Structures and Thermochemistry of Calcium-Containing Molecules

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A variety of theoretical procedures, including the high-level ab initio methods G3, G3[CC](dir,full), and W2C//ACQ, have been used to predict the structures and heats of formation of several small calcium-containing molecules (CaH, CaH_2, CaO, CaOH, $Ca(OH)_2$, CaF, CaF_2, CaS, CaCl, and $CaCl_2$). B3-LYP and CCSD(T) with both the (aug-)cc-pWCVQZ and (aug-)cc-pWCVQ+*d*Z basis sets are found to give molecular geometries that agree well with the experimental results. The CCSD(T)(riv)/(aug-)cc-pWCVQ+*d*Z results are found to be the most accurate, with a mean absolute deviation from experiment of just 0.008 Å. Zero-point vibrational energies (ZPVEs) and thermochemical corrections are found to be relatively insensitive to the level of theory, except in the case of molecules with highly anharmonic calcium-centered bending modes (CaH_2, $Ca(OH)_2$, CaF_2, $CaCl_2$), where special procedures need to be employed in order to obtain satisfactory results. Several potential improvements to the W2C method were investigated, most of which do not produce significant changes in the heats of formation. It was observed, however, that for CaO and CaS the scalar relativistic corrections are unexpectedly large and highly basis set dependent. In these cases, Douglas−Kroll CCSD(T)/(aug-)cc-pWCV5Z calculations appear to give a converged result. The G3[CC](dir,full) and best W2C-type heats of formation are both found generally to agree well with experimental values recommended in recent critical compendia. However, in some cases (CaO, $Ca(OH)_2$, and CaF_2), they differ from one another by more than their predicted error margins. The available experimental data are not sufficiently precise to distinguish definitively between the two sets of results although, in general, when discrepancies exist the W2C heats of formation are lower in energy and tend to be in better agreement with experiment. In the case of CaO, the W2C heat of formation (20.7 kJ mol^{-1}) is ∼20 kJ mol^{-1} lower than the G3[CC](dir, full) result and most of the experimental data. Extensive investigation of possible refinements of the W2C method has failed to reveal any weaknesses that could account for this discrepancy. We therefore believe that the heat of formation of CaO is likely to lie closer to the more recent direct experimental determination of 27 kJ mol^{-1} than to the value of ∼40 kJ mol^{-1} recommended in recent thermochemical reviews.

1. Introduction

A major goal of modern computational chemistry is the calculation of accurate thermochemical properties for molecules of chemical interest.[1] The recent development of composite theoretical methods such as the Gaussian (G*n*) procedures of Curtiss, Raghavachari, and Pople,[2] the complete basis set (CBS) methods of Petersson et al.,[3] and the Weizmann (W*n*) methods of Martin et al.,[4] has made the calculation of such accurate heats of formation almost a routine task for many molecules. For example, for the standard G2-1 test set of molecules containing atoms from the first and second rows, the G2, G3, CBS-Q, W1, and W2 procedures are found to show mean absolute deviations from reliable experimental heats of formation of 5.0, 4.6, 4.2, 2.5, and 2.1 kJ mol^{-1}, respectively.[5]

In recent studies,[6,7] however, we found that the *standard* application of some of these procedures to the determination of the heats of formation of the alkali and alkaline-earth oxides and hydroxides led to unacceptably large errors (more than 100 kJ mol^{-1}) in some cases. For the G2 procedure, we concluded that three aspects of the standard G2 model were contributing to the poor results.[6] In the first place, our calculations confirmed earlier indications[8a,9] 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 (as noted earlier[8a] for CaO) 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 replacement of QCISD(T) with CCSD(T) (denoted G2[CC]). Finally, removal of 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.

The best heats of formation in our initial study[6] were obtained with a procedure denoted G2[CC](dir,full) that includes the modifications to the standard G2 procedure referred to above.

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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. MP2(full)/6-311+G(3df,2p) structures were used in these calculations. With these modifications, G2[CC](dir,full) was found to give heats of formation in reasonable agreement with the available experimental data, although a definitive assessment was difficult because of the large uncertainties in much of the experimental information.[6]

In a subsequent study,[7] we examined the performance of the more recently developed G3[2c] and G3X[10] procedures. We found that, unlike the situation for G2, the use of a simple relaxed-valence (rv) correlation space for the metals in G3 and G3X does lead to reasonable estimates of the heats of formation for most of the metal oxides and hydroxides. This improvement was attributed to the incorporation of core correlation in G3 and G3X through the MP2(full)/G3large calculation. However, even better results were obtained for G3 and G3X with an riv correlation space, and this was recommended as the standard procedure. On the negative side, it was found that additivity still performs poorly in some cases (e.g., for Na_2O), a shortcoming that could be overcome by carrying out direct (dir) calculations. The QCISD(T) calculation is still a problem in cases such as CaO; this is again overcome by using CCSD(T) instead. The best results were obtained with the G3[CC](dir,full) method.

We also examined[7] the performance of the W1 and W2 procedures.[4] We found that standard W1 and W2 give reasonable results for the heats of formation of the metal oxides and hydroxides. However, expansion of the correlation space to riv in the extrapolation calculations leads to spectacular failures in some instances (with errors of more than 100 kJ mol^{-1}). This occurs because the cc-pV*n*Z basis sets prescribed for the metal atoms in the standard formulation do not have sufficient flexibility to adequately describe these inner-valence orbitals. Inclusion of core-correlation functions, as in the newly developed cc-pWCV*n*Z basis sets,[11] removes most of these problems. In the case of calcium, further improvement is seen in the extrapolated results when one and two additional diffuse *d* functions are added to the quadruple- and triple-ζ basis sets, respectively. The resulting basis sets are denoted cc-pWCVQ+*d*Z and cc-pWCVT+2*d*Z. Our best directly calculated heats of formation corresponded to W2-type calculations using these basis sets, and this method was denoted W2C//ACQ (where the ACQ indicates that these new basis sets were also used to calculate the molecular geometry rather than the standard cc-pVQZ+1 sets[12]).

Satisfactory agreement between the heats of formation predicted by the best modified procedures, G3[CC](dir,full) and W2C//ACQ, and experiment was achieved in almost all cases.[7] However, notable among the exceptions were the two calcium-containing molecules, CaO and $Ca(OH)_2$, where the G3[CC](dir,full) and best W2C results differed from one another by 18 and 20 kJ mol^{-1}, respectively. Further improvements beyond W2C did not lead to significant changes in the W2C results. For CaO, these improvements included the use of multireference methods with various active spaces (CASSCF, CAS-ACPF, CAS-AQCC, W2C-ACPF, and W2C-AQCC) and methods based on Brueckner doubles, as well as the investigation of the effects of CCSDT and full CI calculations using smaller basis sets.

Although the W2C procedure is, in principle, a higher level of theory than G3[CC](dir,full), the experimental results for CaO and $Ca(OH)_2$ were not sufficiently precise to be able to distinguish which of the two procedures is performing better in these cases. We therefore felt it desirable to try to address this question by broadening the study to a larger set of Ca-containing molecules (CaH, CaH_2, CaO, CaOH, $Ca(OH)_2$, CaF, CaF_2, CaS, CaCl, and $CaCl_2$) and also to see whether further modifications to the procedures can lead to improved agreement. These are the aims of the present investigation.

Some of these molecules have been the focus of earlier ab initio studies. In the 1980s, Bauschlicher, Partridge, and Langhoff[13] predicted dissociation energies for CaO, CaOH, CaF, CaS, and CaCl using Hartree−Fock (HF) and configuration interaction with single and double excitation (CISD) calculations, coupled with experimental ionization energies and electron affinities for the atoms (with the assumption that these species are largely ionic). The early 1990s saw intense interest in the nature of the geometries of CaH_2 and CaF_2.[14] In particular, it was found that it was necessary to include multiple *d* functions in the Ca basis set in order to correctly predict CaF_2 to be a bent molecule (at the HF level). Most of these calculations were performed using HF or MP2 and in some cases were compared with CISD results. Very recently, detailed investigations of the geometry and vibrational frequencies of CaH_2 and CaF_2 were reported by Koput and Roszczak[15a] and by Koput,[15b] respectively. This work involved the mapping of the potential energy surface at the CCSD(T)/cc-pV5Z level of theory (core−valence basis set used for Ca). The PES was then approximated by a 3D expansion to allow the calculation of vibrational−rotational energy levels and anharmonic frequencies. Apart from our previous work,[6,7] and the original third-row G2 and G3 studies,[8] a literature search has revealed only a small number of other high-level investigations of thermochemical data that have been reported for these molecules. These include CCSD(T) calculations of Trachtman et al.[16a] and Koput and Peterson[16b] for CaOH and a BD(T) investigation of CaF by Yang, Zhang, and Han.[16c]

2. Theoretical Methods

In the present study, the G3[CC](dir,full) and W2C methods have been used to investigate the heats of formation of 10 small calcium-containing molecules: CaH, CaH_2, CaO, CaOH, $Ca(OH)_2$, CaF, CaF_2, CaS, CaCl, and $CaCl_2$. Standard G3 calculations have also been performed for comparison.

The G3[CC](dir,full) method has been described in detail previously.[7] In brief, it involves a high-level geometry optimization (here we have used the CCSD(T)(riv)/(aug-)cc-pWCVQZ level of theory, defined below) followed by a CCSD(T)(full)/G3Large single-point energy calculation. Vibrational frequencies for zero-point energies and thermochemical corrections are calculated using density functional theory (B3-LYP/cc-pVTZ+1, scaled by 0.985). Spin−orbit corrections for atoms and the higher-level correction (as defined by Sullivan et al.[7]) are also included.

The W2C//ACQ method[7] employs the same CCSD(T)(riv)/(aug-)cc-pWCVQZ geometry as used for G3[CC](dir,full). Single-point calculations are performed using CCSD(T)(riv)/(aug-)cc-pWCV*n*Z (n = T, Q, 5), and the resulting HF, CCSD, and triples (T) energies are extrapolated separately to the complete basis set limit. The HF energies are extrapolated using an n^{-5} extrapolation scheme while an n^{-3} scheme is used for CCSD and (T).[4] In the case of the triples extrapolation, only the TZ and QZ energies are used, removing the need to perform the expensive triples calculation with the large quintuple-ζ basis set. Corrections for core−core and core−valence correlation (CV) and for scalar relativistic effects (Darwin[17] and mass−

velocity[18] terms) are estimated at the CCSD(T) and ACPF[19] levels of theory, respectively, in both cases using the MTsmall[4a] basis sets. Spin−orbit effects are included for atomic species where appropriate, and zero-point vibrational energies and thermochemical corrections are determined using B3-LYP/cc-pVTZ+1 vibrational frequencies.

As noted above, new core−valence basis sets have been developed[11] that enable the W1 and W2 methods to give improved results for molecules containing alkali and alkaline-earth metal atoms. For calcium, these include the “standard” cc-pWCV*n*Z sets, along with the augmented cc-pWCVT+2*d*Z and cc-pWCVQ+*d*Z sets. For convenience, in this work we refer to the *d* augmented basis sets as cc-pWCV*n*+*xd*Z basis sets (where n = T, Q, 5 and x = 2, 1, 0) or *n*+*xd*Z for short. W2C//ACQ calculations performed using the standard *n*Z basis sets are denoted W2C-1, while the term W2C-2 is used when the *n*+*xd*Z sets have been employed (with minor modifications from the standard procedure, see below and Table 9).

Correlation-consistent basis sets are also used for the other atoms in these molecules; these include cc-pV*n*Z for H and aug-cc-pCV*n*Z for O and F. Unfortunately, aug-cc-pCV5Z basis sets are not yet available for Cl and S, so it has been necessary to employ the aug-cc-pV*n*Z sets instead. These are improved through the addition of two extra *d* functions (with exponents 2.5 and 6.25 times that of the largest exponent in the set) and one additional *f* function (with exponent 2.5 times the largest in the set) in order to partially compensate for the lack of core-correlation functions (hence aug-cc-pV*n*Z+2*df*).[5] The effects of using aug-cc-pV*n*Z+2*df* basis sets rather than aug-cc-pCV*n*Z for Cl and S were assessed using {T, Q} extrapolations. We find that the two pairs of basis sets give results that are consistent to within 0.6 kJ mol^{-1}, so we do not expect this approximation to have a significant effect on the final results.

For convenience, these combinations of basis sets are denoted (aug-)cc-pWCV*n*Z and (aug-)cc-pWCV*n*+*xd*Z throughout the present work. We also note here that, unless otherwise indicated, a riv correlation space is always used for calcium atoms.[6−8] When determining CV and scalar relativistic corrections, the 1s electrons of Ca, S, and Cl are held frozen in both calculations as the basis sets are not believed to have sufficient flexibility to describe these deep-core electrons adequately.

As noted earlier, density functional theory (B3-LYP[20]) is used to determine harmonic vibrational frequencies. In our previous work,[7] we found that it was necessary in some cases (such as $Ca(OH)_2$) to use “ultrafine” integration grids in order to obtain reliable vibrational frequencies. We have therefore used these grids in all frequency calculations in the present work. For CaH_2, $Ca(OH)_2$, CaF_2, and $CaCl_2$, the potential energy surfaces for the calcium-centered bending modes are found to be extremely anharmonic. In these cases, we have therefore plotted out the potential energy surfaces for these modes and solved the nuclear Schrödinger equation in order to obtain anharmonic vibrational frequencies. These frequencies were used unscaled in the calculation of zero-point energies and thermochemical corrections, the latter being calculated via a sum over the enthalpic contributions of all accessible energy levels at the appropriate temperature (in this case 298 K). This anharmonic treatment was also applied to the OH stretching modes of CaOH and $Ca(OH)_2$.

We have not attempted in the present study to go beyond G3[CC](dir,full) within the G3 framework. However, we have examined several modifications to the standard W2C//ACQ procedure in order to probe for any weaknesses that may account for the discrepancies between the G3[CC](dir,full), W2C, and experimental results. These modifications primarily involve increasing the level of theory and/or the size of the basis sets used to calculate the various components of W2C. We have also estimated the potential effects of basis set superposition error (BSSE) on both the extrapolated valence calculations and the core−valence correlation using the counterpoise method of Boys and Bernardi,[21] and investigated the use of the Douglas−Kroll−Hess approximations[22] in pursuit of a more accurate description of the scalar relativistic effects. In addition, the extension of the coupled cluster method beyond CCSD(T) was also considered for CaO, and calculations with explicit triple-(CCSDT), quadruple-(CCSDTQ), and quintuple-(CCSDTQ5) excitations, along with a full CI computation, were performed. These more demanding calculations naturally required the use of smaller basis sets (double-ζ in most cases) and more restricted valence spaces.

The standard G3 calculations and all the B3-LYP calculations reported in the present study were performed using the Gaussian 03[23] suite of programs. MOLPRO 2002[24] was used for all other calculations (G3[CC](dir,full), W2C, etc.) apart from the work involving the calculation of explicit triple and higher excitations, which was performed using a generalized CI/CC code[25] interfaced with ACESII.[26]

3. Results and Discussion

3.1. Geometries. The experimental and theoretical geometric parameters calculated in the present work are reported in Table 1. Also included are the mean deviation (MD), mean absolute deviation (MAD), and largest deviation (LD) from experiment[27] for each of the theoretical methods considered. There is generally good agreement between theoretical and experimental bond lengths except in the case of CaF_2. We note, however, that this very early experiment[27e] incorrectly predicts CaF_2 to be a linear molecule, which may have an adverse effect on the prediction of the bond length. We have therefore excluded the CaF_2 results from our statistical considerations.

Comparison of the theoretical and experimental results reveals that the large-basis-set CCSD(T) bond lengths (with MAD = 0.008 Å) are, in almost all cases, significantly closer to the experimental values than are the MP2/6-31G(*d*) parameters (employed in the standard G3 procedure) or the HF/6-31G(*d*) and B3-LYP parameters (used in predicting vibrational frequencies). We also note that MP2 and HF incorrectly predict $Ca(OH)_2$ to be slightly bent (with C_{2v} symmetry).

Improvement in the Ca basis sets from cc-pWCVQZ to cc-pWCVQ+*d*Z results in very little change in the predicted bond lengths at the CCSD(T) level of theory. With B3-LYP, however, there is an appreciable improvement in the agreement between theory and experiment with the addition of the two extra *d* functions to the triple-ζ basis sets, such that the B3-LYP/(aug-)cc-pWCVT+2*d*Z results are approaching an accuracy (MAD = 0.009 Å) comparable to that of the coupled cluster values.

As described below, CaF_2 is found to be a bent molecule. The saddle point at the linear geometry is, however, only 0.4 kJ mol^{-1} above the global minimum. Although it would have been desirable to perform the single-point energy calculations for the W2C methods using the bent geometry, the quintuple-ζ calculations are computationally too demanding with our current resources. We therefore used the geometry of the linear molecule for all single-point calculations. This approximation is expected to lead to only a minor overestimation in our final heats of formation (by ~0.4 kJ mol^{-1}).

3.2. Vibrational Frequencies and Thermochemical Corrections. Vibrational frequencies for the molecules of interest

TABLE 1: Geometric Parameters for Calcium Compounds[a,b]

	parameter	HF 6-31G(*d*)	MP2(full) 6-31G(*d*)	B3-LYP cc-pWCVTZ	B3-LYP (aug-)cc-pWCVT+2*d*Z	CCSD(T) (aug-)cc-pWCVQZ	CCSD(T) (aug-)cc-pWCVQ+*d*Z	experiment
CaH	*r*(Ca−H)	2.058	2.067	2.025	1.982	2.006	2.005	2.0025 ± 0.0021[c]
CaH_2 (bent)	*r*(Ca−H)			2.055	2.019			
	<(HCaH)			155.3	137.8			168 ± 4, 166[d]
CaH_2 (linear)	*r*(Ca−H)	2.086	2.088	2.064	2.049	2.050	2.050	
CaO	*r*(Ca−O)	1.822	1.875	1.844	1.809	1.831	1.828	1.8221[c]
CaOH	*r*(Ca−O)	2.006	1.997	1.989	1.973	1.982	1.981	1.9746[e]
	r(O−H)	0.941	0.965	0.954	0.955	0.953	0.953	0.9562[e]
$Ca(OH)_2$	*r*(Ca−O)	2.050	2.042	2.040	2.038	2.036	2.035	
	r(O−H)	0.941	0.964	0.953	0.955	0.952	0.952	
	<(OCaO)	164.2	160.1					
	<(CaOH)	175.6	175.5					
CaF	*r*(Ca−F)	1.962	1.954	1.971	1.950	1.960	1.959	1.967 ± 0.009[c]
CaF_2 (bent)	*r*(Ca−F)	2.002	2.011	2.019	2.000		2.017	
	<(FCaF)	153.1	149.3	160.0	143.8		157.6	
CaF_2 (linear)	*r*(Ca−F)	2.010	2.011	2.023		2.015	2.015	2.10 ± 0.03[f]
CaS	*r*(Ca−S)	2.359	2.382	2.347	2.313	2.333	2.331	2.3178[c]
CaCl	*r*(Ca−Cl)	2.522	2.496	2.469	2.441	2.452	2.451	2.439[c]
$CaCl_2$	*r*(Ca−Cl)	2.515	2.493	2.484	2.472	2.470	2.469	2.483[g]
MD[h]		0.028	0.033	0.015	−0.009	0.003	0.002	
MAD[h]		0.033	0.036	0.016	0.009	0.009	0.008	
LD[h]		0.083	0.064	0.030	−0.021	0.013	−0.014	

[a] Unless otherwise indicated, all molecules are linear. The bent structures for $Ca(OH)_2$ have C_{2v} symmetry with all-cis arrangements. [b] Bond lengths in angstroms, bond angles in degrees. [c] Reference 27a. [d] References 27b and 27c. [e] Reference 27d. [f] Reference 27e. [g] Reference 27f. [h] Mean deviation (MD), mean absolute deviation (MAD), and largest deviation (LD) from experimental values. CaF_2 results are not included in the statistical analysis; see text.

are reported in Table 2. These include the HF/6-31G(*d*) vibrational frequencies (scaled by a factor of 0.8929) that are needed for the standard G3 procedure and the B3-LYP vibrational frequencies (scaled by 0.985) that are used for G3-[CC](dir,full) and W2C calculations. The B3-LYP results have been calculated using the cc-pWCVTZ basis set (for Ca, cc-pVTZ+1 for all other atoms) and the cc-pWCVT+2*d*Z basis set (for Ca, aug-cc-pCVTZ for all other atoms). Also shown are numerical vibrational frequencies calculated at the higher CCSD(T) level of theory with the (aug-)cc-pWCVT+2*d*Z basis sets (unscaled), along with experimental values.[28] The usefulness of the calculated values for our present purposes is best assessed by comparison of the resulting zero-point vibrational energies (ZPVEs) and enthalpic temperature corrections ($H^{298} - H^0$ values), shown in Table 3.

The ZPVEs are found not to vary significantly between the theoretical methods. HF/6-31G(*d*) gives slightly lower ZPVEs, consistent with the rather large mean deviation of its frequencies from experiment (-22 cm^{-1}). However, these are still within 1 kJ mol^{-1} of the other results in almost all cases. The most significant discrepancies between experimental and theoretical ZPVEs are seen for CaOH and $Ca(OH)_2$. These differences (of up to 3 kJ mol^{-1}) stem from the high-energy O−H stretching modes, for which the theoretical predictions are somewhat higher than the experimental values.

Similarly, Table 3 shows that, in most cases, the thermochemical corrections are also quite insensitive to the theoretical method used. The most significant variations occur for CaH_2, $Ca(OH)_2$, CaF_2, and $CaCl_2$. These variations are associated with differences in the very low energy calcium-centered bending modes of these molecules. The closely spaced vibrational levels for these low-energy modes are quickly populated as the temperature rises, so that small discrepancies in the calculated frequencies result in large errors in the thermal corrections. In addition, these modes, as well as the O−H stretching modes, are highly anharmonic. For these reasons, a more careful treatment, involving the calculation of anharmonic vibrational frequencies, was also applied for these modes.

As noted earlier, this was done by plotting out the potential energy surfaces (PESs) for each of these modes while optimizing all other molecular parameters. The nuclear Schrödinger equation was then solved for each PES in order to determine the vibrational energy levels (including the ZPVEs). The thermal contributions of each energy level, based on its population, could then be summed in order to determine the total thermal correction due to this motion. We have assumed that the harmonic approximation is valid for all other modes and that there is no coupling between the bending and stretching modes. These calculations were performed at the B3-LYP/cc-pWCVTZ, B3-LYP/(aug-)cc-pWCVT+2*d*Z, CCSD(T)/(aug-)cc-pWCVTZ, and CCSD(T)/(aug-)cc-pWCVT+2*d*Z levels of theory to allow the effects of both theory and basis set to be evaluated. The comparatively high-energy bending mode of CaOH was also plotted and found to comply well with the harmonic approximation, so anharmonic vibrational frequencies were not evaluated in that case.

For $Ca(OH)_2$, only the B3-LYP anharmonic frequencies could be calculated, as the molecule proved to be too large to allow the mapping of the CCSD(T) PESs. In addition, the O−H bonds in CaOH and $Ca(OH)_2$ were assumed to be sufficiently similar, as evidenced by the almost identical harmonic stretching frequencies, that the anharmonic O−H stretching frequencies calculated for CaOH were also used for $Ca(OH)_2$.

Significant qualitative differences are observed between the bending PESs evaluated at different levels of theory. While the $CaCl_2$ and $Ca(OH)_2$ surfaces have minima at linear geometries in all cases, some of the surfaces for CaH_2 and CaF_2 have small or even significant maxima at bond angles of 180°, that is, there are double-well potentials with minima corresponding to nonlinear structures. The trend is that, as the basis set size increases, the surface becomes more anharmonic and the minimum energy structures start to correspond to nonlinear configurations. This trend is reversed as the level of theory is increased from B3-LYP to CCSD(T).

Thus, for the CaH_2 B3-LYP/cc-pWCVTZ surface there is a maximum at 180° that is 0.4 kJ mol^{-1} above the bottom of the

TABLE 2: Scaled Vibrational Frequencies (cm^{-1})^{a}

	HF 6-31G(*d*)	B3-LYP cc-pWCVTZ	B3-LYP (aug-)cc-pWCVT+2*d*Z	CCSD(T) (aug-)cc-pWCVT+2*d*Z	experiment^{b}
CaH	1156	1247	1281	1270	1298.34
CaH_2^{c}	153	(84)^{d}		86 (88)^{d}	
	153	(84)^{d}	287 (257)^{d}	86 (88)^{d}	
	1128	1221	1231	1246	1216.3^{e}
	1188	1296	1307	1321	1289.7^{e}
CaO	750	734	767	688	733.4
CaOH	343	342	338	342	354^{f}
	343	342	338	344	354^{f}
	574	614	615	615	606^{f}
	3774	3893 (3900)^{d}	3869 (3894)^{d}	3943 (3828)^{d}	3778^{f}
$Ca(OH)_2$		45 (46)^{d}	14 (28)^{d}		
	62	45 (46)^{d}	14 (28)^{d}		110
	387	410	420		340
	392	410	420		340
	392	419	430		340
	393	419	430		340
	495	522	516		510
	595	633	608		660
	3767	3894 (3900)^{d}	3871 (3894)^{d}		3785^{g}
	3767	3894 (3900)^{d}	3871 (3894)^{d}		3785^{g}
CaF	556	571	578	573	587.3
CaF_2 (bent)^{h}	79	33	79 (69)^{d}	84 (19)^{i}	120
	481	487	505	496	490
	578	594	576	592	575
CaF_2 (linear)^{h}		(10)^{d}			
		(10)^{d}			
		480	476	479	
		595	572	587	
CaS	425	448	465	430	462.23
CaCl	311	354	358	359	369.43
$CaCl_2$	41	37 (24)^{d}	23 (14)^{d}	(31)^{d}	75
	41	37 (24)^{d}	23 (14)^{d}	(31)^{d}	75
	245	273	274	270	260
	379	417	410	417	395

[a] Scaling factors are 0.8929 for HF frequencies and 0.985 for B3-LYP; CCSD(T) frequencies are unscaled. [b] Reference 31, unless otherwise noted. [c] B3-LYP/(aug-)cc-pWCVT+2*d*Z predicts CaH_2 to be bent, while CCSD(T)/(aug-)cc-pWCVT+2*d*Z predicts it to be linear. For B3-LYP/cc-pWCVTZ there is a small barrier to linearization, but this lies below the zero-point energy in the bending mode; stretching frequencies are therefore reported for the linear molecule. [d] Anharmonic frequencies in parentheses (unscaled). [e] Reference 27c. Measured in an argon matrix. [f] Reference 28a. [g] Reference 28b. [h] For CaF_2, the PESs show small barriers to linearization (the molecules are bent), but these lie well below the thermal energy in the bending mode at 298 K and, in the case of the B3-LYP/cc-pWCVTZ PES, also below the ZPVE level. We have therefore reported the stretching frequencies calculated for both linear and bent configurations. [i] BSSE-corrected anharmonic bending frequency in parentheses (unscaled).

TABLE 3: Zero-Point Vibrational Energies (ZPVEs, kJ mol^{-1}) and Thermochemical Corrections to 298 K ($H^{298} - H^{0}$, kJ mol^{-1})^{a}

	HF 6-31G(*d*)		B3-LYP cc-pWCVTZ		B3-LYP (aug-)cc-pWCVT+2*d*Z		CCSD(T) (aug-)cc-pWCVT+2*d*Z		expt
	ZPVE	$H^{298} - H^{0}$	ZPVE	$H^{298} - H^{0}$	ZPVE	$H^{298} - H^{0}$	ZPVE	$H^{298} - H^{0}$	ZPVE
CaH	6.9	8.7	7.5	8.7	7.7	8.7	7.6	8.7	7.8
CaH_2^{b,c}	15.7	12.1	16.0 (16.1)	11.7 (10.8)	16.9 (16.7)	11.1 (11.5)	15.9 (16.4)	12.0 (10.4)	
CaO	4.5	8.9	4.4	8.9	4.6	8.9	4.1	9.0	4.4
CaOH^{b}	30.1	11.1	31.1 (31.1)	11.0 (11.0)	30.9 (31.0)	11.0 (11.0)	31.4 (30.7)	11.0 (11.0)	30.3
$Ca(OH)_2$^{b}	61.3	16.4	64.0 (64.0)	17.1 (16.7)	64.3 (63.8)	17.4 (17.8)			61.1
CaF	3.3	9.2	3.4	9.1	3.5	9.1	3.4	9.1	3.5
CaF_2^{b,d}	6.8	13.0	6.7 (6.5)	13.3 (17.0)	6.9 (6.9)	13.0 (16.0)	7.0 (6.6)	13.0 (17.2)	7.1
CaS	2.5	9.4	2.7	9.4	2.8	9.3	2.6	9.4	2.8
CaCl	1.9	9.7	2.1	9.6	2.1	9.6	2.1	9.6	2.2
$CaCl_2$^{b}	4.2	15.3	4.6 (4.4)	15.2 (18.3)	4.4 (4.3)	15.4 (20.7)	(4.4)	(18.2)	4.8

[a] Calculated using the vibrational frequencies reported in Table 2. [b] ZPVEs and thermochemical corrections calculated using anharmonic bending and O−H stretching frequencies shown in parentheses. [c] B3-LYP/cc-pWCVTZ and CCSD(T)/(aug-)cc-pWCVT+2*d*Z predict CaH_2 to be linear at all temperatures, thus the rotational constants and stretching frequencies for the linear molecule were used to calculate $H^{298} - H^{0}$. For B3-LYP/(aug-)cc-pWCVT+2*d*Z the thermal energy in the bending mode at 298 K is still significantly below the barrier height for linearization so the rotational constants and stretching frequencies for the bent molecule were used. [d] Although the PESs for CaF_2 show maxima at a bond angle of 180°, thermal energy in the bending mode at 298 K is well above the height of these linearization barriers, hence the rotational constants and stretching frequencies for the linear molecule were used in the calculation of $H^{298} - H^{0}$.

PES. In the B3-LYP/(aug-)cc-pWCVT+2*d*Z surface, the barrier increases to 4.6 kJ mol^{-1}. However, for the CCSD(T) surfaces it is virtually nonexistent (0.3 and 1.6 cm^{-1} for the TZ and T+2dZ surfaces, respectively). The CCSD(T) PESs are, however, still very square at the bottom. These results are in good agreement with the work of Koput,[15b] whose more extensive

TABLE 4: Components of the W2C Atomization Energies and Extrapolated Results (at 0 K, no ZPVE) (kJ mol^{-1})

	CCSD(T) (aug-)cc-pWCVnZ[a]				CCSD(T) (aug-)cc-pWCV$n+xd$Z[b]					
	TZ	QZ	5Z	extrap.[c]	T+2dZ	Q+dZ	5Z	extrap.[c]	extrap.[d]	CP[e]
CaH	155.6	170.2	172.9	175.3	162.3	170.7	172.9	175.0	175.1	0.0
CaH$_2$	411.5	429.1	432.8	436.3	417.5	429.4	432.8	436.1	436.2	0.0
CaO	329.3	395.1	406.5	416.9	371.0	397.7	406.5	415.6	415.6	0.2
CaOH	818.4	847.3	853.4	859.7	828.6	847.8	853.4	859.0	859.0	0.1
Ca(OH)$_2$	1710.5	1756.7	1767.1	1778.2	1722.3	1757.3	1767.1	1777.3	1777.3	0.3
CaF	511.5	534.4	538.9	543.8	522.1	535.0	538.9	543.0	543.0	0.1
CaF$_2$[f]	1089.3	1123.3	1130.4	1138.2	1101.3	1123.9	1130.4	1137.3	1137.4	0.2
CaS	271.6	318.2	328.2	337.4	294.0	319.7	328.2	336.3	337.0	−0.3
CaCl	383.8	406.5	411.6	416.6	390.9	406.9	411.6	416.1	416.5	−0.4
CaCl$_2$	854.6	892.3	901.5	910.4	863.9	892.8	901.5	909.7	910.5	−0.8

[a] On the basis of CCSD(T)/(aug-)cc-pWCVQZ geometries. [b] On the basis of CCSD(T)/(aug-)cc-pWCVQ+dZ geometries. [c] {Q,5} extrapolation for HF and CCSD and {T,Q} extrapolation for (T). [d] {Q,5} extrapolation for HF, CCSD, and (T). [e] Counterpoise correction for basis set superposition error. [f] Single-point calculations were carried out using linear geometries as the (aug-)cc-pWCV5Z calculations were computationally too demanding to perform for a bent configuration.

CCSD(T) calculations also found the barrier to be effectively negligible (3 and 6 cm^{-1} for the QZ and 5Z PESs, respectively).

For CaF$_2$, the B3-LYP/cc-pWCVTZ surface is very flat between 160° and 200° with a negligible maximum (∼0.01 kJ mol^{-1}). Again the barrier separating nonlinear structures is far more pronounced for the B3-LYP/(aug-)cc-pWCVT+2dZ surface (2.7 kJ mol^{-1}) while being nonexistent for CCSD(T)/(aug-)cc-pWCVTZ. A maximum is observed, however, for the CCSD(T)/(aug-)cc-pWCVT+2dZ surface. This is 0.45 kJ mol^{-1} above the absolute minimum and falls by only 0.08 kJ mol^{-1} (to 0.37 kJ mol^{-1}) when BSSE is considered. These results are consistent with earlier findings[14d] (at the HF level) that for CaF$_2$ the increase from four to six d functions results in a change of geometry from linear to bent. The barrier height is also in good agreement with the CCSD(T)/(aug-)cc-pCVQZ results of Koput and Roszczak,[15a] although when they repeated their calculations with the larger (aug-)cc-pCV5Z basis sets they found the barrier to be 0.23 kJ mol^{-1} higher (at 0.60 kJ mol^{-1}).

These variations in the shapes of the PESs obviously have an appreciable effect on the energy levels of the bending modes and thus on their contributions to the thermal corrections. The changes in the rotational constants, depending on whether the molecule is predicted to be linear or bent, also make significant contributions to $H^{298} - H^0$.

Thus, for the B3-LYP/cc-pWCVTZ CaH$_2$ calculation, the maximum lies below the ZPVE in the bending mode and the molecule was therefore regarded as linear when the ZPVE and $H^{298} - H^0$ were calculated (i.e., the rotational constants and stretching vibrational frequencies of the linear molecule were used). For the B3-LYP/(aug-)cc-pWCVT+2dZ calculation, the linearization barrier is higher than the thermal energy in the bending mode so the molecule was treated as if it were bent in the calculation of the ZPVE and $H^{298} - H^0$. The CCSD(T) PES has its minimum at the linear structure.

For the B3-LYP/cc-pWCVTZ CaF$_2$ calculation, the situation is the same as for CaH$_2$ and was treated accordingly. For the B3-LYP/(aug-)cc-pWCVT+2dZ and CCSD(T) calculations, the barrier to linearization is higher than the ZPVE in the bending motion but well below the thermal energy in the mode at 298 K. In these cases, CaF$_2$ was therefore regarded as being bent when calculating the ZPVE and linear when calculating $H^{298} - H^0$.

In Tables 2 and 3, the anharmonic vibrational frequencies and the resulting ZPVEs and $H^{298} - H^0$ values are shown in parentheses. None of the anharmonic frequencies are scaled. In most cases, the differences between the harmonic and anharmonic frequencies are relatively small, resulting in only minor changes to the ZPVEs. The changes to the thermochemical corrections are more significant, however, particularly in the cases of CaF$_2$ and CaCl$_2$ where the difference is 3−5 kJ mol^{-1}.

The ZPVE and $H^{298} - H^0$ values, obtained using the anharmonic vibrational frequencies, have been used in the calculation of the G3[CC](dir,full) and W2 atomization energies and heats of formation reported below, representing a change from the standard procedures. In the case of Ca(OH)$_2$, where the CCSD(T)/(aug-)cc-pWCVT+2dZ vibrational frequencies (that would normally be used in the W2-best results) could not be calculated, the ZPVE and $H^{298} - H^0$ values obtained with B3-LYP/cc-pWCVTZ were used instead. As can be seen in Table 3, these results (fortuitously) give a better approximation to the CCSD(T)/T+2dZ values than those from the B3-LYP/(aug-)cc-pWCVT+2dZ surface. In light of the significant qualitative differences between the B3-LYP and CCSD(T) surfaces using the $n+xd$Z basis sets, we suspect that B3-LYP may be less reliable in this situation.

3.3. Energies and Extrapolations. Total energies and atomization energies (AEs) were calculated using the molecular geometries determined above. In the W2C procedure, single-point energies are calculated using coupled cluster theory with the triple-, quadruple- and quintuple-ζ basis sets and then extrapolated to the complete basis set limit. AEs calculated with both the nZ and $n+xd$Z versions of each of these sets, and the resulting extrapolated values, are presented in Table 4. The corresponding total energies along with the G3 and G3[CC](dir,full) energies can be found in the Supporting Information.

As mentioned in the methods section, in W2C calculations the HF, CCSD, and (T) components of the energy (or, more conveniently for analysis, AE) are extrapolated separately. Analysis of these data for the $n+xd$Z basis sets reveals that, while the HF component of the AEs is effectively converged at the 5Z level and the (T) components are almost so, there is still significant extrapolation beyond the quintuple-ζ results for the CCSD energies. This extrapolation contributes up to 9.4 kJ mol^{-1} to the CCSD component of the AE (in the case of Ca(OH)$_2$). This degree of extrapolation is not uncommon for molecules of this size, and we do not expect it to lead to a significant error in the W2C heats of formation. We do note, however, that the degree of extrapolation for CaO is rather large in comparison to other molecules of the same size, contributing 8.2 kJ mol^{-1} to the CCSD component of the AE.

Standard W2C uses only the TZ and QZ results for the extrapolation of the (T) contribution so that the expensive quintuple-ζ triples calculations need not be performed. We find that the difference between {TZ, QZ} and {QZ, 5Z} extrapola-

TABLE 5: Core−Core and Core−Valence Correlation (CV) Contributions to Atomization Energies and Associated Counterpoise Corrections (CP) for Basis Set Superposition Error (kJ mol^{-1})

	CCSD(T)/MTsmall[a]	CCSD(T)/MTsmall[b]		CCSD(T)/(aug-)cc-pWCVT+2dZ[b,c]		CCSD(T)/(aug-)cc-pWCVQ+dZ[b,d]	
	CV	CV	CP	CV	CP	CV	CP
CaH	0.0	0.0	−0.1	0.0	0.0	0.2	−0.1
CaH_2	0.0	0.0	−0.1	0.2	0.0	0.5	−0.1
CaO	0.8	0.9	−0.2	0.6	0.0	1.1	−0.1
CaOH	1.6	1.6	−0.1	1.6	0.0	1.9	−0.1
$Ca(OH)_2$	3.1	3.1	−0.2	3.2	0.0	3.7	−0.2
CaF	0.7	0.7	−0.1	0.7	0.0	1.0	−0.1
CaF_2	1.4	1.4	−0.1	1.5	0.0	2.0	−0.1
CaS	0.6	0.6	−0.2	0.4	−0.1	0.9	−0.2
CaCl	0.5	0.5	−0.2	0.5	−0.1	0.9	−0.1
$CaCl_2$	1.0	1.0	−0.3	1.0	−0.2	1.7	−0.3

[a] On the basis of CCSD(T)/(aug-)cc-pWCVQZ geometries. [b] On the basis of CCSD(T)/(aug-)cc-pWCVQ+*d*Z geometries. [c] Using the uncontracted cc-pWCVT+2*d*Z basis set for Ca and the MTsmall basis sets for all other atoms. [d] Using the uncontracted cc-pWCVQ+*d*Z basis set for Ca and the MTVQZ basis sets for all other atoms.

TABLE 6: Contributions of Scalar Relativistic Effects and Spin−Orbit Coupling Effects (for Atoms) to Atomization Energies (kJ mol^{-1})

	Darwin + mass−velocity		Douglas−Kroll				
	ACPF(riiv) MTsmall[a]	ACPF(riiv) MTsmall[b]	CCSD(T) (riiv) MTsmall[b]	CCSD(T) (riiv) (aug-)cc-pWCVT+2dZ[b,c]	CCSD(T) (riiv) (aug-)cc-pWCVQ+dZ[b,d]	CCSD(T) (riiv) (aug-)cc-pWCV5Z[b,e]	spin−orbit[f]
CaH	−2.7	−2.7	−2.4	−2.7	−2.8		0.0
CaH_2	−3.4	−3.4	−3.3	−3.6	−3.8		0.0
CaO			−5.0	−7.4	−8.2	−8.4	−0.9
CaOH	−4.8	−4.8	−4.6	−4.9	−5.0		−0.9
$Ca(OH)_2$	−7.6	−7.6	−7.6	−7.9	−8.1	−8.1	−1.9
CaF	−4.3	−4.3	−4.2	−4.4	−4.5	−4.6	−1.6
CaF_2	−7.0	−7.0	−7.0	−7.3	−7.4		−3.2
CaS	−0.9	−0.9	−4.3	−5.4	−6.1	−6.3	−2.3
CaCl	−4.3	−4.3	−4.0	−4.2	−4.4		−3.5
$CaCl_2$	−7.2	−7.2	−7.1	−7.3	−7.5		−7.0

[a] On the basis of CCSD(T)/(aug-)cc-pWCVQZ geometries. [b] On the basis of CCSD(T)/(aug-)cc-pWCVQ+*d*Z geometries. [c] Using the uncontracted cc-pWCVT+2*d*Z basis set for Ca with MTsmall basis sets for all other atoms. [d] Using the uncontracted cc-pWCVQ+*d*Z basis set for Ca with MTVQZ basis sets for all other atoms. [e] Using the uncontracted cc-pWCV5Z basis set for Ca with MTV5Z basis sets for all other atoms. [f] Taken from ref 2c.

tions is less than 1 kJ mol^{-1} in all cases. We also note that if {Q, 5} extrapolations are performed separately for HF, CCSD, and (T), the result is not significantly different from that obtained by extrapolating the full CCSD(T) AEs. This is not the case, however, for {T, Q} extrapolations.

Finally, the effects of BSSE on the extrapolated results were also estimated and are included in Table 4. This involved estimating the BSSE for each atom in each of the component calculations (TZ, QZ, 5Z) using the counterpoise method and then extrapolating in the same way as for the AEs. The resulting corrections are less than 0.4 kJ mol^{-1} for all the molecules apart from $CaCl_2$ where the BSSE was predicted to contribute ∼0.75 kJ mol^{-1}. Superposition errors are therefore not a serious issue for W2C extrapolations with these basis sets. We note that, although the individual counterpoise corrections are negative in all cases (as they are required to be), they are smaller for larger basis sets so that, when they are extrapolated, the final counterpoise correction to the extrapolated energy may, in fact, be positive.

3.4. Core−Valence Effects. The corrections to the atomization energies associated with core−core and core−valence correlation (CV) are reported in Table 5, along with the corresponding counterpoise corrections for BSSE. Standard W2C theory requires the calculation of the CV correction at the CCSD(T)/MTsmall level of theory. With the introduction of the cc-pWCV*n*+*xd*Z basis sets, however, it has been proposed that the uncontracted triple-ζ set should be preferred to MTsmall for calcium atoms in the calculation of CV and scalar relativistic effects.[11] These results are also included in Table 5, along with calculations performed using the uncontracted cc-pWCVQ+*d*Z basis set (with the MTVQZ sets[4a] for all other atoms) to reveal the effects of any further increase in basis set size.

As is seen in Table 5, CV corrections are very small in all cases and there is very little difference between the results obtained with the three basis sets. The largest discrepancy is 0.7 kJ mol^{-1} between the MTsmall and (aug-)cc-pWCVQ+*d*Z results for $CaCl_2$. Counterpoise corrections to the CV component lie within the range 0.1−0.3 kJ mol^{-1} and therefore do not need to be considered for the routine calculations of CV corrections with these basis sets.

3.5. Scalar Relativistic Effects. The contributions of scalar relativistic corrections to the AEs are shown in Table 6. W2C requires the use of the averaged coupled pair functional (ACPF) method with the MTsmall basis sets to calculate the effects of the Darwin and mass−velocity terms on the total energies. These results are effectively independent of the use of the *n*Z or *n*+*xd*Z reference geometries, as shown in the first two columns of Table 6. Unfortunately, we were unable to obtain convergence in the ACPF calculations for CaO, even though CCSD(T) still appears to be performing acceptably (see below). Similarly, the results for CaS appear to be unreasonably low. The Douglas−Kroll method for the calculation of scalar relativistic effects was therefore also investigated. As shown in the third column of Table 6, this makes very little difference to the prediction of E_{rel} for most molecules apart from CaO (for which the calculation is now successful) and CaS where the result is now more in line with the values predicted for related molecules.

As with the CV corrections, it has been recommended that the uncontracted cc-pWCVT+2*d*Z basis sets be used for Ca (along with MTsmall for other atoms) when calculating scalar relativistic effects.[11] The results with these sets are very similar to those obtained with MTsmall, except in the cases of CaO and CaS. For CaS, the magnitude of the correction increases by 1.1 kJ mol^{-1}, while for CaO it increases by 2.4 kJ mol^{-1}. This large change is unexpected and prompted us to also calculate the Douglas−Kroll relativistic corrections using the cc-pWCVQ+*d*Z basis set (for Ca, MTVQZ[4a] for other atoms) and also with the cc-pWCV5Z basis set (for Ca, MTV5Z[4a] for other atoms) for CaO, $Ca(OH)_2$, CaF, and CaS. While in most cases the correction increases in magnitude by only 0.1 to 0.2 kJ mol^{-1} from the triple- to quadruple-ζ basis sets and by 0.05 kJ mol^{-1} for QZ to 5Z, for CaO and CaS the changes with basis set are more marked. For CaS, there is an increase in magnitude of 0.63 kJ mol^{-1} from TZ to QZ and 0.23 kJ mol^{-1} from QZ to 5Z, while the correction for CaO increases in magnitude by 0.75 kJ mol^{-1} from TZ to QZ and by a further 0.26 kJ mol^{-1} from QZ to 5Z.

The strong basis set dependency of the relativistic corrections for CaO and CaS is surprising and leads to the question of whether this is an artifact of the basis sets that we are using (noting that these basis sets were not specifically designed for estimating relativistic corrections). We therefore repeated the calculations for CaO using core−valence basis sets that had been optimized for Douglas−Kroll calculations by Peterson.[29] These are denoted (aug-)cc-pwCV*n*Z_DK. These calculations confirm the large scalar relativistic corrections predicted with Martin's *n*+*xd*Z basis sets, with the correction to the atomization energy for CaO being −8.0 kJ mol^{-1} at the TZ level and −8.3 kJ mol^{-1} for QZ.

It therefore appears that the unusual nature of the bonding in CaO and CaS (formally Ca−X double bonds but more likely to involve ionic bonding with some covalent contributions) means that the scalar relativistic effects are not straightforward to determine. In general, the T+2*d*Z basis sets are sufficient for the accurate prediction of scalar relativistic effects in calcium compounds. However, in cases with unusual bonding, the use of cc-pWCVQ+*d*Z or the Peterson Douglas−Kroll triple-ζ basis sets is desirable.

3.6. Atomization Energies and Heats of Formation. The G3, G3[CC](dir,full), and W2C AEs and heats of formation at 298 K ($\Delta_f H°_{298}$) are presented in Tables 7 and 8, respectively. Three sets of W2C results are reported: The W2C-1 AEs and $\Delta_f H°_{298}$ values are calculated using the (aug-)cc-pWCV*n*Z basis sets; the W2C-2 columns show the results found with the (aug-)cc-pWCV*n*+*xd*Z basis sets, while the W2C-best results indicate calculations where we have attempted to minimize residual potential errors in W2C. Full details of the methods used to obtain these three sets of results are outlined in Table 9. Basis sets written as "u-cc-p..." are uncontracted.

Comparison of the standard G3 and G3[CC](dir,full) results in Table 8 reveals that for most molecules the heats of formation do not show a significant change accompanying the improvements to the method. The exceptions are CaH and CaH_2 where the $\Delta_f H°_{298}$ decreases by 5.1 and 13.0 kJ mol^{-1}, respectively, and CaS where it increases by 6.1 kJ mol^{-1}. We note that with the changes in going from standard G3 to G3[CC](dir,full), that is, improved geometry, coupled cluster reference energy, and no additivity, each individually has a significant effect on the heats of formation of all molecules. However, the overall effect, coupled with the reoptimization of the higher level correction parameters, appears to be small.

TABLE 7: G3 and W2C Atomization Energies at 0 K (kJ mol^{-1})[a]

	Atomization energies				
	G3	G3[CC] (dir,full)[b]	W2C-1[b,c]	W2C-2[d,e]	W2C-best[d,e]
CaH	160.8	165.9	165.2	164.7	164.7
CaH_2[f]	405.5	417.8	416.8	415.9	416.1
CaO[g]		386.9	407.4	406.0	402.9
CaOH	814.7	816.0	824.6	823.9	824.1
$Ca(OH)_2$[h]	1689.0	1692.3	1707.9	1707.1	1706.8
CaF	525.1	525.3	535.2	534.3	534.3
CaF_2[f]	1104.9	1105.0	1122.9	1121.6	1121.9
CaS[g]	327.1	320.9	328.8	327.6	325.8
CaCl	407.3	405.9	407.2	406.7	406.5
$CaCl_2$	893.1	890.4	892.4	892.3	891.7

[a] See Table 9 for a full description of the W2C-1, W2C-2, and W2C-best methods. [b] On the basis of CCSD(T)/(aug-)cc-pWCVQZ geometries. [c] Using cc-pWCV*n*Z basis sets for Ca. [d] On the basis of CCSD(T)/(aug-)cc-pWCVQ+*d*Z geometries. [e] Using cc-pWCV*n*+*xd*Z basis sets for Ca. [f] CCSD(T)/(aug-)cc-pWCVQ+*d*Z zero-point energies and thermochemical corrections are used for CaH_2 and CaF_2 in W2C-2 calculations as B3-LYP/(aug-)cc-pWCVT+2*d*Z is not considered suitable for predicting the shapes of the bending PESs; see text. [g] Douglas−Kroll CCSD(T)/MTsmall scalar relativistic effects were used for W2C-1 and W2C-2 calculations for CaO and CaS. [h] The B3-LYP/cc-pWCVTZ zero-point energy and thermochemical correction are used for $Ca(OH)_2$ in the W2C-best calculation (see text).

TABLE 8: G3 and W2C Heats of Formation at 298 K (kJ mol^{-1})[a]

	Heats of formation				
	G3	G3[CC](dir,full)	W2C-1	W2C-2	W2C-best
CaH	231.8	226.7	227.4	228.0	227.9
CaH_2	202.4	189.4	189.7	191.3	190.0
CaO		36.6	16.1	17.5	20.7
CaOH	−177.3	−178.6	−187.2	−186.4	−186.7
$Ca(OH)_2$	−591.9	−594.6	−610.5	−608.7	−609.5
CaF	−270.9	−271.2	−281.0	−280.2	−280.1
CaF_2	−774.0	−771.1	−788.0	−787.7	−786.6
CaS	124.8	130.9	123.1	124.2	126.1
CaCl	−110.4	−109.2	−110.4	−109.9	−109.8
$CaCl_2$	−475.6	−469.9	−472.1	−469.4	−471.3

[a] Calculated using atomization energies from Table 7. See Table 7 for comments and details.

It is clear from the W2C-1 and W2C-2 results in Tables 7 and 8 that the introduction of the *n*+*xd*Z basis sets (in W2C-2) does not make a significant impact on the W2C results. The largest change is 2.7 kJ mol^{-1} for $CaCl_2$, where there are significant differences in the thermochemical corrections. This is mostly due to the *n*+*xd*Z basis set not performing very well with B3-LYP in the calculation of the anharmonic bending frequency. In all other cases the difference is below 1.8 kJ mol^{-1}. Similarly, the W2C-best results show very little difference from the *n*+*xd*Z results. The exceptions (in addition to $CaCl_2$) are CaO and CaS where the small changes are associated with the improved evaluation of the scalar relativistic corrections, as noted above. It is therefore clear that, apart from the relativistic problem and the anharmonic treatment of bending modes, the modifications to the W2C method that we have examined do not significantly affect the predicted thermochemical properties of calcium compounds.

The G3[CC](dir,full) and W2C-best heats of formation are compared with experimental values in Table 10. There are a wide range of experimental data available for the various molecules investigated in this study, many of which are,

TABLE 9: Description of Components of W2C-1, W2C-2, and W2C-Best Theoretical Methods[a]

	W2C-1	W2C-2	W2C-best
Ca basis sets	cc-pWCVnZ; n = T,Q,5	cc-pWCVn+xdZ; n = T,Q,5; x = 2,1,0	cc-pWCVn+xdZ; n = T,Q,5; x = 2,1,0
H basis sets	cc-pVnZ; n = T,Q,5	cc-pVnZ; n = T,Q,5	cc-pVnZ; n = T,Q,5
O, F basis sets	aug-cc-pCVnZ; n = T,Q,5	aug-cc-pCVnZ; n = T,Q,5	aug-cc-pCVnZ; n = T,Q,5
S, Cl basis sets	aug-cc-pVnZ+2df; n = T,Q,5	aug-cc-pVnZ+2df; n = T,Q,5	aug-cc-pVnZ+2df; n = T,Q,5
geometry	CCSD(T)/quadruple-ζ	CCSD(T)/quadruple-ζ	CCSD(T)/quadruple-ζ
vibrational frequencies	B3-LYP cc-pWCVTZ (for Ca) cc-pVTZ+1 (all other atoms) anharmonic bending frequencies for CaH_2, $Ca(OH)_2$, CaF_2, and $CaCl_2$ anharmonic OH stretching frequencies for CaOH and $Ca(OH)_2$	B3-LYP cc-pWCVT+2dZ (for Ca) aug-cc-pCVTZ (all other atoms) anharmonic bending frequencies for CaH_2, $Ca(OH)_2$, CaF_2, and $CaCl_2$ anharmonic OH stretching frequencies for CaOH and $Ca(OH)_2$	CCSD(T) cc-pWCVT+2dZ (for Ca) aug-cc-pCVTZ (all other atoms) W2C-1 results for $Ca(OH)_2$ anharmonic bending frequencies for CaH_2, $Ca(OH)_2$, CaF_2, and $CaCl_2$ anharmonic OH stretching frequencies for CaOH and $Ca(OH)_2$
scaling factor for harmonic vibrational frequencies	0.985	0.985	1
SCF extrapolation	$E = A + Bn^{-5}$; n = Q,5	$E = A + Bn^{-5}$; n = Q,5	$E = A + Bn^{-5}$; n = Q,5
CCSD extrapolation	$E = A + Bn^{-3}$; n = Q,5	$E = A + Bn^{-3}$; n = Q,5	$E = A + Bn^{-3}$; n = Q,5
triples extrapolation	$E = A + Bn^{-3}$; n = T,Q	$E = A + Bn^{-3}$; n = T,Q	$E = A + Bn^{-3}$; n = Q,5
BSSE corrections to extrapolations	No	No	Yes
CV correction	CCSD(T) (riiv/riv)/MTsmall	CCSD(T) (riiv/riv)/MTsmall	CCSD(T) (riiv/riv) u-cc-pWCVT+2dZ (for Ca) MTsmall (all other atoms)
BSSE corrections to CV	No	No	Yes
E_{rel} (except CaO and CaS)	ACPF(riiv)/MTsmall Darwin and mass−velocity	ACPF(riiv)/MTsmall Darwin and mass−velocity	CCSD(T) (riiv) Douglas−Kroll u-cc-pWCVQ+dZ (for Ca) MTVQZ (all other atoms)
E_{rel} (CaO and CaS)	CCSD(T) (riiv)/MTsmall Douglas−Kroll	CCSD(T) (riiv)/MTsmall Douglas−Kroll	CCSD(T) (riiv) Douglas−Kroll u-cc-pWCV5Z (for Ca) MTV5Z (all other atoms)
SO	atoms only	atoms only	atoms only

[a] All calculations use a riv correlation space for Ca unless otherwise noted.

TABLE 10: Comparison of Theoretical and Experimental Heats of Formation (kJ mol^{-1})

	G3[CC](dir,full)	W2C-best	JANAF[a]	Gurvich[b]	most recent experiment	year	experimental average	experimental range	no. of expts
CaH	226.7	227.9		229.4 ± 2	229.4 ± 2	1994[c]	231	225 to 239[d]	3
CaH_2	189.4	190.0							
CaO	36.6	20.7	44 ± 21	38 ± 10	37 ± 9	1986[e]	40	5 to 80[f]	14
CaOH	−178.6	−186.7	−194 ± 21	−173 ± 15	−190.8 ± 8	1987[g]	−192	−160 to −250[h]	17
$Ca(OH)_2$	−594.6	−609.5	−611 ± 38	−598 ± 15	−605.8 ± 8	1987[i]	−616	−530 to −700[j]	10
CaF	−271.2	−280.1	−272 ± 8	−276 ± 5	−277 ± 8	1978[k]	−278	−262 to −335[l]	9
CaF_2	−771.1	−786.6	−785 ± 8	−791 ± 8	−787 ± 19	1966[m]	−789	−760 to −805[n]	13
CaS	130.9	126.1	124 ± 8	121 ± 15	124 ± 7	1964(1998)[o]	127	115 to 140[p]	3
CaCl	−109.2	−109.8	−105 ± 15	−104 ± 6	−96.8 ± 7	1973[q]	−105	−85 to −150[r]	11
$CaCl_2$	−469.9	−471.3	−471.5 ± 4	−485 ± 7	−485 ± 21	1973[s]	−475	−400 to −505[t]	14

[a] Reference 30. [b] Reference 31. [c] Reference 31, based on results of several experiments. [d] References 32 and 33, calculated from AEs, using atomic $\Delta_f H^\circ$ values from ref 30. [e] Reference 35a, calculated from the AE, using atomic $\Delta_f H^\circ$ values from ref 30. [f] References 34−36; in most cases calculated from AEs, using atomic $\Delta_f H^\circ$ values from ref 30. [g] Reference 37a. [h] References 34, 36b, 37, and 38, in many cases calculated from Ca−OH dissociation energies, using the O−H dissociation energy from ref 40 and atomic $\Delta_f H^\circ$ values from ref 30. [i] Reference 37a. [j] References 37a−c, 38b, and 39, in many cases calculated from Ca−OH dissociation energies, using the O−H dissociation energy from ref 40 and atomic $\Delta_f H^\circ$ values from ref 30. [k] Reference 41a. [l] References 32 and 41, in many cases calculated from AEs, using atomic $\Delta_f H^\circ$ values from ref 30. [m] Reference 41e. [n] Reference 41e−g and 42, in many cases calculated from sublimation data, using $\Delta_f H^\circ$ values of crystalline forms from ref 30. [o] Reference 35c (reviewed in ref 30), calculated from the AE, using atomic $\Delta_f H^\circ$ values from ref 30. [p] References 35c (reviewed in ref 30) and 43, calculated from AEs, using atomic $\Delta_f H^\circ$ values from ref 30. [q] Reference 38b, calculated from the AE, using atomic $\Delta_f H^\circ$ values from ref 30. [r] References 32, 38, and 44, calculated from AEs, using atomic $\Delta_f H^\circ$ values from ref 30. [s] Reference 38b, calculated from the AE, using atomic $\Delta_f H^\circ$ values from ref 30. [t] References 38, 44a, 44f, and 45, in many cases calculated from sublimation data, using $\Delta_f H^\circ$ values of crystalline forms from ref 30.

unfortunately, of quite low precision. The experimental values are detailed in Table S2 of the Supporting Information. As the majority of the experiments date from the 1960s and early 1970s, improved measurements of the reference data since then have meant that the originally reported heats of formation have needed to be reanalyzed, as in the critical compendia of Chase (JANAF)[30] and Gurvich.[31] We have therefore compared our theoretical heats of formation with the recommended reviewed values, as well as with the most recently reported experimental results, as it appears that, in some cases, these have not been included in the compendia. Table 10 also includes the average and approximate range of the unique experimental results listed by Chase and Gurvich (including uncertainties). These quantities are intended to provide a mean value as well as a rough estimate of the true range within which the experimental heats of formation are likely to lie.

The discerning reader will already have noticed from Table 8 that there are several molecules that still show significant discrepancies between the G3[CC](dir,full) and W2C-best heats of formation. These differences exceed the sum of the uncertainties reported for these classes of methods with the standard test sets. For example, while the results for the hydrides and, surprisingly, the chlorides are in extremely good agreement, differences of 15 to 16 kJ mol^{-1} are seen between G3[CC](dir,full) and W2C-best for CaO, $Ca(OH)_2$, and CaF_2. For CaOH, CaF, and CaS, the results are more consistent and do agree within their error margins. We note that where significant differences exist between G3[CC](dir,full) and W2C-best, the latter consistently predicts a lower heat of formation (i.e., a more stable molecule).

Interestingly, despite the sometimes large discrepancies between the two sets of theoretical results, they are all consistent with the 1998 JANAF recommended heats of formation[30] when uncertainties are taken into consideration (Table 10). The heats of formation from the most recent experiments are generally in better agreement with the W2C-best values, while those from the review of Gurvich[31] are more evenly split. We therefore consider each molecule or class of molecules in turn.

3.6.1. CaH and CaH_2. For both CaH and CaH_2, the two theoretical results show good agreement with one another. For CaH, there is also good agreement between the theoretical values and experiment.[31−33] We have found no reports of experimental thermochemical data for molecular CaH_2, but our result is close to that of a recent theoretical study carried out at a similar level.[15b] We conclude that both theoretical methods are giving a good description of these molecules.

3.6.2. CaO. For CaO, the experimental heats of formation are fairly widely scattered, averaging around 40 kJ mol^{-1}.[34−36] Chase[30] and Gurvich[31] also give ~40 kJ mol^{-1} as the recommended $\Delta_f H°_{298}$ for CaO in their reviews. This value is in good agreement with G3[CC](dir,full) but is a full 20 kJ mol^{-1} higher than the W2C-best result. Our W2C-best heat of formation (20.7 kJ mol^{-1}) also lies outside the error margins of most of the experimental results. Some of the recent experiments,[36] however, do predict slightly lower heats of formation: 27 ± 7 (with a small quoted uncertainty and reportedly a strict upper limit) and 29.4 ± 21 kJ mol^{-1}. These are in better agreement with W2C-best, but according to the Gurvich review, the former result[36a] is less reliable than those from other experiments that predict a $\Delta_f H°_{298}$ closer to 40 kJ mol^{-1}. We have therefore further pursued the possibility of any potential weaknesses in W2C-best for CaO, as described below.

3.6.3. CaOH and $Ca(OH)_2$. In both cases, we see that the G3[CC](dir,full) results are in better agreement with Gurvich while the W2C-best heats of formation are more consistent with JANAF and the recent experiments.[34,36b,37−40] We note, however, that while the W2C-best results fit comfortably within the Gurvich error bars, G3[CC](dir,full) and the most recent experiments only agree within the overlap of their uncertainties. Thus, although we can make no definite conclusions, we are inclined to favor the W2C-best results in these cases.

3.6.4. CaF and CaF_2. The experimental heats of formation are quite consistent for both CaF and CaF_2.[32,41,42] For CaF, these results lie between the two theoretical values, with the JANAF value favoring G3[CC](dir,full), while Gurvich and the most recent experiment are closer to W2C-best. For CaF_2, all the experimental values are in much better agreement with the W2C-best result.

3.6.5. CaS. Here the two theoretical results agree with one another within their uncertainties. While they both also agree with the experimental results[35c,43] within their given error margins, comparison of the experimental values more strongly supports the W2C-best result, the G3[CC](dir,full) value being at the higher end of all error bars.

3.6.6. CaCl and $CaCl_2$. For both of the chlorides, the two theoretical heats of formation are in close agreement. Unfortunately, while these results are consistent with the JANAF review values, agreement with other experiments is not as good.[32,38,44,45] This is particularly the case for CaCl where the experimental values cluster around −100 kJ mol^{-1} (see Supporting Information) while the theoretical results are ~10 kJ mol^{-1} lower. For $CaCl_2$, the most recent experiment is from the laboratory of Gurvich and is, presumably, the data upon which he has based his compendium value.

In summary, although it is not possible to make a definitive statement about the reliability of the two theoretical methods based upon the available experimental data, in most cases where G3[CC](dir,full) and W2C-best differ, the experimental evidence favors the W2C-best results. This is reasonable as W2C is formally a much higher level of theory.

3.7 Further Investigations for Calcium Oxide. As noted above, the W2C methods predict the heat of formation of CaO to be approximately 20 kJ mol^{-1} lower than either G3[CC](dir,full) or the majority of the experimental data. While W2C-best represents the highest level of theoretical treatment that we are currently able to straightforwardly apply to these molecules, and would normally be expected to give accurate results, it is possible that the unusual nature of the bonding in CaO may make it difficult to describe accurately with these methods. For example, a natural bond order (NBO) analysis with the (aug-)cc-pWCVT+2*d*Z basis sets indicates that the atomic charges are ±1.7. This suggests that, although the bonding is dominated by electrostatic interactions between Ca^{2+} and O^{2-} ions, contributions associated with covalent interactions are not insignificant. Although it has been found previously[46] that molecules with semipolar bonds (bonds with both electrostatic and covalent components) present challenges to computational chemistry, we would expect that W2C-best should be a sufficiently high level of theory to give a satisfactory description of these species. Nevertheless, in light of the large discrepancies between W2C-best and experiment, we have investigated three further potential sources of error in the calculations: possible weaknesses in the basis sets themselves, the choice of extrapolation scheme for the single-point energies, and the inclusion of explicit triple and higher-order excitations in the CI expansion.

Recently, Peterson has developed a new set of correlation-consistent basis sets for calcium.[16b,29] In addition to the Douglas−Kroll basis sets mentioned above, these include standard core−valence basis sets, cc-pCV*n*Z, as well as weighted core−valence sets, cc-pwCV*n*Z (note the lower case w). These sets are similar in size to the cc-pWCV*n*+*xd*Z sets developed by Martin, that have been used in the majority of the present work. They include a set of Hartree−Fock 3d functions which negates the need for the extra +*d* functions in cc-pWCV*n*+*xd*Z. We have therefore checked our calculations for CaO by comparison with the results generated using the two Peterson basis sets. We find that the extrapolated valence atomization energies are almost identical when calculated with the cc-pWCVn+xdZ and cc-pwCVnZ basis sets and only 0.7 kJ mol^{-1} higher when the cc-pCVnZ sets are used.

Using these three different types of basis sets, It is also possible to evaluate the reliability of the scheme employed to extrapolate the correlation energies in the W2C procedures. While the n^{-3} scheme is commonly regarded to be the best in most situations[47] there have been instances where other schemes have been suggested to be superior.[48] To probe the extrapolation procedures, AEs were calculated for CaO at the double-, triple-, quadruple-, and quintuple-ζ levels for each of the three series of basis sets. These were then extrapolated using seven different extrapolation schemes: exponential, mixed exponential, n^{-3}, n^{-4}, $n^{-3} + n^{-5}$, $n^{-4} + n^{-5}$, and $n^{-4} + n^{-6}$. For each scheme, the extrapolation was performed with all the available results {DZ, TZ, QZ, 5Z} and also with the {DZ, TZ, QZ} and the {TZ, QZ, 5Z} values. For the two schemes that involve only two parameters, n^{-3} and n^{-4}, extrapolations were also performed with just the {TZ, QZ} pair and also with the {QZ, 5Z} pair. From comparison of the fitted extrapolation curves with the data points, it is clear that, as expected, extrapolations that do not involve the 5Z values generally give inferior fits. The n^{-3}, n^{-4}, and $n^{-3} + n^{-5}$ schemes also give poor results when all four points are included. The remaining curves all approximate the data well, particularly in the higher-ζ regions. The mean AEs from the various extrapolation schemes are quite consistent among the three families of basis sets, being 413.8 kJ mol^{-1} for the cc-pWCVn+xdZ sets, 414.4 kJ mol^{-1} for the cc-pCVnZ sets, and 413.2 kJ mol^{-1} for the cc-pwCVnZ sets. The predicted AEs range over ±2.9 kJ mol^{-1}, ±3.0 kJ mol^{-1}, and ±2.5 kJ mol^{-1}, respectively. The extrapolation scheme that is recommended for W2C procedures (n^{-3}{QZ, 5Z}) is found to give some of the highest AEs, generally 2 kJ mol^{-1} greater than the average. Thus, it is possible that the heat of formation of CaO could be being underestimated by up to a conservative 5 kJ mol^{-1} in our W2C results due to the choice of extrapolation scheme. We emphasize, however, that n^{-3} is currently the generally preferred extrapolation procedure, and so such an underestimation is considered unlikely.[47]

It has been noticed previously that multireference effects may be significant for CaO.[7] In our work we found that the $\boldsymbol{Q}1$ diagnostic[49] of the QCISD(T) calculation of G3 theory is extremely large (0.09), and the $\boldsymbol{T}1$ diagnostics[50] in the components of W2C (~0.035) are also above the normal cutoff limits. While these diagnostics are large enough to suggest that multireference effects may be significant for CaO, the use of multireference versions of W2C in our previous work,[7] denoted W2C-CAS-ACPF and W2C-CAS-AQCC, gave results very similar to the W2C-best value (when our Douglas−Kroll quintuple-ζ relativistic correction is applied). It is possible, nevertheless, that the perturbative treatment of the triple excitations may be performing poorly for this unusual molecule.

We therefore investigated the effects of explicitly including higher-order excitations in the coupled cluster expansion for CaO. This was done using Peterson's cc-pCVnZ basis sets along with the cc-pVnZ sets for oxygen. Naturally, we were quite restricted in the number of electrons that could be correlated at such computationally demanding levels of theory. However, it was possible to perform CCSDT calculations using the riv correlation space with the triple-, quadruple-, and quintuple-ζ basis sets in order to predict the effect of explicitly including the triple excitations (rather than using perturbation theory) on the extrapolated AE. This is found to reduce the atomization energy by 2.4 kJ mol^{-1}.

Of course, it is well-known that the CCSDT method usually gives inferior energies to CCSD(T) as the inclusion of explicit triple excitations tends to underestimate the total energy.[4b,51] This can be corrected for by also calculating the effects of quadruple excitations (CCSDTQ).[4,52] Unfortunately, it was necessary to restrict the active space to include only the 4s electrons of calcium and the 2p electrons of oxygen in order to be able to estimate this effect with anything larger than a double-ζ basis set. At the quadruple-ζ level with this small (six electron) active space, the quadruple excitations are found to increase the extrapolated AE by 2.8 kJ mol^{-1}. Unfortunately, with this small correlation space, calculations on the Ca atom only involve two active electrons and thus only double excitations can be considered (CCSD). The effects of correlating the Ca 3s and 3p and the O 2s electrons were estimated using the double-ζ basis set; this correction is found to be approximately 0.6 kJ mol^{-1}.

The effects of including higher-order terms in the coupled cluster expansion were also investigated by performing CCSDTQ5 and full CI calculations using the small correlation space and the double-ζ basis sets. These effects are estimated to contribute approximately −0.5 kJ mol^{-1} to the extrapolated AE. Thus, in total, the higher-order effects are estimated to increase the AE, and thus decrease the heat of formation, of CaO by approximately 0.5 kJ mol^{-1}. The effects of including diffuse functions on the oxygen atom (potentially important for describing the $Ca^{2+}-O^{2-}$ and $Ca^{+}-O^{-}$ states) were also estimated. In this case the total AE is predicted to be increased by 1.7 kJ mol^{-1}, again reducing the heat of formation.

In summary, while the error associated with the choice of extrapolation scheme may be making our heat of formation too low by up to a conservative estimate of 5 kJ mol^{-1}, the inclusion of higher excitation terms in the coupled cluster expansion would actually act to further reduce our result by up to 1.7 kJ mol^{-1}. Correcting for both of these possible errors would increase the predicted heat of formation by up to ~3 kJ mol^{-1} (but probably less), giving no appreciable improvement in the agreement with G3[CC](dir,full) or the compendia-recommended experimental value. The scatter in even the most recent experimental results indicates that the thermochemistry of CaO is also difficult to investigate experimentally. Nevertheless, our best calculations support one of the more recent experimental estimates of 27 ± 7 kJ mol^{-1} for the heat of formation of CaO. In light of our findings, further experimental investigation would be helpful in determining whether there is a significant error in the prediction of our best theoretical procedure (20.7 kJ mol^{-1}) or if the heat of formation is significantly lower than the value of ~40 kJ mol^{-1} recommended in the compendia.

4. Conclusions

Geometric parameters, atomization energies, and heats of formation have been calculated for a series of small calcium-containing molecules using high-level quantum chemical methods. The CCSD(T)/(aug-)cc-pWCVQ+dZ geometries show good agreement with reliable experimental results. The G3[CC](dir,full) and W2C-best heats of formation are generally in good agreement with experimental values. However, there are discrepancies for a small number of molecules. The large uncertainties in the experimental results make it difficult to definitively assess the reliability of the calculated heats of formation. However, in cases where there are significant differences between the G3[CC](dir,full) and W2C-best results, the experiments tend to favor W2C-best. The exception is CaO where the G3[CC](dir,full) result appears to be in better agreement with the bulk of the experimental data. An intensive investigation of this molecule has failed to reveal any major flaws in the W2C-best procedure that could account for this discrepancy. Our W2C-best heat of formation for CaO supports one of the more recent experimental determinations in preference to values recommended in two recent thermochemical compendia. Further experimental investigations aimed at resolving this issue would be desirable.

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Supporting Information Available: Calculated total energies obtained at the G3, G3[CC](dir,full), CCSD(T)/(aug-)cc-pWCVnZ, and CCSD(T)/(aug-)cc-pWCV$n+xd$Z levels are given in Table S1. Experimental heats of formation are given in Table S2. This material is available free of charge via the Internet at http://pubs.acs.org.

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