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Heats of Formation of Alkali Metal and Alkaline Earth Metal Oxides and Hydroxides: Surprisingly Demanding Targets for High-Level ab Initio Procedures

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High-level ab initio calculations, including variants of the W*n* and G3 procedures, have been used to determine the structures and heats of formation of the alkali metal and alkaline earth metal oxides and hydroxides (M_2O, MOH: M = Li, Na, and K; MO, $M(OH)_2$: M = Be, Mg, and Ca). Our best structures were obtained at the CCSD(T)(riv,rv)/aug′-cc-pWCVQZ level and are in uniformly close agreement with available experimental data, with a mean absolute deviation from experimental metal−oxygen bond lengths of just 0.007 Å.Structures obtained with CCSD(T)/cc-pWCVQZ, B3-LYP/cc-pVTZ, B3-LYP/6-31G(2df,p), and MP2(full)/6-311+G(3df,2p) are also in good agreement with experiment. Zero-point vibrational energies and enthalpy temperature corrections are found to be relatively insensitive to the various procedures employed. However, the heats of formation for these molecules are challenging targets for high-level ab initio procedures. In the W*n*-type procedures, it is found that expanding the correlation space on the metal atoms from the normal relaxed valence (rv) (or frozen-core) specification to relaxed inner valence (riv) requires the use of newly developed core-valence basis sets (cc-pWCV*n*Z) in the extrapolation calculations to obtain reliable results. Our best calculated heats of formation ($\Delta H_{f\ 298}$) come from a procedure designated W2C//ACQ, while G3[CC](dir,full) is the best of the G3-type procedures. Recommended $\Delta H_{f\ 298}$ values, weighted toward the W2C//ACQ results, are -157 ± 5 (Li_2O), -25 ± 5 (Na_2O), -60 ± 5 (K_2O), $+130 \pm 12$ (BeO), $+142 \pm 10$ (MgO), $+26 \pm 17$ (CaO), -239 ± 5 (LiOH), -189 ± 5 (NaOH), -223 ± 5 (KOH), -632 ± 7 ($Be(OH)_2$), -547 ± 5 ($Mg(OH)_2$), and -604 ± 19 ($Ca(OH)_2$) kJ mol^{-1}.

1. Introduction

The oxides and hydroxides of the alkali and alkaline earth metals are of fundamental importance and include commonly occurring substances such as quicklime (calcium oxide) and caustic soda (sodium hydroxide). However, experimental gas-phase data for these molecules, particularly the thermochemistry, are rather patchy, perhaps because of their low volatility and high reactivity. Under these circumstances, theory has a potentially useful role as an alternative source for a complete, satisfactorily reliable set of structures and heats of formation.[1]

In a recent study,[2] we used variants of the G2 theoretical procedure[3] to examine the heats of formation of the alkali metal and alkaline earth metal oxides and hydroxides (M_2O, MOH: M = Li, Na, and K; MO, $M(OH)_2$: M = Be, Mg, and Ca). G2 normally performs very well for thermochemical predictions. For example, it shows a mean absolute deviation from reliable experimental values for the 302 energy comparisons in the G2/97 test set of 6.6 kJ mol^{-1}.[4] However, we found that *standard* G2 theory is quite unsuitable for the prediction of the heats of formation of several of the highly polar metal oxides and hydroxides, with errors greater than 100 kJ mol^{-1} in some cases. We concluded that three aspects of the G2 model were contributing to the poor results. In the first place, our calculations confirmed earlier indications[5] that for systems containing the third-row atoms K and Ca it is essential to include the 3s and 3p orbitals in the correlation space and that more generally an analogous relaxed inner-valence (denoted riv) procedure or a procedure that includes all orbitals in the correlation space (denoted full) is beneficial for the remaining systems. Next, we found that the QCISD(T) component of the G2 energy is poorly described for CaO, Na_2O (in bent structures), and K_2O but that this can be rectified through the replacement of QCISD(T) with CCSD(T) (denoted G2[CC]).[6] Finally, removing the additivity approximation of standard G2 theory through direct (denoted dir) large basis set CCSD(T) calculations was found to have a large effect for the oxides Na_2O, CaO, and K_2O.[7−9]

Our best calculations in the previous study were carried out on structures optimized at the MP2(full)/6-311+G(3df,2p) level. This produced structures that generally agreed well with available experimental information. Our best heats of formation were obtained with the G2[CC](dir,full) procedure that includes the modifications to the standard G2 procedure referred to above. Thus, (a) all orbitals are included in the correlation space (rather than freezing the core), (b) CCSD(T) calculations are used in place of QCISD(T), and (c) the additivity approximation is eliminated by carrying out the large basis set CCSD(T) calculation directly.

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TABLE 1: Occupied Orbitals Included in Correlation Spaces Defined as Relaxed Valence (rv), Relaxed Inner Valence (riv), Relaxed Inner−Inner Valence (riiv), and Relaxed Inner−Inner−Inner Valence (riiiv)

	frozen	active
rv:		
Li, Be	1s[a]	2s, 2p
Na, Mg	1s, 2s, 2p[a]	3s, 3p
K, Ca	1s, 2s, 2p, 3s, 3p[a]	4s, 4p
O	1s[a]	2s, 2p
H		1s
riv:		
Li, Be		1s, 2s, 2p[b]
Na, Mg	1s	2s, 2p, 3s, 3p
K, Ca	1s, 2s, 2p	3s, 3p, 4s, 4p
O		1s, 2s, 2p[b]
riiv:		
Na, Mg		1s, 2s, 2p, 3s, 3p[b]
K, Ca	1s	2s, 2p, 3s, 3p, 4s, 4p
riiiv:		
K, Ca		1s, 2s, 2p, 3s, 3p, 4s, 4p[b]

[a] Equivalent to frozen core. [b] Equivalent to full.

Since the conclusion of our previous study, the G3,[10,11] G3X,[12] W1,[13] and W2[13] techniques have been formulated, and they perform better than G2 for the established test sets. We were interested in examining the performance of the newer methods for the metal oxides and hydroxides. The results of our new study, in which we find that the metal oxides and hydroxides continue to pose special challenges even for these newer methods, are described in the present article, together with the modifications to the standard procedures that we have found most effective in overcoming these shortcomings.

There have been a number of other studies in recent years that have explored deficiencies in standard theoretical descriptions of molecules containing alkali metal or alkaline earth metal atoms.[5,14−26] These have emphasized the need to include inner-valence orbitals in the correlation space,[5,14−25] the need to use flexible basis sets,[16,18] the need to include tight d functions,[15,22] the breakdown of quadratic configuration interaction in some instances,[5] and the importance in some cases of correcting for basis set superposition errors,[16−20] though there has been some debate on this last point.[21]

2. Theoretical Procedures

Standard ab initio molecular orbital theory[27] and density functional theory[28] calculations were carried out using the Gaussian 98,[29] MOLPRO 2000,[30] and ACES II[31] program packages.

Calculations were carried out for a number of choices of correlation spaces, for which we propose the systematic nomenclature specified in Table 1. If only the valence orbitals among the occupied orbitals are included in the correlation space, then we use the notation rv, which stands for relaxed valence. This is often referred to alternatively as frozen core. If the next set of orbitals, the inner-valence orbitals, are included in the correlation space, then we refer to this as relaxed inner valence or riv. Relaxing subsequent sets of orbitals leads to the riiv and riiiv correlation spaces. If all orbitals on all atoms are included in the correlation space, then this is referred to as full in line with common usage. If different types of correlation space are used for the metal and oxygen atoms, then they are specified in the order (metal,oxygen) (e.g., (riv,rv)).

Structures were optimized at a number of levels of theory, primarily those required for the various high-level energy calculations,[32] including MP2(full)/6-31G(d) for G3,[10] B3-LYP/6-31G(2df,p) for G3X,[12] MP2(full)/6-311+G(3df,2p) for G2[CC](dir,full) and G3[CC](dir,full), B3-LYP/cc-pVTZ+1 for W1[13] and W1C (first- and second-row systems), B3-LYP/cc-pWCVTZ for W1C (third-row systems), CCSD(T)(rv,rv)/cc-pVQZ+1 for W2,[13] CCSD(T)(riv,rv)/cc-pWCVQZ for W2C and G3[CC](dir,full), and CCSD(T)(riv,rv)/aug′-cc-pWCVQZ for W2C//ACQ and G3[CC](dir,full). These are described in more detail below.

Vibrational frequencies were obtained at several levels of theory, partly to confirm that the calculated structures are located at minima on the potential energy surfaces and partly to obtain zero-point vibrational energies (ZPVEs) and enthalpy temperature corrections ($\Delta\Delta H_f$) to give heats of formation at 298 K ($\Delta H_{f\ 298}$). For the latter purpose, the vibrational frequencies were scaled either using optimized scale factors[33] or using standard scale factors for the particular methods.[10,12,13] The harmonic approximation was used unless otherwise noted. Heats of formation were obtained using the atomization method, as detailed, for example, by Nicolaides et al.[34]

The heats of formation were obtained using variants of the W1,[13] W2,[13] and G3[10,12] methods. W1 and W2 are high-level theoretical procedures that seek to extrapolate to the (UR)CCSD(T) infinite basis set limit, taking account of core correlation, scalar relativistic effects, first-order spin−orbit coupling, and zero-point vibrational energy.[13] The standard W1 and W2 procedures use B3-LYP/cc-pVTZ+1 and CCSD(T)/cc-pVQZ+1 optimized geometries, respectively, where +1 indicates the addition of a single high-exponent d-type inner polarization function to all second-row atoms. CCSD and CCSD(T) calculations are then performed with basis sets of systematically increasing size: aug′-cc-pVDZ+2d and aug′-cc-pVnZ+2d1f, where $n = T, Q$, or 5 and +2d and +2d1f indicate the addition of high-exponent d and f functions, respectively, to all second-row atoms. The aug′ prefix indicates that diffuse functions are not included on hydrogen atoms. Diffuse functions are also not included on the group I and II metal atoms in the standard W1 and W2 procedures or in the variants considered here (i.e., they are included only on oxygen for the present systems). Separate two-point extrapolations are performed to determine the SCF, CCSD valence-correlation, and triple-excitation components of the total energy at the basis set limit. Core correlation is incorporated by performing CCSD(T) calculations with the MTsmall basis set with and without the core orbitals frozen. However, the deep-lying 1s orbitals on second- and third-row atoms are also held frozen in the core-correlation and scalar relativistic calculations.

The cc-pVnZ basis sets used in the present calculations for Li, Be, Na, and Mg were initially taken from the literature.[35] However, in the course of our study, we found deficiencies in these basis sets in describing the core-valence correlation that is very important for obtaining quantitative accuracy when dealing with molecules containing group I and II metals. These will be discussed further below. However, as a consequence, new core-valence correlation-consistent basis sets, designated cc-pWCVnZ (where W stands for Weizmann to distinguish these basis sets from existing cc-pCVnZ sets), were developed for Li, Be, Na, Mg, K, and Ca.[36] These were used together with existing aug-cc-pCVnZ basis sets for oxygen in new variant procedures that we have designated W1C and W2C that differ from standard W1 and W2 through the use of the new cc-pWCVnZ basis sets in place of cc-pVnZ basis sets for the energy extrapolation calculations. The standard W1C and W2C procedures use riv correlation spaces on the metals and an rv correlation space on oxygen. W1C uses the same geometries as standard W1 (B3-LYP/cc-pVTZ+1) for first- and second-row systems but uses B3-LYP/cc-pWCVTZ for systems containing third-row atoms. Standard W2C uses geometries optimized with CCSD(T)(riv,rv)/cc-pWCVQZ rather than the CCSD(T)(rv,rv)/cc-pVQZ+1 of standard W2 to allow for inner-valence correlation. We have also carried out W2C calculations with CCSD(T)/aug′-cc-pWCVQZ geometries (referred to as W2C//ACQ) to allow for the possibility that structural changes arising from the strong $M^+ O^-$ charge transfer in many of these molecules might affect the W2C energies. As with W1 and W2, core correlation is incorporated into the W1C and W2C procedures by performing CCSD(T) calculations with the MTsmall basis set with and without the core orbitals frozen but taking into account the new choice of core orbitals for the new methods. The deep-lying 1s orbitals on second- and third-row atoms are again held frozen in the core-correlation and scalar relativistic calculations. Except where noted otherwise, scalar relativistic corrections were obtained as the ACPF expectation values of the first-order Darwin and mass−velocity operators.[37] In some cases, they were additionally evaluated using the Douglas−Kroll approximations[38] at the CCSD(T)(full) level.

Some of the systems examined in the present study show evidence of significant multireference character in their wave functions. We have therefore explored the use of multireference versions of the W2 procedure.[1b] Specifically, we have replaced the CCSD(T) parts of W2 by the averaged coupled-pair functional (ACPF)[39] and averaged quadratic coupled cluster (AQCC)[40] procedures. This leads to methods that may be described in general as W2-CAS-ACPF and W2-CAS-AQCC and for the present systems as W2C-CAS-ACPF and W2C-CAS-AQCC. The CAS parts of the calculations are carried out within a full-valence space, and the ACPF and AQCC calculations use an riv,rv correlation space. We have found through representative calculations that W2-CAS-ACPF and W2-CAS-AQCC produce results that are nearly but not quite as good as standard W2 in cases where multireference considerations appear to be relatively unimportant, presumably because of the absence of an explicit connected triples contribution in ACPF and AQCC.[41]

The standard variants of G3[10] and G3X[12] that we use, G3-[CC][42] and G3X[CC],[43] aim to obtain large basis set CCSD(T) energies through the assumption of additivity of correlation and basis set effects. Core correlation is also included by performing the MP2/G3large single-point calculation with correlation of all electrons (full), and a spin−orbit correction is included for atoms. Standard G3 uses MP2(full)/6-31G(d) geometries and HF/6-31G(d) ZPVEs[44], and G3X uses B3-LYP/6-31G(2df,p) geometries and scaled B3-LYP/6-31G(2df,p) ZPVEs. In both cases, individual higher-level corrections (HLCs) that depend on the number of paired and unpaired electrons are incorporated for atoms and molecules. The HLCs were determined using a best fit to the 302 energies of the G2/97 test set (G3[CC])[42] or the 376 energies of the G3/99 test set (G3X[CC]).[43]

We previously found that the use of CCSD(T) in place of QCISD(T) (designated [CC]), elimination of the additivity assumptions of G2 theory (designated dir, standing for direct), and expansion of the correlation space (e.g., full) were all beneficial, leading to the G2[CC](dir,full) procedure as the best theoretical level in our previous study.[2] We use an analogous G3[CC](dir,full) procedure in the present work. The G2[CC](dir,full) calculations used MP2(full)/6-311+G(3df,2p) optimized structures, the best available at the time. The present G3[CC](dir,full) calculations were carried out with MP2(full)/6-311+G(3df,2p) optimized structures as well as with the even better CCSD(T)/cc-pWCVQZ and CCSD(T)/aug′-cc-pWCVQZ geometries obtained in the present study.

An important question that needs to be addressed in the G3[CC](dir,full) calculations is the choice of higher-level correction parameters. We have chosen to reoptimize the HLC parameters for G3[CC](dir,full) using the G2-1 subset of G2/97.[45]

3. Results and Discussion

3.1. Structures. Calculated structures for the metal oxides and hydroxides at the theoretical levels required for the various energy evaluations of the G3- and W-type methods are compared with available experimental data[46] in Tables 2 and 3, respectively. The highest level of theory that we have used for structure determinations is CCSD(T)/aug′-cc-pWCVQZ with the relaxed inner valence (riv) correlation space for the metals and relaxed valence (rv) correlation space for oxygen. We take the geometries at this level to represent our most reliable theoretical predictions. A previous thorough analysis[47] has found that CCSD(T)(full)/cc-pCVQZ gives excellent structures, with a mean absolute deviation (MAD) from their carefully determined reference structures of just 0.009 Å. For the present systems, the MAD between the CCSD(T)/aug′-cc-pWCVQZ and experimental values of the metal−oxygen bond lengths (Table 4) is likewise very small at just 0.007 Å, with a largest deviation (LD) of just +0.011 Å. There have been a number of previous theoretical investigations of the structures of most of these systems but, in all but one case, at lower theoretical levels than CCSD(T)/aug′-cc-pWCVQZ.[2,18,23,48] We note particularly the complete set of calculations of Burk, Sillar, and Koppel[23b] on the alkali metal oxides and hydroxides at the B3-LYP/6-311+G(d,p), B3-LYP/6-311+G(3df,3pd), and CCSD(T)(full)/6-311++G(2df,2pd) levels, the large basis set CCSD and CCSD(T) calculations of Wright et al.[18] on Na_2O, LiOH, and NaOH, and the CCSD(T)/6-311G(2df,2pd)+(2fg) calculations of Schaefer et al. on CaO.[15] Very recently, Koput and Peterson[25] have determined the structure of Li_2O using the CCSD(T)/cc-pCVQZ method and have obtained results totally consistent with those reported here.

Table 4 presents a statistical summary of our results for the M−O bond length predictions, and we will discuss these data before examining results for the individual molecules. In addition to the comparison of the CCSD(T)/aug′-cc-pWCVQZ results with experiment, comparisons are made in Table 4 of the predictions at the other theoretical levels with the CCSD(T)/aug′-cc-pWCVQZ results (i.e., using the latter as a secondary standard to allow a full comparison set).

Compared with CCSD(T)/aug′-cc-pWCVQZ, the best geometries are obtained with CCSD(T)/cc-pWCVQZ, B3-LYP/cc-pVTZ+1 (together with B3-LYP/cc-pWCVTZ for third-row elements), and B3-LYP/6-31G(2df,p), as used in W2C, W1, and G3X, respectively. These have the lowest MAD values (from the CCSD(T)/cc-aug′-pWCVQZ bond lengths) of 0.003, 0.007, and 0.012 Å, respectively, and also the lowest LDs of −0.006, −0.021, and +0.026 Å, respectively. MP2(full)6-311+G(3df,2p), as used in G2[CC](dir,full) and G3[CC](dir,full), also generally produces good geometries, with a comparable MAD (0.011 Å) but a slightly larger LD (+0.031 Å). MP2/6-31G(d), as used in standard G3, has an MAD of 0.028 Å and an LD of +0.054 Å. Results with CCSD(T)/cc-pVQZ+1, the standard method for W2 calculations, depend

TABLE 2: Calculated Structures of Alkali Metal and Alkaline Earth Metal Oxides[a]

			correlation space		geometric parameters		
molecule	method	geometric level of theory	M	O	symmetry	r(M−O)	∠OMO
Li_2O	G3	MP2/6-31G(d)[b]	riv	riv	$D_{\infty h}$	1.653	180.0
	G3X	B3-LYP/6-31G(2df,p)			$D_{\infty h}$	1.620	180.0
	G3[CC](dir,full)	MP2/6-311+G(3df,2p)[b]	riv	riv	$D_{\infty h}$	1.635	180.0
	W1	B3-LYP/cc-pVTZ+1			$D_{\infty h}$	1.611	180.0
	W2	CCSD(T)/cc-pVQZ+1	rv	rv	$D_{\infty h}$	1.629	180.0
		CCSD(T)/cc-pVQZ+1	riv	rv	$D_{\infty h}$	1.616	180.0
	W2C	CCSD(T)/cc-pWCVQZ	riv	rv	$D_{\infty h}$	1.617	180.0
	W2C//ACQ	CCSD(T)/AWCVQZ[c]	riv	rv	$D_{\infty h}$	1.617	180.0
		exptl[d]				1.606	
Na_2O	G3	MP2/6-31G(d)[b]	riiv	riv	C_{2v}	2.036	130.1
	G3X	B3-LYP/6-31G(2df,p)			$D_{\infty h}$	1.984	180.0
	G3[CC](dir,full)	MP2/6-311+G(3df,2p)[b]	riiv	riv	$D_{\infty h}$	2.012	180.0
	W1	B3-LYP/cc-pVTZ+1			$D_{\infty h}$	1.990	180.0
	W2	CCSD(T)/cc-pVQZ+1	rv	rv	$D_{\infty h}$	2.019	180.0
		CCSD(T)/cc-pVQZ+1	riv	rv	$D_{\infty h}$	1.901	180.0
	W2C	CCSD(T)/cc-pWCVQZ	riv	rv	$D_{\infty h}$	1.987	180.0
	W2C//ACQ	CCSD(T)/AWCVQZ[c]	riv	rv	$D_{\infty h}$	1.986	180.0
K_2O	G3	MP2/6-31G(d)	riiiv	riv	$D_{\infty h}$	2.284	180.0
	G3X	B3-LYP/6-31G(2df,p)			$D_{\infty h}$	2.212	180.0
	G3[CC](dir,full)	MP2/6-311+G(3df,2p)[b]	riiiv	riv	$D_{\infty h}$	2.261	180.0
	W1	B3-LYP/cc-pWCVTZ			$D_{\infty h}$	2.227	180.0
	W2C//W2	CCSD(T)/cc-pWCVQZ	rv	rv	$D_{\infty h}$	2.272	180.0
	W2C	CCSD(T)/cc-pWCVQZ	riv	rv	$D_{\infty h}$	2.231	180.0
	W2C//ACQ	CCSD(T)/AWCVQZ[c]	riv	rv	$D_{\infty h}$	2.230	180.0
BeO	G3	MP2/6-31G(d)[b]	riv	riv	$C_{\infty v}$	1.356	
	G3X	B3-LYP/6-31G(2df,p)			$C_{\infty v}$	1.324	
	G3[CC](dir,full)	MP2/6-311+G(3df,2p)[b]	riv	riv	$C_{\infty v}$	1.343	
	W1	B3-LYP/cc-pVTZ+1			$C_{\infty v}$	1.323	
	W2	CCSD(T)/cc-pVQZ+1	rv	rv	$C_{\infty v}$	1.338	
		CCSD(T)/cc-pVQZ+1	riv	rv	$C_{\infty v}$	1.332	
	W2C	CCSD(T)/cc-pWCVQZ	riv	rv	$C_{\infty v}$	1.332	
	W2C//ACQ	CCSD(T)/AWCVQZ[c]	riv	rv	$C_{\infty v}$	1.333	
		exptl[e]				1.3309	
MgO	G3	MP2/6-31G(d)[b]	riiv	riv	$C_{\infty v}$	1.733	
	G3X	B3-LYP/6-31G(2df,p)			$C_{\infty v}$	1.735	
	G3[CC](dir,full)	MP2/6-311+G(3df,2p)[b]	riiv	riv	$C_{\infty v}$	1.745	
	W1	B3-LYP/cc-pVTZ+1			$C_{\infty v}$	1.734	
	W2	CCSD(T)/cc-pVQZ+1	rv	rv	$C_{\infty v}$	1.753	
		CCSD(T)/cc-pVQZ+1	riv	rv	$C_{\infty v}$	1.739	
	W2C	CCSD(T)/cc-pWCVQZ	riv	rv	$C_{\infty v}$	1.740	
	W2C//ACQ	CCSD(T)/AWCVQZ[c]	riv	rv	$C_{\infty v}$	1.742	
		exptl[e]				1.749	
CaO	G3	MP2/6-31G(d)	riiiv	riv	$C_{\infty v}$	1.875	
	G3X	B3-LYP/6-31G(2df,p)			$C_{\infty v}$	1.815	
	G3[CC](dir,full)	MP2/6-311+G(3df,2p)	riiiv	riv	$C_{\infty v}$	1.837	
	W1	B3-LYP/cc-pWCVTZ			$C_{\infty v}$	1.843	
	W2C//W2	CCSD(T)/cc-pWCVQZ	rv	rv	$C_{\infty v}$	1.913	
	W2C	CCSD(T)/cc-pWCVQZ	riv	rv	$C_{\infty v}$	1.827	
	W2C//ACQ	CCSD(T)/AWCVQZ[c]	riv	rv	$C_{\infty v}$	1.831	
		exptl[d]				1.8221	

[a] Bond lengths in angstroms, angles in degrees. [b] Reference 2. [c] AWCVQZ is shorthand for aug′-cc-pWCVQZ. [d] Reference 46c. [e] Reference 46a.

strongly on the correlation space that is used. With an rv space on the metal atoms, the results show a respectable MAD of 0.015 Å and an LD of +0.034 Å. Extending the correlation space to include the important inner-valence orbitals (riv) was expected to improve the results, but in practice it significantly degrades them, with an MAD of 0.023 Å and an LD of −0.084 Å. This may be attributed to deficiencies in the cc-pVQZ+1 basis set in describing inner-valence electrons, and this problem is described in more detail below. Interestingly, this is in sharp contrast with findings for the structures of molecules containing just first-row elements and hydrogen.[47] In that study, it was emphasized that cc-pVQZ calculations with all electrons correlated were significantly more accurate than cc-pVQZ calculations that excluded the core-correlation effects.

Among the worst calculated results are the MP2/6-31G(d) predictions for Li_2O and Na_2O where the M−O bond lengths are overestimated by approximately 0.05 Å in each case. MP2/6-31G(d) also incorrectly predicts a bent structure for Na_2O. The deficiencies of CCSD(T)/cc-pVQZ+1 with the riv correlation space for sodium lead to significant underestimations of the Na−O lengths in Na_2O and NaOH. These errors are markedly reduced by employing the newly developed cc-pWCVQZ basis for sodium.

On the basis of the very good CCSD(T)/cc-aug′-pWCVQZ results for the oxides and hydroxides for which experimental data are available (Li_2O, BeO, MgO, CaO, LiOH, NaOH, and KOH), we can have confidence in the structural predictions of this method for the remaining molecules. Thus, we predict

TABLE 3: Calculated Structures of Alkali Metal and Alkaline Earth Metal Hydroxides[a]

molecule	method	geometric level of theory	correlation space M	correlation space O	symmetry	geometric parameters r(M−O)	r(O−H)	∠MOH	∠OMO
LiOH	G3	MP2/6-31G(d)[b]	riv	riv	$C_{\infty v}$	1.594	0.960	180.0	
	G3X	B3-LYP/6-31G(2df,p)			$C_{\infty v}$	1.581	0.951	180.0	
	G3[CC](dir,full)	MP2/6-311+G(3df,2p)[b]	riv	riv	$C_{\infty v}$	1.591	0.949	180.0	
	W1	B3-LYP/cc-pVTZ+1			$C_{\infty v}$	1.576	0.951	180.0	
	W2	CCSD(T)/cc-pVQZ+1	rv	rv	$C_{\infty v}$	1.590	0.948	180.0	
		CCSD(T)/cc-pVQZ+1	riv	rv	$C_{\infty v}$	1.573	0.948	180.0	
	W2C	CCSD(T)/cc-pWCVQZ	riv	rv	$C_{\infty v}$	1.576	0.948	180.0	
	W2C//ACQ	CCSD(T)/AWCVQZ[c]	riv	rv	$C_{\infty v}$	1.581	0.949	180.0	
		exptl[d]				1.5816(10)	0.9691(21)		
NaOH	G3	MP2/6-31G(d)[b]	riiv	riv	$C_{\infty v}$	1.921	0.962	180.0	
	G3X	B3-LYP/6-31G(2df,p)			$C_{\infty v}$	1.915	0.954	180.0	
	G3[CC](dir,full)	MP2/6-311+G(3df,2p)[b]	riiv	riv	$C_{\infty v}$	1.948	0.952	180.0	
	W1	B3-LYP/cc-pVTZ+1			$C_{\infty v}$	1.937	0.954	180.0	
	W2	CCSD(T)/cc-pVQZ+1	rv	rv	$C_{\infty v}$	1.969	0.951	180.0	
		CCSD(T)/cc-pVQZ+1	riv	rv	$C_{\infty v}$	1.901	0.948	180.0	
	W2C	CCSD(T)/cc-pWCVQZ	riv	rv	$C_{\infty v}$	1.935	0.951	180.0	
	W2C//ACQ	CCSD(T)/AWCVQZ[c]	riv	rv	$C_{\infty v}$	1.941	0.952	180.0	
		exptl[d]				1.95(2)			
KOH	G3	MP2/6-31G(d)	riiiv	riv	$C_{\infty v}$	2.185	0.967	180.0	
	G3X	B3-LYP/6-31G(2df,p)			$C_{\infty v}$	2.184	0.958	180.0	
	G3[CC](dir,full)	MP2/6-311+G(3df,2p)[b]	riiiv	riv	$C_{\infty v}$	2.213	0.955	180.0	
	W1	B3-LYP/cc-pWCVTZ			$C_{\infty v}$	2.191	0.957	180.0	
	W2C//W2	CCSD(T)/cc-pWCVQZ	rv	rv	$C_{\infty v}$	2.200	0.950	180.0	
	W2C	CCSD(T)/cc-pWCVQZ	riv	rv	$C_{\infty v}$	2.198	0.955	180.0	
	W2C//ACQ	CCSD(T)/AWCVQZ[c]	riv	rv	$C_{\infty v}$	2.204	0.955	180.0	
		exptl[d]				2.196(3)	0.960(10)		
Be(OH)$_2$	G3	MP2/6-31G(d)[b]	riv	riv	C_2	1.436	0.963	124.3	177.4
	G3X	B3-LYP/6-31G(2df,p)				1.419	0.954	127.4	177.3
	G3[CC](dir,full)	MP2/6-311+G(3df,2p)[b]	riv	riv	C_2	1.424	0.950	133.3	174.5
	W1	B3-LYP/cc-pVTZ+1			C_2	1.426	0.954	129.0	176.4
	W2	CCSD(T)/cc-pVQZ+1	rv	rv	C_2	1.429	0.951	128.5	176.0
	W2C	CCSD(T)/cc-pWCVQZ	riv	rv	C_2	1.425	0.951	128.4	176.0
	W2C//ACQ	CCSD(T)/AWCVQZ[c]	riv	rv	C_2	1.426	0.951	129.5	175.7
Mg(OH)$_2$	G3	MP2/6-31G(d)[b]	riiv	riv	C_2	1.807	0.963	133.4	178.1
	G3X	B3-LYP/6-31G(2df,p)			C_{2h}	1.779	0.952	142.6	180.0
	G3[CC](dir,full)	MP2/6-311+G(3df,2p)[b]	riiv	riv	$D_{\infty h}$	1.761	0.946	180.0	180.0
	W1	B3-LYP/cc-pVTZ+1			C_2	1.779	0.952	143.2	176.9
	W2	CCSD(T)/cc-pVQZ+1	rv	rv	C_{2h}	1.775	0.947	154.9	180.0
	W2C	CCSD(T)/cc-pWCVQZ	riv	rv	C_{2h}	1.762	0.947	155.4	180.0
	W2C//ACQ	CCSD(T)/AWCVQZ[c]	riv	rv	C_{2h}	1.757	0.947	165.9	180.0
Ca(OH)$_2$	G3	MP2/6-31G(d)	riiiv	riv	C_{2v}	2.042	0.964	175.5	160.2
	G3X	B3-LYP/6-31G(2df,p)			$D_{\infty h}$	2.051	0.953	180.0	180.0
	G3[CC](dir,full)	MP2/6-311+G(3df,2p)[b]	riiiv	riv	$D_{\infty h}$	2.043	0.952	180.0	180.0
	W1	B3-LYP/cc-pWCVTZ			$D_{\infty h}$	2.039	0.954	180.0	180.0
	W2C//W2	CCSD(T)/cc-pWCVQZ	rv	rv	$D_{\infty h}$	2.139	0.960	180.0	180.0
	W2C	CCSD(T)/cc-pWCVQZ	riv	rv	$D_{\infty h}$	2.031	0.951	180.0	180.0
	W2C//ACQ	CCSD(T)/AWCVQZ[c]	riv	rv	$D_{\infty h}$	2.036	0.952	180.0	180.0

[a] Bond lengths in angstroms, angles in degrees. [b] Reference 2. [c] AWCVQZ is shorthand for aug′-cc-pWCVTZ. [d] Reference 46b.

TABLE 4: Mean Absolute Deviations (MADs), Mean Deviations (MDs), and Largest Deviations (LDs) from Experiment and from the Best Theoretical Values for the M−O Bond Length (Å) in Oxides and Hydroxides

method	geometric level of theory	correlation space M, O	MAD	MD	LD	number of comparisons
deviations from experiment:						
W2C//ACQ	CCSD(T)/aug′-cc-pWCVQZ	riv, rv	0.007	+0.002	+0.011	7
deviations from CCSD(T)/aug′-cc-pWCVQZ:						
G3	MP2/6-31G(d)	full	0.028	+0.020	+0.054	12
G3X	B3-LYP/6-31G(2df,p)		0.012	−0.005	−0.026	12
G3[CC](dir,full)	MP2/6-311+G(3df,2p)	full	0.011	+0.011	+0.031	12
W1	B3-LYP/cc-pVTZ[a]		0.007	−0.001	+0.021	12
W2	CCSD(T)/cc-pVQZ+1	rv, rv	0.015	+0.015	+0.034	8
	CCSD(T)/cc-pVQZ+1	riv, rv	0.023	−0.023	−0.084	6
W2C	CCSD(T)/cc-pWCVQZ	riv, rv	0.003	−0.002	−0.006	12

[a] cc-pVTZ+1 for first- and second-row molecules and cc-pWCVTZ for third-row molecules.

metal−oxygen bond lengths of 1.986 (Na_2O), 2.230 (K_2O), 1.426 ($Be(OH)_2$), 1.757 ($Mg(OH)_2$), and 2.036 Å ($Ca(OH)_2$), with an expected uncertainty of better than ±0.01 Å.

3.2. Zero-Point Vibrational Energy and Enthalpy Temperature Corrections. The conversion of raw electronic energies to heats of formation at 298 K ($\Delta H_{f\ 298}$) requires the calculation of zero-point vibrational energies (ZPVE) and adjustments in heats of formation to 298 K ($\Delta\Delta H_f$). Values for these quantities obtained using appropriately scaled vibrational frequencies at three levels of theory, namely, HF/6-31G(d), B3-LYP/6-31G(2df,p), and B3-LYP/cc-pVTZ, are presented in Table 5. The main observation from Table 5 is that both the

TABLE 5: Calculated Zero-Point Energies (ZPVE) and Enthalpy Temperature Corrections ($\Delta\Delta H_f$) to 298 K (kJ mol^{-1})

	HF/6-31G(d)		B3-LYP/6-31G(d)		B3-LYP/6-31G(2df,p)		B3-LYP/cc-pVTZ[a]	
molecule	ZPVE[b]	$(\Delta\Delta H_f)$[c]	ZPVE[d]	$(\Delta\Delta H_f)$[e]	ZPVE[f]	$(\Delta\Delta H_f)$[f]	ZPVE[g]	$(\Delta\Delta H_f)$[g]
Li_2O	12.36	12.68	12.57	12.55	13.04	12.18	12.20	12.71
Na_2O	6.65	13.38	6.67	13.18	6.71	14.36	6.62	14.39
K_2O	5.40	14.84	5.14	14.56[h]	4.71	14.69[h]	5.10	14.68[h]
BeO	9.51	8.69	9.08	8.69	9.13	8.69	9.13	8.69
MgO	4.19	8.99	4.84	8.86	4.95	8.86	4.89	8.87
CaO	4.80	8.90	4.70	8.88	4.70	8.89	4.44	8.93
LiOH	31.85	11.36	31.76	11.40	33.09	11.01	33.10	10.84
NaOH	28.85	11.99	27.34	11.47	27.98	12.99	28.56	12.42
KOH	28.79	11.63	29.40	11.16	29.53	11.40	29.67	11.32
$Be(OH)_2$	69.67	15.31	70.58	14.69	72.57	14.58	71.84	14.75
$Mg(OH)_2$	59.66	19.19	61.55	17.23	61.70	18.37	61.69	18.14
$Ca(OH)_2$	63.56	17.17	63.54[i]	16.79[i]	63.77[i]	17.41[i]	63.90[i]	17.13[i]

[a] cc-pVTZ+1 for first- and second-row molecules and cc-pWCVTZ for third-row molecules. [b] Frequency scale factor of 0.9135 from ref 33, optimized so as to reproduce ZPVEs. [c] Frequency scale factor of 0.8905 from ref 33, optimized so as to reproduce $\Delta\Delta H_f$. [d] Frequency scale factor of 0.9806 from ref 33, optimized so as to reproduce ZPVEs. [e] Frequency scale factor of 0.9989 from ref 33, optimized so as to reproduce $\Delta\Delta H_f$. [f] Frequency scale factor of 0.9854 from ref 12, optimized so as to reproduce ZPVEs. [g] Frequency scale factor of 0.985 from ref 13, optimized so as to reproduce ZPVEs. [h] An ultrafine grid (i.e., pruned (99, 590)) is required to obtain satisfactory values for the low-frequency bending vibrations in K_2O. [i] Ultrafine grid. The standard (75, 302) grid causes an artifactual symmetry breaking.

ZPVE and $\Delta\Delta H_f$ values are generally insensitive to the level of theory used. There are a small number of cases where the corrections differ by more than 1 kJ mol^{-1} among the methods, notably, variations of up to 3 kJ mol^{-1} for the ZPVEs of LiOH, $Be(OH)_2$, and $Mg(OH)_2$. On this basis, we have chosen, unless otherwise noted, to use ZPVE corrections as originally defined for standard procedures such as G3, W1, and W2.

We also note that in the B3-LYP calculations on K_2O and $Ca(OH)_2$ "ultrafine" integration grids (i.e., pruned (99, 590) in energy and gradient evaluation and pruned (50, 194) in coupled perturbed Kohn−Sham) are required for reliable frequencies. Several other examples of the inadequacy for heavy elements of standard integration grids have previously been pointed out.[49]

3.3. Heats of Formation. 3.3.1. W-Type Procedures. Heats of formation calculated with several variants of the W-type procedures of Martin et al. are presented in Table 6. The methods that are included are (a) standard W1, (b) W1C, which is a modification of W1 in which the core-valence correlation cc-pWCV*n*Z basis sets are used instead of standard cc-pV*n*Z basis sets in the energy extrapolation calculations, (c) standard W2, (d) W2C//W2, which is a modification of W2 in which the core-valence correlation cc-pWCV*n*Z basis sets are used instead of standard cc-pV*n*Z basis sets in the energy extrapolation calculations but the standard W2 geometries obtained at the CCSD(T)(rv,rv)/cc-pVQZ+1 level for first- and second-row systems and at the CCSD(T)(rv,rv)/cc-pWCVQZ level for third-row systems[35b] are employed, (e) W2C, which is like W2C//W2 but with CCSD(T)(riv,rv)/cc-pWCVQZ geometries, and (f) W2C//ACQ, which is like W2C but with CCSD(T)-(riv,rv)/aug′-cc-pWCVQZ geometries. In all cases, results with a variety of correlation spaces on the metal and oxygen atoms, designated as rv, riv, riiv, or riiiv, are examined.

Our highest-level procedure in Table 6 is W2C//ACQ. Among the various choices for the correlation space, we propose riv,rv as a standard. We use the heats of formation calculated by W2C or W2C//ACQ with the riv,rv correlation space as the reference with which results at other levels will be compared.

We note initially that the difference between carrying out W2C//ACQ calculations with the riv,rv correlation space or with the larger riv,riv or riiv,riv correlation spaces is small. The mean absolute deviation (MAD) is 0.3 kJ mol^{-1}, with a largest deviation (LD) of 1.4 kJ mol^{-1}.

Incorporating the inner-valence orbitals in the correlation space is more important, particularly for third-row atoms, as has previously been noted. Thus, the MAD between standard W2C//ACQ with riv,rv and W2C//ACQ with rv,rv is 1.1 kJ mol^{-1} with an LD of 2.5 kJ mol^{-1} for the first- and second-row systems, while for the third-row systems, the MAD is 25.7 kJ mol^{-1} with an LD of 33.8 kJ mol^{-1}.

The effect of using improved geometries through the inclusion of the inner-valence orbitals in the correlation space is reflected in the W2C versus W2C//W2 comparisons. The former uses CCSD(T)(riv,rv)/cc-pWCVQZ geometries, and the latter employs the CCSD(T)(rv,rv)/cc-pVQZ+1 geometries that are standard for W2. As we have seen in section 3.1, the CCSD(T)(rv,rv)/cc-pVQZ+1 geometries show significant deviations in some cases. For the first- and second-row systems, there is not much difference between W2C and W2C//W2. The MAD is 0.4 kJ mol^{-1} with an LD of 1.4 kJ mol^{-1}. There is a larger difference for the third-row systems: the MAD is 7.9 kJ mol^{-1} with an LD of 18.1 kJ mol^{-1}.

Improving the geometry further to CCSD(T)(riv,rv)/aug′-cc-pWCVQZ (i.e., comparing W2C with W2C//ACQ) has a minimal effect on the W2C heats of formation. In most cases, the results agree to 0.1 kJ mol^{-1}. The only larger difference for riv,rv results occurs for CaO (0.2 kJ mol^{-1}).

The standard W1 approach when used with the riv,rv correlation space shows some spectacular failures, with some errors greater than 200 kJ mol^{-1}! These arise because of shortcomings in the ability of the standard cc-pV*n*Z basis sets to handle inner-valence correlation.[50] The errors for both the oxides and the hydroxides follow the ordering Na > Li > Mg > Be. The standard W1 (or W2) basis sets are not defined for third-row systems.

The standard W2 approach also shows some spectacular failures when used with the riv,rv correlation space, in this case with largest errors of about 250 kJ mol^{-1}! Interestingly, the ordering of the errors is almost the exact opposite of that for W1: Mg > Be > Li > Na. For W1, the worst case is Na_2O with a difference from W2C//ACQ of 203.2 kJ mol^{-1} compared with a W2 difference in this case of just 4.5 kJ mol^{-1}. However, for W2 the worst system is $Mg(OH)_2$ with a difference from W2C//ACQ of 247.4 kJ mol^{-1} compared with a W1 difference in this case of 35.3 kJ mol^{-1}.

It is interesting that if the standard W1 and W2 methods are used with the smaller rv,rv correlation spaces for the first- and second-row systems then the results are substantially better than with the riv,rv space. None of the huge errors of the latter situation appear. The MAD values from W2C//ACQ results for W1 and W2 are just 1.2 and 1.9 kJ mol^{-1}, respectively, with

TABLE 6: Calculated Heats of Formation for W-Type Procedures ($\Delta H_{f\ 298}$, kJ mol^{-1})

	correlation space							
molecule	M	O	W1[a]	W1C[b]	W2[c]	W2C//W2[d]	W2C[e]	W2C//ACQ[f]
Li_2O	rv	rv	−158.8	−159.1	−157.0	−157.2	−157.5	−157.5
	riv	rv	−186.8	−159.6	−180.9	−158.6	−159.0	−159.0
	riv	riv	−187.8	−159.7	−172.5	−158.6	−159.0	−159.0
Na_2O	rv	rv	−19.6	−21.1	−18.8	−19.1	−20.2	−20.2
	riv	rv	−225.8	−22.8	−18.1	−21.2	−22.6	−22.7
	riv	riv	−219.0	−22.8	−19.5	−21.1	−22.7	−22.7
K_2O	rv	rv		−30.2		−27.2	−27.9	−27.9
	riv	rv		−60.8		−59.6	−61.7	−61.7
	riiv	riv		−62.8		−58.3	−60.3	−60.3
BeO	rv	rv	125.1	124.7	127.2	127.0	126.9	126.9
	riv	rv	124.4	123.5	114.7	126.7	126.6	126.6
	riv	riv	125.7	123.5	116.3	126.7	126.6	126.6
MgO	rv	rv	142.0	140.5	143.1	142.6	142.5	142.5
	riv	rv	127.8	140.0	64.4	142.0	141.7	141.7
	riv	riv	130.4	139.9	63.0	142.0	141.7	141.7
CaO	rv	rv		36.3		42.1	41.3	41.0
	riv	rv		16.9 (23.1)[g]		25.7	14.4	14.6 (20.3)[h]
	riiv	riv		15.7		25.1	13.8	14.0
LiOH	rv	rv	−241.5	−241.6	−239.5	−239.7	−239.8	−239.8
	riv	rv	−256.2	−241.8	−250.7	−240.2	−240.3	−240.3
	riv	riv	−257.1	−241.9	−248.9	−240.3	−240.4	−240.4
NaOH	rv	rv	−187.7	−188.3	−186.5	−186.8	−187.2	−187.2
	riv	rv	−289.1	−189.6	−182.6	−187.5	−188.1	−188.0
	riv	riv	−286.9	−189.6	−185.5	−187.5	−188.1	−188.1
KOH	rv	rv		−205.8		−203.9	−203.9	−203.9
	riv	rv		−224.9		−223.5	−223.5	−223.5
	riiv	riv		−225.3		−222.9	−222.9	−222.9
$Be(OH)_2$	rv	rv	−637.3	−637.4	−633.1	−634.7	−634.8	−634.8
	riv	rv	−638.8	−638.6	−646.8	−635.1	−635.2	−635.2
	riv	riv	−639.4	−638.5	−653.7	−635.2	−635.3	−635.3
$Mg(OH)_2$	rv	rv	−546.5	−547.7	−544.1	−544.7	−544.9	−545.0
	riv	rv	−582.3	−549.3	−794.4	−546.5	−547.0	−547.0
	riv	riv	−581.4	−549.3	−800.4	−546.6	−547.1	−547.1
$Ca(OH)_2$	rv	rv		−591.4		−574.9	−587.1	−587.3
	riv	rv		−614.7 (−613.0)[g]		−592.3	−610.4	−610.3 (−610.3)[h]
	riiv	riv		−616.1		−592.3	−610.6	−610.5

[a] Standard W1 procedure but with correlation spaces as specified. Note that hypothetical cc-pWV*n*Z basis sets (required for standard W1 calculations) have not been developed for K or Ca because of the necessity of the inclusion of core functions for molecules containing these elements. [b] As for standard W1 but uses cc-pWCV*n*Z instead of cc-pV*n*Z basis sets for metals in energy calculations, including diffuse (aug) functions on oxygen. Uses B3-LYP/cc-pWCVTZ geometries for third-row systems. [c] Standard W2 procedure but with correlation spaces as specified. Note that hypothetical cc-pWV*n*Z basis sets (required for standard W2 calculations) have not been developed for K or Ca because of the necessity of the inclusion of core functions for molecules containing these elements. [d] As for standard W2 but uses cc-pWCVnZ instead of cc-pV*n*Z basis sets in energy calculations, including diffuse (aug) functions on oxygen. Uses CCSD(T)(rv,rv)/cc-pVQZ+1 geometries as in standard W2 for first- and second-row systems and CCSD(T)(rv,rv)/cc-pWCVQZ geometries for third-row systems. [e] As for standard W2C//W2 but uses CCSD(T)(riv,rv)/cc-pWCVQZ geometries. [f] As for standard W2C but uses CCSD(T)(riv,rv)/aug′-cc-pWCVQZ instead of CCSD(T)(riv,rv)/cc-pWCVQZ geometries. [g] Standard W1C but with the cc-pWCV(D+3d)Z, cc-pWCV(T+2d)Z, and cc-pWCV(Q+d)Z basis sets on Ca, as recommended in ref 36, and a Douglas−Kroll relativistic correction. [h] Standard W2C//ACQ but with the cc-pWCV(T+2d)Z, cc-pWCV(Q+d)Z, and cc-pWCV5Z basis sets on Ca, as recommended in ref 36, and a Douglas−Kroll relativistic correction.

LDs of 3.1 and 3.9 kJ mol^{-1}. Thus, for first- and second-row systems, W1 and W2 provide results close to those of our best theoretical levels provided that the correlation space is not expanded beyond rv,rv. It would appear that the standard core-correlation correction of W1 and W2 performs satisfactorily and that the effect of not including the inner-valence electrons in the correlation space in the extrapolation calculations is not particularly serious.

The final comparison of W*n* methods from Table 6 is between W2C and W1C. These produce results that are generally quite close to one another. The MAD between W2C and W1C $\Delta H_{f\ 298}$ values is just 2.0 kJ mol^{-1}, with largest deviations observed for $Ca(OH)_2$ (4.3 kJ mol^{-1}), $Be(OH)_2$ (3.4 kJ mol^{-1}), and BeO (3.1 kJ mol^{-1}). We believe that the differences between W2C and W1C provide approximate minimum estimates of the intrinsic uncertainties in our predicted heats of formation.

As pointed out elsewhere,[15,36] the 4s−3d separation in Ca^+ is quite small, and as a result, basis set convergence becomes highly dependent on the inclusion of high-exponent d functions. Iron et al.[36] have proposed the use of the basis set sequence cc-pWCV(D+3d)Z, cc-pWCV(T+2d)Z, cc-pWCV(Q+d)Z, cc-pWCV5Z as an improvement on the standard cc-pWCVDZ, cc-pWCVTZ, cc-pWCVQZ, cc-pWCV5Z sequence in these circumstances. Redoing the W2C calculations with this alternative basis set sequence lowers the binding energy of CaO by 5.7 kJ mol^{-1}; for W1C, the corresponding effect is 6.2 kJ mol^{-1}. In contrast, the W2C binding energy of $Ca(OH)_2$ is barely affected by the corresponding change, and its W1C counterpart changes only slightly. These results are consistent with the differing bonding character in the CaO and $Ca(OH)_2$ species: a natural population analysis[51] reveals that $Ca(OH)_2$ has essentially pure $Ca^{2+}[OH^-]_2$ character while the bonding in CaO is both less polarized and more covalent in character. The CaO HOMO also has appreciable *d* participation.

3.3.2. G*n*-Type Procedures. Heats of formation calculated with variants of the G3 procedure[10−12,42,43] are presented in Table 7.

The results in columns 2 and 3 correspond to G3[CC] and G3X[CC] procedures that use standard additivity approximations but are carried out on MP2(full)/6-311+G(3df,2p) geometries

TABLE 7: Calculated Heats of Formation ($\Delta H_{f\ 298}$, kJ mol^{-1}) for G*n*-Type Procedures and Associated HLCs[a]

energy	G3[CC][b]	G3X[CC][b]	G3[CC] (dir,full)	G3[CC] (dir,full)	G3[CC] (dir,full)	G3[CC] (dir,full)	G3[CC] (dir,full)	G3[CC] (dir,full)	G3[CC] (dir,full)
geometry	//MP2[c]	//MP2[c]	//AWCVQZ[d]	//AWCVQZ[d]	//AWCVQZ[d]	//MP2[c]	//WCVQZ[e]	//AWCVQZ[d]	//AWCVQZ[d]
ZPVE	HF/V[f]	B3X/Z[g]	B3X/Z[g]	B3X/Z[g]	B3X/Z[g]	B3X/Z[g]	B3X/Z[g]	HF/Z[h]	B3/Z[i]
HLC type	[CC][j]	X[CC][k]	[CC][l]	[CC][m]	[CC](dir,full)[n]	[CC](dir,full)[n]	[CC](dir,full)[n]	[CC](dir,full)[n]	[CC](dir,full)[n]
HLC test set	G2/97	G3/99	G2-1	G2/97	G2-1	G2-1	G2-1	G2-1	G2-1
Li_2O	−151.1	−151.6	−151.2	−150.9	−153.9	−153.7	−153.9	−154.1	−154.0
Na_2O	32.1	32.4	−26.0	−25.7	−28.7	−28.1	−28.7	−29.8	−30.0
K_2O	−20.9	−16.6	−46.9	−41.3	−57.3	−56.8	−57.3	−57.3	−57.8
BeO	144.0	144.7	140.1	141.5	136.8	136.8	136.8	137.2	136.7
MgO	153.5	155.0	144.4	145.9	141.1	141.1	141.1	140.5	141.0
CaO	48.5	51.9	45.5	49.6	38.3	38.4	38.4	38.4	38.3
LiOH	−239.5	−238.8	−233.8	−233.5	−236.5	−236.5	−236.5	−237.4	−237.5
NaOH	−192.9	−193.0	−187.3	−187.0	−190.0	−190.0	−190.0	−190.2	−192.2
KOH	−218.7	−215.9	−214.8	−211.9	−221.4	−221.4	−221.4	−221.9	−221.8
$Be(OH)_2$	−627.6	−623.9	−619.0	−617.2	−625.0	−624.8	−624.9	−627.2	−626.9
$Mg(OH)_2$	−549.7	−547.2	−542.2	−540.4	−548.2	−548.4	−547.4	−549.4	−549.4
$Ca(OH)_2$	−590.7	−586.4	−580.5	−576.1	−590.4	−590.3	−590.4	−590.8	−591.1
A[o]	6.211	6.635	6.743	6.451	6.597	6.597	6.597	6.597	6.597
B[o]	2.941	3.085	2.211	3.122	1.934	1.934	1.934	1.934	1.934
C[o]	5.973	6.645	6.411	6.367	5.895	5.895	5.895	5.895	5.895
D[o]	1.079	1.076	1.251	1.014	1.107	1.107	1.107	1.107	1.107

[a] Unless otherwise specified, all of the G*n* results correspond to CCSD(T) calculations without additivity assumptions (dir) with all electrons correlated (full) and with higher-level correction (HLC) parameters (*A*, *B*, *C*, and *D*) as presented. [b] Calculated using standard additivity assumptions but with an riv,rv correlation space for all systems. For an rv,rv correlation space, the G3[CC] heats of formation are −147.1 (Li_2O), 33.2 (Na_2O), −17.5 (K_2O), 145.7 (BeO), 155.5 (MgO), 68.7 (CaO), −237.7 (LiOH), −192.7 (NaOH), −217.8 (KOH), −624.6 ($Be(OH)_2$), −548.0 ($Mg(OH)_2$), and −573.9 ($Ca(OH)_2$) kJ mol^{-1}. For an rv,rv correlation space, the G3X[CC] heats of formation are −147.6 (Li_2O), 33.4 (Na_2O), −13.1 (K_2O), 146.3 (BeO), 157.0 (MgO), 72.2 (CaO), −237.1 (LiOH), −192.8 (NaOH), −215.0 (KOH), −620.9 ($Be(OH)_2$), −545.5 ($Mg(OH)_2$), and −571.3 ($Ca(OH)_2$) kJ mol^{-1}. [c] Calculated using MP2(full)/6-311+G(3df,2p) optimized structures. [d] Calculated using CCSD(T)/aug′-cc-pWCVQZ optimized structures. [e] Calculated using CCSD(T)/cc-pWCVQZ optimized structures. [f] HF/V signifies ZPVEs calculated using HF/6-31G(d) vibrational frequencies scaled by 0.8929. [g] B3X/Z signifies ZPVEs calculated using B3-LYP/6-31G(2df,p) vibrational frequencies scaled by 0.9854. [h] HF/Z signifies ZPVEs calculated using HF/6-31G(d) vibrational frequencies scaled by 0.9135. [i] B3/Z signifies ZPVEs calculated using B3-LYP/6-31G(d) vibrational frequencies scaled by 0.9806. [j] Calculated using HLC parameters optimized for G3[CC]. From ref 42. [k] Calculated using HLC parameters optimized for G3X[CC]. From ref 43. [l] Calculated using HLC parameters optimized for G3[CC] with the G2-1 test set. From ref 45. [m] Calculated using HLC parameters optimized for G3[CC] with the G2/97 test set. From ref 42. [n] Calculated using HLC parameters optimized for G3[CC](dir,full) with the G2-1 test set. From ref 45. [o] Higher-level correction parameters: $\mathrm{HLC} = -An_\beta - B(n_\alpha - n_\beta)$ for molecules, and $\mathrm{HLC} = -Cn_\beta - D(n_\alpha - n_\beta)$ for atoms.

and with an riv,rv correlation space. This expanded correlation space has been previously recommended as standard for G3 calculations on molecules containing the second- and third-row elements Na, Mg, K, and Ca,[11] but in light of our previous experience with G2 calculations,[2] we also use it here for molecules containing Li and Be. Because G3 and G3X both include MP2(full) calculations with the G3large basis set that could potentially address core-correlation difficulties, it is of interest to determine whether the problems associated with the use of a nonexpanded valence space that we detected in previous G2-based calculations[2] occur if the G3 calculations are also carried out with a nonexpanded rv,rv correlation space, and these results are included as a footnote to Table 7.

The G3[CC] and G3X[CC] results are all within 5 kJ mol^{-1} of one another. Differences of more than 3 kJ mol^{-1} are observed only for CaO (3.4 kJ mol^{-1}), $Be(OH)_2$ (3.7 kJ mol^{-1}), and $Ca(OH)_2$ (4.3 kJ mol^{-1}). Comparing these riv,rv results with the rv,rv results listed in footnote b of Table 7 shows that for both G3[CC] and G3X[CC] the effect of moving from an rv,rv correlation space to the riv,rv correlation space is generally minor. This means that the MP2(full) calculations with the G3large basis set are generally almost as effective at capturing the core correlation through an additive correction to the rv,rv result as they are through an additive correction to the riv,rv results. Larger errors with rv,rv are observed for CaO and $Ca(OH)_2$ where there are differences between the rv,rv and riv,rv results of up to 20 kJ mol^{-1}. Confirmation of the importance of the MP2(full)/G3large calculation comes from the observation that if the MP2/G3large calculations in G3[CC] are carried out with MP2(rv,rv) rather than MP2(full) then poor results are obtained (e.g., 140.9 kJ mol^{-1} for the heat of formation of K_2O compared with the standard G3[CC] result of −20.9 kJ mol^{-1}). Because the riv,rv space leads to improved results in virtually all of the cases examined here, it is recommended as standard for the compounds of all of the alkali and alkaline earth metals. Although these aspects of the performance of G3[CC] and G3X[CC] are encouraging, comparison with W2C//ACQ values (Table 6) suggests that the heats of formation for Na_2O and K_2O reflect continuing problems associated with the standard G3 additivity approximations.

The G3[CC] results in columns 4 and 5 are obtained without any additivity approximations (dir) and with all electrons included in the correlation space (full). However, the HLC parameters are those optimized for standard G3[CC] (with the G2-1 or G2/97 test sets) rather than those reoptimized for G3[CC](dir,full). There are only relatively minor variations between the two sets of results.

Results obtained when the HLC parameters are reoptimized using the G2-1 test set for G3[CC](dir,full) are presented in column 6. Significant differences of up to 16 kJ mol^{-1} are observed between the G3[CC](dir,full) results obtained using the HLC parameters optimized for G3[CC](dir,full) (column 6) and those obtained using standard G3[CC] HLC parameters (columns 4 and 5).

The remaining columns of results correspond to the use of optimized G3[CC](dir,full) HLC parameters. The three sets of results in columns 6, 7, and 8 corresponding to three different geometries (MP2(full)/6-311+G(3df,2p), cc-pWCVQZ, and aug′-cc-pWCVQZ, respectively) are very similar to one another, with a largest variation of 0.7 kJ mol^{-1} (for Na_2O). This

TABLE 8: Comparison of Calculated Electron Affinities (EA), Ionization Energies (IE), and Double Ionization Energies (DIE) with Experimental Values (eV[a])

	G3	G3X	G3[CC] (dir,full)	W1[b]	W1C (riv,rv)	W2[b]	W2C (riv,rv)	exptl[c]
$O^- \rightarrow O$	1.338	1.356	1.252	1.446	1.449	1.449	1.448	1.461
$Li \rightarrow Li^+$	5.397	5.396	5.403	5.387	5.395	5.387	5.393	5.392
$Na \rightarrow Na^+$	5.114	5.113	5.132	5.129	5.137	5.129	5.152	5.139
$K \rightarrow K^+$	4.305	4.304	4.316		4.332		4.335	4.341
$Be \rightarrow Be^+$	9.458	9.477	9.423	9.322	9.322	9.318	9.325	9.323
$Mg \rightarrow Mg^+$	7.785	7.804	7.725	7.633	7.642	7.633	7.649	7.646
$Ca \rightarrow Ca^+$	6.183	6.202	6.197		6.105		6.114	6.113
$Be \rightarrow Be^{2+}$	27.656	27.674	27.628	27.525	27.538	27.521	27.538	27.534
$Mg \rightarrow Mg^{2+}$	22.744	22.762	22.702	22.651	22.680	22.651	22.695	22.681
$Ca \rightarrow Ca^{2+}$	17.971	17.989	17.993		17.975		17.986	17.985
MAD	0.073	0.080	0.064	0.012	0.005	0.012	0.006	
MD	+0.034	+0.046	+0.016	−0.012	−0.004	−0.012	0.002	
LD	+0.139	+0.158	−0.209	−0.030	−0.012	−0.030	0.014	

[a] 1 eV = 96.485 kJ mol^{-1}. [b] Note that hypothetical cc-pV*n*Z basis sets (required for standard W1 and W2 calculations) have not been developed for K or Ca because of the necessity of the inclusion of core functions for molecules containing these elements. Hence, there are no entries in these cases. [c] From ref 56a.

indicates that any choice among these three sets of geometries would be satisfactory for the energy calculations.

Columns 6, 9, and 10 show the effect of using different zero-point energies (and correspondingly optimized HLCs with the ACQ geometries). Again, the variation is small, the largest difference being just 2.3 kJ mol^{-1} (for $Be(OH)_2$).

Our best G3-type heats of formation correspond to G3[CC](dir,full) calculations with optimized HLC parameters using aug′-cc-pWCVQZ optimized structures and B3-LYP/6-31G(2df,p) (B3X/Z) ZPVEs. These are the values shown in column 6. Comparison with W2C//ACQ and experimental results is deferred until section 3.3.7.

3.3.3. Calculation of Electron Affinities and Ionization Energies. Because of the highly ionic character of the metal oxides and hydroxides, it is desirable to use theoretical procedures that yield reasonably accurate values for the electron affinity of oxygen and for the ionization energies of the alkali and alkaline earth metals. Values obtained with our principal theoretical procedures are compared with experiment in Table 8.

G3 performs slightly better than G3X, the MADs being 0.073 and 0.080 eV, respectively. The worst results are obtained for the IEs of Be and Mg, with errors of 0.13−0.16 eV.

G3[CC](dir,full) almost always leads to an improvement over standard G3 and G3X, as might have been expected. The major exception is the electron affinity of the oxygen atom where G3[CC](dir,full) gives 1.252 eV, an error of more than 0.2 eV compared with the experimental value of 1.461 eV, perhaps reflecting insufficient diffuse functions in the G3large basis set. The better results for G3 and G3X must reflect a partial cancellation of errors in the additivity approximations.

Standard W1 and W2 give uniformly good values for the EA of oxygen and the IEs of the first- and second-row metal atoms. In each case, the MADs are just 0.012 eV and the LD is just 0.030 eV. The W1 and W2 methods are not defined for third-row metals because of the absence of appropriate basis sets, so the comparisons are less extensive than for the other methods.

The standard W1C and W2C procedures (i.e., with riv,rv correlation spaces) give a significant improvement over W1 and W2 in most cases. Agreement with experiment is uniformly very good, with MAD values of just 0.005 and 0.006 eV, respectively.

3.3.4. Basis Set Superposition Errors. We have explored the importance of intramolecular basis set superposition errors (BSSEs)[16−19] for W1C and W2C calculations on the alkali metal hydroxides and the alkaline earth metal oxides, with the results shown in Table 9. The BSSEs were calculated using the counterpoise method,[52] and for the MOH molecules, the fragments were taken as M and OH. For the M_2O and $M(OH)_2$ systems, application of the counterpoise corrections in an objective manner is less straightforward, and they were therefore not included here. In addition, intramolecular BSSEs probably should not be considered in G3-type calculations of heats of formation obtained by the atomization method because they would have been partially corrected for already with the empirical higher-level corrections. Their explicit incorporation would thus amount to applying corrections for the same effect twice.

TABLE 9: Calculated Basis Set Superposition Errors (BSSE) for W1C and W2C (kJ mol^{-1})

molecule	W1C (riv,rv)	W2C (riv,rv)
BeO	0.3	−0.2
MgO	0.5	−0.3
CaO	0.6	−0.1
LiOH[a]	0.3	−0.2
NaOH[a]	0.3	−0.4
KOH[a]	0.7	−0.6

[a] Using M and OH as the fragments.

The calculated BSSEs are uniformly small, with a largest absolute value of 0.6 kJ mol^{-1}. This is an encouraging sign of basis set convergence. Because of the small magnitudes of the estimated BSSEs, they were not incorporated into the $\Delta H_{f\ 298}$ calculations. In addition, we note that BSSEs should by definition be positive because they reflect the greater binding in supermolecules compared with that in fragments because of the availability of additional basis functions in the former. The appearance of negative numbers must therefore reflect the "noise" in the components of the composite W1C and W2C procedures.

3.3.5. Multireference Considerations. A value for the $\mathscr{T}_1$ diagnostic[53] of more than 0.02 and a small contribution of the SCF component to the total atomization energy[1b] have each been proposed as an indication of a system with substantial multireference character. For the molecules considered here, all of the oxides except for Li_2O show the multireference warning sign with both diagnostics (Table 10). The extreme case is MgO where the % SCF diagnostic is negative, meaning that MgO is unbound at the SCF level.

To address this point, we have carried out multireference calculations for a selection of the present systems using the

TABLE 10: Diagnostics for Multireference Character in W2C Calculations

molecule	$\mathcal{T}_1$ diagnostic[a]	% SCF[b]
Li_2O	0.018	50.9
Na_2O	0.024	21.2
K_2O	0.027	20.0
BeO	0.035	40.5
MgO	0.036	−38.5
CaO	0.037	16.7
LiOH	0.013	65.8
NaOH	0.011	61.3
KOH	0.012	61.8
$Be(OH)_2$	0.011	76.0
$Mg(OH)_2$	0.011	70.6
$Ca(OH)_2$	0.013	70.4

[a] Value of the $\mathcal{T}_1$ diagnostic in the CCSD(riv,rv)/aug′-cc-pWCVQZ calculation defined in ref 53. [b] Percentage of SCF contribution to the W2C atomization energy.

TABLE 11: Calculated Heats of Formation Using W2C-CAS Procedures ($\Delta H_{f\ 298}$, kJ mol^{-1})[a]

molecule	W2C-CAS-ACPF	W2C-CAS-AQCC	W2C//ACQ
BeO	123.7	122.8	126.6
MgO	139.8	141.4	141.7
CaO	16.5	17.0	14.6
LiOH	−244.1	−246.2	−240.3
NaOH	−191.4	−193.0	−188.0
KOH	−227.9	−230.3	−223.5

[a] The (riv,rv) correlation space was used in the ACPF and AQCC calculations, which were carried out using the ACQ optimized geometry. Standard W2C basis sets (i.e., without the additional tight d functions) were used.

W2C-CAS-ACPF and W2C-CAS-AQCC procedures, and the results are shown in Table 11. We find that for reference systems without significant multireference effects the W2-CAS procedures do not perform quite as well as standard W2, presumably because of the absence of triples in the CCSD treatment,[41] so it is not clear beforehand which set of results in Table 11 is better. For the hydroxides, for which multireference character appears not to be an issue, the W2C-CAS $\Delta H_{f\ 298}$ values are uniformly more negative than our W2C//ACQ values. The average differences are 3.9 (W2C-CAS-ACPF) and 5.9 (W2C-CAS-AQCC) kJ mol^{-1}, respectively. These differences are very similar to those found for the reference H_2O molecule (3.7 and 5.8 kJ mol^{-1}, respectively).[41] However, the W2C-CAS results for CaO are more *positive* than those for W2C//ACQ. This *may* reflect a multireference contribution. If we use the standard differences above to apply an additive correction to the results for the oxides, then we obtain $\Delta H_{f\ 298}$ values for CaO of 20.4 (ACPF) and 22.9 (AQCC) kJ mol^{-1}. The BeO results change marginally to 127.6 (ACPF) and 128.7 (AQCC) kJ mol^{-1}, and the MgO values become 143.7 (ACPF) and 147.3 (AQCC) kJ mol^{-1}. It is not clear whether such corrections are useful, but overall our results suggest that multireference effects do not play a major role in the calculated heats of formation.

3.3.6. Higher-Order Electron Correlation Effects. Because BeO, MgO, and CaO all exhibit significant nondynamical correlation effects, it cannot be automatically assumed that methods based on CCSD will yield the correct answer. However, the systems are sufficiently small that, at least with a double-ζ basis set (cc-pWVDZ without polarization functions, denoted cc-WVDZ), full configuration interaction (FCI) calculations with all valence electrons correlated are feasible. In addition, particularly in MgO and definitely in CaO, the gap between the metal valence orbitals and the oxygen 2s orbital is sufficiently large that the latter can be constrained to be doubly occupied without overly distorting the energetic picture. In this manner, full CI calculations become possible in an augmented polarized double-ζ basis set (aug-cc-pWVDZ). Total energies are given in Table 12.

From the structure of the FCI wave function, it is clear that MgO exhibits the strongest multireference character of the three oxides. Nevertheless, the effect of connected triple excitations is surprisingly well reproduced by the (T) quasiperturbative treatment, as witnessed by the small CCSDT − CCSD(T) differences. The CCSDT − FCI differences suggest a comparatively large contribution of connected quadruple excitations (which increase the binding energy by about 5 kJ mol^{-1} in a polarized double-ζ basis set). Full-valence CAS-ACPF and CAS-AQCC appear to reproduce the full CI result with the cc-VDZ basis set very well, giving credence to the W2C-CAS numbers.

In contrast to the situation in MgO, the quasiperturbative triples treatment performs somewhat more poorly in BeO, but the CCSDT − FCI difference (expected to be dominated by connected quadruples contributions) is fairly small. For both BeO and MgO, the CCSD(T) − FCI difference is approximately 5 kJ mol^{-1} with the cc-VDZ basis set. Although we have not made such a correction in our final recommended heats of formation for these molecules (see below), we have increased the assigned uncertainty by this amount.

It has been claimed on several occasions[54] that methods based on Brueckner doubles (BD) are more appropriate than CC-based methods for systems with significant nondynamical correlation effects. In the present case, however, BD(T) energies consistently deviate further from FCI than CCSD(T), which means that a putative W2C-BD(T) method (akin to variants of the G2[55] and G3X[43] methods) would in fact be less reliable than standard W2C.

As noted in section 3.2.2 and previously,[15,36] the low-lying 3d orbitals in Ca^+ cause an exceedingly high sensitivity to the presence of high-exponent d functions in the calculated properties of CaO. As a result, a calculation using a valence-only cc-pVDZ basis set on Ca erroneously yields an essentially biconfigurational wave function. Adding core-correlation functions (particularly the higher-exponent d functions) causes both a dramatic improvement in the SCF energy and a change in the character of the wave function to a regime similar to BeO. Because of the low-lying 3d orbitals in Ca, the 6-in-7 active space employed for BeO and MgO is no longer as appropriate for CaO. When using a 6-in-12 active space, the full CI energy can be reproduced nearly exactly at both the CAS-ACPF and CAS-AQCC levels.

3.3.7. Comparison of Theoretical and Experimental Heats of Formation. Literature experimental values for the heats of formation of the metal oxides and hydroxides are presented in Table 13.[46a,56] The listed values come from several widely used compendia plus a small number of recent individual studies. We have generally not included references to the older experimental heats of formation that underlie the analyses in the compendia.

It is striking that there are very large variations among the different experimental values for many of the systems, and there are also large error bars in many cases. Clearly, unlike the situation for standard organic molecules, very few of the metal oxides and hydroxides could be said to have definitive experimental heats of formation. This indicates that these molecules are not straightforward targets for experimental gas-phase study and that theory has a potentially useful role to play in assigning reliable heats of formation.

TABLE 12: Comparison of Calculated Total Energies (hartrees) of BeO, MgO, and CaO

method	BeO[a]	MgO[a]	BeO[b]	MgO[b]
SCF	−89.391964	−274.336263	−89.419340	−274.356732
CCSD(T)	−89.574322	−274.547806	−89.612909	−274.576600
CCSDT	−89.575578	−274.548258	−89.613575	−274.576333
BD(T)	−89.573283	−274.544607	−89.612209	−274.573823
CASSCF	−89.553198[c]	−274.514308[c]	−89.542146[d]	−274.510740[d]
CAS-ACPF	−89.576065[c]	−274.550094[c]	−89.614019[d]	−274.577537[d]
CAS-AQCC	−89.575943[c]	−274.549798[c]	−89.613499[d]	−274.576890[d]
FCI	−89.576077	−274.549965	−89.614303	−274.578253

CaO	AWVDZ	AWCVDZ	AWCVTZ	AWCVQZ
SCF	−751.478199	−751.527242	−751.574623	−751.594011
CCSD	−751.675449	−751.710125	−751.776767	−751.804956
BD	−751.676974	−751.707367	−751.774927	−751.803388
CCSD(T)	−751.707783	−751.724675	−751.791375	−751.820537
BD(T)	−751.693626	−751.72181	−751.790608	−751.819917
CCSDT	−751.695151	[e]	[e]	[e]
CASSCF(6/7)	−751.637167	−751.656348	−751.698994	−751.720192
CAS(6/7)-ACPF	−751.696699	−751.723532	−751.790601	−751.819468
CAS(6/7)-AQCC	−751.696279	−751.723029	−751.789855	−751.818684
CASSCF(6/12)	−751.681424	−751.703379	−751.751459	−751.772523
CAS(6/12)-ACPF	−751.697204	−751.724376	−751.791467	−751.820404
CAS(6/12)-AQCC	−751.697124	−751.724292	−751.791305	−751.820202
FCI	−751.697344			

[a] Using cc-VDZ on metal and aug-cc-VDZ on oxygen (i.e., cc-pVDZ and aug-cc-pVDZ without polarization functions) with all valence electrons correlated. [b] Using cc-pVDZ on metal and aug-cc-pVDZ on oxygen with all valence electrons except the 2s on oxygen correlated. [c] Using an 8-in-8 (8/8) active space. [d] Using a 6-in-7 (6/7) active space. [e] Could not be calculated because of near-linear dependence problems.

TABLE 13: Experimental and Best Predicted Heats of Formation ($\Delta H_{f\ 298}$, kJ mol^{-1})

molecule	G2[CC] (dir,full)[a]	G3[CC] (dir,full)[b]	W1C[c]	W2C//ACQ[c]	recommended[d]	experimental
Li_2O	−160.9	−153.9	−159.6	−159.0	−157 ± 5	−166.94 ± 10.5,[e] −160.7[f]
Na_2O	−29.5	−28.7	−22.8	−22.7	−25 ± 5	−36.0 ± 8,[g] −35.6[f]
K_2O	−46.2	−57.3	−60.8	−61.7	−60 ± 5	−142 ± 15,[h] −63[f]
BeO	+134.4	+136.8	+123.5	+126.6	+130 ± 12[i]	136.4 ± 13,[e] 117,[f] 122.4,[j] 128.9 ± 11,[k] 138.5 ± 14.3[l]
MgO	+145.1	+141.1	+140.0	+141.7	+142 ± 10[i]	58.16 ± 25.1,[e] 151 ± 21,[m] 17,[f] 32.27 ± 10,[k] 33.1 ± 12.6[l]
CaO	+59.0	+38.3	+23.1[n]	+20.3[o]	+26 ± 17	43.9 ± 21,[e] 44.9[f,p], ≥ −35.9 ± 14.5,[j] 38.01 ± 10,[k] 24.9 ± 16.7[l]
LiOH	−245.3	−236.5	−241.8	−240.3	−239 ± 5	−234.30 ± 6.3,[e] −229.0 ± 5,[q] −238.1[f]
NaOH	−195.7	−190.0	−189.6	−188.0	−189 ± 5	−197.76 ± 12.6,[e] −191 ± 8,[q] −207.1[f]
KOH	−223.4	−221.4	−224.9	−223.5	−223 ± 5	−232.63 ± 12.6,[e] −231.0[f]
$Be(OH)_2$	−634.7	−625.0	−638.6	−635.2	−632 ± 7	−677 ± 38,[e] −661,[f] −638.01 ± 15[k]
$Mg(OH)_2$	−549.8	−548.2	−549.3	−547.0	−547 ± 5	−572.37 ± 33.5,[e] −561,[f] −522.02 ± 20[k]
$Ca(OH)_2$	−596.7	−590.4	−613.0[n]	−610.3[o]	−604 ± 19	−610.76 ± 37.7,[e] −544,[f] −598.29 ± 15[k]

[a] From ref 2. [b] From Table 7. [c] From Table 6. [d] See Section 3.3.7. [e] JANAF Tables, 4th ed.[56a] [f] Wagman et al.[56c] [g] Steinberg and Schofield.[56d] [h] Lias et al.[56b] [i] The recommended values for BeO and MgO do not include the 5 kJ mol^{-1} correction discussed in Section 3.3.6. [j] Calculated from D_0 values of 4.6_0 (BeO), 3.5_3 (MgO), and 4.7_6 (CaO) eV in Huber and Herzberg.[46a] [k] As cited in Gurvich et al.[56h] [l] Calculated from D_{298} values of 434.7 (BeO), 363.2 (MgO), and 402.1 (CaO) kJ mol^{-1} in Kerr and Stocker.[56i] [m] Operti et al.[56e] [n] Standard W1C but with the cc-pWCV(D+3d)Z, cc-pWCV(T+3d)Z and cc-pWCV(Q+d)Z basis sets on Ca, as recommended in ref 36, and the Douglas−Kroll scalar relativistic correction. [o] Standard W1C but with the cc-pWCV(T+2d)Z, cc-pWCV(Q+d)Z and cc-pWCV5Z basis sets on Ca, as recommended in ref 36, and the Douglas−Kroll scalar relativistic correction. [p] Obtained using $\Delta H_{f\ 0}$ value of 46.0 kJ mol^{-1} from Wagman et al.[56c] and theoretical temperature correction to 298 K. [q] Gurvich et al.[56g]

Table 13 includes a comparison of (a) our best previous $\Delta H_{f\ 298}$ predictions,[2] obtained at the G2[CC](dir,full) level using MP2(full)/6-311+G(3df,2p) geometries, (b) the best G3-type results obtained in the present study, namely, G3[CC](dir,full) calculations with optimized HLC parameters using aug′-cc-pWCVQZ optimized structures and B3-LYP/6-31G(2df,p) (B3X/Z) ZPVEs, (c) W1C heats of formation, (d) W2C//ACQ heats of formation, and (e) the experimental $\Delta H_{f\ 298}$ values.

An examination of the results in Table 13 shows that the best agreement between G3[CC](dir,full) and W2C//ACQ occurs for the oxides and hydroxides of Mg, followed by those of K, Na, and Li. In all of these cases, the two sets of heats of formation agree to within 6 kJ mol^{-1}. However, larger discrepancies of 10 kJ mol^{-1} occur for BeO and $Be(OH)_2$, 18 kJ mol^{-1} for CaO, and 20 kJ mol^{-1} for $Ca(OH)_2$, discrepancies that intriguingly are roughly the same for the two members of each set. Our recommended $\Delta H_{f\ 298}$ values are obtained as weighted averages of the W2C//ACQ and G3[CC](dir,full) values. Because the W2C values are considered to be the more reliable, we have assigned them twice the weight of the G3[CC](dir,full) values. The uncertainties are taken as 5 kJ mol^{-1} or the difference between the G3[CC](dir,full) values and the weighted average, whichever is greater. In addition, on the basis of the higher-order correlation effects (section 3.3.6), we have added 5 kJ mol^{-1} to the uncertainty interval for BeO, MgO, and CaO. Confirmatory evidence for the heats of formation of BeO and CaO in particular would be highly desirable. It is intriguing that MgO and $Mg(OH)_2$ show the greatest internal consistency in calculated heats of formation among the various methods whereas CaO and $Ca(OH)_2$ (and to a lesser extent BeO and $Be(OH)_2$) show the greatest variation.

It is instructive to examine in more detail possible reasons for the discrepancy between the G3[CC](dir,full) and W2C//ACQ $\Delta H_{f\ 298}$ values for CaO. For G3[CC](dir,full), the contribution to the heat of formation at CCSD(T)/G3large is +58.3 kJ mol^{-1}, to which must be added the higher-level correction of −24.4 kJ mol^{-1} and a spin−orbit correction of +0.9 kJ mol^{-1}, leading to +34.8 kJ mol^{-1} for the "vibrationless" heat of formation. Adding in ZPVE (+4.7 kJ mol^{-1}) and temperature (−1.2 kJ mol^{-1}) corrections leads to a final $\Delta H_{f\ 298}$ of +38.3 kJ mol^{-1} (as in Table 13). For the W2C method, we have carried out an additional CCSD(T)/aug′-cc-pWCV5Z//ACQ calculation on CaO to help with the analysis. The raw heats of formation calculated at the CCSD(T) level with the aug′-cc-pWCV(Q+d)Z and aug′-cc-pWCV5Z basis sets are +26.9 and +18.1 kJ mol^{-1}, respectively. These are already significantly lower than the CCSD(T)/G3large + HLC value of +33.9 kJ mol^{-1}. Extrapolation to an infinite basis set leads to +9.0 kJ mol^{-1}, to which must be added spin−orbit (+0.9 kJ mol^{-1}), core correlation (−0.8 kJ mol^{-1}), and scalar relativistic (+7.4 kJ mol^{-1}) corrections, giving +16.5 kJ mol^{-1} for the vibrationless value. Adding in ZPVE (+4.4 kJ mol^{-1}) and temperature (−1.1 kJ mol^{-1}) corrections leads to a $\Delta H_{f\ 298}$ of +19.8 kJ mol^{-1} (which is close to the value of +20.3 kJ mol^{-1} in Table 13).[57] Thus, it would seem that a rather large basis set is required for calcium to obtain an accurate description of the thermochemistry for CaO (and presumably also $Ca(OH)_2$).

The experimental heats of formation for most of the metal oxides and hydroxides (Table 13) span a wide range, often with significant error bars, and they therefore do not offer definitive reference points. We believe that our recommended theoretical values probably represent the most reliable estimates of $\Delta H_{f\ 298}$, either experimental or theoretical, currently available. In most cases, our recommended heats of formation are consistent with at least one of the listed experimental values. For K_2O and MgO, the calculated values are able to discriminate between two quite separated experimental results in each case, to favor −63 kJ mol^{-1} for K_2O[56c] and +151 kJ mol^{-1} for MgO.[56e]

4. Conclusions

Several important points emerge from the current study of the structures and heats of formation of alkali metal and alkaline earth metal oxides and hydroxides.

(1) All of the standard methods that we have used produce reasonable geometries for these molecules. The best results are obtained with CCSD(T)(riv,rv)/aug′-cc-pWCVQZ (MAD = 0.007 Å), but good results are also obtained with CCSD(T)(riv,rv)/cc-pWCVQZ, B3-LYP/cc-pVTZ, B3-LYP/6-31G(2df,p) and MP2/6-311+G(3df,2p). The excellent results obtained with CCSD(T)(riv,rv)/aug′-cc-pWCVQZ (abbreviated ACQ) lend confidence to predictions in cases where experimental structures are not available.

(2) Calculated zero-point vibrational energies do not vary much between the various methods used and therefore are unlikely to contribute significantly to uncertainties in the calculated heats of formation.

(3) Obtaining reliable thermochemistry for the metal oxides and hydroxides, however, provides a challenge for high-level theoretical procedures.

(4) Unlike the situation for G2, the use of an rv,rv correlation space in the G3 and G3X procedures leads to reasonable estimates of the heats of formation for most of the metal oxides and hydroxides because of the incorporation of core correlation through the MP2(full)/G3large calculation. Even better results are obtained for G3 and G3X with an riv,rv correlation space, and this is the recommended standard procedure. However, (a) additivity sometimes fails badly (e.g., for Na_2O), a shortcoming that may be overcome by carrying out direct (dir) calculations, and (b) QCISD(T) sometimes fails badly (e.g., for CaO) but this may be overcome by carrying out CCSD(T) calculations instead. The best results are obtained with the G3[CC](dir,full) method.

(5) Standard W1 and W2 calculations give reasonable results for the heats of formation of the metal oxides and hydroxides. However, expanding the correlation space (riv) in the extrapolation calculations can lead to spectacular failures in some instances. The inclusion of core-correlation functions, as in the cc-pWCV*n*Z basis sets, removes these problems. Our best directly calculated heats of formation correspond to W2 calculations using these basis sets on ACQ geometries and are denoted W2C//ACQ.

(6) On the basis of comparisons among the methods that we have used, our recommended heats of formation, obtained as weighted averages of the W2C//ACQ and G3[CC](dir,full) values, carry an uncertainty of 5−10 kJ mol^{-1}, with a somewhat larger uncertainty in the cases of BeO, CaO, and $Ca(OH)_2$.

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