

Heats of Formation for CrO, CrO₂, and CrO₃: An Extreme Challenge for Black-Box Composite Procedures

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S Supporting Information

ABSTRACT: In the present study, we use composite methods, denoted CM(S)_Λ and CM5, with post-CCSD(T) terms up to CCSDTQ(S)_Λ and CCSDTQ5, respectively, to evaluate the atomization energies for CrO, CrO₂, and CrO₃. The heats of formation ($\Delta H_{f,298}$) based on our best estimated atomization energies are 198.3 ± 5 kJ mol⁻¹ (CrO), -81.3 ± 5 kJ mol⁻¹ (CrO₂), and -286.8 ± 20 kJ mol⁻¹ (CrO₃). Standard G4-type composite methods yield atomization energies that are adequate for CrO, less good for CrO₂, and least good for CrO₃. CrO₃ is highly multireference in character, and therefore, a “black box” approach of using a single-reference RHF wave function is inadequate, even for “high-level” G4-type methods. We find that, for CrO₃, there is a very large difference in the G4 atomization energies depending on whether an RHF or a UHF reference is used, which is mainly associated with large differences in the MP4 components. In general, we propose that a large R-versus-U difference is likely to be an indication of potential problems in the theoretical treatment. Going beyond G4 to a more rigorous UCCSD(T)-based composite scheme [termed U-CM(3:[DZ,TZ]) in the present study], we again find a large difference (but significantly smaller than that for G4) between the CrO₃ atomization energies based on RHF or UHF references. Intriguingly, the use of Brueckner orbitals as reference orbitals in all components, as in the corresponding Brueckner Doubles (BD) procedure [B-CM(3:[DZ,TZ])], produces results for CrO₃ that are independent of whether RHF or UHF orbitals are used as the starting point.

1. INTRODUCTION

Since the introduction of the G1 protocol,^{1a} the G_n family of composite procedures¹ has grown to become very widely used in computational chemistry. These methods combine a series of calculations of relatively modest computational cost to approximate a higher-level procedure, with the target level typically corresponding to CCSD(T) with a relatively large basis set. The latest among these procedures, namely G4 and related methods,^{1,2} have been shown to achieve chemical accuracy of ~ 5 kJ mol⁻¹ for a wide range of thermochemical properties for main-group molecules. In addition, while earlier G_n procedures, namely G1–G3 and related methods,^{1a–c,3} are formulated only for main-group molecules, G4^{1d} and G4(MP2)^{2a} have been extended to include first-row transition metals, that is, G4(rel) and G4(MP2,rel).⁴

However, while G4 and G4(MP2) perform very well for main-group chemistry, the uncertainties associated with transition metals have been found to be considerably greater. For example, for a test set of 20 small transition metal compounds, the mean absolute deviations from experiment for G4(rel) and G4(MP2,rel) are 17.0 and 11.9 kJ mol⁻¹, respectively.⁴ Perhaps a more intriguing observation is that, while G4 generally outperforms the more economical G4(MP2) procedure for main-group chemistry, G4(MP2,rel) gives somewhat smaller deviations from experiment than G4(rel) in many of the 20 test cases in ref 4. In the particular case of CrO₃, G4(MP2,rel) deviates from the quoted experimental heat of formation⁵ of -323.4 kJ mol⁻¹ by 18.0 kJ mol⁻¹, while G4(rel) gives a much more substantial deviation

of 89.2 kJ mol⁻¹! We note that an alternative composite procedure, namely ccCA-TM, also gives a sizable deviation of 33.5 kJ mol⁻¹ from this experimental value.^{6,7}

Given that these discrepancies occur not only between theory and experiment but also among several reasonably high-level composite procedures, it is important to obtain a better understanding of these intriguing observations for CrO₃, in order to help the further advancement of cost-effective composite methods for transition metal chemistry. In the present study, we focus on the series CrO, CrO₂, and CrO₃, and we aim particularly to identify the cause of the large deviation for CrO₃ for G4(rel).

2. COMPUTATIONAL DETAILS

Standard molecular orbital theory calculations⁸ were carried out with the Gaussian 09,⁹ MOLPRO 2010,¹⁰ MRCC,¹¹ and Orca¹² programs. For the correlation calculations, we employ all-electron (full, FU) calculations as well as two types of frozen-core approximations, namely the LC (large core) scheme where the 1s orbital of O and the 1s, 2s, 2p, 3s, and 3p orbitals for Cr are frozen, and the SC (small core) scheme in which for Cr only the 1s, 2s, and 2p orbitals are frozen. Basis sets that are external to these programs were obtained from the EMSL basis-set library.¹³ We will use the following abbreviations for the basis sets: VnZ for cc-pVnZ, WCVnZ for cc-pWCVnZ, a prefix “A” for “aug-”, SV for Ahlrichs-VDZ, VDZ(no df) for VDZ with

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the exclusion of d functions on O and f functions on Cr, and CBS for the complete-basis-set limit.

Geometries were optimized with the CCSD(T)(LC) procedure with the WCVTZ basis set. Following each geometry optimization, harmonic frequency analysis was carried out to confirm the nature of the stationary point as an equilibrium structure. To obtain the zero-point vibrational energies (ZPVEs) and thermal corrections for enthalpies at 298 K (ΔH_{298}), we used unscaled CCSD(T)(LC)/WCVTZ harmonic vibrational frequencies.¹⁴ Scalar relativistic effects were obtained at the CCSD(T) level within the second-order Douglas–Kroll–Hess (DKH) approximation.¹⁵ A standard literature value for the correction for spin–orbit coupling was included for the oxygen atom (−0.36 mhartree).^{1d} The spin–orbit corrections for CrO (−0.56) and CrO₂ (−0.004) (mhartree) were calculated at the MRCI/def2-SVP level.¹⁶ To obtain the 298 K heat of formation (ΔH_f) values for the chromium oxides, experimental 0 K ΔH_f values were used for the Cr (395.4 kJ mol^{−1}) and O (246.8 kJ mol^{−1}) atoms, together with their respective temperature corrections of 4.1 and 4.4 kJ mol^{−1}.¹⁷

Our benchmark single-point energies¹⁸ were obtained with composite procedures that include post-CCSD(T) components. Thus, we start with a series of CCSD and CCSD(T) calculations to approximate the all-electron relativistic CCSD(T)/CBS limit followed by post-CCSD(T) contributions up to the CCSDTQ5 level using smaller basis sets. We will use the abbreviation CM5 for composite methods with CCSDTQ5 as the highest-excitation component, and CM(5)_Λ for a composite method with CCSDTQ(5)_Λ as the highest level.^{19,20} The (*n*) and (*n*)_Λ approaches represent two alternative perturbative corrections to coupled-cluster theory with *n*th order excitations.²¹ It has been previously found that the CCSDTQ(5)_Λ procedure provides a better approximation to CCSDTQ5 than does CCSDTQ(5) for a relatively large set of main-group molecules.²²

In addition to G4(rel)⁴ and G4(MP2,rel)⁴ (which we will refer to simply as G4 and G4(MP2), respectively), we have also examined the performance of more rigorous CCSD(T)-based composite schemes, and we will refer to these protocols as CM(3)-type procedures. These methods are more expensive than G4-type procedures, but they usually provide better approximations to the all-electron relativistic CCSD(T)/CBS limit. However, they do not incorporate the effect of the higher excitations that are included in CM5 and CM(5)_Λ.

For the CM(3)-type procedures, we use the prefixes U-, B- or R- to designate that UHF, Brueckner, or ROHF orbitals are employed for all the component single-point energy calculations for open-shell systems (CrO, CrO₂, Cr, and O). The two basis sets employed in the two-point CBS extrapolation are represented by “[XZ,YZ]” in the parentheses, where XZ and YZ indicate whether the basis sets used for the extrapolation of the (T) perturbative triples contribution are double zeta (DZ), triple zeta (TZ) or quadruple zeta (QZ). Thus, for example, U-CM(3:[DZ,TZ]) represents a procedure that uses UHF reference wave functions for open-shell systems, and where the $\Delta(T)$ /CBS component is obtained using DZ-type and TZ-type basis sets. For all the CM-type methods, the two-point CBS extrapolation is carried out using the formula $E_L = E_{\text{CBS}} + AL^{-\alpha}$,²³ where *L* is the cardinal number of the basis set.^{24,25} The value of the exponent α is 5 for the extrapolation of HF energies, 3 for correlation components in CM5 and CM(5)_Λ, and 3.22 for those in CM(3)-type methods.^{26,27}

The chromium oxides CrO, CrO₂, and CrO₃ have quintet, triplet, and singlet ground states, respectively. Thus, in the case of CrO₃, calculations would conventionally be carried out using a restricted reference. However, as we shall see, the wave function exhibits an RHF-to-UHF instability. As a result, we have examined the use of two types of reference wave functions for the calculations on CrO₃: (1) conventional RHF wave functions, and this is indicated by an “RHF*.” prefix, and (2) broken-spin-symmetry UHF wave functions, indicated by “UHF*.” The UHF procedures are applicable only to G4, G4(MP2), U-CM(3), and B-CM(3) calculations for CrO₃. Acronyms for the various procedures are described in Table 1.

Table 1. Acronyms and Abbreviations Used in the Present Study

acronym	description
Basis Sets	
VnZ	cc-pVnZ
WCVnZ	cc-pWCVnZ
prefix “A”	“aug.”
SV	Ahlrichs-VDZ (split-valence)
VDZ(no df)	cc-pVDZ with the exclusion of d functions on O and f functions on Cr
CBS	complete-basis-set limit
Core-Correlation Options	
LC	large core: the 1s orbital for O, and the 1s, 2s, 2p, 3s, and 3p orbitals for Cr are frozen
SC	small core: the 1s orbital for O, and the 1s, 2s, and 2p orbitals for Cr are frozen
FU	full (i.e., all electrons are correlated)
Reference Wave Function (Applicable Only for CrO ₃)	
prefix “RHF*”	Conventional RHF wave function
prefix “UHF*”	Broken-spin-symmetry UHF wave function
Composite Methods (CMs) ^{a,b}	
U-CM(3:[DZ,TZ])	Approximate UCCSD(T)/CBS with $\Delta(T)$:[DZ,TZ], that is, the $\Delta(T)$ /CBS contribution is obtained by extrapolation with DZ-type and TZ-type basis sets, see Table 4.
B-CM(3:[DZ,TZ])	BD(T) analogue to the UCCSD(T)-based U-CM(3:[DZ,TZ]), i.e., approximate BD(T)/CBS including $\Delta(T)$:[DZ,TZ], see Table 4.
R-CM(3:[DZ,TZ])	ROCCSD(T) analogue to U-CM(3:[DZ,TZ]), that is, approximate ROCCSD(T)/CBS including $\Delta(T)$:[DZ,TZ], see Tables 2 and 4.
R-CM(3:[TZ,QZ])	ROCCSD(T)/CBS including $\Delta(T)$:[TZ,QZ], that is, the various components are extrapolated to CBS using larger basis sets when compared with R-CM(3:[DZ,TZ]), see Table 2.
CM5	R-CM(3:[TZ,QZ]) + Δ CCSDTQ5, that is, R-CM(3:[TZ,QZ]) plus post-CCSD(T) terms up to CCSDTQ5, see Table 2.
CM(5) _Λ	R-CM(3:[TZ,QZ]) + Δ CCSDTQ(5) _Λ , see Table 2.

^aApproximations to core–valence correlation and scalar relativistic effects are included for all CMs. ^bEnergies corresponding to excitations of lower order than the top-level excitations are generally obtained using (increasingly) larger basis sets; see, for example, Table 2.

We note that for CrO, CrO₂, and CrO₃, the experimental ΔH_f values obtained by Ebbinghaus⁵ are generally considered to be the most accurate, and they have been used as benchmark values for G4 and ccCA-TM.^{4,6} In the present study, in addition to this set of experimental values, we will also make comparison with the NIST-JANAF values²⁸ and those from Yungman’s compilation.²⁹

Table 2. R-CM(3:[TZ,QZ]) and CM5 [or CM(5)_Λ] Total Atomization Energies (0 K, kJ mol⁻¹) for CrO, CrO₂, and CrO₃^a

component	full expression ^b		CrO	CrO ₂	CrO ₃
HF	HF/AVSZ		-81.1	-52.2	-261.6
ΔCC	CCSD(LC)/AVSZ - HF/AVSZ		431.6	824.4	1352.5
Δ(T)	CCSD(T)(LC)/AVQZ - CCSD(LC)/AVQZ		77.7	176.6	287.8
ΔCBS[HF]	HF/AV[Q,5]Z - HF/AVSZ		0.1	0.1	0.1
ΔCBS[ΔCC]	ΔCC(LC)/AV[Q,5]Z - ΔCC(LC)/AVSZ		3.2	6.6	8.5
ΔCBS[Δ(T)]	Δ(T)(LC)/AV[TZ,QZ]Z - Δ(T)(LC)/AVQZ		1.6	3.4	4.8
ΔCV	CCSD(T)(SC)/AWCV[TZ,QZ]Z - CCSD(T)(LC)/AWCV[TZ,QZ]Z		-3.8	-5.4	-10.9
ΔFU	CCSD(T)(FU)/AWCVTZ - CCSD(T)(SC)/AWCVTZ		0.5	1.8	1.6
ΔDKH	CCSD(T)(LC,DKH)/AV[TZ,QZ]Z-DK - CCSD(T)(LC)/AV[TZ,QZ]Z		16.9	21.8	35.6
ΔSO			0.5	-1.9	-2.8
ZPVE ^c			-5.5	-13.0	-23.2
R-CM(3:[TZ,QZ])			441.8	962.3	1392.2
ΔT	CCSDT(LC)/V[TZ,QZ]Z - CCSD(T)(LC)/V[TZ,QZ]Z	CrO	-1.2	-11.7	-16.0
	CCSDT(LC)/V[DZ,TZ]Z - CCSD(T)(LC)/V[DZ,TZ]Z	CrO ₂ ,CrO ₃			
ΔQ	CCSDTQ(LC)/V[DZ,TZ]Z - CCSDT(LC)/V[DZ,TZ]Z	CrO	5.5	19.6	30.5
	CCSDTQ(LC)/VDZ - CCSDT(LC)/VDZ	CrO ₂			
	CCSDTQ(LC)/VDZ(no df) - CCSDT(LC)/VDZ(no df)	CrO ₃			
ΔS or Δ(5) _Λ	CCSDTQ5(LC)/VDZ(no df) - CCSDTQ(LC)/VDZ(no df)	CrO	-1.9 ^d	1.0 ^e	10.4
	UCCSDTQ5(LC)/SV - UCCSDTQ(LC)/SV	CrO ₂			
	UCCSDTQ(5)(LC) _Λ /SV-UCCSDTQ(LC)/SV	CrO ₃			
CM5 or CM(5) _Λ			444.3	969.1	1419.1
expt ^{f,g}			460.2	987.0	1455.7

^aRestricted reference wave functions were employed unless otherwise noted (with a “U” prefix). ^bLC: the 1s orbital for O and the 1s, 2s, 2p, 3s, and 3p orbitals for Cr are frozen. SC: the 1s orbital for O and the 1s, 2s, and 2p orbitals for Cr are frozen. FU: all-electron calculation. ^cObtained with unscaled CCSD(T)(LC)/WCVTZ harmonic vibration frequencies. ^dThe Δ(5)_Λ/VDZ(no df) contribution is 0.1 kJ mol⁻¹. ^eThe Δ(5)_Λ/VDZ contribution is 0.3 kJ mol⁻¹. ^fObtained from experimental ΔH_f values at 298 K [CrO (188.3), CrO₂ (-75.3), CrO₃ (-323.4), kJ mol⁻¹], back-corrected to 0 K ΔH_f using unscaled CCSD(T)(LC)/WCVTZ frequencies and experimental thermal corrections (kJ mol⁻¹) for Cr (4.1) and O (4.4), and converted to atomization energies using experimental 0 K ΔH_f values (kJ mol⁻¹) for Cr (395.4) and O (246.8). ^gExperimental ΔH_f values for the chromium oxides are obtained from ref 5, while the ΔH_f values and thermal corrections for the Cr and O atoms are obtained from ref 17.

3. RESULTS AND DISCUSSION

3.1. CM5 and CM(5)_Λ Total Atomization Energies for CrO, CrO₂ and CrO₃. Table 2 shows the composite-CCSDTQ5 (CM5) atomization energies for CrO and CrO₂, and the CM(5)_Λ atomization energy for CrO₃, and the components used to obtain them. For the calculation of contributions to the all-electron relativistic CCSD(T)/CBS limit, that is, the CM(3)-type component, the same protocol is employed for all species. We will denote this CM(3) scheme as R-CM(3:[TZ,QZ]), with R signifying the use of restricted reference wave functions for open-shell systems and [TZ,QZ] indicating that the highest-order excitation for valence electrons, namely the (T) component in CCSD(T), is obtained by extrapolation using the AVTZ and AVQZ basis sets.

For post-CCSD(T) contributions, several different protocols are used, as some of the calculations for higher-order excitations that are attainable for CrO are computationally too demanding for the larger CrO₂ and CrO₃ systems. We use approximate focal-point-analysis-type schemes³⁰ to determine the levels of theory that are likely to be most accurate (for obtaining the post-CCSD(T) contributions). Thus, we evaluate different levels of post-CCSD(T) components using both the full scheme, that is, CCSDT, CCSDTQ and CCSDTQ5,³¹ as well as two types of perturbative schemes, first CCSDT(Q) and CCSDTQ(5),³¹ and second CCSDT(Q)_Λ and CCSDTQ(5)_Λ,³¹ all in combination with a number of basis sets.

The complete set of results for our focal-point analysis is given in the Supporting Information. Here, we simply note several key observations from those results that lead to the

choice of our final protocols that correspond to the results in Table 2.

1. We sometimes find large differences between values obtained for the higher-order correlation contributions with unrestricted (U) and restricted (R) reference wave functions. As the underlying R-CM(3:[TZ,QZ]) energies are calculated using the restricted formalism, we use the RCCSDT, RCCSDTQ, and RCCSDTQ5 energies whenever possible.
2. Large differences in the calculated relative energies are often observed for the two perturbative approaches [(*n*) and (*n*)_Λ] used to approximate the full values. In a majority of the cases where the full CC...*n* (i.e., CCSDTQ or CCSDTQ5) energies are also available, we find for the current systems that the CC...(*n*)_Λ approach often yields relative energies that are in closer agreement with the CC...*n* energies than does CC...(*n*).
3. The basis-set convergence for the CC...(*n*)_Λ approach appears to be more rapid than that for CC...(*n*). Nonetheless, we caution that it may not be realistic to expect adequately converged results for the higher correlation contributions for basis sets that are smaller than VTZ, even for reasonably high-order excitations (e.g., CCSDTQ).
4. On the basis of these observations, our preference for the methods used for obtaining post-CCSD(T) contributions in the current systems increases in the order: CC...(*n*) → CC...(*n*)_Λ → CC...*n*.

We now proceed to analyze the contributions to the atomization energies for CrO, CrO₂, and CrO₃, as presented

Table 3. Comparison of G4(MP2) and G4 Total Atomization Energies (kJ mol⁻¹) for CrO₃^a

component	full expression ^b	G4(MP2)		G4	
		RHF*	UHF*	RHF*	UHF*
CCSD(T)	CCSD(T)(SC)/6-31G(d)	1310.4	1215.7	1310.4	1215.7
ΔPoTZ	sum of Δ+, Δ2df and ΔLXP	86.7 ^c	92.1 ^c	187.7	109.1
Δ+	MP _n (SC)/6-31+G(d) – MP _n (SC)/6-31G(d) <i>n</i> = 4 [G4] or 2 [G4(MP2)]	34.7	13.1	77.5	14.1
Δ2df	MP _n (SC)/6-31G(2df) – MP _n (SC)/6-31G(d) <i>n</i> = 4 [G4] or 2 [G4(MP2)]	127.4	109.8	189.3	122.4
ΔLXP	[MP2(FU)/G3LargeXP: (G4) or MP2(SC)/G3MP2LargeXP: G4(MP2)] – MP2(SC)/6-31+G(d) – MP2(SC)/6-31G(2df) + MP2(SC)/6-31G(d)	–75.4	–30.7	–79.1	–27.4
ΔCBS	G4(MP2): HF/AV[TZ,QZ] – HF/G3MP2LargeXP G4: HF/AV[QZ,SZ] – HF/G3LargeXP	–21.4	–17.0	–22.0	–17.4
ΔDKH	CCSD(T)(SC,DKH)/6-31G(d) – CCSD(T)(SC)/6-31G(d)	27.8	24.3	27.8	24.3
HLC		80.8	80.8	64.6	64.6
ΔSO		–2.8	–2.8	–2.8	–2.8
ZPVE ^d		–23.2	–23.2	–23.2	–23.2
total		1458.2	1369.8	1542.5	1370.3

^aUnrestricted reference wave functions were employed for Cr and O atoms. For singlet CrO₃, the reference wave functions were either RHF (RHF*) or broken-spin-symmetry UHF (UHF*). ^bLC: the 1s orbital for O, and the 1s, 2s, 2p, 3s and 3p orbitals for Cr are frozen. SC: the 1s orbital for O, and the 1s, 2s and 2p orbitals for Cr are frozen. FU: all-electron calculation. ^cThe ΔPoTZ term for G4(MP2) is formally calculated as a single difference of MP2(SC)/G3MP2LargeXP – MP2(SC)/6-31G(d). We nonetheless decompose this term into the three components to allow for a direct comparison with G4. ^dObtained with unscaled CCSD(T)(LC)/WCVTZ harmonic vibration frequencies.

in Table 2. We first focus on the components up to the CCSD(T) level, that is, R-CM(3:[TZ,QZ]). Among these, HF predicts all three molecules to be unbound (i.e., the atomization energies are negative). The inclusion of CCSD correlation energy (ΔCC) already recovers a large portion of the atomization energy. Nonetheless, there still remains a substantial contribution to the binding energy that is recovered by the Δ(T) component, specifically 77.7 (CrO), 176.6 (CrO₂), and 287.8 (CrO₃) kJ mol⁻¹.

We can see that, while the HF relative energies are effectively converged with the AVSZ basis set (i.e., the ΔCBS[HF] component is very small), there are still non-negligible ΔCBS[ΔCC] and ΔCBS[Δ(T)] contributions. In addition, we can see that there are also non-negligible outer-core–valence correlations (ΔCV), that is, correlation between the “core” 3s and 3p electrons of Cr with the “valence” electrons, but further inclusion of inner-core electrons in the correlation (ΔFU) contributes little to the atomization energies. As expected for systems containing third-row atoms such as chromium, the inclusion of scalar relativistic effects (ΔDKH) is important for obtaining accurate atomization energies.

Before proceeding to a more detailed discussion of the post-CCSD(T) contributions, we first note that the generally good performance of CCSD(T) in computational chemistry can typically be attributed to the significant degree of cancellation between higher-order triples contributions (which tend to decrease the atomization energies) and quadruples and quintuples contributions (which tend to increase the atomization energies). In this regard, we find that, for the three chromium oxides, the extent of cancellation of the positive and negative contributions appears to be imperfect, with the magnitudes of the total post-CCSD(T) contributions estimated to increase in the order: CrO (2.5 kJ mol⁻¹) < CrO₂ (6.9 kJ mol⁻¹) < CrO₃ (26.9 kJ mol⁻¹).

For CrO and CrO₂, all the post-CCSD(T) contributions are obtained either from values that are close to the CBS limit or they are small in magnitude.³² Therefore, it is likely that the final CM5 values for these two species have relatively small residual errors, and we thus conservatively assign an uncertainty of ±5 kJ mol⁻¹ to our CM5 atomization energies. For CrO₃, however, the Δ(S)_Λ contribution (10.4 kJ mol⁻¹) is evaluated

with the small SV basis set and it is very different from the Δ(S)/SV value of –31.9 kJ mol⁻¹. We consider it more appropriate to adopt the Δ(S)_Λ value, based on the closer agreement of Δ(S)_Λ with Δ5 for CrO and CrO₂, even in cases where Δ(S) deviates considerably from Δ5 (Supporting Information).³³ We assign an uncertainty of ±10 kJ mol⁻¹ for this term for CrO₃.

Taking all of this into account, we believe a relatively large uncertainty for the CM(5)_Λ atomization energy for CrO₃ is warranted, and we assign a value of ±20 kJ mol⁻¹. This covers an uncertainty of ±5 kJ mol⁻¹ for the ΔQ/VDZ(no df) contribution and ±10 kJ mol⁻¹ for Δ(S)_Λ/SV, plus ±5 kJ mol⁻¹ for potential post-CCSDTQ5 contributions. For all three chromium oxides, we note that the CM5-type values are smaller than the experimental atomization energies of Ebbinghaus,⁵ and the difference is larger for CrO₃ (36.6 kJ mol⁻¹) than for CrO (15.9 kJ mol⁻¹) and CrO₂ (17.8 kJ mol⁻¹).

3.2. Performance of the Various Composite Procedures for CrO₃. In the previous section, we have seen that, among the series CrO, CrO₂, and CrO₃, the monoxide and dioxide appear to be adequately described by the CM5 procedure. On the other hand, the trioxide emerges as the most challenging case for our CM(5)_Λ theoretical treatment. As we shall see in section 3.3, these observations also generally hold for the less costly composite procedures. In this section, we focus on CrO₃, due partly to the large discrepancy between the G4 and experimental values quoted in ref 4 and partly to the difficulty in the theoretical treatment, as demonstrated in the previous section. In reference 4, CrO₃ was calculated as a closed-shell singlet, which corresponds to a bonding situation consisting of three Cr=O double bonds. The closed-shell singlet state is also the reference state used in our CM(5)_Λ calculation.

However, it is easy to envisage alternative bonding patterns that may also be low in energy. In fact, a stability analysis on the RHF/G4MP2LargeXP wave function of singlet CrO₃ reveals an RHF-to-UHF instability, with the resulting UHF wave function having an ⟨S²⟩ value of 2.56!³⁴ This is indicative of the highly multireference character in CrO₃, as has also been commented on elsewhere.³⁵ As discussed in the previous section, there remains a non-negligible uncertainty, even at the

Table 4. Comparison of U-CM(3:[DZ,TZ]) and B-CM(3:[DZ,TZ]) Total Atomization Energies (kJ mol⁻¹) for CrO₃^a

component	full expression ^b	U-CM(3:[DZ,TZ])		B-CM(3:[DZ,TZ])
		RHF*	UHF*	RHF* ^c
ref	[HF or BDréf]/AVQZ	-314.2	170.9	-451.5
ΔCC	[CCSD or BD](LC)/AVQZ - [HF or BDréf]/AVQZ	1394.2	943.3	1483.3
Δ(T)	[CCSD or BD](T)(LC)/AVTZ - [CCSD or BD](LC)/AVTZ	281.9	199.2	339.3
ΔCBS[ref]	ref/AV[TZ,QZ]Z - ref/AVQZ	0.3	0.5	0.7
ΔCBS[ΔCC]	ΔCC(LC)/AV[TZ,QZ]Z - ΔCC(LC)/AVQZ	13.6	11.8	13.0
ΔCBS[Δ(T)]	Δ(T)(LC)/AV[DZ,TZ]Z - Δ(T)(LC)/AVTZ	9.6	10.1	9.1
ΔCV	[CCSD or BD](T)(SC)/AWCVTZ - [CCSD or BD](T)(LC)/AWCVTZ	-4.4	-5.4	10.4
ΔFU	[CCSD or BD](T)(FU)/AWCVTZ - [CCSD or BD](T)(SC)/AWCVTZ	4.1	1.6	3.8
ΔDKH	[CCSD or BD](T)(LC,DKH)/AVTZ-DK - [CCSD or BD](T)(LC)/AVTZ	35.5	35.8	35.2
ΔSO		-2.8	-2.8	-2.8
ZPVE ^d		-23.2	-23.2	-23.2
total		1394.6	1341.7	1417.3

^aUnrestricted reference wave functions were employed for Cr and O atoms. For singlet CrO₃, the reference wave functions were either an RHF (RHF*) or a broken-spin-symmetry UHF (UHF*). ^bLC: the 1s orbital for O, and the 1s, 2s, 2p, 3s and 3p orbitals for Cr are frozen. SC: the 1s orbital for O, and the 1s, 2s, and 2p orbitals for Cr are frozen. FU: all-electron calculation. ^cStarting with a UHF wave function as the initial guess leads to a final wave function in which the orbitals are identical within numerical noise to those obtained starting with an RHF wave function. ^dObtained with unscaled CCSD(T)(LC)/WCVTZ harmonic vibration frequencies.

CCSDTQ(5)_A level. Thus, it is not surprising that more approximate composite schemes may yield less accurate values.

3.2.1. G4 and G4(MP2). We now examine the individual components of the CrO₃ atomization energies obtained with the G4 and G4(MP2) protocols (Table 3). For the Cr and O atoms, the unrestricted formalism for the reference wave functions, as required in standard G4 and G4(MP2) for open-shell systems, is adopted. For singlet CrO₃, we use either the restricted or the broken-spin-symmetry unrestricted reference wave functions. We will use the RHF*- and UHF*- prefixes to make such a distinction in the treatment for the CrO₃ molecule (e.g., RHF*-G4 and UHF*-G4) and more generally for CM(3)-type methods to be discussed in the next section.

For G4 and G4(MP2), the CCSD(T)/6-31G(d) contribution has a strong dependence on the underlying reference wave function. Thus, the RHF*-CCSD(T) value is larger than the UHF*-CCSD(T) value by almost 100 kJ mol⁻¹. For G4(MP2), the total contribution associated with the extension to a large Pople-type triple-ζ basis set (ΔPoTZ), interestingly, has only a very mild dependence on the type of reference (R - U = -5.4 kJ mol⁻¹). This is a consequence of a somewhat fortuitous cancellation of larger differences for its components, namely Δ+ (R - U = +21.6 kJ mol⁻¹), Δ2df (+17.6 kJ mol⁻¹), and ΔLXP (-44.7 kJ mol⁻¹).

For G4, there is a difference of 78.6 kJ mol⁻¹ for RHF*-ΔPoTZ versus UHF*-ΔPoTZ. We find that this is mainly due to the larger R-versus-U differences for two of its components, namely Δ+ (R - U = +63.4 kJ mol⁻¹) and Δ2df (+66.9 kJ mol⁻¹), when compared with those for G4(MP2). The difference in the ΔLXP term (-51.7 kJ mol⁻¹), on the other hand, is comparable to that for G4(MP2). The two large and positive terms (Δ+ and Δ2df) based on the RHF wave function lead to a significantly more positive RHF*-ΔPoTZ for G4 than the corresponding UHF*-ΔPoTZ value.

Other single-point-energy components of G4 and G4(MP2), namely ΔCBS calculated at the HF level and ΔDKH evaluated with CCSD(T), are quite insensitive to the RHF-versus-UHF choice. Overall, the significant difference between the RHF*-G4(MP2) and UHF*-G4(MP2) atomization energies for CrO₃ can be attributed to a large extent to the difference in the CCSD(T)/6-31G(d) energies. For G4, this difference is

compounded by the difference in the ΔPoTZ contribution, which then leads to a very large difference between RHF*-G4 (1542.5 kJ mol⁻¹) and UHF*-G4 (1370.3 kJ mol⁻¹).

The main difference between G4 and G4(MP2) is the use of MP4 for parts of ΔPoTZ in G4, and we have already seen that this is indeed a major cause for the substantially different CrO₃ atomization energy value for RHF*-G4 when compared with RHF*-G4(MP2). We also note that, while there is a very large difference between RHF*-G4 and RHF*-G4(MP2), UHF*-G4 and UHF*-G4(MP2) yield almost identical atomization energies. This is not entirely coincidental, as can be seen from the relatively comparable values for each of the components for UHF*-G4 and UHF*-G4(MP2).

3.2.2. U-CM(3:[DZ,TZ]) and B-CM(3:[DZ,TZ]). We now turn our attention to the CM(3)-type methods (Table 4). For U-CM(3:[DZ,TZ]), we first note that the final RHF*-U-CM(3:[DZ,TZ]) and UHF*-U-CM(3:[DZ,TZ]) atomization energies, that is, values obtained using unrestricted wave functions for Cr and O atoms, and either RHF or UHF references for CrO₃, differ from one another by 52.9 kJ mol⁻¹. A survey of the components for the U-CM(3:[DZ,TZ]) energies quickly reveals that this difference is mainly a result of the large RHF-versus-UHF differences in the three fundamental components, namely the HF reference and the ΔCC and Δ(T) valence-correlation components.

We note that the UHF*-HF/AVQZ atomization energy for CrO₃ is +170.9 kJ mol⁻¹, which is in stark contrast to the -314.2 kJ mol⁻¹ for RHF*-HF/AVQZ. These correspond to a difference of nearly 500 kJ mol⁻¹ between the two methods! However, this large difference in the HF values is almost entirely compensated for at the CCSD level, with the RHF*-ΔCC value being more positive than the UHF*-ΔCC value by 450.9 kJ mol⁻¹. Thus, the more positive RHF*-Δ(T) value (by 82.7 kJ mol⁻¹) when compared with that for UHF*-Δ(T) is a major contributing factor to the RHF*-U-CM(3:[DZ,TZ]) value being more positive by 52.9 kJ mol⁻¹ than that for UHF*-U-CM(3:[DZ,TZ]).

Given the very large differences observed for some of the components for the two types of U-CM(3:[DZ,TZ]), the results for B-CM(3:[DZ,TZ]) are striking. Specifically, when a UHF reference wave function (with an ⟨S²⟩ value of 2.57) is

Table 5. Summary of Theoretical and Experimental Total Atomization Energies for CrO, CrO₂ and CrO₃ (0 K, kJ mol⁻¹)

	CrO	CrO ₂	CrO ₃
G4(MP2)	451.3	949.5	1458.2 (1369.8) ^a
G4	447.1	943.7	1542.5 (1370.3) ^a
U-CM(3:[DZ,TZ])	428.3	939.1	1394.6 (1341.7) ^a
B-CM(3:[DZ,TZ])	434.4	959.6	1417.3 (1416.3) ^a
R-CM(3:[DZ,TZ])	443.8	961.9	1394.2
R-CM(3:[TZ,QZ])	441.8	962.3	1392.2
CM5 or CM(5)_Λ	444.3	969.1	1419.1
ccCA-TM ^{b,c,k}	457.3	981.1	1422.3
NIST-JANAF ^{b,d}	454.3 ± 42	963.1 ± 42	1425.5 ± 42
Yungman ^{b,e}	452.5 ± 29	948.5 ± 63	1427.2 ± 84
Ebbinghaus ^{b,f}	460.2 ± 6.7	987.0 ± 5.0	1455.7 ± 4.2

^aFor singlet CrO₃, energies are obtained using both UHF and RHF reference wave functions (denoted elsewhere as UHF* and RHF*), while UHF references are used for Cr and O atoms. The UHF values (for CrO₃) are shown in parentheses. ^bObtained from ΔH_f at 298 K, back-corrected to 0 K atomization energies using unscaled CCSD(T)(LC)/WCVTZ frequencies and experimental quantities for Cr and O atoms. ^cRef 6. ^dExperimental values from ref 28. ^eExperimental values from ref 29. ^fExperimental values from ref 5. These were the experimental values chosen in references 4 and 6 owing to their small quoted uncertainties.

used as the initial guess, the subsequent BD calculation yields a final reference wave function in which the orbitals are identical within numerical noise to those obtained with an RHF starting wave function. In other words, the BD orbitals do not show an R-to-U instability.

3.3. Comparison of the Different Composite Procedures. Table 5 summarizes our theoretical atomization energies obtained using the different composite procedures discussed. We have also included for comparison, the R-CM(3:[DZ,TZ]) method, which is analogous to U-CM(3:[DZ,TZ]) but uses restricted reference wave functions for the open-shell systems (CrO, CrO₂, Cr and O). The R-CM(3:[DZ,TZ]) protocol is also closely related to the R-CM(3:[TZ,QZ]) procedure but utilizes smaller basis sets for the extrapolation to the CCSD(T)/CBS limit. Several experimental values for the three oxides are also included for comparison.^{5,26,27}

We can see that R-CM(3:[DZ,TZ]) gives values that are very similar to those for R-CM(3:[TZ,QZ]), supporting the use of smaller basis sets for the extrapolation. Results for the various CM-type procedures span ranges of ~ 20 kJ mol⁻¹ for all three oxides. The “outlier CM(3) procedure” for CrO and CrO₂ is U-CM(3:[DZ,TZ]), while for CrO₃, the B-CM(3:[DZ,TZ]) and CM(5)_Λ values are close to one another, but they differ considerably from the results for the other CM(3)-type procedures. This exemplifies the considerable dependence of the results on the underlying reference wavefunctions for these three molecules. The G4 and G4(MP2) procedures agree well with CM5 for CrO, but the agreement is less good for CrO₂ and least good for CrO₃, and this further highlights the difficulty in the treatment of these molecules.

It is noteworthy to once again point out that, for G4 and G4(MP2), the ΔH_f values for CrO₃ obtained using UHF reference wave functions (UHF*) are significantly different from the corresponding RHF values (RHF*). We thus highlight the potential danger when a large R-versus-U difference is found. Under such circumstances, it would, in principle, be desirable to employ a high-level multireference procedure. Unfortunately, there is currently no protocol for the choice of active orbitals for multireference computations that is both systematic and practical in a wide sense. Robust single-reference methods thus continue to have an important role to play. As discussed, the use of Brueckner orbitals, that is, BDref, eliminates the difference associated with the use of RHF or

UHF starting orbitals for CrO₃, even when there is a nearly 500 kJ mol⁻¹ difference between the RHF and UHF energies and an exceedingly large amount of spin-contamination in the UHF wave function. While generalization of the use of BDref as a solution to the R-versus-U dilemma would be premature at this point, further investigation in this direction is desirable, especially in the context of “black-box” composite procedures where robustness is crucial.

The CM5 [or CM(5)_Λ] atomization energies obtained in the present study are, to the best of our knowledge, the highest level theoretical values to date for these three chromium oxides. Nonetheless, as mentioned earlier, they differ significantly from the experimental values of Ebbinghaus.⁵ On the other hand, we find that the atomization energies of 454.3 (CrO), 963.1 (CrO₂), and 1425.2 (CrO₃) kJ mol⁻¹, derived from the NIST-JANAF ΔH_f values, although having a large quoted uncertainty of ± 42 kJ mol⁻¹, are in closer agreement with our best theoretical values (444.3, 969.1, and 1419.1 kJ mol⁻¹, respectively) (Table 5). Equivalently, our best theoretical estimates of the heats of formation ($\Delta H_{f,298}$) are 198.3 ± 5 (CrO), -81.3 ± 5 (CrO₂), and -286.8 ± 20 (CrO₃) kJ mol⁻¹, which compare well with values obtained from the NIST JANAF tables²⁶ of 188.3 (CrO), -75.3 (CrO₂), and -292.9 (CrO₃) kJ mol⁻¹. Further experimental and theoretical investigations are desirable in order to improve confidence in these quantities.

4. CONCLUDING REMARKS

In the present study, we use high-level composite methods with contributions up to CCSDTQ(5)_Λ (i.e., the CM(5)_Λ protocol) and CCSDTQ5 (CM5) to evaluate the total atomization energies for CrO (by CM5), CrO₂ (CM5) and CrO₃ (CM(5)_Λ). We investigate the features in the more approximate CCSD(T)-based methods (CM(3)-type procedures), and in G4 and G4(MP2) protocols, that may represent shortcomings in the evaluation of these quantities. The following major conclusions can be drawn from the present study:

1. Our best estimates of the atomization energies for the three chromium oxides provided by the CM5 or CM(5)_Λ procedures are 444.3 ± 5 (CrO), 969.1 ± 5 (CrO₂), and 1419.1 ± 20 (CrO₃) kJ mol⁻¹. These correspond to theoretical $\Delta H_{f,298}$ values of 198.3 ± 5 (CrO), -81.3 ± 5

- (CrO₂), and -286.8 ± 20 (CrO₃) kJ mol⁻¹. They compare well with NIST JANAF values of 188.3 (CrO), -75.3 (CrO₂), and -292.9 (CrO₃) kJ mol⁻¹.
- The large uncertainty for CrO₃ is associated, in part, with the use of rather small basis sets in the calculation of some of the post-CCSD(T) contributions. In addition, the use of a single-reference RHF wave function appears to be a poor starting point for CrO₃, which is highly multireference in character and seems to require correlation corrections beyond CCSDTQ(5)_A.
 - For CrO₃, there is a very large difference in the calculated G4 atomization energies depending on whether the reference wave function is RHF or UHF. The MP4 components in the basis-set extension appear to be more sensitive to the underlying reference than the corresponding MP2 components in the G4(MP2) procedure. We note that the differences between MP4 and MP2 are more significant with an RHF reference than with UHF orbitals.
 - In the context of CM(3)-type procedures, there is still a large difference between the calculated CrO₃ atomization energies based on RHF or broken-spin-symmetry UHF reference wave functions for the CrO₃ molecule. Intriguingly, we find that the use of a BD procedure in this case eliminates the spin-contamination in the UHF wave function, so that the results are independent of whether UHF or RHF orbitals are used as the starting point.
 - We propose that a large RHF-versus-UHF energy difference could be a good indicator of a potential problem for a single-reference theoretical treatment.

■ ASSOCIATED CONTENT

■ Supporting Information

Geometries optimized at the CCSD(T)(LC)/WCVTZ level (Table S1), calculated CCSD(T)(LC)/WCVTZ zero-point vibrational energies (ZPVEs), enthalpy corrections at 298 K (ΔH_{298}), and relevant electronic energies (Table S2), and focal-point analysis for post-CCSD(T) contributions to total atomization energies for CrO (Table S3), CrO₂ (Table S4), and CrO₃ (Table S5). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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■ Notes

The authors declare no competing financial interest.

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(14) We have briefly examined the effect of including anharmonicity using a one-dimensional anharmonic potential in our vibrational frequency calculations with a variety of density functional theory (DFT) procedures. We find that such effects are small and are adequately accounted for by using the appropriate frequency scale factors, with deviations of scaled harmonic ZPVEs from anharmonic ZPVEs being less than 0.5 kJ mol^{-1} . We note in addition that, since the CCSD(T) procedure with a triple- ζ -type basis set typically has a scale factor that is close to unity, we do not apply scaling to our calculated CCSD(T)(LC)/WCVTZ harmonic frequencies.

(15) We have also employed a number of DFT procedures to probe the effect of using, as an alternative, the zeroth-order regular approximation (ZORA) method for the evaluation of scalar-relativistic effects. We find that the differences in the scalar-relativistic contribution to the total atomization energies obtained with the two approaches are small ($<2 \text{ kJ mol}^{-1}$) relative to the uncertainties in the other components of our composite schemes.

(16) We include all π -type valence electrons and orbitals in the active space for our MRCI calculations. Our brief benchmark calculations indicate that, for a spin-orbit correction of moderate magnitude ($\sim 10 \text{ kJ mol}^{-1}$), the use of the MRCI/def2-SVP procedure and such a partition scheme for the active space is likely to yield an uncertainty of better than 1 kJ mol^{-1} . We note that our calculated values of -0.56 (CrO) and -0.004 (CrO₂) mhartree are similar to those (-0.46 and -0.01 mhartree for CrO and CrO₂, respectively) used in ref 6c.

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(Supporting Information). It is therefore likely that the ΔQ value is also already close to the CBS limit.

(33) Indeed, we note that for CrO₂ the quintuples corrections evaluated with the SV basis set are $-29.2 [\Delta(S)]$, $0.9 [\Delta(S)_A]$, and $-1.0 [\Delta S] \text{ kJ mol}^{-1}$. Moving to the larger VDZ(no df) basis set has a large effect on $[\Delta(S)]$ (which becomes $-18.6 \text{ kJ mol}^{-1}$) but only a small effect on $[\Delta(S)_A]$ (which becomes 0.3 kJ mol^{-1}). These results for CrO₂ lend confidence to our $[\Delta(S)_A]/\text{SV}$ estimate for CrO₃.

(34) We note that the UHF/G3MP2LargeXP $\langle S^2 \rangle$ values for quintet CrO, triplet CrO₂, and singlet CrO₃ are 6.66, 3.65, and 2.56, respectively. For CrO, this represents a value that is 11% larger than the ideal $\langle S^2 \rangle$ of 6, while the value for CrO₂ is 83% larger than the ideal value of 2. The progression of spin contamination for CrO (0.66, 11%), CrO₂ (1.65, 83%), and CrO₃ (2.56) is in accord with CrO being the least difficult of the three chromium oxides for our theoretical treatments, while CrO₃ is the most difficult.

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