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Structures and Heats of Formation of Simple Alkaline Earth Metal Compounds II: Fluorides, Chlorides, Oxides, and Hydroxides for Ba, Sr, and Ra

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Abstract

Geometry parameters, vibrational frequencies, heats of formation, bond dissociation energies, cohesive energies, and selected fluoride affinities (difluorides) are predicted for the late alkaline earth (Sr, Ba and Ra) oxides, fluorides, chlorides, and hydroxides at the coupled cluster theory [CCSD(T)] level. Additional corrections (scalar relativistic and pseudopotential corrections, vibrational zero-point energies, and atomic spin-orbit effects) were included to accurately calculate the total atomization energies and heats of formation following the Feller-Peterson-Dixon methodology. The calculated values are compared to the experimental data where available. In some cases, especially for Ra compounds, there are no experimental results or the experimental energetics and geometries are not reliable or have very large error bars. All of the Sr, Ba and Ra difluorides, dichlorides and dihydroxides are bent structures with the OMO bond angles decreasing going down the group. The cohesive energy of bulk Be dihalides are predicted to be quite low while those of Ra are relatively large. The fluoride affinities show that

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the difluorides are moderately strong Lewis acids and that such trifluorides may form under the appropriate experimental conditions.

Introduction

Simple alkaline earth compounds play an important role in flame chemistry[1,2,3] and in other high temperature regimes such as magnetohydrodynamic (MHD) plasmas[4] and stellar atmospheres.[5] Molecules containing Sr and Ba have also been observed in atmospheric release experiments.[6] Important species include the metal monohydroxides[7] and the oxides.[8] Severe nuclear accidents can release a wide range of species, and BaO and SrO are among those that have been considered in the gas phase from the interaction of the core with concrete.[9] The alkaline earth hydroxides may also play a role. Furthermore, molten salt nuclear reactors may generate various gas phase alkaline earth fluorides or chlorides depending on the anion used in the salt and the nuclear fission products, and thermodynamic information about these materials is needed.[10,11,12,13,14] In addition, one can obtain information about cohesive energies of solid materials by combining the calculated heats of formation of the gaseous species with the experimental heats of formation of the solid.[15,16]

Reliable structural, spectroscopic and thermodynamic information about alkali and alkaline earth compounds have previously been predicted using accurate computational chemistry methods[17,18] based on the Feller-Peterson-Dixon (FPD) composite approach.[19,20,21] The FPD approach is based on correlated molecular orbital theory using coupled cluster methods starting at the CCSD(T) level[22,23,24,25] extrapolated to the complete basis set (CBS) limit using the correlation consistent basis sets with additional corrections.[26,27,28,29,30,31] Additional high level calculations for the alkaline earth hydroxides, oxides, fluorides, and chlorides up to Ca have been previously reported.[32,33,34,35,36,37,38,39,40] Martin and co-workers[37] emphasized the need to include the core electrons in the correlation calculations. Recently, Neese and co-workers[41] have reported results at the CCSD(T) and DLPNO-CCSD(T) level for SrF_2, $SrCl_2$, BaF_2, $BaCl_2$, and BaO. They calculated a range of reaction energetics and compared them to experimental values and also emphasized the need to correlate the outer core electrons. In addition,

The recent design of systematically convergent, correlation consistent basis sets for the third, fourth and fifth row main group and transition elements using relativistic effective core potentials[42,43,44,45,46] has been essential to the application of highly accurate correlation methods. With the new basis sets developed by Hill, Peterson, and co-workers[47,48] for M = Sr, Ba and Ra, we can expand our predictions of the thermodynamic properties of the alkaline earth metals. Herein, we report the properties of M = Sr, Ba, and Ra halides (chlorides and fluorides), oxides and hydroxides.

Computational Methods

We used the coupled-cluster method at the CCSD(T) level including core-valence (CV) correlation corrections with the aug-cc-pV*n*Z (H)/aug-cc-pwCV*n*Z (O, F, Cl)/aug-cc-pwCV*n*Z-PP (Sr, Ba, Ra) basis sets for n = D, T, Q and 5 (abbreviated as awCV*n*Z) to predict the structural characteristics and thermodynamic properties of the alkaline earth compounds for M = Sr, Ba, and Ra fluorides, chlorides, oxides and hydroxides.[26,27,47,49] The 28 electrons in the 1s2s2p3s3p3d orbitals of Sr, the 46 electrons in the 1s2s2p3s3p3d4s4p4d orbitals of Ba, and the 78 electrons in the 1s through 5d orbitals of Ra are replaced by relativistic energy-consistent pseudopotentials (PPs).[50] Equilibrium geometries were optimized at the CCSD(T)(CV)/awCV*n*Z level with n = D and T, except for the diatomic compounds which were optimized with n = D, T and Q. The CCSD(T) total energies were extrapolated to the CBS limit by using Eq. 1[51,52] for basis sets with n = 4 and 5 (awCVQZ and awCV5Z)

$$E(n) = E_{\mathrm{CBS}} + A/[n + 0.5]^4 \qquad (1)$$

We label the values obtained from Eq. 1 as CBS-Q5. Alternative extrapolated values using a mixed Gaussian/exponential (Eq. 2) for n=2-4:[53]

$$E(n) = E_{\mathrm{CBS}} + B \exp[-(n-1)] + C \exp[-(n-1)^2] \qquad (2)$$

are given in the Supporting Information.

The harmonic frequencies (ω_e) and anharmonic constants ($\omega_e x_e$) of the diatomic molecules were obtained at the CCSD(T)/awCVQZ level using a 7-point Dunham expansion.[54,55] Harmonic vibrational frequencies for the remaining alkaline earth compounds were calculated at the CCSD(T)/awCVTZ level. The anharmonic corrections[56,57,58] of the closed shell polyatomic molecules were calculated via 2nd-order vibrational perturbation theory at the MP2[59,60]/awCVTZ/wCVTZ-PP(Sr,Ba,Ra) level using Gaussian09 (Supporting Information).[61] For the MOH compounds, the anharmonic corrections were obtained from analytical fits (polynomials in simple displacement coordinates) to the near-equilibrium potential energy surfaces (defined by 50 symmetry-unique geometries) at the MP2/awCVTZ/wCVTZ-PP(Sr,Ba,Ra) level using Molpro[62,63] and the Surfit program.[64] The appropriate frequencies were used in the zero point energy (ZPE) corrections to the total atomization energy.

Total atomization energies (TAEs or ΣD_0) at 0 K were calculated from the following expression (Eq. 3) with ΔE referring to the difference between the molecule (reactant) and the atomic products for each energy component:

$$\Sigma D_0 = \Delta E_{\mathrm{CBS}} + \Delta E_{\mathrm{rel}} + \Delta E_{\mathrm{ZPE}} + \Delta E_{\mathrm{SO}} \qquad (3)$$

Additional corrections to the CCSD(T)/CBS energy (ΔE_{CBS}) are necessary to reach chemical accuracy (±1 kcal/mol). Scalar relativistic corrections for light elements together with corrections for the PP approximation, ΔE_{rel}, were obtained using the 2nd or 3rd order Douglas-Kroll-Hess (DKH) Hamiltonian at the CCSD(T)/aug-cc-pwCVTZ-DK[48,65] level of theory (abbreviated as awCV*n*Z-DK). The atomic spin-orbit corrections, $\Delta E_{SO} = \{\Sigma_J[(2J + 1)\cdot E(J)]\}/[\Sigma_J(2J + 1)]$, were calculated from the experimental values for the ground states of the atoms using Moore's tables[66] (ΔE_{SO}(O) = -0.22, ΔE_{SO}(F) = -0.39, ΔE_{SO}(Cl) = -0.84 kcal/mol and 0 kcal/mol for H, Sr, Ba and Ra).

Heats of formation at 0 K were calculated by combining our computed ΣD_0 values with the known enthalpies of formation at 0 K for the elements[67] [$\Delta H_{f,0K}$(O) = 58.98 ± 0.02, $\Delta H_{f,0K}$(F) = 18.47 ± 0.07, $\Delta H_{f,0K}$(Cl) = 28.59, $\Delta H_{f,0K}$(H) = 51.63, $\Delta H_{f,0K}$(Sr) = 39.3 ± 0.4, and $\Delta H_{f,0K}$(Ba) = 43.0 ± 1.2 kcal/mol]. Two values for $\Delta H_{f,0K}$(Ra) of 36.35 kcal/mol[68] and 38.95 ± 2.0 kcal/mol[69] have been reported. Since we cannot distinguish which one is better without reliable data for other Ra containing compounds determined independently of this gas phase value, we report results using both atomic heats of formation. Heats of formation at 298 K were calculated by following the procedures outlined by Curtiss et al.[70]

The CCSD(T) calculations were performed with the MOLPRO 2012.1 program package.[62,63] The open-shell calculations were done with the R/UCCSD(T) approach where a restricted open shell Hartree-Fock (ROHF) calculation was initially performed and the spin constraint was then relaxed in the coupled cluster calculation.[24,71,72,73] The calculations were mainly performed on Linux clusters at The University of Alabama.

Results and Discussion

Geometries The optimized geometries of the diatomic Sr, Ba and Ra compounds are reported in Table 1 and compared to the available experimental values. The M-A bond distances of the diatomics where M = Sr, Ba or Ra and A = O, Cl or F are in good agreement with experiment.[74,75,76,77,78,79,80,81,82,83,84,85] In general, the calculated Sr-O and Ba-O bond distances are longer than experiment by about 0.01 Å suggesting that a similar error is likely for Ra-O, where the experimental data has not been reported. The Ba-O bond is only slightly longer than the SrO bond and there is a much larger difference between RaO and BaO for the bond distance. The monofluorides and monochlorides exhibit a similar difference of 0.01 Å between the CCSD(T) values and experiment for Sr and Ba. The trends in the M-X bond distances are different from the M-O bond distances as there is an approximately equal spacing between the Sr-F, Ba-F and Ra- F bonds and a similar but larger spacing between the M-Cl bonds.

Table 1. CCSD(T) Calculated and Experimental Bond Distances in Å for the Alkaline Earth Metal Oxides, Monochlorides and Monofluorides.

Molecule	awCVQZ	awCV5Z	awCVQZ-DK[a]	Expt.
SrO ($^1\Sigma^+$)	1.935	1.929	1.927	1.919809[77,78,80, 85]
BaO ($^1\Sigma^+$)	1.947	1.943	1.950	1.939630[74,75,77, 78,80,81,85]
RaO ($^1\Sigma^+$)	2.061	2.052	2.052	
SrF ($^2\Sigma^+$)	2.085	2.082	2.082	2.07537[84,85]
BaF ($^2\Sigma^+$)	2.172	2.168	2.177	2.163[77,85]
RaF ($^2\Sigma^+$)	2.262	2.256	2.253	
SrCl ($^2\Sigma^+$)	2.588	2.584	2.599	2.576[80,83,84]
BaCl ($^2\Sigma^+$)	2.701	2.694	2.700	2.682765(10)
RaCl ($^2\Sigma^+$)	2.801	2.794	2.802	

[a] Using DKH2 for Sr compounds and DKH3 for Ba and Ra compounds. The O and F 1s, and Cl 2s and 2p orbitals have been rotated into the correlated electron space.

Based partially on the diatomic results above, the current predicted geometries for the triatomic dihalides (Table 2) should be more reliable than the estimated values reported in the JANAF Tables.[67] The values in the JANAF Tables are not directly measured for the isolated molecules but are derived from krypton matrix isolation infrared spectroscopy measurements in combination with a normal coordinate/force field analysis.[86,87] We now discuss the periodic trends in the bending angle in the Group 2 dihalides. BeF_2 is a linear molecule from both experiment and theory.[18,88] MgF_2 is predicted at the CCSD(T)/awCVTZ level[18] to be linear in contrast to some of the experimental data. Krypton matrix isolation infrared spectroscopy measurements have been interpreted to show that the molecule is bent with an $\angle$FMgF = 158°[89] but electron diffraction[90] and beam deflection measurements[91] suggest a linear structure, consistent with the CCSD(T) one. The low calculated bending frequency of 154 cm^{-1} suggests that the Kr matrix is causing a bent structure. Hassett and Marsden[40] examined the effect of the basis set and correlation level on the bending frequency for linear MgF_2 and found modest effects. CaF_2 is predicted[18] to have a bent structure with $\angle$FCaF = 157°, consistent with the experimental result that CaF_2 has a permanent electric dipole moment.[88,92] As found for MgF_2, the experimental $\angle$FCaF angle of 135 ± 7° derived from a Kr matrix isolation experiment is 20° smaller than our calculated value.[86] Hassett and Marsden[93] examined the effect of the basis set on the angle for CaF_2 at the Hartree-Fock level and found that large d-orbital basis sets are needed to find a bent structure. Kaupp et al.[94] predicted that CaF_2 is bent with a bond angle of 157.5º ad the CISD+Q (configuration interaction single and doubles with the Davidson correction) level with a 6s6p5d1f valence basis set with a pseudopotential on the Ca. The trend in the difluorides being bent beginning at CaF_2 continues for the heavier Group 2 elements with the bond angle decreasing from Sr to Ra, with a much smaller difference between Ba and Ra than between Sr and Ba. Kaupp et al.[94] predict SrF_2 and BaF_2 to be bent with bond angles of 138.8º and 123.0º at the level given above consistent with our CCSD(T) results.

$BeCl_2$, $MgCl_2$, and $CaCl_2$ are all predicted[18] to be linear molecules in agreement with experiment.[67,95,96] and the results of Kaupp et al.[94] at the CISD+Q level. The potential energy surface for bending in $SrCl_2$ is very flat and the linear structure is only 0.04 kcal/mol above the structure with an angle of 160°. This leads to a very anharmonic bend with a very low bending frequency of 7 cm^{-1} as compared to a harmonic value of 26 cm^{-1}. Hargittai and co-workers[97] have studied $SrCl_2$ in detail experimentally using high temperature (1500 K) electron diffraction and computationally at the MP2 level including all electrons with large basis sets. They also checked their MP2 results with limited CCSD(T) calculations. They describe $SrCl_2$ as being quasilinear and having a complex bending potential. They also showed that the angle is very temperature dependent. They predict the molecule to be bent with a bond angle between 155º and 160º. They predict a harmonic bending frequency of 25.5 cm^{-1} as predicted by us with a barrier to linearity of 0.1 kcal/mol. They solved for the frequencies in a one-dimensional approximation but did not report the values for the bend except to note that the results show splitting due to the presence of the small barrier and that the ZPE is quite low. All of the results for $SrCl_2$ point to a very low frequency bend with a contribution to the ZPE of < 0.05 kcal/mol. The bond angles for $BaCl_2$ and $RaCl_2$ are significantly smaller, both near 130° and the molecules are clearly bent. The bond angles for the chlorides are larger than for the fluorides. The CISD+Q results of Kaupp et al.[94] are consistent with our results for the bond angles of $SrCl_2$ and $BaCl_2$.

Table 2. Calculated [CCSD(T)/awCVTZ] and Experimental Bond Distances and Angles for the Alkaline Earth Fluorides and Chlorides.

Molecule	CCSD(T) M–X (Å)	Expt.[67] M–X (Å)	CCSD(T) ∠XMX (°)	Expt.[67] ∠XMX (°)
SrF_2 ($^1A_1$, C_{2v})	2.139	2.20 ± 0.03	136.4	108
BaF_2 ($^1A_1$, C_{2v})	2.246	2.32 ± 0.03	123.1	[95]
RaF_2 ($^1A_1$, C_{2v})	2.321		120.7	
$SrCl_2$ ($^1A_1$, C_{2v})	2.635	2.67 ± 0.03 2.625 ± 0.010[a] 2.606 ± 0.008[a]	161.4	120 ± 20 142.4 ± 4.0[a]
$BaCl_2$ ($^1A_1$, C_{2v})	2.761	2.82 ± 0.03	133.5	100 ± 20
$RaCl_2$ ($^1A_1$, C_{2v})	2.845		130.4	

[a] Ref. 97. First bond distance is measured value at 1500 K. Second bond distance is thermally corrected value. The angle is the value at 1500 K.

The geometry parameters for the mono and dihydroxides are reported in Table 3. The triatomic monohydroxides are linear.[98,99,100,101,102] The M-O bond distances (Table 3) follow the same patterns as for the fluorides. The bond distances are in reasonable agreement with the values reported in the JANAF Tables.[67] The dihydroxides are bent with larger OMO bond angles than found for the difluorides but smaller than for the dichlorides. The M-OH bond angles for the dihydroxides are no longer linear and deviate by about 5 - 10° from linearity. The bond distance down the column increases from Sr to Ra following the pattern of the difluorides.

Table 3. Calculated [CCSD(T)/awCVTZ] and Experimental Bond Distances and Angles for the Alkaline Earths Hydroxides.

Molecule	CCSD(T) M–O (Å)	CCSD(T) O–H (Å)	CCSD(T) ∠OMO (°)	CCSD(T) ∠MOH (°)	Expt.[67] M–O (Å)
SrOH ($^2\Sigma^+$, $C_{\infty v}$)	2.118	0.955		180.0	2.111
BaOH ($^2\Sigma^+$, $C_{\infty v}$)	2.220	0.957		180.0	2.201
RaOH ($^2\Sigma^+$, $C_{\infty v}$)	2.306	0.957		180.0	
$Sr(OH)_2$ ($^1A_1$, C_{2v})	2.176	0.955	151.0	174.5	
$Ba(OH)_2$ ($^1A_1$, C_{2v})	2.291	0.957	128.9	169.8	
$Ra(OH)_2$ ($^1A_1$, C_{2v})	2.365	0.957	125.6	169.7	

Vibrational Frequencies The vibrational frequencies for the diatomics are given in Table 4. The frequencies for SrO and BaO are less than experiment by 5-15 cm^{-1} for ω_e due to the predicted bond lengths being longer than the experimental values. The values for $\omega_e x_e$ are larger than experiment by about 1 cm^{-1} for SrO[77,78,80] and essentially identical to experiment for BaO.[74,75,77,78,80,81] The value for $\omega_e x_e$ for RaO is predicted to be larger than for BaO.

Table 4. CCSD(T) Calculated and Experimental Harmonic Frequencies (ω_e) and Anharmonicities ($\omega_e x_e$) in cm^{-1} for the Alkaline Earth Metal Oxides, Monochlorides and Monofluorides.

Molecule	ω_e				$\omega_e x_e$			
	awCVQZ	awCV5Z	awCVQZ-DK[a,b]	Expt.	awCVQZ	awCV5Z	awCVQZ-DK[a,b]	Expt.
SrO ($^1\Sigma^+$)	639.4	647.0	646.0	653.49[77,78,80]	5.00	4.58	4.64	3.96
BaO ($^1\Sigma^+$)	660.3	663.3	666.0	669.76[74,75,77, 78,80,81]	1.98	1.92	1.99	2.028
RaO ($^1\Sigma^+$)	596.5	603.2	611.9		2.98	2.58	2.61	
SrF ($^2\Sigma^+$)	499.5	500.6	500.6	502.4[84]	2.17	2.19	2.47	2.27
BaF ($^2\Sigma^+$)	463.4	465.9	465.1	468.9[77]	1.84	1.84	1.86	1.79
RaF ($^2\Sigma^+$)	432.8	435.0	434.6		1.65	1.70	1.51	
SrCl ($^2\Sigma^+$)	300.8	301.4	290.0	302.3[80,83,84]	1.10	0.96	1.30	0.95
BaCl ($^2\Sigma^+$)	276.3	278.4	276.9	279.3[85]	0.79	0.84	0.96	0.89
RaCl ($^2\Sigma^+$)	253.6	254.5	250.5		0.70	0.73	0.73	

[a] Using DKH2 for Sr compounds and DKH3 for Ba and Ra compounds.

[b] The O and F 1s, and Cl 2s and 2p orbitals have been rotated into the correlated electron space.

Table 5. Calculated [CCSD(T)/awCVTZ] and Experimental Vibrational Frequencies in cm^{-1} for the Alkaline Earth Dihalides.

Molecule	Symmetry	Calculated CCSD(T)/awCVTZ	Anharm corrected[a]	Expt.[67]
SrF_2 ($^1A_1$)	ν_1(sym stretch - b_2)	478.3	473.7	443
	ν_2(asym stretch - a_1)	469.9	465.2	442
	ν_3(bending - a_1)	75.9	72.7	82
BaF_2 ($^1A_1$)	ν_1(sym stretch - a_1)	437.4	433.7	413
	ν_2(asym stretch - b_2)	418.5	414.8	390
	ν_3(bending - a_1)	88.0	86.3	[64]
RaF_2 ($^1A_1$)	ν_1(sym stretch - a_1)	418.4	415.2	
	ν_2(asym stretch - b_2)	397.4	394.3	
	ν_3(bending - a_1)	79.8	78.0	
$SrCl_2$($^1A_1$)[b]	ν_1(asym stretch - b_2)	313.0	310.9	300
	ν_2(sym stretch - a_1)	262.7	260.1	270
	ν_3(bending - a_1)	26.1	7.7	44
$BaCl_2$ ($^1A_1$)	ν_1(asym stretch - b_2)	259.7	258.8	265
	ν_2(sym stretch - a_1)	270.0	267.2	255
	ν_3(bending - a_1)	41.1	39.7	[36]
$RaCl_2$ ($^1A_1$)	ν_1(asym stretch - b_2)	248.0	247.2	
	ν_2(sym stretch - a_1)	247.6	246.9	
	ν_3(bending - a_1)	37.7	37.8	

[a] CCSD(T)/awCVTZ with anharmonic corrections from MP2/awCVTZ/wCVTZ-PP(Sr,Ba,Ra).

[b] The frequencies for $SrCl_2$ were evaluated at 160°.

The values for ω_e are within about 5 cm^{-1} of experiment for diatomic M-F, and the M-F values are in better agreement with experiment[77,84] than for diatomic M-O. Again, the M-F values are lower than experiment consistent with the predicted bond lengths being too long. For the diatomic chlorides, all of the results are within 5 cm^{-1} of experiment[,80,83,84,85] except for the awCVQZ-DK result for SrCl where the difference is about 10 cm^{-1}. The estimated values in the JANAF Tables[67] are consistent with our calculated values including anharmonic corrections for the difluorides and dichlorides (Table 5). $SrCl_2$ is discussed in more detail above.

For the monohydroxides, the calculated Sr-O stretch for SrOH is essentially the same as the reported experimental value and the SrOH bend is ~12 cm^{-1} above the experimental value.[98,99] For BaOH, the calculated Ba-O stretch is in within 10 cm^{-1} of experiment and the calculated bend is too high by about 20 cm^{-1}.[100] For $Ba(OH)_2$, the two calculated OH stretches are within better than 10 cm^{-1} of experiment.[102] In this case, the agreement with experiment for the two Ba-O stretches is not as good suggesting a possible role for matrix effects.

Heats of Formation As the TAEs are the prime component of the heats of formation predictions, these are discussed first. The CBS-DTQ TAEs (Supporting Information) obtained with Eq. 2 are mostly within 0.5 kcal/mol of the CBS-Q5 values calculated with Eq. 1. The components for the total CBS-Q5 atomization energies are given in Table 7 and the heats of formation are given in Table 8. The comparison to experiment for the diatomic dissociation energies is given below in the discussion of the bond energies. The T_1 diagnostic values[103] (Supporting Information) show that the wavefunctions are dominated by a single configuration. The largest T_1 values are for the monoxides. We found that there are no doubles amplitude values above 0.05 for any of these monoxides, so they are truly dominated by a single configuration. In our previous work on BeO and MgO,[18] we found that there was one doubles amplitude above 0.05 for BeO and MgO with that for MgO being the largest. For these two molecules, calculations were performed up to CCSDTQ and the correction was found to be 0.98 kcal/mol to the total atomization energy. Thus the corrections for higher order excitations will be smaller than this value for SrO, BaO, and RaO as they have even less multi-reference character.

The only additional contribution to the total atomization energy to be discussed is that of ΔE_{rel} which includes a pseudopotential correction and scalar relativistic corrections for O, F, and Cl. The values of this correction range from -1.9 to +2.3 kcal/mol. The largest ΔE_{rel} corrections

Table 6. Calculated and Experimental Vibrational Frequencies in cm^{-1} for the Alkaline Earth Hydroxides.

Molecule	Symmetry	Calculated[a]	Anharm corrected[b]	Expt.
SrOH($^2\Sigma^+$)	ν_1(O-H stretch - σ)	3935.7	3766.9	3766 ± 10[98]
	ν_2(Sr-O stretch - σ)	536.6	523.6	526.99[99]
	ν_3(Sr-O-H bend - π)	400.6	375.3	363.69[99]
BaOH($^2\Sigma^+$)	ν_1(O-H stretch - σ)	3904.0	3734.9	
	ν_2(Ba-O stretch - σ)	493.6	483.1	494.4 ± 0.8[100]
	ν_3(Ba-O-H bend - π)	379.9	363.7	341.6 ± 0.6[100]
RaOH($^2\Sigma^+$)	ν_1(O-H stretch - σ)	3903.7	3733.7	
	ν_2(Ba-O stretch - σ)	461.5	451.6	
	ν_3(Ba-O-H bend - π)	378.7	366.5	
Sr(OH)$_2$ ($^1A_1$)	ν_1(O-H sym stretch - b_2)	3931.8	3763.7	
	ν_2(O-H asym stretch - a_1)	3930.7	3762.7	
	ν_3(O-Sr-O sym stretch - b_2)	508.7	496.4	
	ν_4(O-Sr-O asym stretch - a_1)	500.3	489.0	
	ν_5(H-O out-of-plane-wag - a_2)	454.6	419.2	
	ν_6(H-O out-of-plane-twist - b_1)	449.7	418.6	
	ν_7(H-O in-plane-wag - a_1)	444.8	415.3	
	ν_8(H-O in-plane-twist - b_2)	440.2	405.2	
	ν_9(O-Sr-O bend - a_1)	44.8	43.0	
Ba(OH)$_2$ ($^1A_1$)	ν_1(O-H sym stretch - b_2)	3897.4	3725.8	3723[102]
	ν_2(O-H asym stretch - a_1)	3897.0	3725.3	3718[102]
	ν_3(O-Ba-O sym stretch - a_1)	469.7	387.4	410[102]
	ν_4(O-Ba-O asym stretch - b_2)	442.2	374.7	422.8[102]
	ν_5(H-O out-of-plane-wag - a_2)	425.0	389.8	
	ν_6(H-O out-of-plane-twist - b_1)	422.1	359.2	
	ν_7(H-O in-plane-wag - a_1)	405.3	317.9	
	ν_8(H-O in-plane-twist - b_2)	384.9	370.3	
	ν_9(O-Ba-O bend - a_1)	72.2	76.4	
Ra(OH)$_2$ ($^1A_1$)	ν_1(O-H sym stretch - b_2)	3898.0	3730.7	
	ν_2(O-H asym stretch - a_1)	3897.8	3730.7	
	ν_3(O-Ra-O sym stretch - a_1)	451.6	442.0	
	ν_4(O-Ra-O asym stretch - b_2)	422.4	402.4	
	ν_5(H-O out-of-plane-wag - a_2)	416.0	397.8	
	ν_6(H-O out-of-plane-twist - b_1)	415.6	404.7	

	ν_7(H-O in-plane-wag - a_1)	399.5	375.3	
	ν_8(H-O in-plane-twist - b_2)	378.6	357.9	
	ν_9(O-Ra-O bend - a_1)	67.1	67.3	

[a] CCSD(T)/awCVTZ. [b] CCSD(T)/awCVTZ with Anharmonic correction from MP2/awCVTZ /wCVTZ-PP(Sr,Ba,Ra) and UMP2/awCVTZ /wCVTZ-PP(Sr,Ba,Ra) for open shells.

are found for compounds containing Ra. For all atoms, the oxides show the largest corrections with that for BaO being -1.9 kcal/mol and that for RaO being +2.2 kcal/mol. The value for SrO is 1.3 kcal/mol. We note that the only other two large corrections are for RaF of 0.8 kcal/mol and for RaF_2 of 1.1 kcal/mol.

The experimental heats of formation and the corresponding bond dissociation energies of SrO and BaO have been previously reviewed.[8] For SrO, the heat of formation is within the experimental[8,67] error bars of ±4 kcal/mol and very similar to the value derived in a review from spectroscopic measurements.[8] For BaO, the calculated heat of formation is in very good agreement with the experiment; within the ±1.9 kcal/mol error bar for the more negative experimental value,[67] and is significantly more negative than the average value given in a review.[8] Thus, we suggest that the experimental value for the heat of formation from thermodynamic Knudsen cell measurements of BaO be further examined, and we confirm the value for SrO derived from the spectroscopic information. The heats of formation of SrF and BaF are in excellent agreement with experiment[67] considering the ±2 kcal/mol error bars from experiment. The same is true for SrCl and BaCl and we note that the BaCl experimental[67] error bar is larger at ±3 kcal/mol.

For the difluorides, the calculated heats of formation are significantly more negative than the experimental values[67] which have small error bars of ±1 kcal/mol suggesting an issue with the experimental values. We note that the heats of formation of the dichlorides are closer to experiment, with $BaCl_2$ just outside of the experimental[67] ±4 kcal/mol error bars.

Table 7. CCSD(T) Calculated and Experimental Total Atomization Energies at 0 K in kcal/mol.

Molecule	ΔE_{CBS}[a]	ΔE_{rel}[b]	ΔE_{ZPE}[c]	ΔE_{SO}[d]	$\Sigma D_{0,0K}$	
					CCSD(T)[e]	Expt.
SrO ($^1\Sigma^+$)	98.62	1.30	-0.92	-0.22	98.79	101.9±1.5 (298 K)[105] 115.53[85]
BaO ($^1\Sigma^+$)	134.20	-1.89	-0.95	-0.22	131.15	134.3±3.2 (298 K)[105] 133.52[85]
RaO ($^1\Sigma^+$)	106.44	2.22	-0.85	-0.22	107.58	
SrF ($^2\Sigma^+$)	128.48	0.02	-0.72	-0.39	127.40	128.67[85]
BaF ($^2\Sigma^+$)	138.81	-0.25	-0.66	-0.39	137.50	139.51[85]
RaF ($^2\Sigma^+$)	128.01	0.82	-0.62	-0.39	127.82	
SrCl ($^2\Sigma^+$)	99.97	-0.10	-0.43	-0.84	98.60	97.8 (298 K)[105] 95.92[85]
BaCl ($^2\Sigma^+$)	109.24	0.16	-0.40	-0.84	108.16	104.92[85]
RaCl ($^2\Sigma^+$)	99.97	0.22	-0.36	-0.84	98.99	82±18[69]
SrF_2 ($^1A_1$)	266.47	-0.25	-1.45	-0.78	264.98	
BaF_2 ($^1A_1$)	279.59	-0.03	-1.35	-0.78	277.43	
RaF_2 ($^1A_1$)	261.84	1.08	-1.28	-0.78	260.86	
$SrCl_2$ ($^1\Sigma_g$)	214.74	-0.21	-0.80	-1.68	212.05	
$BaCl_2$ ($^1A_1$)	226.42	0.13	-0.76	-1.68	224.11	
$RaCl_2$ ($^1A_1$)	210.68	0.15	-0.71	-1.68	208.44	
SrOH ($^2\Sigma^+$)	203.75	-0.16	-7.42	-0.22	195.94	
BaOH ($^2\Sigma^+$)	213.66	-0.10	-7.27	-0.22	206.07	
RaOH ($^2\Sigma^+$)	202.28	0.63	-7.23	-0.22	195.47	
$Sr(OH)_2$ ($^1A_1$)	417.71	-0.68	-15.02	-0.44	401.57	
$Ba(OH)_2$ ($^1A_1$)	428.29	-0.02	-14.48	-0.44	413.34	
$Ra(OH)_2$ ($^1A_1$)	410.25	0.61	-14.55	-0.44	395.87	

[a] Extrapolated CCSD(T)/awCV*n*Z energies with n = Q and 5 using Eq. 1. [b] $\Delta E_{rel} = \Delta E_{awCVTZ\text{-}DK} - \Delta E_{awCVTZ}$. [c] CCSD(T)/awCV*n*Z, n = Q for diatomics and n = T for the rest including anharmonic corrections from MP2/awCVTZ/wCVTZ-PP(Sr,Ba,Ra) (see supporting Information). [d] Experimental atomic spin-orbit corrections (-0.22, -0.84 and -0.39 kcal/mol for O, Cl and F and 0 kcal/mol for H, Sr, Ba and Ra); Reference 66. [e] Eq. 3: $\Sigma D_0 = \Delta E_{CBS} + \Delta E_{rel} + \Delta E_{ZPE} + \Delta E_{SO}$.

Table 8. CCSD(T) Calculated and Experimental Heats of Formation at 0 K and 298 K in kcal/mol.[a]

Molecule	$\Delta H_{f,0K}$		$\Delta H_{f,298K}$	
	CCSD(T)	Expt.[67]	CCSD(T)	Expt.[67]
SrO ($^1\Sigma^+$)	-0.5	-2.8 ± 4.0	-1.0	-3.2 ± 4.0 0.4 ± 3.6[8]
BaO ($^1\Sigma^+$)	-29.2	-29.1 ± 1.9	-29.7	-29.6 ± 1.9 -26.9 ± 1.2[8]
RaO ($^1\Sigma^+$)	-12.3/-9.7		-12.8/-10.2	
SrF ($^2\Sigma^+$)	-69.6	-70.0 ± 2.0	-70.0	-70.4 ± 2.0
BaF ($^2\Sigma^+$)	-76.0	-76.5 ± 2.0	-76.5	-77.0 ± 2.0
RaF ($^2\Sigma^+$)	-73.0/-70.4		-73.4/-70.8	
SrCl ($^2\Sigma^+$)	-30.7	-29.3 ± 2.0	-31.0	-29.6 ± 2.0
BaCl ($^2\Sigma^+$)	-36.6	-33.6 ± 3.0	-37.0	-34.0 ± 3.0
RaCl ($^2\Sigma^+$)	-34.0/-31.4		-34.4/-31.8	
SrF_2 ($^1A_1$)	-187.7	-182.6 ± 1.0	-188.3	-183.1 ± 1.0
BaF_2 ($^1A_1$)	-197.5	-191.6 ± 1.5	-198.1	-192.1 ± 1.5
RaF_2 ($^1A_1$)	-187.6/-185.0		-188.1/-185.5	
$SrCl_2$ ($^1\Sigma_g$)	-115.6	-112.8 ± 1.5	-116.7	-113.1 ± 1.5
$BaCl_2$ ($^1A_1$)	-123.9	-118.9 ± 4.0	-124.3	-119.2 ± 4.0
$RaCl_2$ ($^1A_1$)	-114.9/-112.3		-115.2/-112.6	
SrOH ($^2\Sigma^+$)	-46.0	-48.11 ± 5.0	-47.0	-49.1 ± 5.0
BaOH ($^2\Sigma^+$)	-52.5	-53 ± 7	-53.4	-54 ± 7
RaOH ($^2\Sigma^+$)	-48.5/-45.9		-49.5/-46.9	
$Sr(OH)_2$ ($^1A_1$)	-141.0	-141 ± 10	-143.6	-142 ± 10
$Ba(OH)_2$ ($^1A_1$)	-149.1	-148 ± 9	-151.8	-150 ± 9
$Ra(OH)_2$ ($^1A_1$)	-138.3/-135.7		-140.0/-137.4	

[a] The Ra values are given in the order of using the heat of formation of Ra, $\Delta H_{f,0K}$(Ra) = 36.35 kcal/mol from Ref. 68 and after the slash $\Delta H_{f,0K}$(Ra) = 38.95 ± 2.0 kcal/mol from Ref 69.

For the monohydroxides, the calculated heats of formation are within the range of the rather large experimental[67] error bars of up to ±7 kcal/mol, with the calculated values within 1 to

2 kcal/mol of experiment. For the dihydroxides, the calculated values are in excellent agreement with experiment[67] even though there are very large error bars.

Neese and co-workers[41] calculated the energies of reaction 4 where M = Sr, Ba and X = F, Cl at the CCSD(T) and DLPNO-CCSD(T) levels of theory. We can also calculate these values from the current heats of formation

$$M(g) + X_2(g) \rightarrow MX_2(g) \tag{4}$$

using the atomic heats of formation for the atoms and the heats of formation of F_2 and Cl_2 which are 0.0 kcal/mol at this level of theory in agreement with experiment.[104] The calculated values at 298 K from Neese and co-workers[41] (-229.0, -242.9, -156.9, and -168.8 kcal/mol for SrF_2, BaF_2, $SrCl_2$, and $BaCl_2$, respectively) are within 2.5 kcal/mol of our values (-227.5, -240.9, -155.9, and -167.1 kcal/mol for SrF_2, BaF_2, $SrCl_2$, and $BaCl_2$, respectively). This is reasonable agreement considering that they used different geometries and frequencies obtained from density functional theory calculation and we have included additional relativistic corrections. The agreement between the two sets of calculations confirms the assessment that there are issues with the experimental heats of formation of SrF_2 and BaF_2.

Bond Dissociation Energies (BDEs) The BDEs[85,105,106] and heats of formation are obviously linked for the diatomics. Less reliable BDEs for the MO diatomics have been reported in the literature.[107] The calculated BDEs are reported in Table 9. The calculated values for SrO and BaO are smaller than either of the experimental measurements.[85,105] The SrO BDE is closer to the value[105] of 101.9 kcal/mol; the BaO BDE is within the experimental error bars and closer to the experimental value of 133.5 kcal/mol. A crossed beam chemiluminescence study of the reaction of the alkaline earths with ClO_2 gave lower limit BDEs.[108] The calculated BDE for SrO is significantly below the chemiluminescence value but the calculated BDE for BaO is in good

Table 9. CCSD(T) Calculated and Experimental Bond Dissociation Energies in kcal/mol at 0 K.

Molecule	Product	CCSD(T)	Expt.[105]
SrO ($^1\Sigma^+$)	Sr + O	98.8	101.9 ±1.5, 115.5,[85] ≥107.7±3.5[108]
BaO ($^1\Sigma^+$)	Ba + O	131.1	134.3 ±3.2, 133.5,[85] ≥133.6±3.5,[108] 133.5±1.3[109]
RaO ($^1\Sigma^+$)	Ra + O	107.6	
SrF ($^2\Sigma^+$)	Sr + F	127.4	129.5±1.6, 126.8, 128. 7[85]
BaF ($^2\Sigma^+$)	Ba + F	137.5	140.3 ±1.6 , 136.6 , 138.8, 139.5[85]
RaF ($^2\Sigma^+$)	Ra + F	127.8	
SrCl ($^2\Sigma^+$)	Sr + Cl	98.6	97.8, 95.6 ± 1.6,[106] 95.92[85]
BaCl ($^2\Sigma^+$)	Ba + Cl	108.2	104.2 ±2, 105.8, 106.8 ± 2.2,[106] 104.9[85]
RaCl ($^2\Sigma^+$)	Ra + Cl	99.0	82±18[69]
SrF_2 ($^1A_1$)	SrF + F	136.6	131.7
BaF_2 ($^1A_1$)	BaF + F	139.9	134.1
RaF_2 ($^1A_1$)	RaF + F	133.0	
$SrCl_2$ ($^1\Sigma_g$)	SrCl + Cl	113.5	112.5
$BaCl_2$ ($^1A_1$)	BaCl + Cl	116.0	114.2
$RaCl_2$ ($^1A_1$)	RaCl + Cl	109.4	
SrOH ($^2\Sigma^+$)	Sr + OH	94.2	97.2, 92 ±4, 95 ± 3[106]
	SrO + H	97.2	98.0
BaOH ($^2\Sigma^+$)	Ba + OH	104.4	107, 107 ±4, 105.8, 111± 14[106]
	BaO + H	74.9	76.6
RaOH ($^2\Sigma^+$)	Ra + OH	93.8	
	RaO + H	87.9	
$Sr(OH)_2$ ($^1A_1$)	SrOH + OH	103.9	102.0
$Ba(OH)_2$ ($^1A_1$)	BaOH + OH	105.6	99, 104.5
$Ra(OH)_2$ ($^1A_1$)	RaOH + OH	98.7	

agreement, within the experimental error bars. Another chemiluminescent reaction study[109] of the reaction Ba + CO_2 gave a BDE value with smaller error bars in excellent agreement with our calculated value. The experimental BDEs from these experiments were not included in the evaluation[8] of the heat of formation of BaO but they do confirm our calculated value for

ΔH_f(BaO), suggesting that there is a consistent error in the Knudsen cell measurements. However, the calculated value for the SrO BDE is in excellent agreement with the average spectroscopic value from an extensive review,[8] which suggests an issue with the chemiluminescence values for SrO. We note that there is a significant increase in the BDE from SrO to BaO followed by a decrease from BaO to RaO. The BDE for RaO is larger than that for SrO.

The calculated BDEs for Sr-F and Ba-F are in agreement with the available experimental values[85,105] given the error bars of the latter quantities. The M-F BDE increases from Sr-F to Ba-F and then decreases to Ra-F, just as found for the oxides. The Sr-F and Ra-F BDEs are almost identical. The M-F BDEs are larger than the M-O BDEs even though we would formally write a single bond for the M-F and a double bond for the M=O. The BDEs for Sr-F and Ra-F are substantially larger than those of Sr-O and Ra-O, respectively, and the Ba-F BDE is only slightly larger than for Ba-O.

The calculated BDEs for Sr-Cl and Ba-Cl are in agreement with experiment[85,105,106] and that for Ra-Cl is within the larger error bound of the experimental value.[69] The M-Cl BDEs follow the same trend as the M-F BDEs as one goes down the column. The Sr-Cl and Ra-Cl BDEs are comparable to the corresponding Sr-O and Ra-O BDEs.

The first BDEs for SrF_2 and $SrCl_2$ are larger than the second value. The values are more similar to each other than for the monohalides, and the Sr-X and Ba-X dissociation energies are closer to each other even though the Ba-X values are always the largest. The Ra-X first BDEs are always the smallest. The first Sr-F BDE is larger than experiment and the first Sr-Cl BDE is in good agreement with experiment suggesting that the M-F values need to be reevaluated.[105]

There are two BDEs to consider for MOH, the M-OH and the MO-H. For SrOH, the O-H BDE is larger than the Sr-OH BDE and this is reversed for BaOH. The change is probably due to the strength of the BaO BDE. For RaOH, the Ra-OH BDE is larger than the RaO-H BDE. The M-OH BDEs follow the same trends as the M-F and M-Cl BDEs with the Ba-OH BDE being the largest and the Sr-OH and Ra-OH BDEs being comparable. The M-OH BDEs are smaller than the M-F BDEs. For $M(OH)_2$, the first BDE for Sr and Ba are comparable and slightly larger than that for Ra. In all cases, the first M-OH BDE is larger than the second just as found for the dihalides. The M-OH and MO-H BDEs for Sr and Ba are in very good agreement with the experimental values[105] for MOH given the lack of any error bars on the experimental values. In a similar way, the M-OH BDE for $M(OH)_2$ is also in good agreement with experiment.[105]

Cohesive energies The cohesive energy of a solid[67,69] is the energy required to convert the solid into the gas. The cohesive energy is usually applied to metals and is equivalent to the sublimation energy. All that is required to calculate the cohesive energy are the heat of formation of the solid and that of the gas phase species. We are interested in vaporizing to the particular molecular monomer. The cohesive energies for all alkaline earths are reported in Table 10. The cohesive energy of the oxides decreases from BeO/MgO to BaO and then increases to RaO. There is a large decrease from SrO to BaO. The difluorides behave in a different manner. There is a substantial increase from BeF_2 to MgF_2 and the values increase to CaF_2. The cohesive energy for SrF_2 is comparable to that for CaF_2 and there is decrease to BaF_2 followed by an increase to RaF_2. The decrease for BaF_2 is consistent with the strong bonds in BaF_2. The chlorides show an interesting pattern of increasing from a low value of 32 kcal/mol for $BeCl_2$ to a value of ~95 kcal/mol for $RaCl_2$. The dihydroxides show an increase from $Be(OH)_2$ to $Mg(OH)_2$ and the

Table 10. CCSD(T) Calculated Cohesive Energies in kcal/mol.[a]

Molecule	$\Delta H_{f,298K}$ (gas)	$\Delta H_{f,298K}$ (solid)	Cohesive Energy
	CCSD(T)	Expt.[67]	CCSD(T) - Expt.
BeO	30.1	-145.4	175.5
MgO	32.3	-143.7	176.0
CaO	4.7	-151.8	156.5
SrO	-1.0	-141.5 ± 0.8	140.5
BaO	-29.7	-131.0 ± 0.5	101.3
RaO	-12.8/-10.2	-123.0[69]	110.2/112.8
BeF_2	-190.1	-245.4	55.4
MgF_2	-174.4	-268.7	94.3
CaF_2	-189.1	-293.0	103.9
SrF_2	-188.3	-290.9 ± 0.7	102.6
BaF_2	-198.1	-288.9 ± 1.0	90.8
RaF_2	-188.1/-185.5	-282.4[69]	94.3/96.9
$BeCl_2$	-86.5	-118.6	32.1
$MgCl_2$	-95.1	-153.3	58.2
$CaCl_2$	-114.9	-190.2	75.3
$SrCl_2$	-116.7	-198.1 ± 0.6	81.4
$BaCl_2$	-124.3	-205.2 ± 3	80.9
$RaCl_2$	-115.2/-112.6	-207.7[69]	92.5/95.1
$Be(OH)_2$	-150.8	-216.5	65.7
$Mg(OH)_2$	-132.8	-221.0	88.2
$Ca(OH)_2$	-146.6	-235.7	89.1
$Sr(OH)_2$	-143.6	-231.6 ± 2.2	88.0
$Ba(OH)_2$	-151.8	-226.2 ± 1.5	74.5
$Ra(OH)_2$	-140.0/-137.4	-221.2[69]	81.2/83.8

[a] The Ra values are given in the order using the heat of formation of Ra, $\Delta H_{f,0K}$(Ra) = 36.35 kcal/mol from Ref. 68 and after the slash $\Delta H_{f,0K}$(Ra) = 38.95 ± 2.0 kcal/mol from Ref 69. The gas phase values for Be, Mg, and Ca are from Ref. 18.

values for Mg to Sr are comparable. There is a decrease from Sr to Ba followed by an increase to Ra.

We note that the cohesive energies for the Be compounds are actually quite low with only 32 kcal/mol required for the enthalpy of sublimation for $BeCl_2$ and only 55 kcal/mol required for

BeF_2. The energy required to sublime $MgCl_2$ is also low at 58 kcal/mol. Of further interest is the result that the Ra compounds have reasonably large enthalpies of sublimation from 80 to 110 kcal/mol with the lowest being near 81 kcal/mol for $Ra(OH)_2$.

Fluoride affinity The gas phase fluoride affinity (FA) provides a measure of the Lewis acidity[110] and is defined as the negative of the enthalpy of reaction (5).

$$A + F^{-} \rightarrow AF^{-} \qquad (5)$$

Addition of an F^- to MF_2 leads to a D_{3h} MF_3^- anion and the M-F bond distances increase by 0.07 to 0.14 Å (Table 11). The smallest M-F bond distance increase is predicted for Mg which has the highest FA, and the largest M-F increase in the distance is predicted for Ra which has the lowest calculated FA. The trend in the bond distance changes does follow the increase in atomic size of the central atom as one proceeds down the column, excluding Be which has a larger change in the bond distance. The FAs are also given in Table 11 for the MF_2 molecules The fluoride affinities decrease from MgF_2 to RaF_2 consistent with a larger M-F bond distance and less stabilization of the F^- by the M(II). The FA for BeF_2 is slightly smaller than that for MgF_2 due to

Table 11. CCSD(T) Calculated Fluoride Affinities in kcal/mol at 0 K and M-F Bond Distances in Å for all the alkaline earth MF_2 and MF_3^-.[a]

Molecule	FA	CCSD(T)/awCVTZ M–F (Å) in MF_2	CCSD(T)/awCVTZ M–F (Å) in MF_3^{-b}	Δr(M-F)[c]
BeF_2 ($^1\Sigma_g^+$)	88.1	1.377	1.472	0.095
MgF_2 ($^1\Sigma_g^+$)	91.1	1.742	1.812	0.070
CaF_2 ($^1A_1$, C_{2v})	83.7	2.013	2.090	0.077
SrF_2 ($^1A_1$, C_{2v})	80.0	2.139	2.238	0.099
BaF_2 ($^1A_1$, C_{2v})	71.5	2.246	2.380	0.134
RaF_2 ($^1A_1$, C_{2v})	69.9	2.321	2.458	0.137

[a] MF_2 for M = Be, Mg and Ca are from Reference 18. [b] All the MF_3^- are $^1A_1'$, D_{3h}. [c] Increase in the M-F bond distance on adding F^-.

steric crowding in the former. The FAs show that the difluorides are modestly strong Lewis acids. The FAs are relevant to which species could be formed in molten salt reactors when fluoride is the dominant anion.

Natural Population Analysis (NPA) The Natural Population Analysis based on the Natural Bond Orbitals (NBOs)[111,112] using NBO6[113,114] (Supporting Information) with wavefunctions calculated at the B3LYP/awCVTZ/wCVTZ-PP(Sr,Ba,Ra) using optimized CCSD(T) geometries was performed using Gaussian09.[61] For the oxides under consideration, the positive charge on the alkaline earth is about 0.4 e less than the formal oxidation state charge of +2.0 e. Most of this charge difference from the formal charge is due to backbonding from the O^{2-} to the alkaline earth valence *d* orbitals. The mono-substituted (halides and hydroxides) radicals have a charge that is within ~0.1 e of the formal charge of +1.0 e. The excess α spin is mostly localized in the valence s orbital of the alkaline earth. There is about 0.1 e of backbonding into the valence d orbital of the alkaline earth with the largest amount of backbonding predicted for BaCl, which has the lowest positive charge on the alkaline earth. The larger ionic character in the M-F bonds than the M-O bonds may contribute to the apparent increased strength of the M-F bonds as compared to the M-O bonds.

The NPA calculated charges for the Sr, Ba, and Ra compounds show that the di-substituted compounds (halides and hydroxides) are more ionic than the oxides. The mono-substituted halide compounds are slightly more ionic than the corresponding di-substituted ones. The di-substituted compounds for Sr, Ba, and Ra all have positive charges of 1.8 to 1.9 e on the alkaline earth.

We compare the NPA charges for all of the alkaline earth dihalides. For the difluorides, the least ionic molecule is BeF_2. The backbonding from the two F^- groups is split between the 2s and 2p orbitals almost evenly. For MgF_2, most of the backbonding is into the 3s with a small contribution into the 3p. Both BeF_2 and MgF_2 are linear. The valence d orbitals become available for CaF_2 and all of the backbonding for the remainder of the alkaline earth difluorides is into the valence d. Beginning with CaF_2, all of the heavier difluorides are bent. Thus the ability to bend correlates with the availability of the valence d orbital. The role of the d orbitals for CaF_2 has been noted previously by Gole et al.[115]

For the dichlorides, $BeCl_2$ is the least ionic with 0.36 e in the 2s and 0.18 e in the 2p. $MgCl_2$ is also less ionic than all of the fluorides and has 0.26 e in the valence 3s with only 0.05 e in the valence 3p. Both $BeCl_2$ and $MgCl_2$ are linear. Again, the availability of a valence d orbital shifts the backbonding into this orbital at $CaCl_2$ and increases the ionicity. In contrast to the difluorides, however, there is a small backbonding into the valence s on the order of 0.03 to 0.06 e for $CaCl_2$ to $RaCl_2$. $CaCl_2$ has the most backbonding into the valence d and s orbitals and is still linear. $SrCl_2$ has less valence s and d backbonding than $CaCl_2$ and is thus more ionic; $SrCl_2$ is slightly bent, although it may be best described as highly fluxional and quasilinear as discussed above. $BaCl_2$ has more valence d backbonding and less valence s backbonding than $SrCl_2$ and is clearly bent even though it is less ionic than $SrCl_2$. $RaCl_2$ has essentially the same orbital backbonding as does $SrCl_2$, yet it is clearly bent. Thus, the types of orbitals available for the backbonding and the size of the anion are key factors in determining if the molecules are bent or linear. The bent molecules, of course, show deviations from simple valence shell electron pair repulsion theory.[116]

Conclusions

Reliable geometry parameters and frequencies are reported at the CCSD(T) level of theory for the late alkaline earth metal (Sr, Ba and Ra) oxides, fluorides, chlorides and hydroxides. Our calculated geometry parameters, frequencies, heats of formation and bond energies were compared with available experimental data and good agreement is found (within experimental errors) with reliable experimental results. The effects of anharmonicity on the quasilinear molecules for the ZPE are expected to be very small, < 0.1 kcal/mol. We suggest that our values for the thermodynamic heats of formation and the BDEs are the most accurate available with estimated uncertainties of ± 1 to 2 kcal/mol for all except the compounds containing Ra. The heats of formation of the Ra compounds have additional uncertainty due to the uncertainty in the heats of formation of the Ra atom and the lack of additional thermodynamic information against which to test the values for the heat of formation of gaseous Ra. The higher order corrections for the oxides which potentially have the most multi-reference character are expected to be significantly below 1 kcal/mol. This suggests that significant revisions may be needed for some of the gas phase heats of formation. We report the first reliable energetics, geometry parameters and frequencies for Ra oxides, fluorides, chlorides and hydroxides. The cohesive energies (heats of sublimation of the monomer) show that the values for the Be dihalides are quite low. In addition, the results show that the cohesive energies for the Ra compounds are substantial. The fluoride affinities show that the difluorides are moderately strong Lewis acids and that such trifluorides may form under the appropriate experimental conditions. The calculated charges on the alkaline earth suggest that di-substituted compounds (dihalides and dihydroxides) are more ionic than the corresponding monoxides. In addition, the charges for the dihalides and backbonding into the available valence orbitals on the alkaline earth correlate with whether these molecules are bent or linear. These calculated values provide a consistent set of thermodynamic data for use in further macroscopic simulations, for example, of molten salt reactors.

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Supporting Information Complete references for Ref. 61 and 62. Energy contributions to the total atomization energies. T_1 diagnostic values at CCSD(T)/ aug-cc-pwCVQZ Level. Calculated ZPE including anharmonic corrections. Calculated and Experimental Vibrational Frequencies in cm^{-1} including anharmonic corrections. Calculated heats of formation at 0 K and 298K from the total atomization energies in kcal/mol at CCSD(T)/CBS-DTQ and CCSD(T)/CBS-TQ5 Levels**.** Total CCSD(T) and CBS energies in hartrees. The Natural Population Analysis based on the Natural Bond Orbitals. DFT optimized geometries for all group 2 dihalides. $SrCl_2$ CCSD(T)/awCVTZ Frequencies.

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