7522 J. Phys. Chem. A **1999,** *103,* 7522−7527

Heats of Formation of Alkali and Alkaline Earth Oxides and Hydroxides: Some Dramatic Failures of the G2 Method

Axel Schulz,[†,‡] Brian J. Smith,*[,§] and Leo Radom*[,†]

Research School of Chemistry, Australian National University, Canberra, ACT 0200, Australia,
Institut für Anorganische Chemie, Ludwig-Maximilians University of Munich, Butenandtstrasse 1,
D-81377 München, Germany, and Biomolecular Research Institute, 343 Royal Parade,
Parkville, VIC 3052, Australia

Received: May 14, 1999; In Final Form: July 7, 1999

High-level ab initio calculations with a variety of G2-based methods have been used to determine the structures and heats of formation of the alkali and alkaline earth oxides and hydroxides (M_2O, MOH with M = Li, Na, and K; M′O, M′$(OH)_2$ with M′ = Be, Mg, and Ca). Standard G2 theory, which is normally very reliable for the prediction of molecular thermochemistry, is shown to be quite unsuitable for the prediction of the heats of formation of several of these highly polar species, with errors greater than 100 kJ mol^{-1} in some cases. Our calculations confirm 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. Interestingly, an analogous relaxed-inner-valence (denoted riv) procedure is more beneficial for the Li- and Be-containing oxides and hydroxides than for the Na- and Mg-containing molecules. Inclusion of all orbitals in the correlation space (denoted full) generally provides only a slight further improvement to the results. Removal of the additivity approximation of standard G2 theory through direct large basis set QCISD(T) calculations [e.g., G2(dir,full)] has a large effect for the oxides CaO and K_2O. The QCISD(T) component of the G2 energy is poorly described for CaO, Na_2O, and K_2O, but this can be rectified through replacement of QCISD(T) with CCSD(T) [e.g., G2[CC](dir,full)]. For five molecules (CaO, $Be(OH)_2$, $Mg(OH)_2$, $Ca(OH)_2$, and K_2O) where significant discrepancies (10−30 kJ mol^{-1}) remain between the best theoretical heats of formation (i.e., G2[CC](dir,full)) and experimental values, we suggest that experimental reexamination is desirable. Structures determined at the MP2/6-311+G(3df,2p) level are in good agreement with available experimental data. Structures obtained at the standard MP2/6-31G(d) level of G2 theory are not as good, but the impact of using the simpler geometries on calculated heats of formation is generally relatively small.

1. Introduction

The oxides and hydroxides of alkali and alkaline earth metals represent highly ionic systems where bonding is predominantly electrostatic. They are known to include some of the strongest known bases in the gas phase. Most experimental information about such species is based on the solid state. Their study in the gas phase is made difficult because of low volatility, high reactivity, and complex vapor composition.

An alternative means of obtaining reliable information on systems of this type comes from high-level ab initio molecular orbital calculations. One such method is G2 theory,[1,2] which has proved to be an accurate and efficient procedure for the prediction of molecular thermochemistry. G2 and its more economical variants G2(MP2)[3] and G2(MP2,SVP)[4] are found to consistently predict atomization energies, electron and proton affinities, ionization energies, and heats of formation to within 10 kJ mol^{-1} of experiment. However, there are a number of cases where G2 fails to give accurate estimates of energies,[5−7] and further assessment of molecules not strongly represented in the G2 test set is desirable. In the present study, we provide critical documentation and evaluation of several different G2 approaches to the estimation of the heats of formation for alkali (Li, Na, and K) and alkaline earth (Be, Mg, and Ca) oxides and hydroxides. Some of these molecules have been the subject of important previous theoretical studies.[1,8−14]

2. Theoretical Procedures

Standard ab initio molecular orbital calculations[15] have been carried out with the GAUSSIAN 94,[16] MOLPRO,[17] and ACESII[18] program packages.

Structures were optimized at the MP2(full) level with the following basis sets: 6-31G(d) (standard in G2), 6-311G(d,p), 6-311+G(2df,p), and 6-311+G(3df,2p). Geometry optimizations were also performed at the computationally more expensive CCSD(T) level with a subset of these basis sets. Comparisons are made with experimental structures taken from standard compendia.[19,20]

Energies were initially obtained at the standard G2 level of theory.[1] This is a composite method that corresponds effectively to calculations at the QCISD(T)/6-311+G(3df,2p) level on MP2-(full)/6-31G(d) optimized geometries, incorporating scaled (by 0.8929) HF/6-31G(d) zero-point energies (ZPE) and a “higher-level correction” (HLC) term. The HLC is an empirical correction designed to compensate for incomplete basis sets and other deficiencies in the theoretical treatment. It is given by HLC $= -Bn_\alpha - An_\beta$, where n_α and n_β are the number of α and β valence electrons, respectively. In all the calculations presented in this paper, A and B take the values 4.81 and 0.19 mhartrees, respectively.

[†] Australian National University.
[‡] Permanent address: University of Munich.
[§] Biomolecular Research Institute.

10.1021/jp991577+ CCC: $18.00

TABLE 1: Core and Valence Orbitals Included in the Correlation Space

	frozen	active
	G2	
Li, Be	1s	2s,2p
Na, Mg	1s,2s,2p	3s,3p
K, Ca[a]	1s,2s,2p,3s,3p	4s,4p
O	1s	2s,2p
H		1s
	G2(riv)[b]	
Li, Be		1s,2s,2p[c]
Na, Mg	1s	2s,2p,3s,3p
K, Ca	1s,2s,2p	3s,3p,4s,4p
O	1s[d]	2s,2p
H		1s
	G2(full)	
Li, Be		1s,2s,2p
Na, Mg		1s,2s,2p,3s,3p
K, Ca		1s,2s,2p,3s,3p,4s,4p
O		1s,2s,2p
H		1s

[a] Blaudeau et al.[14] have recommended that standard G2 calculations on K- and Ca-containing molecules should include the 3s and 3p orbitals of K and Ca in the correlation space. However, for consistency with our notation for the elements of the first and second rows, we use the G2 label to refer to a calculation with a 4s,4p correlation space for K and Ca. [b] The notation riv stands for relaxed-inner-valence. [c] Same as full. [d] Remains frozen core.

In standard G2 theory, the component energies are evaluated using the frozen-core approximation. We have investigated the adequacy of this approximation by examining the effect of extending the correlation space to include, in addition to the valence orbitals, the next shell of orbitals for the metal atoms. We denote this level as G2(riv) to indicate *relaxed-inner-valence* orbitals. Such a procedure has previously been found to be important for molecules containing K and Ca.[14] Indeed, Blaudeau et al.[14] have recommended the inclusion in the correlation space of the 3s and 3p orbitals of K and Ca as standard for G2 calculations.[21] The importance of the inclusion of inner-valence electrons in the correlation space in MP, CI, and CC calculations for molecules containing Na and K has been pointed out,[22] and it has also been demonstrated in G2 calculations on molecules containing Na bound to electronegative elements such as F.[23] In a related vein, it has been found that inclusion of 3d orbitals in the correlation space is important for molecules in which an electropositive third-row element such as Ga is bonded to an electronegative element such as O or F, leading to the suggestion of a G2(d) procedure in such situations.[24] In all of these cases, mixing of orbitals that would normally not be included in the correlation space with valence orbitals of attached atoms is the key reason that their exclusion is inappropriate and can lead to poor results. In addition to the G2(riv) calculations, we have also performed calculations in which all electrons are included in the electron correlation treatment. These are denoted in standard fashion as G2(full). The correlation spaces used in the various procedures are summarized in Table 1.

In a second series of calculations, the effectiveness of the additivity approximations in standard G2 theory was investigated through *direct* QCISD(T)/6-311+G(3df,2p) calculations.[25a] These calculations were carried out for the three different correlation spaces and are denoted as G2(dir), G2(dir,riv), and G2(dir,full) where dir denotes direct, i.e., without additivity.

In a third series of calculations, the effect of geometry variation was examined by carrying out the G2(dir,full) calculations with MP2/6-311+G(3df,2p) geometries for comparison with results obtained using the MP2/6-31G(d) geometries that are standard for G2.

TABLE 2: Calculated Structures of Alkaline Earth Oxides M′O (M′ = Be, Mg, Ca)[a]

	6-31G(d)	6-311G(d,p)	6-311+ G(2df,p)	6-311+ G(3df,2p)	exptl[b]
		BeO			
MP2, r(M′−O)	1.356	1.348	1.346	1.343	1.3309
CCSD(T), r(M′−O)	1.349	1.343	1.337	1.333	
		MgO			
MP2, r(M′−O)	1.733	1.740	1.746	1.745	1.749
CCSD(T), r(M′−O)	1.768	1.775	1.759	1.751	
		CaO			
MP2, r(M′−O)	1.811	1.908	1.826	1.837	1.8221
CCSD(T), r(M′−O)	1.948	2.014	1.848	1.856	

[a] Bond lengths in angstrom. [b] Reference 19.

Finally, we examined the replacement of the QCISD(T) component of G2 theory with a coupled-cluster CCSD(T) energy.[25b] We denote such methods as G2[CC]. These were performed using the MP2/6-311+G(3df,2p) optimized geometries. The influences of the correlation space and additivity approximations were also investigated for this method, leading to G2[CC], G2[CC](riv), G2[CC](full), G2[CC](dir), G2[CC](dir,riv), and G2[CC](dir,full) energies. A small number of the G2[CC] calculations were performed using an analogue of the G2+ approach[26] to investigate the effect of including diffuse functions in the reference basis set of the G2 additivity scheme.

Molecular heats of formation at 298 K (ΔH_{f298}) were obtained from the calculated total energies and experimental heats of formation and temperature corrections for the elements,[27,28] using the atomization method, as described by Nicolaides et al.[29] Temperature corrections for the oxides and hydroxides were derived using the calculated vibrational frequencies and standard statistical thermodynamics methods.[30] Low-frequency internal rotations (below 260 cm^{-1}) were treated as free rotors, each contributing $RT/2$. The theoretical ΔH_{f298} values are compared with available experimental values taken primarily from the compendia of Lias et al.,[27] Wagman et al.,[28] Chase et al.,[31] and Gurvich et al.[32] Charge distributions were obtained using the atoms-in-molecules (AIM) procedure.[33]

3. Results and Discussion

3.1. Structures. Structural parameters at the various levels of theory are compared with experimental data from standard compendia[19,20] in Tables 2−5. All species with the exception of $Be(OH)_2$ are predicted to be linear at the MP2/6-311+G(3df,2p) level.

3.1.1 Oxides. The structurally simplest systems of the present study are the alkaline earth oxides, characterized by a single M′−O bond length (Table 2). Except for CaO, the calculated bond length is not particularly sensitive either to the size of basis set or to the correlation procedure. It is interesting that the 6-311G(d,p) lengths for CaO appear to be worse than either the smaller or larger basis set results and that there appear to be significant errors with both CCSD(T)/6-31G(d) and CCSD(T)/6-311G(d,p). The MP2/6-311+G(3df,2p) bond lengths for all the M′O systems lie within 0.02 Å of the experimental values.[19]

TABLE 3: Calculated Structures of Alkali Metal Oxides M_2O (M = Li, Na, K)[a]

	6-31G(d)	6-311G(d,p)	6-311+G(2df,p)	6-311+G(3df,2p)	exptl[b]
Li_2O					
MP2	$D_{\infty h}$	$D_{\infty h}$	$D_{\infty h}$	$D_{\infty h}$	$D_{\infty h}$
r(M−O)	1.653	1.635	1.634	1.635	1.60(5)
CCSD(T)	$D_{\infty h}$	$D_{\infty h}$	$D_{\infty h}$	$D_{\infty h}$	
r(M−O)	1.644	1.626	1.622	1.621	
Na_2O					
MP2	C_{2v}	C_{2v}	C_{2v}	$D_{\infty h}$	
r(M−O)	2.036	2.037	2.021	2.012	
∠MOM	130.1	132.6	160.7	180.0	
CCSD(T)	C_{2v}	C_{2v}	$D_{\infty h}$	$D_{\infty h}$	
r(M−O)	2.031	2.038	1.997	1.992	
∠MOM	124.8	124.5	180.0	180.0	
K_2O					
MP2	C_{2v}	C_{2v}	$D_{\infty h}$	$D_{\infty h}$	
r(M−O)	2.234	2.276	2.254	2.261	
∠MOM	158.5	160.2	180.0	180.0	
CCSD(T)	$D_{\infty h}$				
r(M−O)	2.232				
∠MOM	180.0				

[a] Bond lengths in angstrom, angles in degrees. [b] Reference 20.

TABLE 4: Calculated Structures of Alkali Metal Hydroxides MOH (M = Li, Na, K)[a]

	6-31G(d)	6-311-G(d,p)	6-311+G(2df,p)	6-311+G(3df,2p)	exptl[b]
LiOH					
MP2					
r(M−O)	1.594	1.575	1.592	1.591	1.5816(10)
r(O−H)	0.960	0.950	0.953	0.949	0.9691(21)
CCSD(T)					
r(M−O)	1.594	1.575	1.587	1.588	
r(O−H)	0.961	0.950	0.952	0.948	
NaOH					
MP2					
r(M−O)	1.921	1.932	1.956	1.948	1.95(2)
r(O−H)	0.962	0.952	0.955	0.952	
CCSD(T)					
r(M−O)	1.921	1.932	1.950	1.944	
r(O−H)	0.964	0.952	0.954	0.951	
KOH					
MP2					
r(M−O)	2.155	2.188	2.213	2.213	2.196(3)
r(O−H)	0.964	0.954	0.958	0.955	0.960(10)
CCSD(T)					
r(M−O)	2.159	2.192	2.216	2.216	
r(O−H)	0.966	0.955	0.957	0.954	

[a] Bond lengths in angstrom, angles in degrees. All structures have $C_{\infty v}$ symmetry. [b] Reference 20.

The alkali oxides are found to be linear with our largest basis set correlated calculations (Table 3). However, for several of the smaller-sized basis sets, bent structures are found both for Na_2O and for K_2O. For example, MP2(full) and CCSD(T)(full) calculations with the 6-311G(d,p) basis set reveal shallow minima for bent Na_2O and K_2O structures, lying 1.9 and 0.1 kJ mol^{-1} (MP2/6-311G(d,p)), respectively, lower in energy than the linear structures. The bending potentials are in fact very flat in all cases. The M−O and O−H bond lengths do not show a strong variation with level of theory, and there is satisfactory agreement with experimental results for the Li−O length of Li_2O.[20]

3.1.2 Hydroxides. Microwave and infrared spectra indicate that the gaseous alkali hydroxide molecules have linear or near-linear structures and possess low-frequency bending vibrations.[34] Our calculations are in agreement with these findings, linear structures being predicted at all levels of theory (Table 4). It has been suggested[13] that the linear structures result from strong Coulombic repulsion between hydrogen and the metal atoms, both of which bear considerable positive charge (see Table 6). Linear structures would also maximize the overlap between the donor p orbitals on oxygen and acceptor p orbitals on the metal atom, which would be important for those molecules with significant covalent character. The MP2 and CCSD(T) results are very close to one another with all basis sets, the largest difference in bond lengths being just 0.006 Å. Our best structures are in close agreement with experimental results,[20] all bond lengths agreeing to within 0.02 Å.

TABLE 5: Calculated Structures of Alkaline Earth Hydroxides M′$(OH)_2$ (M′ = Be, Mg, Ca)[a]

	6-31G(d)	6-311G(d,p)	6-311+G(2df,p)	6-311+G(3df,2p)
$Be(OH)_2$				
MP2	C_2	C_2	C_2	C_2
r(M′−O)	1.436	1.434	1.428	1.424
r(O−H)	0.963	0.954	0.954	0.950
∠OM′O	177.4	178.2	174.6	174.5
∠HOM′	124.3	121.7	131.1	133.3
∠HOM′O	134.5	139.4	133.9	132.9
CCSD(T)	C_2	C_2		
r(M′−O)	1.435	1.433		
r(O−H)	0.965	0.954		
∠OM′O	177.5	177.1		
∠HOM′	123.8	121.5		
∠HOM′O	134.0	138.6		
$Mg(OH)_2$				
MP2	C_2	C_2	$D_{\infty h}$	$D_{\infty h}$
r(M′−O)	1.807	1.808	1.767	1.761
r(O−H)	0.963	0.951	0.950	0.946
∠OM′O	178.1	177.2	180.0	180.0
∠HOM′	133.4	136.0	180.0	180.0
∠HOM′O	129.0	137.5	180.0	180.0
CCSD(T)	C_2	C_2		
r(M′−O)	1.807	1.806		
r(O−H)	0.964	0.951		
∠OM′O	177.9	177.1		
∠HOM′	133.6	136.8		
∠HOM′O	126.4	133.8		
$Ca(OH)_2$				
MP2	C_{2v}	C_{2v}	$D_{\infty h}$	$D_{\infty h}$
r(M′−O)	2.014	2.034	2.040	2.043
r(O−H)	0.960	0.951	0.955	0.952
∠OM′O	154.2	162.5	180.0	180.0
∠HOM′	173.2	175.5	180.0	180.0
∠HOM′O	0.0	0.0	0.0	0.0
CCSD(T)	C_{2v}			
r(M′−O)	2.017			
r(H−O)	0.962			
∠OM′O	154.2			
∠HOM′	173.2			
∠HOM′O′	0.0			

[a] Bond lengths in angstrom, angles in degrees.

TABLE 6: Calculated AIM Charges[a]

	LiOH	NaOH	KOH	$Be(OH)_2$	$Mg(OH)_2$	$Ca(OH)_2$
M (M′)	+0.92	+0.93	+0.91	+1.72	+1.79	+1.71
O	−1.47	−1.45	−1.41	−1.47	−1.49	−1.41
H	+0.55	+0.52	+0.51	+0.61	+0.60	+0.56
	Li_2O	Na_2O	K_2O	BeO	MgO	CaO
M (M′)	+0.89	+0.78	+0.79	+1.54	+1.22	+1.26
O	−1.79	−1.55	−1.58	−1.54	−1.22	−1.26

[a] MP2/6-311+G(3df,2p) geometry, MP2/6-311+G(d,p) density.

The M−O bond lengths in the alkali metal hydroxides (MOH) are considerably shorter than in the corresponding oxides (M_2O).

TABLE 7: Calculated and Experimental Heats of Formation for G2-Type Procedures (ΔH_{f298}, kJ mol^{-1})

	G2	G2(riv)	G2(full)	G2(dir)	G2(dir,riv)	G2(dir,full)	G2(dir,full)[a]	exptl
Li_2O	−144.0	−155.7	−157.6	−148.2	−159.6	−162.1	−163.2	−166.9 ± 1.5[b]
Na_2O	68.5	63.3	61.3	−11.1	7.5	−2.0	−32.1	−36.0 ± 8[c]
K_2O	192.7	102.6	92.2	120.5	9.5	4.3	−3.5	−63.0[d]
BeO	148.1	141.6	139.5	141.9	135.0	132.5	131.6	136.4 ± 13[e]
MgO	145.3	146.0	144.3	141.2	142.0	139.8	139.2	146.0 ± 21[f]
CaO	413.2	132.6	129.8	111.6	297.4	262.9	321.3	43.9 ± 21[g]
LiOH	−238.2	−244.1	−246.9	−237.0	−242.9	−245.9	−246.3	−245.6 ± 8[h]
NaOH	−194.7	−195.4	−198.3	−192.9	−193.2	−196.2	−196.8	−197.8 ± 13[i]
KOH	−76.8	−222.2	−225.8	−75.8	−218.8	−222.6	−224.6	−231.0[j]
$Be(OH)_2$	−622.3	−631.1	−637.7	−618.4	−627.5	−634.2	−636.4	−661.0[k]
$Mg(OH)_2$	−543.5	−539.1	−545.6	−538.8	−535.6	−542.3	−551.7	−561.0[l]
$Ca(OH)_2$	−525.0	−590.3	−598.4	−523.0	−586.5	−594.9	−599.2	−610.8 ± 38[m]

[a] Obtained with MP2/6-311+G(3df,2p) optimized geometries instead of MP2/6-31G(d). [b] Reference 31. Other values: −160.7 (ref 28), −167.0 (ref 27). [c] Reference 36. Other values: −35.6 (ref 28), −27.0 (ref 27). [d] Reference 28. [e] Reference 27. Other value: 117.0 (ref 28). [f] Reference 35. Other values: 58.2 ± 25 (ref 31), 17.0 (ref 27), 150.62 (ref 31). [g] Reference 31. Other values: 46.0 (0 K) (ref 28), 27 ± 21 (ref 27). [h] Reference 32. Other values: −241.1 ± 12 (ref 32), −238.1 ± 6 (ref 28), −234.3 ± 6 (ref 31), −229.0 ± 5 (ref 32). [i] Reference 31. Other values: 187.4 ± 12 (ref 32), −207.1 (ref 28), −185.6 ± 10 (ref 32), −191 ± 8 (ref 32). [j] Reference 28. Other value: 232.6 ± 13 (ref 31). [k] Reference 28. Other value: −676.6 ± 38 (ref 31). [l] Reference 28. Other value: −572.4 ± 33.5 (ref 31). [m] Reference 31. Other value: −544.0 (ref 28). Other value: −142.0 ± 15 (ref 27).

TABLE 8: Calculated and Experimental Heats of Formation for G2[CC]-Type Procedures (ΔH_{f298}, kJ mol^{-1})

	G2[CC]	G2[CC](riv)	G2[CC](full)	G2[CC](dir)	G2[CC](dir,riv)	G2[CC](dir,full)	exptl[a]
Li_2O	−142.0	−154.1	−156.1	−146.4	−158.7	−160.9	−166.9 ± 1.5
Na_2O	17.5	14.1	24.4	−24.5	−27.2	−29.5	−36.0 ± 8
K_2O	169.1	20.5	45.4	119.3	−42.4	−46.2	−63.0
BeO	145.4	137.9	136.1	143.8	136.4	134.4	136.4 ± 13
MgO	151.5	152.1	150.5	146.9	147.0	145.1	146.0 ± 21
CaO	115.1	74.0	71.0	89.3	62.2	59.0	43.9 ± 21
LiOH	−237.4	−243.3	−246.2	−236.4	−242.3	−245.3	−245.6 ± 8
NaOH	−195.0	−195.0	−197.9	−193.2	−192.7	−195.7	−197.8 ± 13
KOH	−78.5	−223.5	−227.0	−77.3	−219.8	−223.4	−231.0
$Be(OH)_2$	−621.9	−631.3	−638.2	−618.0	−627.5	−634.7	−661.0
$Mg(OH)_2$	−548.0	−545.4	−553.1	−543.4	−541.8	−549.8	−561.0
$Ca(OH)_2$	−545.3	−592.7	−600.8	−542.8	−588.3	−596.7	−610.8 ± 38

[a] References to experimental heats of formation are given in Table 7.

This may be attributed to increased π-overlap between oxygen and the metal when there is only a single metal atom.

The calculated geometries of the alkaline earth hydroxides show a great structural diversity, with symmetries ranging from bent C_2, C_{2h}, and C_{2v} to linear $D_{\infty h}$, depending on the basis set and method applied (Table 5). Both the ∠HOM and ∠OMO bending potentials are very flat for these molecules, and it is difficult to determine definitively whether the structures are linear or bent with regard to these angles. Our best calculations (MP2/6-311+G(3df,2p)) predict linear structures for $Mg(OH)_2$ and $Ca(OH)_2$ but a bent structure for $Be(OH)_2$, lying 9.2 kJ mol^{-1} below a constrained (optimized) linear form. The calculated M′−O bond lengths for the alkaline earth hydroxides do not show a strong dependence on the level of theory.

3.2. Heats of Formation. The heats of formation (ΔH_{f298}) calculated using a variety of G2-type procedures are compared with available experimental values[27,28,31,32,35,36] in Tables 7 and 8. Since there are often several different experimental estimates, sometimes with large limits of uncertainty, we have chosen to include in the main body of Tables 7 and 8 the experimental values that provide the best agreement with the highest level of theory applied (G2[CC](dir,full)); i.e., we use our calculations to suggest which experimental value is best supported by theory. However, this is clearly not definitive, and so other experimental values are also included in the tables as footnotes.

In agreement with experimental results, all the alkali and alkaline earth hydroxides as well as the alkali oxides are predicted to be exothermic molecules. However, the alkaline earth oxides represent endothermic species. A striking feature is that the second-row oxides and hydroxides are less exothermic (or more endothermic) than their first-row or third-row analogues. Intriguingly, the charges also show nonmonotonic behavior in going from the first- to the second- to the third-row systems; the positive charges on the metal in the second-row hydroxides are greater than in the first- or third-row analogues, while the positive charges on the metal in the second-row oxides are smaller than in the first- or third-row analogues.

3.2.1. Comparisons of G2, G2(riv), and G2(full). Inspection of Table 7 shows that the heats of formation generally decrease as the correlation space is expanded from G2 to G2(riv) to G2(full); i.e., the molecules benefit more than the atoms from an increase in the correlation space.

The major part of the change occurs in relaxing the inner-valence electrons, i.e., in going from G2 to G2(riv). Very substantial changes (65−280 kJ mol^{-1}) are observed for Ca- and K-containing molecules, as noted previously by Blaudeau et al.,[14] confirming the necessity of including the 3s and 3p orbitals in the correlation space. In these cases, the 2s basis functions on oxygen mix strongly with the 3s and 3p orbitals on K or Ca, making exclusion of the latter orbitals inappropriate. Interestingly, the relaxed-inner-valence effect is larger for the Li- and Be-containing oxides and hydroxides (approximately 5−10 kJ mol^{-1}) than for the Na- and Mg-containing molecules (0−5 kJ mol^{-1}, except for bent structures of Na_2O where there is a QCISD(T) problem; see below). The further changes in going from G2(riv) to G2(full) are relatively small; 6−8 kJ mol^{-1} for the alkaline earth hydroxides and generally 2−4 kJ mol^{-1} in all the other cases.

At the G2(full) level, heats of formation that are within 10 kJ mol^{-1} of experimental values are obtained for Li_2O, BeO, MgO, LiOH, NaOH, and KOH. However, discrepancies of more than 30 kJ mol^{-1} remain for Na_2O (97.3 kJ mol^{-1}), K_2O (155.2 kJ mol^{-1}), and CaO (85.9 kJ mol^{-1}).

3.2.2. Comparisons with G2(dir), G2(dir,riv), and G2(dir,full). An Evaluation of the G2 Additivity Approximations. To assess whether the additivity approximations of G2 theory are adequate for the metal oxides and hydroxides or whether they are contributing to the discrepancies pointed out in section 3.2.1, we have carried out *direct* QCISD(T)/6-311+G(3df,2p) calculations, leading to the G2(dir), G2(dir,riv), and G2(dir,full) results in Table 7. We can see that for most of the systems examined in this study (MgO, Li_2O, $Be(OH)_2$, $Mg(OH)_2$, $Ca(OH)_2$, LiOH, NaOH, and KOH), the heats of formation obtained through use of the additivity approximations are close to those obtained through direct calculations, with differences of less than 5 kJ mol^{-1}. For BeO, the deviation is slightly larger but still less than 10 kJ mol^{-1}. However, additivity totally breaks down when applied to Na_2O, K_2O, and CaO, with errors of 63.3, 87.9, and 133.1 kJ mol^{-1}, respectively (in the full calculations), though part of these errors is associated with problems with QCISD(T) for these three molecules (see below). The additivity problem is similar to that noted by Gronert[26] for G2 calculations on anions. The absence of diffuse functions in the QCISD(T) calculation with the 6-311G(d,p) basis set leads to a poor estimate of this component of the G2 energy for anionic systems. The same difficulty arises in molecules such as Na_2O, K_2O, and CaO where the large amount of negative charge on oxygen (Table 6) gives the diffuse functions an essential role.

At the G2(dir,full) level, i.e., with all orbitals included in the correlation space and with direct calculations that do not require additivity assumptions, there remain three molecules, namely, Na_2O ($\Delta\Delta H_{f298} = 34.0$ kJ mol^{-1}), K_2O ($\Delta\Delta H_{f298} = 67.3$ kJ mol^{-1}), and CaO ($\Delta\Delta H_{f298} = 219.0$ kJ mol^{-1}), for which the discrepancy with experimental results exceeds 30 kJ mol^{-1}.

3.2.3 Influence of Geometry. The heats of formation discussed so far have all been obtained using G2 theories that employ MP2/6-31G(d) optimized geometries. We noted in section 3.1 that there are small but perhaps significant differences between MP2/6-31G(d) geometries and those obtained with larger basis sets. It is of interest to examine the effect on calculated heats of formation of using the better geometries. To this end, the G2(dir,full) calculations have been repeated using MP2/6-311+G(3df,2p) geometries, and the results are included in Table 7.

Comparison of the G2(dir,full) heats of formation obtained with MP2/6-31G(d) and MP2/6-311+G(3df,2p) geometries shows that in most cases the difference is less than 3 kJ mol^{-1}. Slightly larger differences are found for K_2O (7.8 kJ mol^{-1}), $Mg(OH)_2$ (9.4 kJ mol^{-1}), and $Ca(OH)_2$ (4.3 kJ mol^{-1}). The very large difference (58.4 kJ mol^{-1}) in the heat of formation for CaO calculated using geometries that only differ by 0.026 Å in the Ca−O bond length emphasizes the complete failure of the standard G2 procedures, in particular the QCISD(T) component, for this molecule. Likewise, the large difference (30.1 kJ mol^{-1}) in the heats of formation in the case of Na_2O for similarly modest changes in geometry reflects the apparent failure of QCISD(T) to adequately describe bent structures of this molecule. Close agreement with the experimental heat of formation for Na_2O is observed when the (linear) MP2/6-311+G(3df,2p) structure is used.

3.2.4. G2 vs G2[CC]. Blaudeau et al.[14] recently noted that QCISD(T) does not perform well for CaO, giving an unrealistic triples contribution. We also find generally poor QCISD(T) behavior for CaO, bent Na_2O, and bent K_2O, in some cases the triples even producing a positive contribution. Boehme and Frenking[37] and Hrusac et al.[38] found a similar problem in the $CuCH_3$ system. For all of these molecules, CCSD(T) gives results that do not appear to show the same deficiency. In an attempt to remove the remaining deficiencies in our results, we have therefore examined the effect of replacing the QCISD(T) component of the G2 energy with CCSD(T).[25b] Results obtained with variants of this G2[CC] procedure are presented in Table 8. All the G2[CC] calculations have been performed using the MP2/6-311+G(3df,2p) optimized geometries.

Comparison of the G2(full) results of Table 7 with the G2[CC](full) results of Table 8 shows that in most cases the differences do not exceed 4 kJ mol^{-1}. Larger differences are observed for Na_2O (36.9 kJ mol^{-1}), K_2O (46.8 kJ mol^{-1}), MgO (6.2 kJ mol^{-1}), CaO (58.8 kJ mol^{-1}), and $Mg(OH)_2$ (7.5 kJ mol^{-1}).

Comparison of the G2(dir,full) results (on MP2/6-311+G(3df,2p) optimized structures) of Table 7 with the G2[CC](dir,full) results of Table 8 shows even closer agreement, to within 3 kJ mol^{-1} in most cases. Larger differences are now found only for K_2O (42.7 kJ mol^{-1}), MgO (5.9 kJ mol^{-1}), and CaO (262.3 kJ mol^{-1}). The heats of formation for K_2O and CaO are now within 17 kJ mol^{-1} of the experimental value, while for MgO the deviation from experiment is less than 1 kJ mol^{-1}. Clearly, the coupled-cluster procedure is essential for obtaining reliable thermochemistry for the third-row oxides K_2O and CaO.

We noted in section 3.2.2 that the additivity approximation of G2-type methods fares poorly for several of the oxides, namely, Na_2O, K_2O, and CaO. Difficulties of this type in the case of anions have previously been overcome by Gronert using his G2+ procedure that removes the additivity approximation for diffuse functions.[26] We have tested such an approach here by applying an analogous G2+[CC](full) method to Li_2O, Na_2O, K_2O, and CaO. The resultant heats of formation of −160.5 kJ mol^{-1} for Li_2O and −28.5 kJ mol^{-1} for Na_2O differ from the G2[CC](dir,full) values by less than 1 kJ mol^{-1}. For K_2O, the G2+[CC](full) heat of formation is −34.0 kJ mol^{-1}, differing from G2[CC](dir,full) by 12.2 kJ mol^{-1}. For CaO, the G2+[CC](full) procedure leads to a heat of formation (53.2 kJ mol^{-1}) that differs by only 5.8 kJ mol^{-1} from the G2[CC](dir,full) value. These results suggest that the G2+[CC](full) procedure provides a cost-effective means of improving the reliability for molecules such as Na_2O, K_2O, and CaO where diffuse functions play an important role.

Our best heats of formation in the present study correspond to G2[CC](dir,full) calculations, obtained with MP2/6-311+G(3df,2p) optimized geometries. At this level, most of the heats of formation calculated for the oxides and hydroxides show good agreement with experimental values. However, discrepancies greater than 10 kJ mol^{-1} remain for K_2O, CaO, $Be(OH)_2$, $Mg(OH)_2$, and $Ca(OH)_2$. We believe that, at least in some of these cases, the theoretical values are likely to be the more accurate, and thus experimental reexamination is desirable.

4. Conclusions

Several important conclusions emerge from the present study.

1. The alkali (M = Li, Na, or K) and alkaline earth (M′ = Be, Mg, or Ca) oxides and hydroxides are all found to be linear with the exception of $Be(OH)_2$ for which our best calculations predict a bent structure. The M_2O and $M'(OH)_2$ systems are all very floppy molecules with large-amplitude low-frequency vibrations. There is good agreement between our calculated structural data and available experimental information.

2. Without relaxation of inner-valence electrons, the G2 method performs well only for a minority of the molecules investigated (MgO, LiOH, and NaOH). Nonrelaxed G2 heats of formation are in poor agreement with experimental results for Li_2O, Na_2O, K_2O, CaO, KOH, $Be(OH)_2$, and $Ca(OH)_2$, with deviations of 20−370 kJ mol^{-1}.

3. Extension of the correlation space for these species, either by relaxing the inner-valence orbitals (G2(riv)) or by inclusion of all the orbitals in the correlation space (G2(full)), leads to accurate heats of formation for Li_2O, BeO, KOH, and $Ca(OH)_2$ but does not improve the agreement with experimental results to an acceptable level for Na_2O, K_2O, CaO, and $Be(OH)_2$, for which the deviations are 20−140 kJ mol^{-1}.

4. Removal of the additivity approximations through direct calculations (e.g., G2(dir,full)) leads to a major improvement in the results for Na_2O and K_2O.

5. The effect of using MP2/6-311+G(3df,2p) optimized geometries instead of the standard MP2/6-31G(d) optimized geometries is generally relatively small, though there are larger differences for Na_2O because of QCISD(T) problems with the bent MP2/6-31G(d) structure.

6. For most of the systems studied here, there is only a slight overall improvement in the agreement with experimental results when the G2[CC] approaches are used, in which QCISD(T) is replaced by CCSD(T). However, large improvements (approximately 40−260 kJ mol^{-1}) are found for CaO and K_2O, and there are also significant improvements for bent structures of Na_2O.

7. Our most accurate heats of formation correspond to the G2[CC](dir,full) level and are in good agreement with experimental values for most of the molecules. However, significant differences (10−30 kJ mol^{-1}) from experimental heats of formation remain even at this level for CaO, $Be(OH)_2$, $Mg(OH)_2$, $Ca(OH)_2$, and K_2O. Experimental reexamination seems warranted in these cases.

8. In summary, determination of reliable heats of formation using G2-type methods for highly ionic molecules such as those examined in the present study requires careful consideration of the extent of the correlation space, the validity of additivity approximations, and the use of CCSD(T) in place of QCISD(T). With these precautions in place, we believe that theory has a very useful role to play in predicting the thermochemistry of these experimentally difficult molecules.

Acknowledgment. We gratefully acknowledge the award (to A.S.) of a Visiting Fellowship in the Research School of Chemistry of the Australian National University and a generous allocation of time on the Fujitsu VPP300 and SGI Power Challenge computers of the Australian National University Supercomputing Facility. We thank Dr. Tony Scott, Professor Magdalena Hargittai, Mr. David Smith, and Dr. Tim Lee for many helpful comments and discussions.

References and Notes

(1) Curtiss, L. A.; Raghavachari, K.; Trucks, G. W.; Pople, J. A. *J. Chem. Phys.* **1991**, *94*, 7221.

(2) (a) Curtiss, L. A.; Raghavachari, K. In *Quantum Mechanical Electronic Structure Calculations with Chemical Accuracy*; Langhoff, S. R., Ed.; Kluwer Academic: Netherlands, 1995. (b) Raghavachari, K.; Curtiss, L. A. In *Modern Electronic Structure Theory*; Yarkony, D. R., Ed.; World Scientific: Singapore, 1995.

(3) Curtiss, L. A.; Raghavachari, K.; Pople, J. A. *J. Chem. Phys.* **1993**, *98*, 1293.

(4) (a) Smith, B. J.; Radom, L. *J. Phys. Chem.* **1995**, *99*, 6468. (b) Curtiss, L. A.; Redfern, P. C.; Smith, B. J.; Radom, L. *J. Chem. Phys.* **1996**, *104*, 5148.

(5) Nicolaides, A.; Radom, L. *J. Phys. Chem.* **1994**, *98*, 3092.

(6) Curtiss, L. A.; Raghavachari, K.; Redfern, P. C.; Pople, J. A. *J. Chem. Phys.* **1997**, *106*, 1063.

(7) Curtiss, L. A.; Redfern, P. C.; Raghavachari, K.; Pople, J. A. *J. Chem. Phys.* **1998**, *109*, 42.

(8) Bauschlicher, C. W.; Langhoff, S. R.; Partridge, H. *J. Chem. Phys.* **1986**, *84*, 901.

(9) Langhoff, S. R.; Bauschlicher, C. W.; Partridge, H. *J. Chem. Phys.* **1986**, *84*, 4474.

(10) Gardner, P. J.; Preston, S. R.; Siertsma, R.; Steele, D. *J. Comput. Chem.* **1993**, *14*, 1523.

(11) Bauschlicher, C. W.; Partridge, H. *Chem. Phys. Lett.* **1993**, *205*, 479.

(12) Garcia Cuesta, I.; Sandez de Meras, A.; Nebot Gill, I. *Chem. Phys. Lett.* **1993**, *203*, 484.

(13) Burk, P.; Koppel, I. *Int. J. Quantum Chem.* **1994**, *51*, 313.

(14) Blaudeau, J.-P.; McGrath, M. P.; Curtiss, L. A.; Radom, L. *J. Chem. Phys.* **1997**, *107*, 5016.

(15) Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley: New York, 1986.

(16) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. *GAUSSIAN 94*, revision E.2; Gaussian, Inc.: Pittsburgh, 1995.

(17) MOLPRO 96 is a package of ab initio programs written by H.-J. Werner and P. J. Knowles with contributions from J. Almlof, R. D. Amos, M. J. O. Deegan, S. T. Elbert, C. Hampel, W. Meyer, K. Peterson, R. Pitzer, A. J. Stone, P. R. Taylor, and R. Lindh.

(18) Stanton, J. F.; Gauss, J.; Watts, J. D.; Lauderdale, W. J.; Bartlett, R. J. *ACES II*; Quantum Theory Project; Departments of Chemistry and Physics, University of Florida: Gainsville, FL, 1992.

(19) Huber, K. P.; Herzberg, G. *Molecular Spectra and Molecular Structures, Vol. IV, Constants of Diatomic Molecules*; van Nostrand: New York, 1979.

(20) Kuchitsu, K., Ed. Landolt-Bornstein Structure Data for Free Polyatomic Molecules. New Series, Group II, Vol. 25; Springer-Verlag: Berlin-Heidelberg, 1998.

(21) For consistency with our notation for the elements of the first and second rows, we use the G2 label in this paper to refer to a calculation with a 4s,4p correlation space for K and Ca. When the 3s and 3p orbitals are also included in the correlation space for K and Ca, the relaxed-inner-valence (riv) description is used, but we emphasize that this has been recommended[14] as standard for G2.

(22) Hofmann, H.; Hänsele, E.; Clark, T. *J. Comput. Chem.* **1990**, *11*, 1147.

(23) Petrie, S. *J. Phys. Chem. A* **1998**, *102*, 6138.

(24) Duke, B. J.; Radom, L. *J. Chem. Phys.* **1998**, *109*, 3352.

(25) (a) Curtiss, L. A.; Carpenter, J. E.; Raghavachari, K.; Pople, J. A. *J. Chem. Phys.* **1992**, *96*, 9030. (b) Curtiss, L. A.; Raghavachari; Pople, J. A. *J. Chem. Phys.* **1995**, *103*, 4192.

(26) (a) Gronert, S. *Chem. Phys. Lett.* **1996**, *252*, 415. (b) Gronert, S. *J. Am. Chem. Soc.* **1993**, *115*, 10258.

(27) Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, W. G. *J. Phys. Chem. Ref. Data* **1988**, *17* (Suppl. 1).

(28) Wagman, D. D.; Evans, W. H.; Parker, V. B.; Schumm, R. H.; Halow, I.; Bailey, S. M.; Churney, K. L.; Nuttall, R. L. *J. Phys. Chem. Ref. Data* **1982**, *11* (Suppl. 2).

(29) Nicolaides, A.; Rauk, A.; Glukhovtsev, M. N.; Radom, L. *J. Phys. Chem.* **1996**, *100*, 17460.

(30) McQuarrie, D. A. *Statistical Mechanics*; Harper & Row: New York, 1976.

(31) Chase, M. W.; Davies, C. A.; Downey, J. R.; Frurip, D. J.; McDonald, R. A.; Syverud, A. N. JANAF Thermochemical Tables. *J. Phys. Chem. Ref. Data* **1985**, *14* (Suppl. 1).

(32) Gurvich, L. V.; Bergman, G. A.; Gorokhov, L. N.; Iorish, V. S.; Leonidov, V. Ya.; Yungman, V. S. *J. Phys. Chem. Ref. Data* **1996**, *25*, 1211.

(33) Bader, R. F. W. *Atoms in Molecules. A Quantum Theory*; Oxford Press: New York, 1990.

(34) Pearson, E. F.; Winnewisser, B. P.; Trueblood, M. B. *Z. Naturforsch.* **1976**, *31*, 1259 and references therein.

(35) Operti, L.; Tews, E. C.; MacMahon, T. J.; Freiser, B. S. *J. Am. Chem. Soc.* **1989**, *111*, 9152.

(36) Steinberg, M.; Schofield, K. *J. Chem. Phys.* **1991**, *94*, 3901.

(37) Boehme, M.; G. Frenking, G. *Chem. Phys. Lett.* **1994**, *224*, 195.

(38) Hrusak, J.; Tenno, S.; Iwata, S. *J. Chem. Phys.* **1997**, *106*, 7185.