High-Level *Ab Initio* Composites: Thermochemical Bond Dissociation Energies for Vanadium Species

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Abstract

Bond dissociation energies (BDE) are key descriptors for molecules and are among the most sought-after properties in chemistry. Despite their importance, the accurate prediction of BDE's for transition metal species can be particularly daunting for both experiment and computation. Experimental data has been limited and, when available, often has large error bars, making the critical evaluation and identification of suitable computational methods difficult. However, recent advancements in the experimental determination of BDE's with techniques such as Velocity Map Imaging and 2 Photon Ionization now provide useful gauges for computational strategies and new methodologies, providing energies with unprecedented accuracies. The vanadium diatomics (VX, X=B, C, N, O, F, Al, Si, P, S, Cl) have been challenging for computational chemistry methods, and, thus, a new experimental gauge enables methods to be reevaluated and developed for these species. Herein, the super-correlation consistent Composite (super-ccCA or s-ccCA), a new thermochemical scheme centered around CCSD(T)/complete basis set (CBS) limit computations with additional contributions that account for scalar-relativistic effects, and coupled cluster contributions beyond CCSD(T) up to quintuple excitations has been considered. The agreement between determinations made by the s-ccCA scheme and by recent experiment is excellent, demonstrating the utility of the new approach in addressing challenging metal systems, even those of multireference nature. In light of recent experimental BDE's, the longstanding correlation consistent composite approach (ccCA) is also evaluated for the VX species and find that the mean absolute deviation (MAD) is greatly reduced compared to previously used experimental values.

Keywords: Electronic structure, transition metals, thermochemistry, ab initio composite, s-ccCA

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1.Introduction

Thermochemistry is central to the chemical sciences, enabling the understanding of reaction processes, and is key to technological advancement in areas from batteries to cellular machinery. Through the years, much work has been done to obtain thermochemical data to aid in describing the equilibria and the kinetics of transition metal reactions for processes such as catalysis. For all of these applications, there is often sensitivity in the prediction of thermochemical energies, where small errors in the prediction of a thermochemical property can lead to substantial errors in the reaction rate.For example, a ~3 kJ mol^{-1} error in an enthalpy prediction, can translate to an order of magnitude in the rate constant. Often in catalytic models, many reaction rates are used and such an error would propagate throughout a reaction model. Additionally, many steps in reaction models often involve transient intermediates that are difficult to isolate and study experimentally, and thus require a theoretical approach.

In considering thermochemical properties, vital is the bond dissociation energy (BDE), indicating the strength of a chemical bond and providing insight about the reactivity of a molecule. To describe thermochemical energies such as binding energies, *ab initio* thermochemical composite schemes are commonly used. Composite schemes aim to achieve a certain level of accuracy through an additive scheme of computations, aiming for results that would be achievable by more advanced methods. Among the available composite schemes are the ccCA approaches[1,2], the W1 and W2 families[3], the Gn (i.e., G2, G3) series[4–8], as well as approaches that strive towards sub-kilojoule per mole accuracies such as the W4[910] HEAT[11-14], and the FPD scheme.[15,16].

Composite strategies have been widely applied to early main group species, and less so to transition metal species where the number of electrons can become daunting in terms of the computational cost (memory, disk space, CPU or GPU time) for routine calculations. As well, particularly for transition metal species, the number of low lying electronic states or degenerate states may require that multireference wavefunction methods be utilized due to substantial multireference character of many transition metal species[17,18]. Nonetheless, a number of single reference wavefunction-based composite schemes have been developed and successfully applied to the transition metals. The first such method broadly applied to the transition metals are the ccCA schemes, with application to over 300 3*d* and 4*d* species, as well as more recent application to 5d species[19,20]. The FPD composite scheme has been applied to 3d transition metals[21–23]. Aoto and workers have utilized a composite scheme using a coupled cluster approach, with a correction for multireference character with MRCCSD(T)[24]. A variation of HEAT has been applied to the 3dMLBE20 database, a dataset of 20 3*d* transition metal species, and was used in conjunction with re-determined amine bond dissociation energies to reevaluate results of 3*d* hydride BDE's. This was due to both the known need for better amine BDE's, and the large discrepancy between 3d hydrides and computation[25]. Multireference composite strategies also are available for thermochemical predictions, such as a multireference form of ccCA, MR-ccCA, which has largely been applied to main group species with a few exceptions[26,27]. Starting from a single reference the CR-ccCA(2,3) scheme makes use of CR-CCSD(T) to handle multireference systems such as biradicals[28].

For early main group species, there are well over a thousand energies from experiment with uncertainties of 1 kcal mol^{-1} or less which provide a rich source for gauging the utility of computational chemistry methods. In contrast to the early main group where there is a plethora of available thermochemical energies with small experimental uncertainties, there is a limited amount of thermochemical data available for transition metal species, and, some of the available data has significant uncertainties[19,20,22,25,29]. In fact, in earlier work, the Wilson group introduced the term "transition metal chemical accuracy", to indicate the overall average experimental uncertainty (± 3 kcal mol^{-1}) in the enthalpies of formation for a set of ~200 3*d* transition metal species, which included some uncertainties as large as ~20 kcal mol^{-1} to represent the diversity of the transition metal species[20]. For main group chemistry, the Active Thermochemical Tables (ATcT), generated with a thermochemical network approach, have provided a reliable analysis of thermochemical determinations for main group species, and have enabled a route for significant reduction in the uncertainty of many main group enthalpies of formation[30,31]. The transition metals have yet to benefit from such a useful analysis, in part, due to the limited amount of necessary experimental data.

However, significant strides have been made recently in terms of experiment, that have resulted in high quality dissociation energies with small experimental uncertainties for MX and MM diatomics[32–38]. These newer studies have provided sources of accurate dissociation energies that can be used as a gauge of computational chemistry methodologies. These metrics are often an important first step of confidence in the utility of methodologies for high quality calculations for other studies. Among the experiments are high quality studies on VX (X=first- or second-row non-metal) compounds.

Previously, a study was done to investigate three VX compounds for which the Morse group has provided high quality dissociation energies[39]. The three species are highly multireference in character, and the utility of a number of approaches from a broad range of density functional approaches to multireference configuration approaches were considered. In this prior study, an advanced composite strategy, s-ccCA, which attempts to approximate the CCSDTQP energy was introduced and utilized. In the current study, our approach is utilized to gain more insight for first- and second-row VX compounds. Note, however, that not all of the diatomics have dissociation energies from experiment with small uncertainties, and, thus, a part of this study provides predictions for a number of compounds that had not previously been studied or were not yet well-resolved by experiment, using the recent high quality dissociation energies from experiment as a gauge before venturing to new predictions.

2.Theoretical Approach

The thermochemical composite approach recently introduced – the super correlation consistent composite approach (s-ccCA) – is utilized and expanded here to strive towards an energy that approximates the full-configuration interaction (FCI) energy[40] s-ccCA relies upon the unique convergence of each component of the composite that contributes to the total energy

CCSD(T) and CCSDT on the other hand converge much more slowly (ℓ^{-3} and less than ℓ^{-3} where ℓ represents the cardinal number of the basis set) and require larger basis sets and extrapolation schemes to accurately capture their contributions to the total energy[9,41] The s-ccCA approach described here is akin to composites such as HEAT[11–13], W4[10], FPD[15,16], and FPA[42–44]. Similarities to these composite schemes include large basis sets extrapolated to the complete basis set extrapolations for CCSD(T), treatments for electron correlation beyond CCSD(T), and scalar relativity.

The geometries for the series of molecules in Table 1 were optimized with CCSD(T)[45,46] and the cc-pVQZ basis set[47–49]. The frequencies were also determined with this method. The frequency for each diatomic was used to convert D_e to D_o to facilitate direct comparison to experiment. The optimized geometry was then used for all single point computations. To obtain the s-ccCA energy the contributions to the total s-ccCA energy are shown in equation 1:

$$E(\text{s-ccCA})=E_0(\text{s-ccCA})+\Delta E(\text{Rel})+\Delta E(\text{HOC})+\Delta E(\text{CV})+\Delta E(\text{SO})+\Delta E(\text{ZPVE}) \quad (1)$$

E_0(s-ccCA) is the reference energy for s-ccCA, ΔE(Rel) a contribution for relativistic effects, ΔE(HOC) corresponds to higher order coupled cluster contributions including CCSDT, CCSDTQ, and CCSDTQP. ΔE(CV) is a higher order coupled cluster correction for the core-valence contribution computed with CCSDT, and ΔE(SO) is the spin-orbit correction. Finally, ΔE(ZPVE) is the zero-point energy for molecules that allows for direct comparison with experiment. Atomic energies are computed in the same manner except for spin-orbit being derived from experimental levels, and there being no ZPVE contribution.

The total CCSD(T) energy term, E_0(s-ccCA), was computed with the augmented core weighted basis sets (aug-cc-pwCV*n*Z, *n*=T,Q,5)[47]. The augmented core weighted basis sets aug-cc-pwCV*n*Z, *n*=T,Q,5 were applied to the first and second row atoms as well[50]. The core electrons were correlated for E_0(s-ccCA). For vanadium the core includes the 3s and 3p orbitals. For the first-row main group this includes the 1s orbital; for the second-row species this includes the 2s and 2p orbitals. The CCSD(T) calculations are done with a series of correlation consistent basis sets, and the resulting energies are extrapolated to the CBS limit[51]. The three-point ℓ^{-3} extrapolation of Helgaker was used to extrapolate the CCSD(T) energies to obtain the E_0(s-ccCA) term [52].

Scalar relativistic effects were accounted for as the energy difference arising between CCSD(T) determined using second-order Douglas-Kroll-Hess (DKH) and the aug-cc-pVQZ-DK basis set[47,53], and CCSD(T) with the aug-cc-pVQZ basis set[47–49]

$$\Delta E(\text{Rel})=E[\text{CCSD(T)/aug-cc-pVQZ-DK}] - E[\text{CCSD(T)/aug-cc-pVQZ}] \quad (2)$$

As noted earlier, transition metals are notorious for their multireference character[17]. Coupled cluster-based thermochemical approaches generally are useful for small molecules as long as the CCSD(T) method is paired with large basis sets extrapolated to the complete basis set limit[22,24,25,54]. Higher-order coupled cluster contributions noted here as higher order correlation (HOC), can help further improve thermochemical results[41,55] For small main group molecules with significant multireference character, higher-order coupled cluster methods can contribute 1 kcal mol^{-1} or more towards the atomization energy[56,57]. Considering that HOC is important to obtain sub-chemical accuracy for main group atomization energies suggests that this contribution will be important for transition metal thermochemistry to reach even 3 kcal mol^{-1} accuracy, *transition metal chemical accuracy*. Prior work on several transition metal dissociation energies indicated the utility of the HOC[25].

In the current study, the HOC was obtained with CCSDT, CCSDTQ, and CCSDTQP[58,59]. Equation 3 presents the contributions to the HOC term.

$$\Delta E(\mathrm{HOC}) = \Delta E(\mathrm{CCSDT/CBS}) + \Delta E(\mathrm{CCSDTQ/PVTZ}) + \Delta \mathrm{ECCSDTQP/PVDZ} \quad (3)$$

ΔE(CCSDT/CBS) was obtained in the following manner: The CCSDT contribution was found as the difference between CCSDT and CCSD(T) energies at the cc-pVTZ (PVTZ) and cc-pVQZ (PVQZ) levels extrapolated to the complete basis set (CBS) limit using the two-point ℓ^{-3} formula of Helgaker[52].

$$\Delta E(\mathrm{CCSDT/CBS}) = E[\mathrm{CCSDT/CBS}] - E[\mathrm{CCSD(T)/CBS}] \quad (4)$$

The ΔE(CCSDTQ) contribution was determined as the difference between CCSDTQ and CCSDT energies determined at the cc-pVTZ basis level.

$$\Delta E(\mathrm{CCSDTQ/PVTZ}) = E[\mathrm{CCSDTQ/cc\text{-}pVTZ}] - E[\mathrm{CCSDT/cc\text{-}pVTZ}] \quad (5)$$

The ΔE(CCSDTQP/PVDZ) contribution was obtained as the difference between CCSDTQP and CCSDTQ energies determined with the cc-pVDZ basis set.

$$\Delta E(\mathrm{CCSDTQP/PVDZ}) = E[\mathrm{CCSDTQP/cc\text{-}pVDZ}] - E[\mathrm{CCSDTQ/cc\text{-}pVDZ}] \quad (6)$$

The higher level correlation (HOC) contribution to the core-valance (CV), ΔE(CV), was computed as the difference between the CCSDT/CV and CCSD(T)/CV, and CCSDT/VAL(VAL=valence) and CCSD(T)/VAL energies determined with the cc-pwCVTZ basis set[47,50].

$$\Delta E(\mathrm{CV}) = [E[\mathrm{CCSDT/CORE/cc\text{-}pwCVTZ}] - E[\mathrm{CCSD(T)/CORE/cc\text{-}pwCVTZ}]] -$$

$$[E[\mathrm{CCSDT/VAL/cc\text{-}pwCVTZ}] - E[\mathrm{CCSD(T)/VAL/cc\text{-}pwCVTZ}]] \quad (7)$$

Accounting for spin-orbit effects is necessary for a correct description of dissociation energies, as transition metal atoms can have spin-orbit splittings of multiple kJ mol^{-1}. Neglecting these would lead to erroneously more positive dissociation energies outside the range of experimental error bars, or even outside of transition metal thermochemical accuracy of 3 kcal mol^{-1}. So, here, the atomic spin-orbit is derived from energy levels reported in the NIST database by j-averaging the levels[60]. For molecules with electronic states $\Lambda>0$ (i.e., $\Pi(1)$ and $\Delta(2)$) spin-orbit splitting was found as the difference between the lowest spin-orbit state and the state-averaged energy, determined with CASSCF using the Breit-Pauli operator[61,62]. For VC, VN, VCl, computed spin-orbit energies were taken from literature[25,63]. For VF and VP the spin-orbit contributions were computed with CASSCF/aug-cc-pVTZ. A valence orbital and electrons active space was used.

$$\Delta E(\mathrm{SO}) = E[\mathrm{CASSCF/Spin\text{-}orbit}] - E[\mathrm{CASSCF/State\ averaged}] \quad (8)$$

To make direct comparisons with experiment the dissociation energy was computed as follows:

$$D_0 = E(A) + E(B) - E(AB) \quad (9)$$

A and B are the atomic constituents of molecule AB. E is the energy obtained by s-ccCA. Due to the inclusion of ZPVE in equation 1 a direct comparison with experiment can be made.

All CCSD(T) computations[45,46] were performed with MOLPRO 2015.1[64] For all HOC contributions, the MRCC code was used[65]. MOLPRO was used to generate reference molecular orbitals for use by MRCC. The s-ccCA thermochemical composite scheme used is summarized in Table 1. ccCA-TM has also been used in this study for comparison to s-ccCA. It was implemented as described in [20].

3.Results and Discussion

The D_0 are summarized in Table 5. Included in this table are the contributions that arise from each of the components of the s-ccCA composite scheme. Table 6 presents these D_0 and previous literature determinations. In the section that follows, each of the molecules is described, including an overview of some of the prior studies for each species.

3.1.*Vanadium boride (VB,$^7\Sigma$+)*

Resonant 2 Photon Ionization (R2PI) provided the first experimental prediction of the dissociation energy of VB, with a determination of 207.44±1.54 kJ mol^{-1}[66]. The s-ccCA value of 205.89 kJ mol^{-1} is in excellent agreement with the R2PI experiment. This same composite energy was performed by this group for ref [40]

In prior work, Tzeli and Mavridis computed potential energy curves for the entire series of 3*d* borides including VB[67]. For MRCI+Q they obtained a D_0 of 226.2 kJ mol^{-1}, which is in fair agreement with the R2PI and s-ccCA values. To note, if a contribution such as CCSD(T)-DKH had been added to their MRCI-Q value to account for relativistic effects, their D_0 would have resulted in 217.2 kJ mol^{-1}, in somewhat better agreement with the Do's determined by Morse and coworkers and the current study.

3.2.*Vanadium carbide (VC,$^2\Delta$)*

VC has been the subject of a number of experimental [68-71] and theoretical studies[68,72–75]. There are two experimental values: one obtained by mass spectrometry[70] and another by recent R2PI experiments[69]. The s-ccCA value of 390.70 kJ mol^{-1} is in reasonable agreement with the V2PI value of Johnson et al.[69] of 396.42±0.24 kJ mol^{-1} and falls within the lower bound of the mass spectrometry Knudsen effusion value by Satish and Gingerich of 418.75±24.12 kJ mol^{-1}[70].

Vanadium carbide has been studied theoretically, using methods ranging from different types of DFT to *ab initio* schemes that include methods beyond CCSD(T). An earlier DFT study with the B3LYP functional by Maclagan et al resulted in a D_0 of 367.8 kJ mol^{-1}[74]. This value is in poor agreement with the experimental and our composite scheme values; however, it does not account for scalar relativity, which would likely be beneficial. A preliminary composite scheme introduced by our group and similar to the s-ccCA presented here resulted in a D_0 of 395.35 kJ mol^{-1}, near the s-ccCA energy already mentioned (390.79 kJ mol^{-1}), and is also in very good agreement with R2PI experiment[63]. Our prior approach includes all of the components in s-ccCA, but with a perturbative quadruples treatment for the core-valence contribution[63]. If one removes this additional contribution the D_0 presented here and in [40] is the same. A MRCI+Q computation of Kalemos et al, also is in good agreement with experiment, differing by less than 2 kJ mol^{-1}[73]. However, the Kalemos study did not include the treatment of scalar relativity or the treatment of core correlation in the active space.

An *ab initio* scheme that includes higher order coupled cluster contributions up to CCSDTQ used by Chang et al differs by ~2 kJ mol^{-1} from s-ccCA (390.70 kJ mol^{-1})[68]. Part of the difference between their composite and s-ccCA comes from their inclusion of relativistic effects in all aspects of the higher order correlation. Our composite treats scalar relativity using CCSD(T). The other difference is that s-ccCA has a contribution from CCSDTQP. As shown in Table 5, CCSDTQP contributes 3.57 kJ mol^{-1} to the s-ccCA D_0.

3.3. *Vanadium nitride (VN,$^3Δ$)*

Vanadium nitride is a well-studied molecule[69,76–78]. There are three experimental values with varying levels of precision. The first is an equilibria experiment resulting in a D_0 of 473.74±8.68 kJ mol^{-1}. The s-ccCA D_0 of 481.89 kJ mol^{-1} falls within the upper bound of their uncertainty. The next value of 478.57±5.79 kJ mol^{-1} which comes from the use of a thermochemical cycle; the s-ccCA value is in close agreement. The s-ccCA value also is in excellent agreement (<0.30 kJ mol^{-1}) with the R2PI dissociation energy of 482.12±0.19 kJ mol^{-1} in [69].

In comparison to prior computational work, the s-ccCA D_0 is in great agreement with the D_0 of 481.47 kJ mol^{-1} from our prior work[63]. Our approach from [62] includes a term for the treatment of core-valence with CCSDT(Q), which contributes 0.42 kJ mol^{-1} to the D_0 The MCSCF computation in Ref [79] results in a value of 355.07 kJ mol^{-1} which is in poor agreement with both experiment and our results, certainly not accounting for necessary electron correlation. A later TPSSh calculation predicted a dissociation energy of 457.44 kJ mol^{-1}, which is in better agreement with experiment, though still ~25 kJ mol^{-1} lower than via R2PI energy[80]. However, this computation does not include relativistic effects through either a scalar relativistic approach or an ECP. A multireference CCSD(T) approach of Aoto et al[24]. resulted in 477.71 kJ mol^{-1}, differing by ~5 kJ mol^{-1} from R2PI and ~5 kJ mol^{-1} from our value. The approach by Aoto et al. accounted for some of the HOC using a multireference CCSD(T) contribution to the total energy.

3.4. *Vanadium oxide (VO,$^4Σ^-$)*

Vanadium oxide is one of the most studied molecules among this vanadium series. It has a wide range of uses in industry[81], and has been detected in stars[82] and the atmosphere of extra-solar planets[83]. It has been studied both experimentally[36,84–86] and theoretically[25,87,88]. In terms of experimental results, two Knudsen effusion experiments were done, resulting in D_0's of 620.88±18.81 kJ mol^{-1} and 625.5±8.5 kJ mol^{-184}.[84,85], and more recent D_0's were predicted by Velocity Map Imagine (VMI) and R2PI experiments of Gentleman et al.(635.28±3.15)[36] and Merriles et al.(631.50±0.19) [86], respectively. The s-ccCA D_0 prediction of 633.21 kJ mol^{-1} falls within the error bars of the Knudsen experiments, and is in very good agreement with the V2PI D_0.

Miliordos and Mavridis computed both MRCI and CCSD(T) D_0's[87]. Their CCSD(T) value is 624.21 kJ mol^{-1}, and for MRCI, they utilized relativistic and core-correlation corrections and obtained 628.72 kJ mol^{-1}, which in good agreement with our value and the experimental values. Miliordos did not include a basis set extrapolation, which we are showing is key to obtaining more accurate dissociation energies for these species. (Even with a quadruple-ζ basis set, the VO D_0 has not reached convergence as demonstrated in Table 2.) Cheng et al. also caried out a HEAT-like thermochemical computation, including higher order correlation contributions from CCSDT and CCSDTQ[25]. Converting the s-ccCA value to D_e, 639.25 kJ mol^{-1} is obtained, which is near to their value of 636.00 kJ mol^{-1}. The difference between the HEAT-like method of Cheng et al and s-ccCA is due to the more extensive treatment of HOC in s-ccCA. The CCSD(T) contributions for the HEAT-like approach in [25] (HF+CCSD+(T)+CV) results in a D_e of 641.4 kJ mol^{-1}, while our CCSD(T) +DKH contribution is 641.7 kJ mol^{-1}. The total HOC contribution to s-ccCA is ~2.2 kJ mol^{-1} while the HEAT-like composite has a triples and quadruples contribution of -0.9 kJ mol^{-1}. Aoto et.al obtained a D_0 of 626.56 kJ mol^{-1}[24]. As mentioned previously, their higher-order correlation was determined via MR-CCSD(T). Fang et al. [22] predicted a Do of 626.05 kJ mol^{-1} using an FPD scheme which does not include higher order coupled cluster contributions. Bross and coworkers on the other hand did use an FPD scheme including higher order coupled cluster up to pentuples for VO and obtained a D_0 of 628.01 kJ mol^{-1} [23]. This FPD composite used explicitly correlated CCSD, and made use of UHF references for the higher order correlation.

3.5. *Vanadium fluoride (VF,$^5\Pi$)*

There have been very few studies of VF. While a study by Ram et al.[89] focused on the emission spectroscopy of VF, there has been no reported D_0 from experiment. In terms of computation, Koukounas et al.[90] reported an MRCI D_0 of 528.3 kJ mol^{-1}, which is in fair agreement with our value of 545.28kJ mol^{-1}. The prior MRCI dissociation energy includes corrections for core-correlation and relativity, and the authors of this earlier study further recommend an adjusted value of 539.89 kJ mol^{-1}, based on a larger quintuple-ζ basis set computation, which provides an energy that is in much better agreement with our value. This substantial improvement in energy increase (~10 kJ mol^{-1}) demonstrates the importance of large basis sets with correlated methods for these species.

3.6. *Vanadium alumide (VAl,$^5\Sigma^+$)*

The only study on the vanadium alumide diatomic is an R2PI experiment by Behm et al [91], providing a dissociation energy of 143.67±0.19 kJ mol^{-1}. Our value of 141.96kJ mol^{-1} is in excellent agreement with the experimental dissociation energy. As VAl has significant multireference character, based on the very large [%TAE(T)] and [%TAE(T_4+T_5)] shown in section V, this is a particularly good result for a single reference CCSD(T)-based composite scheme.

3.7. *Vanadium silicide (VSi,$^4\Pi$)*

The dissociation energy of vanadium silicide was only recently experimentally determined using R2PI, resulting in a BDE of 215.55±0.33 kJ mol^{-1}[92], compared to the s-ccCA Do of 208.02 kJ mol^{-1}. As will be shown in section V, VSi has the most significant multireference character of these vanadium molecules, based upon the multireference diagnostics, so a multireference wavefunction approach will be important in reducing the gap between experiment and theory.

3.8. *Vanadium phosphide (VP,$^3\Delta$)*

For vanadium phosphide, there has been limited gas phase experiments. Currently, determination of the electronic spectra of VP is the only experiment of note[93], and an experimental dissociation energy has not been determined. Even the computational work is limited, with only a single DFT study[94]. In the DFT study, the D_0 of 312.21 kJ mol^{-1}was found with B3LYP paired with a triple-ζ quality basis set, and no relativistic treatment. s-ccCA resulted in a D_0 of 290.73 kJ mol^{-1}

This extent of difference between s-ccCA and B3LYP is not at all surprising. In considering prior studies on the performance of density functionals, including B3LYP, on 3*d* transition metal species, a similar overall error for B3LYP was determined, in comparison to the best experimental energies available for enthalpies of formation[95] An earlier study of B3LYP and a triple-ζ for 19 3*d* species showed very significant efforts for experiment, of 66.5 kJ mol^{-1}[29]. While the neglect of relativistic effects, and spin-orbit can lead to discrepancy, it is clear that the underlying functional does not capture enough correlation to compare more favorably with s-ccCA.

3.9. *Vanadium sulphide (VS,$^4\Sigma^-$)*

Vanadium sulphide is an extensively studied molecule with multiple bond dissociation energy determinations[69,96–98]. The most recent experimental determination was by Johnson et al with the R2PI technique[69]. Though the s-ccCA value of 435.15 kJ mol^{-1}is in poor agreement with older mass spec determinations of 483.35±16.40 kJ mol-1[96], 479.15±3.28 kJ mol-1[97] and 472.59±1.93 kJ mol-1[97] it is, however in excellent agreement with this recent R2PI measurement of Johnson et al. of 437.59±0.24 kJ mol^{-1}

In terms of computation, an early CCSD(T) study using a quadruple-ζ quality basis set obtained a value of 387.87 kJ mol^{-1}, in poor agreement with our determination[99] This computation is lacking a treatment of core-correlation and relativistic effects. A later determination with B3LYP is closer at 406.20 kJ mol^{-1}[100] This result was obtained with the 6-311G(df) basis set[100]. As noted in the section on VP, this difference is not surprising. A computation with Diffusion Monte Carlo (DMC) and triple-ζ basis sets is in much better agreement with the s-ccCA value at 432.45±0.68 kJ mol^{-1} differing by ~3 kJ mol^{-1}[101]. This DMC computation accounts for relativity with pseudopotentials, and does account for a significant amount of electronic correlation necessary for the prediction of accurate dissociation energies. A high-level composite by Bao et al[63]. including core-valence CCSDT(Q) and valence CCSDTQP resulted in a D_0 of 435.07 kJ mol$^-$, ,in excellent agreement with s-ccCA and the V2PI determination of Johnson et al. Work by the Wilson group used a slightly modified s-ccCA composite that included tight d functions in the basis sets for the determination of the higher order dissociation energy contributions. They obtained a D_0 of 435.02 kJ mol^{-1}[40].Based on the multireference diagnostics in the Multireference Character section this system is relatively free of multireference character and a CCSD(T)-centric approach is sufficient for the treatment of this system.

3.10. *Vanadium chloride (VCl,$^5\Delta$)*

There have been more experimental studies on vanadium chloride than on vanadium fluoride, including the determination of D_0[102,103] Our value of 411.86 kJ mol^{-1}is in fair agreement with the determination of Hildenbrand et al. who found the D_0 of VCl to be 426.35±8.37 kJ mol^{-1}[102] There has not yet been a V2PI experiment reported.

In terms of computational studies, a prior MRCI study[104] resulted in a D_0 of 400.40 kJ mol^{-1}, differing by ~11 kJ mol-1 from our value. This MRCI computation made use of core-valence MRCI-Q paired with the aug-cc-pwCV5Z basis set, and a aug-cc-pwCV5Z-DK set for the relativistic contribution. A coupled cluster computation using the same quintuple-ζ set as for MRCI performed in the same work resulted in a prediction of 408.36 kJ mol^{-1}, in much better agreement with our value. Fang et al. obtained a D_0 of 407.65 kJ mol-1 using an FPD composite scheme; this scheme did not include a higher order coupled cluster contributions[22].

Converting our s-ccCA D_0 to D_e, a D_e of 414.27 kJ mol^{-1}is obtained, in excellent agreement with the HEAT-like composite D_0 of Cheng et al. (414.6 kJ mol-1)[25] Considering the two *ab* *initio* composite schemes (work of Cheng et al. and the present work), CCSD(T), and MRCI studies, it is suggested that the experimental D_0 be re-evaluated in light of these computations.

4. Basis Set Convergence

Table 2 provides the D_0 energies for the aug-cc-pwCV*n*Z *(n*=T, Q, 5) as well as the three-point extrapolated complete basis set (CBS) energies for the molecules considered. For all of the molecules, the convergence of CCSD(T) is slow; from aug-cc-pwCVTZ to aug-cc-pwCV5Z, there is at least a 10 kJ mol^{-1} increase in the D_0. For VC and VN, this increase is more than 20 kJ mol^{-1}. Complete basis set limit extrapolation is necessary because even with the aug-cc-pwCV5Z basis set, the dissociation energies are not fully converged.

For the scalar relativistic correction, all species considered show little change (0.10-0.20 kJ mol^{-1}) when the basis set size is increased from aug-cc-pVTZ-DK to aug-cc-pVQZ-DK, indicating its near-convergence, even at the triple-ζ level. This fast convergence of the scalar relativistic contribution has been observed previously for main group species[10]. All of the scalar relativistic contributions to the D_0 are negative.

The contribution to the D_0 from higher order correlation including the ΔE(CCSDT), ΔE(CCSDTQ), and ΔE(CCSDTQP) terms is approximately an order of magnitude smaller than the reference CCSD(T), and are presented in Table 3. For example, VSi has a CCSD(T) reference energy of 194.94 kJ mol^{-1} while the ΔE(CCSDT) contribution is -1.43 kJ mol^{-1}. Table 3 lists the contributions that arise from higher order correlation energies. For VC, VN, VAl, VSi, and VS, it is clear that CBS extrapolation is needed for the ΔE(CCSDT) contribution, as there is a significant change between the cc-pVTZ and cc-pVQZ ΔE(CCSDT) dissociation energy contributions. These differences are not surprising, as CCSDT electronic energies are known to converge more slowly than CCSD(T) energies to the CBS limit[105,106]. For the ΔE(CCSDTQ) contribution, there is still a multiple kJ mol^{-1} change between the cc-pVDZ and cc-pVTZ level calculations. To illustrate, for VP, the ΔE(CCSDTQ) contribution increases from 7.61 kJ mol^{-1} to 11.32 kJ mol^{-1}, a nearly 4 kJ mol^{-1} difference as the basis set is changed from cc-pVDZ to cc-pVTZ. Even the ΔE(CCSDTQP)/cc-pVDZ level contribution is >2 kJ mol^{-1} for these species, and positive. Larger basis sets were not considered for the pentuples term due to the extreme N^{12} scaling. However, it is anticipated that any change in contribution upon a basis set change for the ΔE(CCSDTQP) contribution will be quite small, overall.

For five of the molecules ΔE(CCSDT) does not cancel or reduce the positive ΔE(CCSDTQ) contribution. Instead, ΔE(CCSDT) is positive and further increases D_0. It also leads to an overall larger higher-order coupled cluster contribution, which increases the D_0. ΔE(CCSDTQ) for these molecules is also positive, further increasing the D_0. For the rest of the systems considered the negative ΔE(CCSDT) does not cancel the positive quadruples contributions, leading to an overall positive higher-order coupled cluster contribution to the D_0 for all species except VO and VCl. It also demonstrates that CCSDT must be paired with CCSDTQ and CCSDTQP to obtain accurate dissociation energies.

5. Multireference Character

Some molecules are not well-represented by a single-reference wavefunction, and instead, because of characteristics such as degenerate electronic states, they require treatment with methods that can account for static correlation, such as multireference wavefunction approaches. For transition metal species, where there are many electronic states, degenerate states, and open shell species, a multireference wavefunction approach may be necessary. Interestingly, however, prior work has demonstrated that a more extensive treatment of the single-reference electronic structure with methods beyond CCSD(T) can prove to be an effective route to describe some molecules that may be of multireference nature[41,106,107]

While for some molecules, the need for multireference treatment is obvious, for others, this necessity is far less clear. Multireference diagnostics provides a useful route to assess the potential need for a multireference (MR) or MR-like strategy, and gives insight about why there may be large errors in prediction by single-reference wavefunction approaches.

In Table 4, several MR metrics are considered, which are detailed in earlier work (see, e.g., [10,17,57,108–110]). One metric is the percentage of the atomization energy arising from the perturbative triples, %TAE[(T)] from the coupled cluster calculation. The %TAE[(T)] provides a rough estimate of the importance of higher order coupled cluster to the total atomization energy. For main group species, a %TAE[(T)] of 5-10% suggests that CCSD(T) should be used with caution, and >10% suggests that CCSD(T) is not an appropriate methodology for the molecule under consideration. Another metric is the T_4+T_5 % TAE, which is the percentage of the contribution to the total atomization energy from the CCSDTQ and CCSDTQP dissociation energy contribution [10] Other metrics are the T_1, the Frobenius norm of the t_1 vector, and D_1, the matrix 2-norm of t_1. These metrics, which easily can be determined in any coupled cluster computation, provide insight into the importance of singly excited determinants in a molecule. Another metric is via the norms of the singles and doubles amplitudes, T_1 and T_2. The absolute value of the largest T_1 and T_2 amplitudes is also considered known as T_{1Max} and T_{2Max} T_{1Max} and T_{2Max} are also measures of the importance of single and doubly excited determinants in CCSD[25]. Prior work has suggested that the T_1, D_1, and %TAE[(T)] diagnostics utilized for main group species are not appropriate for main group species, and, instead, criteria that are suitable for 3*d* and 4*d* transition metal-containing molecules have been introduced and are now well-utilized[17,18,20] For 3*d* systems, diagnostics of T_1>0.15, D_1>0.05, and %TAE[(T)]>10, can suggest possible multireference character[17]. T_{2Max}, a measure of double excitations, can be useful for systems, such as those where T_1, D_1, and %TAE[(T)] do not provide sufficient clarity.

In this work the %TAE[(T)] was obtained at the aug-cc-pwCV5Z basis set level. The T_1 and D_1 diagnostics, as well as the T_1 and T_2 norms, and T_{1max} and T_{2max} are all determined using a CCSD(T)/aug-cc-pwCV5Z computation. In terms of the diagnostics, the only species with T_1<0.15 and D_1<0.15 are VO and VAl. The other species have T_1>0.15 and D_1>0.05. Considering %TAE[(T)], all species but VF and VCl have %TAE[(T)]>10%, and for VSi and VP have >35%. Such a large %TAE[(T)] suggests possible multireference character and the importance of higher-order coupled cluster contributions (T_4+T_5). VSi has a %TAE[T_4+T_5] of 9.23% and VP has a %TAE[T_4+T_5] of 4.94% . Of the species considered here, six, VB, VC, VN, VAl, VSi, VP have TAE[T_4+T_5]>1%. %TAE[(T)]>20% corresponds with a %TAE[T_4+T_5]>1%, which for these species can easily be more than 10 kJ mol^{-1}.Considering this metric, as well as the T_1, D_1 and %TAE[(T)] suggests that these species have substantial non-dynamical/static correlation energy. None of the species has a T_{2max} above 0.10, but two, VB and VSi have a T_{2max} of 0.09. A T_{2max} above 0.10 would indicate that there are important doubly excited determinants. For all of the species considered, the T_1 norms are very large. Large T_1 norms are common for transition metal compounds and can be attributed to orbital relaxation. The T_2 norms while large, are not dominated by large T_2 amplitudes, as none of the T_{2max} are above 0.10. Rather the T_2 norms consist of many small T_2 amplitudes.

6. Accuracy and Transition Metal Chemical Accuracy

Having the means to gauge computational approaches for thermochemical predictions is vital to understand the utility of the methods, so that they can be applied broadly for the prediction of the thermochemistry of other species. As mentioned earlier many of the main group elements are a part of ATcT[[30]] which synthesizes new thermochemical data and updates uncertainty and thermochemical quantities. Unfortunately, such a broad, useful compilation and analysis of data is not available for the transition metals. Until recently, some of the best comparison for transition metal species have been via Knudsen Effusion experiments, though many of these experiments have large uncertainties [[111]]. The 3 kcal mol^{-1} "transition metal chemical accuracy" was determined with these Knudsen Effusion dissociation energies, considering their experimental uncertainties.

With the two-photon(R2PI) dissociation energies, a new level of assessment is possible in gauging theoretical approaches. An overall summary of results for the ccCA method for the vanadium molecules is shown in Table VII, and a summary for s-ccCA is provided in Table V.

The s-ccCA method resulted in a MAD of 2.97 kJ mol^{-1}or 0.71 kcal mol^{-1}, much smaller than the 3.0 kcal mol^{-1} "transition metal thermochemical accuracy". If VSi is omitted from the evaluation, a MAD of 2.21 kJ mol^{-1}is obtained. This level of accuracy demonstrates that the super-ccCA composite scheme can be highly effective in predicting thermochemical energies. This also suggests a new tighter metric for transition metal thermochemical accuracy is possible, reaching a level where "sub-chemical accuracy" for transition metals of <1 kcal mol^{-1} from experiment is possible, and is overall achievable via s-ccCA for the vanadium diatomics.

Though s-ccCA is very effective, the performance of the ccCA transition metal (ccCA-TM) approach can also be assessed via the new experiments. For the vanadium diatomics, ,VC, VN, VO, and VS have both Knudsen and 2 Photon dissociation energies. In comparing ccCA, very different MAD's from the 2 Photon vs. the Knudsen effusion dissociation energies are obtained 15.94 kJ mol^{-1} vs. 31.94 kJ mol^{-1}, respectively, for these four molecules. The new experiment results in ccCA error reduction by nearly two times. The MAD for the Knudsen effusion experiments as a whole is 36.19 kJ mol^{-1} while the MAD for the 2 Photon experiments with ccCA is 19.11 kJ mol^{-1}. In comparing the s-ccCA results to the Knudsen experiments cited in Ref [20] , a MAD of 26.65 kJ mol^{-1} is obtained. This is only a ~20% decrease from the ccCA MAD. The four molecules for which there are both 2 photon and Knudsen Effusion experiments has a MAD of 25.77 kJ mol^{-1}, and the 2 photon results have a MAD of 2.51 kJ mol^{-1}, ten times smaller!

7. Conclusion

A new version of ccCA for highly accurate dissociation energies, super ccCA (s-ccCA), was applied to first- and second-row vanadium diatomics. The recent advances in two-photon experiments have enabled unprecedented gauges of comparisons for D_0, providing a clear understanding of the performance of various theoretical methods. Our results are in excellent agreement with current V2PI dissociation energies with a MAD of 2.97 kJ mol^{-1}. Our work has made it clear that large basis sets with CBS extrapolations are important for accurate coupled cluster predictions. Composite thermochemical schemes that incorporate single reference coupled cluster methods with high-order excitations can be applied to transition metal diatomic systems with multireference character and lead to energetics in agreement with experiment. In the absence of experiment, s-ccCA BDE predictions should be used as gauges for VF and VP molecules. For VCl, based on our composite scheme, and other computational work, it is recommended that prior experiments be revisited.

Table and Figures

Table 1: Contributions to Super-ccCA (s-ccCA)

Contribution	Method and Basis set
Geometry	CCSD(T)/PVQZ
Frequency	CCSD(T)/PVQZ
Total CCSD(T)	APWCVXZ, X=T, Q, 5, ℓ^{-3} extrapolation
Scalar Relativistic	CCSD(T)/APVQZ-DK
Atomic Spin-Orbit	NIST
Molecular Spin-Orbit	Literature or CASSCF+BP operator
CCSDT	CC-PVXZ, X=T, Q ℓ^{-3} extrapolation
CCSDTQ	CCSDTQ/PVTZ-CCSDT/PVTZ
CCSDTQP	CCSDTQP/PVDZ-CCSDTQ/PVDZ
Core CCSDT	ΔCCSDT(core)-ΔCCSDT(val), PWCVTZ

Acronyms used: PVQZ=cc-pVQZ. APWCVXZ=aug-cc-pWCV*n*Z,

APVQZ-DK=aug-cc-pVQZ-DK, PVTZ=cc-pVTZ,

PWCVTZ=cc-pWCVTZ, PVDZ=cc-pVDZ

Table 2: Total CCSD(T) energies and scalar relativistic contributions to the dissociation energies (kJ mol^{-1})

Molecule	APWCVTZ	APWCVQZ	APWCV5Z	CBS	APVTZ-DK	APVQZ-DK
VB	204.10	209.84	211.99	214.12	-8.81	-8.84
VC	374.48	390.34	396.79	402.62	-12.53	-14.39
VN	453.06	469.03	475.14	481.05	-1.74	-1.67
VO	620.81	634.61	638.81	644.06	-2.36	-2.34
VF	539.13	548.48	551.04	554.65	-6.57	-6.56
VAl	138.13	142.66	144.23	145.93	-5.84	-6.05
VSi	180.69	188.92	191.83	194.91	-3.07	-3.23
VP	253.35	266.92	271.95	276.99	-3.02	-3.11
VS	417.08	429.95	435.03	439.78	-6.50	-6.56
VCl	408.12	418.46	422.11	425.97	-7.66	-7.77

CBS = $a+b\,\ell^{-3}$

Table 3: Higher-order correlation energy contributions (kJ mol^{-1})

Molecule	**T/cc-pVTZ**	**T/cc-pVQZ**	**CBS**	**Q/cc-pVDZ**	**Q/cc-pVTZ**	**P/cc-pVDZ**
VB	2.18	1.94	1.76	3.48	3.18	0.30
VC	-7.46	-8.56	-9.37	11.13	12.44	3.57
VN	-4.38	-5.51	-6.33	7.69	9.12	2.73
VO	-4.11	-4.98	-5.62	5.01	5.94	-2.61
VF	0.91	0.70	0.54	1.14	0.79	-0.22
VAl	5.77	5.30	4.91	4.44	4.85	4.85
VSi	0.77	-0.50	-1.43	13.97	15.31	3.58
VP	-1.29	-3.04	-4.31	7.61	11.32	3.09
VS	6.34	5.44	4.84	2.31	4.98	-2.52
VCl	-0.81	-0.88	-0.94	0.39	0.57	-0.06

Acronyms: T=CCSDT, Q=CCSDTQ, P=CCSDTQP

Table 4: Multireference metrics

Molecule	(T) % TAE	T_4+T_5 % TAE	T_1 Norm	T_1 Max[a]	T_2 Norm	T_2 Max[a]	T_1 Diag	D_1 Diag
VB	22.53	1.66	0.62	0.26	0.58	0.09	0.05	0.15
VC	24.81	4.03	0.59	0.11	0.56	0.05	0.09	0.25
VN	21.65	2.43	0.36	0.13	0.47	0.05	0.05	0.15
VO	13.73	0.52	0.33	0.08	0.43	0.03	0.04	0.11
VF	2.59	0.10	0.37	0.15	0.38	0.02	0.05	0.24
VAl	23.91	3.54	0.29	0.11	0.49	0.05	0.04	0.12
VSi	35.39	9.23	0.66	0.31	0.62	0.09	0.06	0.18
VP	35.94	4.94	0.72	0.22	0.65	0.06	0.08	0.21
VS	13.89	0.56	0.49	0.17	0.52	0.04	0.07	0.18
Vcl	1.76	0.12	0.41	0.22	0.43	0.02	0.05	0.27

[a] T_1, T_2 Max are absolute values

Table 5: Composite thermochemical scheme contributions to D_0 (kJ mol^{-1})

Molecule	CCSD(T)	SR[1]	MSO[2]	ASO[3]	CCSDT	CCSDTQ	CCSDTQP	Core	ZPVE	Total
VB	214.12	-8.84	0.00	-3.89	1.76	3.18	0.30	2.85	-3.59	205.89
VC	402.62	-14.93	1.76	-4.18	-9.37	12.44	3.57	3.94	-5.06	390.79
VN	481.05	-1.67	1.97	-3.82	-6.33	9.12	2.73	5.27	-6.43	481.89
VO	644.06	-2.34	0.00	-4.70	-5.62	5.94	-2.61	4.53	-6.05	633.21
VF	554.65	-6.56	2.25	-5.38	0.54	0.79	-0.22	3.20	-3.99	545.28
VAl	145.93	-6.05	0.00	-4.66	4.91	4.85	0.18	-1.62	-1.58	141.96
VSi	194.91	-3.23	1.51	-5.56	-1.43	15.31	3.58	5.08	-2.15	208.02
VP	275.31	-3.11	1.74	-3.77	-4.31	11.32	3.09	11.52	-2.74	289.05
VS	439.78	-6.56	0.00	-6.28	4.84	4.98	-2.52	4.10	-3.20	435.14
VCl	425.97	-7.77	1.67	-7.28	-0.94	0.57	-0.06	2.10	-2.40	411.86
MAD	2.97									

[1] scalar relativistic

[2] molecualr spin-orbit

[3] atomic spin-orbit

Table 6: Comparisons with literature values for D_0 in kJ mol^{-1}

Molecule	Determination	Type	D0	Reference
VB	Tzeli and Mavridis	MRCI	226.2	[67]
	Merriles *et al.*	2 Photon	207.44±1.54	[66]
	Present Work	Composite	205.89	
VC	Johnson *et al.*	2 Photon	396.42±0.24	[69]
	Chang *et al.*	Composite	388.16	[68]
	Satish and Gingerich	Knudsen	418.75±24.12	[70]
	Kalemos *et al.*	MRCI	392.56	[73]
	Maclagan and Scuseria	DFT	367.8	[74]
	Bao *et al.*	Composite	395.35	[63]
	Present Work	Composite	390.79	
VN	Bao *et al*.	Composite	481.47	[63]
	Huang *et al*.	Thermocycle	478.57±5.79	[76]
	Harrison	MCSCF	355.07	[77]
	Farber and Srivastava	Equilibria	473.74±8.68	[78]
	Johnson *et al.*	2 Photon	482.12±0.19	[69]
	Furche and Perdew	DFT	457.44	[80]
	Aoto *et al.*	MR-CCSD(T)	477.71	[24]
	Present Work	Composite	481.89	
VO	Gentleman *et al.*	VMI	635.28±3.15	[36]
	Miliordos and Mavridis	CCSD(T)	624.21	[87]
	Pedley *et al.*	Kndusen	620.88±18.81	[85]
	Balducci *et al.*	Knudsen	625.5±8.5	[84]
	Merriles *et al.*	2 Photon	631.50±0.19	[86]
	Cheng *et al*.	Composite	636.00	[25]
	Fang *et al*	CCSD(T)	626.05	[22]
	Bross et al	FPD	628.02	[23]
	Aoto *et al*.	MR-CCSD(T)	626.56	[24]
	Present Work	Composite	633.21	

Table 6 Continued

Molecule	Determination	Type	D0	Reference
VF	Koukounas *et al.*	MRCI	528.3	[90]
	Present Work	Composite	545.28	
VAl	Behm *et al.*	2 Photon	143.67±0.19	[91]
	Present Work	Composite	141.96	
VSi	Sevy *et al*.	2 Photon	215.55±0.30	[92]
	Present Work	Composite	208.02	
VP	Tong *et al*	DFT	312.21	[94]
	Present Work	Composite	290.73	
VS	Owzarski and Franzen	Mass Spec	483.35±16.40	[96]
	Edwards *et al*.	Mass Spec	479.15±3.28	[97]
	Botor and Edwards	Mass Spec	472.59±1.93	[98]
	Johnson *et al*.	2 Photon	437.59±0.24	[69]
	Bauschlicher and Maitre	CCSD(T)	387.87	[99]
	Wu *et al.*	DFT	406.2	[100]
	Petz and Luchow	DMC	432.45±0.68	[101]
	Bao *et al.*	Composite	435.07	[63]
	Welch *et al.*	Composite	435.02	[40]
	Present Work	Composite	435.14	
VCl	Hildenbrand *et al.*	Knudsen Effusion	426.35±8.37	[102]
	Cheng *et al*.	Composite	414.6	[25]
	Fang *et al*.	CCSD(T)	407.64	[22]
	Kardahakis and Mavridis	MRCI	396.77	[104]
	Present Work	Composite	411.86	

Table 7: TM-ccCA dissociation energies compared to experiment. MAD is obtained for results where both R2PI and previous results exist, VC, VN, VO, and VS. All results are in kJ mol^{-1}.

Molecule	ccCA D_0	Yungman D_0 [112]	R2PI D_0[67,69,86,91,92]
VB	185.43		207.44±0.15
VC	367.43	465.66±62.76	396.42±0.24
VN	473.36	463.15±13.39	482.12±0.19
VO	622.76	625.50±41.84	631.50±0.18
VF	528.66	545.28±62.76	
VAl	126.13		143.67±0.96
VSi	183.77		215.55±0.29
VP	269.82		
VS	420.31	446.89±12.55	437.59±0.24
VCl	395.98	426.35±62.76	
MAD Knudsen	36.19		
MAD 2 Photon	19.11		

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References

[[1] N.J. DeYonker, T.R. Cundari, and A.K. Wilson, "The correlation consistent composite approach (ccCA): An alternative to the Gaussian-n methods," J. Chem. Phys. **124**(11), 114104 (2006).

[2] N.J. DeYonker, T. Grimes, S. Yockel, A. Dinescu, B. Mintz, T.R. Cundari, and A.K. Wilson, "The correlation-consistent composite approach: Application to the G3/99 test set," J. Chem. Phys. **125**(10), 104111 (2006).

[3] J.M.L. Martin, and G. De Oliveira, "Towards standard methods for benchmark quality ab initio thermochemistry - W1 and W2 theory," J. Chem. Phys. **111**(5), 1843–1856 (1999).

[4] J.A. Pople, M. Head-Gordon, D.J. Fox, K. Raghavachari, and L.A. Curtiss, "Gaussian-1 theory: A general procedure for prediction of molecular energies," J. Chem. Phys. **90**(10), 5622–5629 (1989).

[5] L.A. Curtiss, C. Jones, G.W. Trucks, K. Raghavachari, and J.A. Pople, "Gaussian-1 theory of molecular energies for second-row compounds," J. Chem. Phys. **93**(4), 2537–2545 (1990).

[6] L.A. Curtiss, K. Raghavachari, P.C. Redfern, and J.A. Pople, "Assessment of Gaussian-2 and density functional theories for the computation of enthalpies of formation," J. Chem. Phys. **106**(3), 1063–1079 (1997).

[7] L.A. Curtiss, K. Raghavach Ari, P.C. Redfern, V. Rassolov, and J.A. Pople, "Gaussian-3 (G3) theory for molecules containing first and second-row atoms," J. Chem. Phys. **109**(18), 7764–7776 (1998).

[8] L.A. Curtiss, P.C. Redfern, and K. Raghavachari, "Gaussian-4 theory," J. Chem. Phys. **126**(8), 084108 (2007).

[9] A. Karton, P.R. Taylor, and J.M.L. Martin, "Basis set convergence of post-CCSD contributions to molecular atomization energies," J. Chem. Phys. **127**(6), 064104 (2007).

[10] A. Karton, E. Rabinovich, J.M.L. Martin, and B. Ruscic, "W4 theory for computational thermochemistry: In pursuit of confident sub-kJ/mol predictions," J. Chem. Phys. **125**(14), 144108 (2006).

[11] A. Tajti, P.G. Szalay, A.G. Császár, M. Kállay, J. Gauss, E.F. Valeev, B.A. Flowers, J. Vázquez, and J.F. Stanton, "HEAT: High accuracy extrapolated ab initio thermochemistry," J. Chem. Phys. **121**(23), 11599–11613 (2004).

[12] Y.J. Bomble, J. Vázquez, M. Kállay, C. Michauk, P.G. Szalay, A.G. Császár, J. Gauss, and J.F. Stanton, "High-accuracy extrapolated ab initio thermochemistry. II. Minor improvements to the protocol and a vital simplification," J. Chem. Phys. **125**(6), 064108 (2006).

[13] M.E. Harding, J. Vázquez, B. Ruscic, A.K. Wilson, J. Gauss, and J.F. Stanton, "High-accuracy extrapolated ab initio thermochemistry. III. Additional improvements and overview," J. Chem. Phys. **128**(11), 114111 (2008).

[14] J.H. Thorpe, C.A. Lopez, T.L. Nguyen, J.H. Baraban, D.H. Bross, B. Ruscic, and J.F. Stanton, "High-accuracy extrapolated ab initio thermochemistry. IV. A modified recipe for computational

efficiency," J. Chem. Phys. **150**(22), 224102 (2019).

[15] D. Feller, K.A. Peterson, and D.A. Dixon, "Further benchmarks of a composite, convergent, statistically calibrated coupled-cluster-based approach for thermochemical and spectroscopic studies," Mol. Phys. **110**(19–20), 2381–2399 (2012).

[16] D. Feller, K.A. Peterson, and B. Ruscic, "Improved accuracy benchmarks of small molecules using correlation consistent basis sets," Theor. Chem. Acc. **133**(1), 1–16 (2014).

[17] W. Jiang, N.J. Deyonker, and A.K. Wilson, "Multireference character for 3d transition-metal-containing molecules," J. Chem. Theory Comput. **8**(2), 460–468 (2012).

[18] J. Wang, S. Manivasagam, and A.K. Wilson, "Multireference Character for 4d Transition Metal-Containing Molecules," J. Chem. Theory Comput. **11**(12), 5865–5872 (2015).

[19] N.J. DeYonker, K.A. Peterson, G. Steyl, A.K. Wilson, and T.R. Cundari, "Quantitative computational thermochemistry of transition metal species," J. Phys. Chem. A **111**(44), 11269–11277 (2007).

[20] W. Jiang, N.J. Deyonker, J.J. Determan, and A.K. Wilson, "Toward accurate theoretical thermochemistry of first row transition metal complexes," J. Phys. Chem. A **116**(2), 870–885 (2012).

[21] S. Li, J.M. Hennigan, D.A. Dixon, and K.A. Peterson, "Accurate thermochemistry for transition metal oxide clusters," J. Phys. Chem. A **113**(27), 7861–7877 (2009).

[22] Z. Fang, M. Vasiliu, K.A. Peterson, and D.A. Dixon, "Prediction of Bond Dissociation Energies/Heats of Formation for Diatomic Transition Metal Compounds: CCSD(T) Works," J. Chem. Theory Comput. **13**(3), 1057–1066 (2017).

[23] D.H. Bross, J.G. Hill, H.J. Werner, and K.A. Peterson, "Explicitly correlated composite thermochemistry of transition metal species," J. Chem. Phys. **139**(9), 094302 (2013).

[24] Y.A. Aoto, A.P. De Lima Batista, A. Köhn, and A.G.S. De Oliveira-Filho, "How to Arrive at Accurate Benchmark Values for Transition Metal Compounds: Computation or Experiment?," J. Chem. Theory Comput. **13**(11), 5291–5316 (2017).

[25] L. Cheng, J. Gauss, B. Ruscic, P.B. Armentrout, and J.F. Stanton, "Bond Dissociation Energies for Diatomic Molecules Containing 3d Transition Metals: Benchmark Scalar-Relativistic Coupled-Cluster Calculations for 20 Molecules," J. Chem. Theory Comput. **13**(3), 1044–1056 (2017).

[26] G.A. Oyedepo, and A.K. Wilson, "Multireference correlation consistent composite approach [MR-ccCA]: Toward accurate prediction of the energetics of excited and transition state chemistry," J. Phys. Chem. A **114**(33), 8806–8816 (2010).

[27] B. Mintz, T.G. Williams, L. Howard, and A.K. Wilson, "Computation of potential energy surfaces with the multireference correlation consistent composite approach," J. Chem. Phys. **130**(23), 214103 (2009).

[28] S.A. Nedd, N.J. DeYonker, A.K. Wilson, P. Piecuch, and M.S. Gordon, "Incorporating a completely renormalized coupled cluster approach into a composite method for thermodynamic

properties and reaction paths," J. Chem. Phys. **136**(14), 144109 (2012).

[29] S.M. Tekarli, M.L. Drummond, T.G. Williams, T.R. Cundari, and A.K. Wilson, "Performance of density functional theory for 3d transition metal-containing complexes: Utilization of the correlation consistent basis sets," J. Phys. Chem. A **113**(30), 8607–8614 (2009).

[30] B. Ruscic, R.E. Pinzon, M.L. Morton, G. Von Laszevski, S.J. Bittner, S.G. Nijsure, K.A. Amin, M. Minkoff, and A.F. Wagner, "Introduction to active thermochemical tables: Several 'Key' enthalpies of formation revisited," J. Phys. Chem. A **108**(45), 9979–9997 (2004).

[31] S.J. Klippenstein, L.B. Harding, and B. Ruscic, "Ab Initio Computations and Active Thermochemical Tables Hand in Hand: Heats of Formation of Core Combustion Species," J. Phys. Chem. A **121**(35), 6580–6602 (2017).

[32] M.D. Morse, "Predissociation Measurements of Bond Dissociation Energies," Acc. Chem. Res. **52**(1), 119–126 (2019).

[33] G.A. Cooper, A.S. Gentleman, A. Iskra, and S.R. Mackenzie, "Photofragmentation dynamics and dissociation energies of MoO and CrO," J. Chem. Phys. **147**(1), 013921 (2017).

[34] I.S. Parry, A.C. Hermes, A. Kartouzian, and S.R. MacKenzie, "Imaging the photodissociation dynamics of neutral metal clusters: Copper dimer, Cu2, and copper oxide, CuO," Phys. Chem. Chem. Phys. **16**(2), 458–466 (2014).

[35] W.S. Hopkins, S.M. Hamilton, P.D. McNaughter, and S.R. Mackenzie, "VUV photodissociation dynamics of diatomic gold, Au2: A velocity map imaging study at 157 nm," Chem. Phys. Lett. **483**(1–3), 10–15 (2009).

[36] A.S. Gentleman, A. Iskra, H. Köckert, and S.R. MacKenzie, "Photodissociation dynamics and the dissociation energy of vanadium monoxide, VO, investigated using velocity map imaging," Phys. Chem. Chem. Phys. **21**(28), 15560–15567 (2019).

[37] D.M. Merriles, E. Tieu, and M.D. Morse, "Bond dissociation energies of FeB, CoB, NiB, RuB, RhB, OsB, IrB, and PtB," J. Chem. Phys. **151**(4), 44302 (2019).

[38] E.M. Spain, and M.D. Morse, "Bond strengths of transition metal diatomics: VNi and V2," Int. J. Mass Spectrom. Ion Process. **102**(C), 183–197 (1990).

[39] E.L. Johnson, Q.C. Davis, and M.D. Morse, "Predissociation measurements of bond dissociation energies: VC, VN, and VS," J. Chem. Phys. **144**(23), 234306 (2016).

[40] B.K. Welch, N.M.S. Almeida, and A.K. Wilson, "Super ccCA (s-ccCA): an approach for accurate transition metal thermochemistry," Mol. Phys., e1963001 (2021).

[41] A. Karton, "Post-CCSD(T) contributions to total atomization energies in multireference systems," J. Chem. Phys. **149**(3), 034102 (2018).

[42] M.S. Schuurman, S.R. Muir, W.D. Allen, and H.F. Schaefer, "Toward subchemical accuracy in computational thermochemistry: Focal point analysis of the heat of formation of NCO and [H,N,C,O] isomers," J. Chem. Phys. **120**(24), 11586–11599 (2004).

[43] A.G. Császár, W.D. Allen, and H.F. Schaefer, "In pursuit of the ab initio limit for conformational energy prototypes," J. Chem. Phys. **108**(23), 9751–9764 (1998).

[44] A.L.L. East, and W.D. Allen, "The heat of formation of NCO," J. Chem. Phys. **99**(6), 4638–4650 (1993).

[45] J.D. Watts, J. Gauss, and R.J. Bartlett, "Coupled-cluster methods with noniterative triple excitations for restricted open-shell Hartree-Fock and other general single determinant reference functions. Energies and analytical gradients," J. Chem. Phys. **98**(11), 8718–8733 (1993).

[46] P.J. Knowles, C. Hampel, and H.J. Werner, "Coupled cluster theory for high spin, open shell reference wave functions," J. Chem. Phys. **99**(7), 5219–5227 (1993).

[47] N.B. Balabanov, and K.A. Peterson, "Systematically convergent basis sets for transition metals. I. All-electron correlation consistent basis sets for the 3d elements Sc-Zn," J. Chem. Phys. **123**(6), 064107 (2005).

[48] T.H. Dunning, "Gaussian basis sets for use in correlated molecular calculations. I. The atoms boron through neon and hydrogen," J. Chem. Phys. **90**(2), 1007–1023 (1989).

[49] D.E. Woon, and T.H. Dunning, "Gaussian basis sets for use in correlated molecular calculations. III. The atoms aluminum through argon," J. Chem. Phys. **98**(2), 1358–1371 (1993).

[50] K.A. Peterson, and T.H. Dunning, "Accurate correlation consistent basis sets for molecular core-valence correlation effects: The second row atoms Al-Ar, and the first row atoms B-Ne revisited," J. Chem. Phys. **117**(23), 10548–10560 (2002).

[51] W. Kutzelnigg, and J.D. Morgan, "Rates of convergence of the partial-wave expansions of atomic correlation energies," J. Chem. Phys. **96**(6), 4484–4508 (1992).

[52] T. Helgaker, W. Klopper, H. Koch, and J. Noga, "Basis-set convergence of correlated calculations on water," J. Chem. Phys. **106**(23), 9639–9646 (1997).

[53] W.A. De Jong, R.J. Harrison, and D.A. Dixon, "Parallel Douglas-Kroll energy and gradients in NWChem: Estimating scalar relativistic effects using Douglas-Kroll contracted basis sets," J. Chem. Phys. **114**(1), 48–53 (2001).

[54] D. Feller, "Estimating the intrinsic limit of the Feller-Peterson-Dixon composite approach when applied to adiabatic ionization potentials in atoms and small molecules," J. Chem. Phys. **147**(3), 034103 (2017).

[55] A. Karton, "Basis set convergence of high-order coupled cluster methods up to CCSDTQ567 for a highly multireference molecule," Chem. Phys. Lett. **737**, 136810 (2019).

[56] A. Karton, "A computational chemist's guide to accurate thermochemistry for organic molecules," Wiley Interdiscip. Rev. Comput. Mol. Sci. **6**(3), 292–310 (2016).

[57] A. Karton, S. Daon, and J.M.L. Martin, "W4-11: A high-confidence benchmark dataset for computational thermochemistry derived from first-principles W4 data," Chem. Phys. Lett. **510**(4–6), 165–178 (2011).

[58] M. Kállay, and P.R. Surján, "Higher excitations in coupled-cluster theory," J. Chem. Phys. **115**(7), 2945–2954 (2001).

[59] M. Kallay, J. Gauss, and P.G. Szalay, "Analytic first derivatives for general coupled-cluster and configuration interaction models," J. Chem. Phys. **119**(6), 2991–3004 (2003).

[60] C.E.Moore, "Atomic energy levels," Natl. Bur. Stand. Ref. Data Ser., Natl. Bur. Stand., (1971).

[61] P.J. Knowles, and H.J. Werner, "An efficient second-order MC SCF method for long configuration expansions," Chem. Phys. Lett. **115**(3), 259–267 (1985).

[62] H.J. Werner, and P.J. Knowles, "A second order multiconfiguration SCF procedure with optimum convergence," J. Chem. Phys. **82**(11), 5053–5063 (1985).

[63] J.L. Bao, B.K. Welch, I.S. Ulusoy, X. Zhang, X. Xu, A.K. Wilson, and D.G. Truhlar, "Predicting Bond Dissociation Energies and Bond Lengths of Coordinatively Unsaturated Vanadium-Ligand Bonds," J. Phys. Chem. A **124**(47), 9757–9770 (2020).

[64] T.T. and M.W. P. J Knowles, G. Knizia, F. R. Manby, M. Schutz, P. Celani, W. Gyorffy, D. Kats, T. Korona, R. Lindh, A. Mitrushenkov, G. Rauhut, K. R. Shamasundar, T. B. Adler, R. D. Amos, A. Bernhardsson, A. Berning, D. L. Cooper, M. J. O. Deegan, A. J. Dobbyn, F. Ecke, "MOLPRO, Version 2015.1, A Package of Ab Initio Programs," (2015).

[65] M. Kállay, P.R. Nagy, D. Mester, Z. Rolik, G. Samu, J. Csontos, J. Csóka, P.B. Szabó, L. Gyevi-Nagy, B. Hégely, I. Ladjánszki, L. Szegedy, B. Ladóczki, K. Petrov, M. Farkas, P.D. Mezei, and Á. Ganyecz, "The MRCC program system: Accurate quantum chemistry from water to proteins," J. Chem. Phys. **152**(7), 074107 (2020).

[66] D.M. Merriles, C. Nielson, E. Tieu, and M.D. Morse, "Chemical Bonding and Electronic Structure of the Early Transition Metal Borides: ScB, TiB, VB, YB, ZrB, NbB, LaB, HfB, TaB, and WB," J. Phys. Chem. A, (2021).

[67] D. Tzeli, and A. Mavridis, "Electronic structure and bonding of the 3d transition metal borides, MB, M=Sc, Ti, V, Cr, Mn, Fe, Co, Ni, and Cu through all electron ab initio calculations," J. Chem. Phys. **128**(3), 154321 (2008).

[68] Y.C. Chang, Z. Luo, Y. Pan, Z. Zhang, Y.N. Song, S.Y. Kuang, Q.Z. Yin, K.C. Lau, and C.Y. Ng, "Rotationally resolved state-to-state photoionization and the photoelectron study of vanadium monocarbide and its cations (VC/VC+)," Phys. Chem. Chem. Phys. **17**(15), 9780–9793 (2015).

[69] E.L. Johnson, Q.C. Davis, and M.D. Morse, "Predissociation measurements of bond dissociation energies: VC, VN, and VS," J. Chem. Phys. **144**(23), 234306 (2016).

[70] S.K. Gupta, and K.A. Gingerich, "Mass spectrometric study of the stabilities of gaseous carbides of vanadium, niobium, and molybdenum," J. Chem. Phys. **74**(6), 3584–3590 (1981).

[71] O. Krechkivska, and M.D. Morse, "Electronic spectroscopy of diatomic VC," J. Phys. Chem. A **117**(50), 13284–13291 (2013).

[72] G.L. Gutsev, L. Andrews, and C.W. Bauschlicher, "Similarities and differences in the structure of 3d-metal monocarbides and monoxides," Theor. Chem. Acc. **109**(6), 298–308 (2003).

[73] A. Kalemos, T.H. Dunning, and A. Mavridis, "The electronic structure of vanadium carbide, VC," J. Chem. Phys. **123**(1), 14301 (2005).

[74] R.G.A.R. Maclagan, and G.E. Scuseria, “An ab initio study of VC: A comparison of different levels of theory including density functional methods,” Chem. Phys. Lett. **262**(1–2), 87–90 (1996).

[75] D. Majumdar, and K. Balasubramanian, “A theoretical study of potential energy curves and spectroscopic constants of VC,” Mol. Phys. **101**(9), 1369–1376 (2003).

[76] H. Huang, Z. Luo, Y.C. Chang, K. Lau, and C.Y. Ng, “State-to-state Photoionization Dynamics of Vanadium Nitride by Two-color Laser Photoionization and Photoelectron Methods,” Chinese J. Chem. Phys. **26**(6), 669 (2014).

[77] J.F. Harrison, “Electronic structure of the transition metal nitrides TiN, VN, and CrN,” J. Phys. Chem. **100**(9), 3513–3519 (1996).

[78] M. Farber, and R.D. Srivastava, “Effusion-mass spectrometric study of thermodynamic properties of vanadium and vanadium nitride,” J. Chem. Soc. Faraday Trans. 1 Phys. Chem. Condens. Phases **69**(0), 390–398 (1973).

[79] J.F. Harrison, “Electronic structure of the transition metal nitrides TiN, VN, and CrN,” J. Phys. Chem. **100**(9), 3513–3519 (1996).

[80] F. Furche, and J.P. Perdew, “The performance of semilocal and hybrid density functionals in 3d transition-metal chemistry,” J. Chem. Phys. **124**(4), 044103 (2006).

[81] R. Grabowski, S. Pietrzyk, J. Sloczyński, F. Genser, K. Wcislo, and B. Grzybowska-wierkosz, “Kinetics of the propane oxidative dehydrogenation on vanadia/titania catalysts from steady-state and transient experiments,” Appl. Catal. A Gen. **232**(1–2), 277–288 (2002).

[82] L. Delrez, A. Santerne, J.M. Almenara, D.R. Anderson, A. Collier-Cameron, R.F. Díaz, M. Gillon, C. Hellier, E. Jehin, M. Lendl, P.F.L. Maxted, M. Neveu-VanMalle, F. Pepe, D. Pollacco, D. Queloz, D. Ségransan, B. Smalley, A.M.S. Smith, A.H.M.J. Triaud, S. Udry, V. Van Grootel, and R.G. West, “WASP-121 b: A hot Jupiter close to tidal disruption transiting an active F star,” Mon. Not. R. Astron. Soc. **458**(4), 4025–4043 (2016).

[83] L.K. McKemmish, S.N. Yurchenko, and J. Tennyson, “ExoMol line lists - XVIII. The high-temperature spectrum of VO,” Mon. Not. R. Astron. Soc. **463**(1), 771–793 (2016).

[84] G. Balducci, G. Gigli, and M. Guido, “Thermochemical properties of the gaseous molecules VO, VO2, and V2O4,” J. Chem. Phys. **79**(11), 5616–5622 (1983).

[85] J.B. Pedley, and E.M. Marshall, “Thermochemical Data for Gaseous Monoxides,” J. Phys. Chem. Ref. Data **12**(4), 967–1031 (1983).

[86] D.M. Merriles, A. Sevy, C. Nielson, and M.D. Morse, “The bond dissociation energy of VO measured by resonant three-photon ionization spectroscopy,” J. Chem. Phys. **153**(2), (2020).

[87] E. Miliordos, and A. Mavridis, “Electronic structure of vanadium oxide. Neutral and charged species, VO0,±,” J. Phys. Chem. A **111**(10), 1953–1965 (2007).

[88] M. Pykavy, and C. van Wüllen, “Multireference correlation calculations for the ground states of VO+/0/- using correlation consistent basis sets,” J. Phys. Chem. A **107**(29), 5566–5572 (2003).

[89] R.S. Ram, P.F. Bernath, and S.P. Davis, “Infrared emission spectroscopy of the [10.5]5Δ-X5Δ system of VF,” J. Chem. Phys. **116**(16), 7035–7039 (2002).

[90] C. Koukounas, S. Kardahakis, and A. Mavridis, “Ab initio investigation of the ground and low-lying states of the diatomic fluorides TiF, VF, CrF, and MnF,” J. Chem. Phys. **120**(24), 11500–11521 (2004).

[91] J.M. Behm, D.J. Brugh, and M.D. Morse, “Spectroscopic analysis of the open 3d subshell transition metal aluminides: AlV, AlCr, and AlCo,” J. Chem. Phys. **101**(8), 6487–6499 (1994).

[92] A. Sevy, J.J. Sorensen, T.D. Persinger, J.A. Franchina, E.L. Johnson, and M.D. Morse, “Bond dissociation energies of TiSi, ZrSi, HfSi, VSi, NbSi, and TaSi,” J. Chem. Phys. **147**(8), 084301 (2017).

[93] R. Li, and W.J. Balfour, “Transition metal monophosphides: Electronic spectra of TiP, VP and CrP,” Chem. Phys. Lett. **403**(1–3), 102–106 (2005).

[94] G.S.M. Tong, G.H. Jeung, and A.S.-C. Cheung, “Theoretical studies of the first-row transition metal phosphides,” J. Chem. Phys. **118**(20), 9224–9232 (2003).

[95] W. Jiang, M.L. Laury, M. Powell, and A.K. Wilson, “Comparative study of single and double hybrid density functionals for the prediction of 3d transition metal thermochemistry,” J. Chem. Theory Comput. **8**(11), 4102–4111 (2012).

[96] T.P. Owzarski, and H.F. Franzen, “High temperature mass spectrometry, vaporization, and thermodynamics of vanadium monosulfide,” J. Chem. Phys. **60**(3), 1113–1117 (1974).

[97] J.G. Edwards, M. Pelino, and J.S. Starzynski, “Vapor pressures, vaporization reactions, and thermodynamics of vaporization of VS(s),” J. Chem. Phys. **79**(5), 2351–2355 (1983).

[98] J.P. Botor, and J.G. Edwards, “Thermodynamics of VS(s) and its equilibrium vapor by Knudsen-cell mass spectrometry,” J. Chem. Phys. **81**(4), 2185–2186 (1984).

[99] C.W. Bauschlicher, and P. Maitre, “Theoretical study of the first transition row oxides and sulfides,” Theor. Chim. Acta **90**(2–3), 189–203 (1995).

[100] Z.J. Wu, M.Y. Wang, and Z.M. Su, “Electronic structures and chemical bonding in diatomic ScX to ZnX (X = S, Se, Te),” J. Comput. Chem. **28**(3), 703–714 (2007).

[101] R. Petz, and A. Lüchow, “Energetics of diatomic transition metal sulfides ScS to FeS with diffusion quantum Monte Carlo,” ChemPhysChem **12**(10), 2031–2034 (2011).

[102] D.L. Hildenbrand, K.H. Lau, J. Perez-Mariano, and A. Sanjurjo, “Thermochemistry of the gaseous vanadium chlorides VCl, VCl2, VCl3, and VCl4,” J. Phys. Chem. A **112**(40), 9978–9982 (2008).

[103] D.T. Halfen, L.M. Ziurys, and J.M. Brown, “Fine structure and hyperfine perturbations in the pure rotational spectrum of the VCl radical in its X5 Δ r state,” J. Chem. Phys. **130**(16), 164301 (2009).

[104] S. Kardahakis, and A. Mavridis, “First-principles investigation of the early 3d transition metal diatomic chlorides and their ions, ScCl0= TiCl0, ±, VCl0’ and CrCl0±,” J. Phys. Chem. A **113**(24), 6818–6840 (2009).

[105] A. Karton, "Post-CCSD(T) contributions to total atomization energies in multireference systems," J. Chem. Phys. **149**(3), 034102 (2018).

[106] A. Karton, "Effective basis set extrapolations for CCSDT, CCSDT(Q), and CCSDTQ correlation energies," J. Chem. Phys. **153**(2), 024102 (2020).

[107] B. Chan, A. Karton, K. Raghavachari, and L. Radom, "Heats of formation for CrO, CrO 2, and CrO 3: An extreme challenge for black-box composite procedures," J. Chem. Theory Comput. **8**(9), 3159–3166 (2012).

[108] T.J. Lee, and P.R. Taylor, "A diagnostic for determining the quality of single-reference electron correlation methods," Int. J. Quantum Chem. **36**(23 S), 199–207 (1989).

[109] T.J. Lee, J.E. Rice, G.E. Scuseria, and H.F. Schaefer, "Theoretical investigations of molecules composed only of fluorine, oxygen and nitrogen: determination of the equilibrium structures of FOOF, (NO)2 and FNNF and the transition state structure for FNNF cis-trans isomerization," Theor. Chim. Acta **75**(2), 81–98 (1989).

[110] C.L. Janssen, and I.M.B. Nielsen, "New diagnostics for coupled-cluster and Møller-Plesset perturbation theory," Chem. Phys. Lett. **290**(4–6), 423–430 (1998).

[111] K.A. Gingerich, "Mass Spectrometric Determination of Bond Energies of High Temperature Molecules," Chimia (Aarau). **26**, 619–623 (1972).

[112] V.. Yungman, *Thermal Constants of Substances Wiley* (New York, 1999).