obtained herein. Again, our D_0 value may be straightforwardly converted to a ΔH_f^{298} value, yielding ΔH_f^{298}(CsOH) = −55.1 kcal mol^{-1}, which is less than the recommendation of −61.2 ± 1 kcal mol^{-1} from ref 9 and −62 ± 3 kcal mol^{-1} from JANAF.[26]

For the cation, we obtain $D_e = 9.6$ kcal mol^{-1}, which may be corrected to $D_0 = 8.8$ kcal mol^{-1}. As for RbOH, this value is significantly higher than that of the corresponding monoxide, D_0(CsO$^+$) = 3.0 kcal mol^{-1}.

TABLE 13: Computed D_e (with CP) at RCCSD(T)/CRE[11s10p5d4f3g];aug-cc-pV5Z(no h) (Frozen O 1s) Level[a]

	D_e (kcal mol^{-1})	
	RCCSD	RCCSD(T)
$FrOH \rightarrow Fr^+ + OH^-$	134.1	134.4
$FrOH \rightarrow Fr + OH$	83.2	83.5
$Fr^+OH\ (\tilde{X}^2\Pi) \rightarrow Fr^+ + OH\ (\tilde{X}^2\Pi)$	9.3	9.4

[a] The RCCSD(T) E_{tot} for the ground states of FrOH and the two lowest-lying of its cation at their respective minimum-energy geometries are −94.982 206 7 and −94.715 581 6 E_h, respectively.

(iii) FrOH and FrOH$^+$. Table 13 gives the corresponding values for FrOH and FrOH$^+$. In all cases, the full counterpoise correction (CP) was employed in order to account for basis set superposition error, where the optimized geometries were used in each case and EA(OH) was used as for RbOH, with IE(Fr) = 4.035 eV.[44] Our best value for the neutral is $D_e = 83.5$ kcal mol^{-1}, which may be corrected to $D_0 = 81.9$ kcal mol^{-1}. For the cation, we obtain $D_e = 9.4$ kcal mol^{-1}, which may be corrected to $D_0 = 8.5$ kcal mol^{-1}, which is significantly higher than D_0[FrO$^+$] = 2.8 kcal mol^{-1}. There are no experimental data to which to compare either of the two calculated values.

IV. Conclusions

High-level calculations have been performed employing methods up to the RCCSD(T) level and large valence basis sets together with quasirelativistic effective core potentials. Previous experience with such calculations suggests that these should be very reliable and able to produce results close to experiment. However, for RbOH and CsOH, we find large discrepancies with previously reported experimental values. The high consistency in the calculated values suggests that the results ought to be reliable.

For the Rb−O and Cs−O bond lengths, the experimental r_e values have been derived from B_e values that have in turn been derived from B_v values. It turns out that there is some uncertainty in the treatment of the rotational constants (obtained from microwave experiments) and the derivation of the equilibrium geometries from these. Consequently, we conclude that there is still some work to be done in this area. With regard to the vibrational frequencies, there is a wide range of values in the literature for the ω_1 and ω_2 values, with some estimates of ω_2 being significantly larger than the ω_1 value. The most-cited values are, however, the matrix isolation values. These latter values are based on an assignment that took into account annealing/temperature studies and deuteration. The presence of dimers (and possible other *n*-mers) complicates the issue, and it is very possible that a misassignment of these spectra has occurred. For RbOH and CsOH, we obtain good agreement for ω_1, but we conclude that it is likely that ω_2 has been misassigned. The above may possibly have affected the derivation of D_0 values from ΔH measurements at high temperatures. We therefore conclude that there is a necessity for remeasurement of the infrared spectra and that further consideration of the interpretation of the microwave measurements is needed in order to establish the molecular parameters of RbOH and CsOH more firmly.

There is reasonable agreement between the calculated ionization energies for CsOH. Clearly it would be desirable to have photoelectron measurements for RbOH and CsOH. The ground states of the cations are $^2\Pi$ and so will be subject to a Renner–Teller splitting. In addition, spin–orbit splitting in these states is expected to be very similar to that in free OH($X^2\Pi$), and so it will be approximately 126 cm^{-1}. Again, there is some disparity among the previous work on dissociation energies, but we find that we obtain good agreement with most previous calculations.

Our work on FrOH and its cation represents the only such data on this species.

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