Accurate Enthalpies of Formation for CrX(g), X = O, OH, and F. A Computational Study

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CrOH(g) is studied for the first time by theory, using accurate configuration interaction (CI) methods in conjunction with large basis sets. The ground and lowest excited state are established for the neutral and singly ionized molecule. The ionization potential is computed to 7.54 ± 0.05 eV, which, when applied to experimental results for $CrOH^+$ [Magnera, T. F.; David, D. E.; Michl, J. *J. Am. Chem. Soc.* **1989**, *111*, 4100. Kang, H.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1986**, *108*, 7502] opens access to experimental data on the bond dissociation energy in Cr−OH. Accurate quantum chemical methods have been applied to the calculation of bond dissociation energies of gaseous CrOH, CrF, and CrO. For the singly bound molecules the values obtained, $D_0(\mathrm{Cr{-}OH}) = 3.74 \pm 0.10$ eV and $D_0(\mathrm{CrF}) = 5.04 \pm 0.10$ eV, constitute the most accurate thermodynamical data available for these compounds. The high accuracy has been realized through the use of a dissociation process which is analogous to electron-attachment induced dissociation, leading to a high degree of cancelation of errors in the calculation of bond strengths in polar systems. In chromium monoxide, higher-than-triply excited configurations are important in the CI expansion, and an extrapolation procedure is applied to take these effects into account. The resulting estimate, $D_0(\mathrm{CrO}) = 4.69 \pm 0.10$ eV, confirms the experimental finding of Kang and Beauchamp [Kang, H.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1986**, *108*, 5663]. Enthalpies of formation are calculated for the title molecules based on the computed bond dissociation energies.

1. Introduction

The gas-phase chemistry of chromium is of importance to properties as diverse as the stability of solid materials[1] and loss of chromium to the environment.[2] Chromium oxides, hydroxides, and halides, as exemplified by the title molecules, are postulated to participate in the release of chromium to the atmosphere during waste incineration processes.[2] Interest in gaseous molecules containing chromium also arises in connection with solid oxide fuel cells (SOFCs). This concept holds great promise of efficient conversion of chemical energy into electricity,[3] but major obstacles remain within material design.[4] One particular problem relates to the stability of the material used to couple single fuel cells into stacks. Both alloys and ceramic materials based on chromium are used as interconnector material,[5] and loss of Cr is attributed to chromium oxo hydroxides.[1,5] The number of chemical species participating in these processes may be large, and in combination with the short lifetimes often found for molecules containing low-coordinate transition metals, this makes characterization of the gas-phase composition difficult. An attractive alternative is to obtain thermodynamical data for the candidate species, and then determine the equilibrium composition of the gas phase at the conditions of the process under study.

Accurate measurements of the enthalpy of formation ($\Delta_f H$) of a short-lived molecule are hard to carry out. During the past 20 years, progress has been made[6] for transition-metal-containing molecules by considering a series of reactions involving the specimen of interest and then to classifying the reactions as being endothermic or exothermic. By relating the reaction energies to enthalpies of formation for reactants and products, it has been possible to bracket the wanted enthalpy of formation. However, the experimental techniques are usually based on a thermodynamical cycle, implying that accurate data are required for all species apart from one to facilitate determination of an unknown datum. In the following, the situation with respect to experimental information concerning the enthalpy of formation of the title molecules, CrO, CrF, and CrOH, will be reviewed briefly.

Only a single experiment is available for the enthalpy of formation for CrOH. Gorokhov et al.[7] used high-temperature Knudsen effusion mass spectrometry to determine K_p for two equilibria involving CrO and CrO_2, in addition to CrOH. They then used the third law and entropies estimated by the molecular constant method to determine the enthalpy of formation for chromium monohydroxide. Two measurements are reported for the bond dissociation energy of $CrOH^+$.[8,9] Combined with accurate values for the ionization potential of chromium and chromium hydroxide, these values may be used to deduce bond energies also for the neutral molecule. However, only wide upper and lower limits to IP(CrOH) were available to the researchers, and even today, the most recent measurement carries error bars of ±0.3 eV.

The stability of chromium monofluoride has been studied by means of Knudsen effusion mass spectrometry,[10−12] and the results were reviewed in ref 12. Kent and Margrave[10] employed an tantalum cell, which is not inert under the conditions of the experiment. Their value for the dissociation energy of CrF probably suffers from this. The two later experiments are both based on an equilibrium between the three lowest chromium fluorides, and essentially links the enthalpies of formation of CrF, CrF_2, and CrF_3. A value for CrF is then computed from prior knowledge of $\Delta_f H$ for the two other species. The accuracy of the thus obtained estimate of $D_0(\mathrm{CrF})$ is determined by the accuracy with which $\Delta_f H$ is known for CrF_2 and CrF_3, and the most reliable estimate is probably the one presented by Boltalina et al.,[12] since it involves a consistent and updated set of enthalpy data for the di- and trifluorides.

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TABLE 1: Experimental Enthalpies of Formation and Dissociation Energies of $CrOH^+$(g) and CrX(g), X = OH, F, and O[a]

ref	$\Delta_f H°_{0K}$	D_0
	$CrOH^+$	
Kang and Beuchamp[9]		3.17 ± 0.22
Magnera et al.[8]		3.22 ± 0.13
	CrOH	
Gorokhov et al.[7]	62 ± 14	3.86 ± 0.15[b]
Ebbinghaus (reevaluation)[17]	81 ± 8[c]	3.66 ± 0.09
	CrF	
Kent and Margrave[10]	32 ± 15	4.57 ± 0.15[c]
Malkerova et al.[11]	41 ± 21[b,d]	4.47 ± 0.21
Boltalina et al.[12]	−50 ± 20[b,e]	5.42 ± 0.20
Ebbinghaus (reevaluation)[f]	19 ± 10[c]	4.70 ± 0.11
	CrO	
Grimley et al.[13]	220 ± 29	4.38 ± 0.30[b]
Balducci et al.[14]	206 ± 10	4.52 ± 0.09[b]
Kang and Beauchamp[15]	182 ± 10	4.77 ± 0.09[b]
Georgiadis and Armentrout[16]	200 ± 7	4.58 ± 0.07[b,g]
Ebbinghaus (reevaluation)[17]	182 ± 9[c]	4.77 ± 0.10

[a] Enthalpies of formation: $\Delta_f H°_{0K}$, in kJ/mol. Dissociation energies: D_0, in eV. [b] Original value. [c] Adjusted to 0 K. [d] Given explicitly by Boltalina et al.,[12] based solely on Malkerova et al.'s data.[11] [e] Partly based on Malkerova et al.'s data,[11] with Boltalina et al.'s improved enthalpies of formation for CrF_2 and CrF_3. [f] Ebbinghaus, B. B. *Combust. Flame* **1995**, *101*, 311. [g] Lower bound.

The value for D_0(CrO) which appears in most reference works is due to Grimley et al. (1961)[13] and is based on a compositional analysis of gaseous equilibria over solid Cr_2O_3. Twenty years later, Balducci et al.[14] used a gas-phase reaction between Cr and WO_3 to determine the bond dissociation energy of CrO. The accuracy of the thus obtained bond dissociation energy is determined by the accuracy of the estimated difference in bond energies between the trioxide and dioxide of tungsten. It is likely that the error bars suggested by Balducci et al. are overly optimistic. The most accurate value of D_0(CrO) is probably due to Kang and Beauchamp,[15] who allowed the chromium oxide cation, CrO^+, to react with unsaturated organic molecules. By controlling the energy of the chromium oxide cation and measuring the energy and abundance of product ions by means of mass spectrometry, they were able to bracket the bond strength of CrO^+. Combined with known values of the ionization potential of the neutral chromium monoxide and atomic chromium, this allows the calculation of bracketing values also of the bond strength in CrO. A strict lower bound of 4.71 eV and an upper bound of 4.82 eV were obtained. However, due to competing reaction channels, the upper bound is somewhat uncertain. Georgiadis and Armentrout[16] repeated and confirmed the experiments by Kang and Beauchamp. Furthermore, they used a side reaction to establish another lower bound to the dissociation energy. This value was also presented as an estimate of the bond strength, and is included in Table 1. Ebbinghaus[17] reevaluated the data obtained by Grimley et al.,[13] and based his determination of the dissociation energy of CrO on data which minimize internal inconsistency. However, it is doubtful whether significantly tighter error bars may be attached to the reevaluated dissociation energy than originally estimated by Grimley et al.

From the data presented in Table 1 and reviewed above, a considerable spread is immediately apparent among available experimental values of $\Delta_f H$ for each of the three molecules CrO, CrF, and CrOH. The inaccuracy stems from the lack of precise bond dissociation energies for these molecules. At this point, computational chemistry offers an attractive alternative to experiment, in that bond energies may be computed for a single molecule without the need of a thermochemical cycle. In the present contribution, high-level ab initio quantum chemical methods are used to form accurate enthalpies of formation for the title chromium compounds. Furthermore, a reliable estimate of IP(CrOH) is computed, which subsequently is used to derive estimates of D_0(Cr−OH) on the basis of experimental bond energies of the corresponding cation, cf. Table 1. For chromium hydroxide, the present work represents the first report on the electronic and geometric structure of the molecule. Work in progress aims at providing enthalpies of formation for a series of molecules obeying the generic formula $CrO_m(OH)_n$.

TABLE 2: Overview of Computational Strategies

	Approach I	Approach II
geometry optimization	UB3LYP/TZD1P	ACPF/ANO-M
relativity	1. order PT: RHF/TZD2P	
reference states	UHF	RHF
vSD	UCCSD/TZD2P	MCPF/ANO-M
vT	UCCSD(T)/TZD2P	
vΔBasis	UCCSD(T)/SEG-L	MCPF/ANO-L
cSDT	UCCSD(T)/SEG-L	MCPF/ANO-L

2. Computational Details

To increase confidence in the results, two different computational strategies, denoted by capital roman numerals, have been applied throughout this work. The main features of the two approaches are summarized in Table 2, one important difference being that orbitals are optimized separately for alpha and beta spin in approach I, whereas approach II is kept strictly in a restricted formalism. All calculations in approach I (II) were performed with the GAUSSIAN 94[18] (MolCas-3)[19] suite of programs.

2.1. Geometry Optimization. In approach I, geometry optimizations and determination of vibrational frequencies were performed using a hybrid gradient-corrected density functional method, Becke3LYP,[20] as implemented in GAUSSIAN 94. Convergence criteria were set to 4.5×10^{-4} and 1.8×10^{-4} au for the maximum gradient and displacement, respectively. Molecular orbitals were formed in atom-centered spherical harmonic bases of valence triple-ζ quality, extended by diffuse and polarization functions. For Cr, Wachters primitive basis[21] was used with the 4p exponents multiplied by 1.5 and with a set of diffuse d functions ($\alpha_d = 0.0912$) added. The contraction of (14s11p6d) follows Wachters Scheme 3, except for decontraction of the second d function, leading to a [8s6p4d] contracted set. The main group elements were described by Huzinagas primitive sets[22] (H, (5s); O, F, (10s6p)) contracted according to Dunning[23] (H, [3s]; O, F, [5s3p]) and augmented by diffuse functions (H, s; O, F, s,p) in an even-tempered manner. A single set of polarization functions were added to H ($\alpha_p = 1.0$), O ($\alpha_d = 0.85$), and F ($\alpha_d = 1.00$), to form the TZD1P sets.

In approach II, molecular geometries were obtained in the single-reference average coupled-pair functional[24] approximation (ACPF). The actual search for minima were performed by means of MolOpt,[25] which is an object-oriented Unix script utility which automates optimization based on energy evaluations only. Typically, geometry parameters were converged to 0.5 pm and degrees for bond lengths and angles, respectively. Atomic natural orbital (ANO) bases comparable to the TZD2P sets in flexibility were used. These sets are referred to as ANO-M (medium), and contain the following contractions: H, (8s4p)/[3s2p];[26] O and F, (14s9p4d)/[4s3p2d]; [26] and Cr, (21s15p10d6f)/[6s5p4d2f].[27]

2.2. Energy Evaluation. Final energies were computed by means of coupled-cluster expansions[28] in approach I, either including only singly and doubly excited determinants

(UCCSD)[29−32] relative to an unrestricted Hartree−Fock (UHF) reference, or alternatively, including the contributions from triply excited determinants by means of perturbation theory; UCCSD(T).[28] In approach II, dynamic correlation was included in terms of the modified coupled pair functional (MCPF)[33] method, which employs a single reference state and is close to size-consistent.

To increase resolution, the electronic energy is decomposed into a number of contributions when estimating observables such as bond dissociation energies, ionization potentials, and electron affinities. The starting point is always taken to be the independent particle model, either RHF or UHF, where large bases[52] are used to ensure energies essentially at the Hartree−Fock limit. Effects from electron correlation are split into four terms, denoted by vSD, vT, cSDT, and vΔBasis, respectively. The vSD term is the most important one, and includes valence electron correlation as recovered by CI expansions limited to singly and doubly excited determinants. When computing vSD in approach I, the basis sets used for geometry optimizations (TZD1P) were extended to form the TZD2P sets by employing two sets of polarization functions on each atomic center. For the main group elements, the two polarization functions were formed by multiplying the polarization exponents listed above for TZD1P by $\sqrt{3}$ and $1/\sqrt{3}$, respectively. For chromium, two sets of contracted f functions were adopted from ref 27. In approach II, ANO-M sets were used to form the vSD estimates.

Next, the importance of higher excitations (vT) is examined for the valence electrons by including triple excitations in approach I. vT is thus formed as the difference between UCCSD(T) and UCCSD energies, as computed using TZD2P bases. The correlation method used in approach II, MCPF, is usually found to perform intermediate between RCCSD and RCCSD(T), and thus contains some contribution from triple excitations. Still, some tests were made with multireference ACPF to include higher excitations in CrOH. Only after optimizing orbitals for a weighted average of the four lowest roots (weights 16:1:1:2) in a CASSCF active space containing all Cr 3d- and 4s-derived orbitals, was any appreciable energy lowering obtained. This rather exotic procedure proved necessary in order to obtain orbitals suitable to describe the contribution from both the ^{6}D and ^{6}S states of Cr$^+$ in this molecule. However, the resulting energy lowering was only 0.06 eV for CrOH, and since its inclusion only for the bound molecules would probably lead to a biased description of the bond strengths, it has not been added to any energies to be discussed in this work.

cSDT denotes the contribution from core−core and core-valence electron correlation, where "core" is taken to mean Cr 3s and 3p. Operationally, this contribution is obtained by computing the quantity in question (D_0, IP, EA) twice with the methods and bases indicated in Table 2: first correlating both valence and core electrons, and next, correlating only the valence electrons. The difference between these results then gives cSDT. To compute this term, larger basis sets than those used this far have to be employed. For use in approach I, large segmented bases (SEG-L) were composed as follows. For Cr, the set described for TZD2P was decontracted to make the five outermost p and all six sets of d functions primitive. Furthermore, four (two) sets of f (g) functions were generated by splitting the "4f" ("5g") function from ref 27 into contraction lengths of 2, 1, 1, and 2 (2 and 2). The innermost f function provides angular correlation of the 3s and 3p orbitals. The resulting Cr basis set may be summarized as (14s11p6d6f4g)/[8s7p6d4f2g]. As for the ligands, correlation consistent bases classified as aug-cc-pVTZ by Dunning[34] were chosen. In approach II, ANO-M was extended by increasing the number of contracted functions significantly, while keeping the primitive sets. The resulting bases, denoted by ANO-L,[27,26] were formed by adding one set of s, p, and d functions to each of O, F, and Cr, in addition to two extra sets of f functions to chromium. Furthermore, the bases were extended to higher angular momentum as follows: H, (3d)/[1d];[26] O and F, (3f)/[2f];[26] and Cr, (4g)/[3g].[27] Equivalency of the large bases employed in approaches I and II was checked for by computing MCPF estimates of cSDT, which gave essentially identical values irrespective of whether SEG-L or ANO-L bases were used. Furthermore, the basis set superposition error (BSSE) is similar for these bases, and at the core-correlated level of accuracy, a counter-poise correction of 0.05 eV (0.06 eV) was computed in approach I (approach II), using ghost orbitals at the equilibrium distance in CrO, thus providing upper limits to the BSSE in CrOH and CrF. The resulting numbers are taken as an indication that BSSE effects are small, and the counterpoise correction has not been included in any computed bond dissociation energies.

Extension of the one-particle bases leads to recovery of a larger fraction of the valence correlation energy, and the resulting energetic effect is included in the term vΔBasis. In approach I, this correction is determined at the valence-correlated UCCSD(T) level of accuracy as the difference between results obtained by basis sets SEG-L and TZD2P. Correspondingly, in approach II, MCPF was used in conjunction with basis sets ANO-L and ANO-M.

Based on the RHF wave function, relativistic effects are included by means of first-order perturbative estimates of the mass−velocity and Darwin terms.[35,36] The TZD2P sets were used, due to their flexibility[37] in the outer core: Cr 3s3p.

3. Results and Discussion

3.1. Electronic States. In this section, emphasis is put on establishing the ground state and the energy required to reach the first excited state of the title molecules. For CrO and CrF, the ground state, as well as several excited states, have been reported in the literature. The ground state[38] of chromium monoxide, X$^5\Pi$, is dominated by the configuration $(8\sigma)^2(9\sigma)^2(3\pi)^4(10\sigma)^1(1\delta)^2(4\pi)^1(11\sigma)^0$. Orbitals 9$\sigma$ and 3π are bonding orbitals, whereas orbitals 4π and 11σ have antibonding character. The first excited quintet state, A$^5\Sigma^+$, is found[39] 1.03 eV above the ground state, and states of higher multiplicity are predicted to be even further up in energy.[40] The ground state[41] of CrF is X $^6\Sigma^+$, having one additional electron in 4π compared to the ground state of CrO. The lowest excited states, A$^6\Sigma^+$ and B$^6\Pi$, are found to have term values (T_e) of 1.19 and 0.97 eV, respectively.[42]

For CrOH the ground state, as well as the first excited sextet and quartet states within each of the two irreducible representations in Cs-symmetry, have been determined. The ground state is found to be ^{6}A′, which apart from changes due to the lower symmetry, fits the description given for the ground state of CrF. This holds true also for the first excited state, which in CrF is the doubly degenerate B$^6\Pi$ state. In the bent CrOH molecule, this state is split into ^{6}A″+ ^{6}A′, of which the former is the lowest in energy by some 0.3 eV. It is obtained by promoting one electron from the 4π-derived orbital perpendicular to the molecular plane, to an orbital of σ antibonding character between chromium and oxygen ("11σ" in the orbital sequence laid out for CrO above). At the valence correlated level of accuracy, single-reference ACPF leads to an estimate of the adiabatic excitation energy of 0.74 eV. It is likely that the excitation energies from "4π" will increase as the description of the electron correlation is improved, due to larger multireference

TABLE 3: Structure Parameters and Vibrational Frequencies

	structures				frequencies (cm^{-1})		
state	bond lengths (Å) or angles (deg)	theory I[a]	theory II[a]	exptl (r_e)	theory I[a] (ω_e)	exptl (ω_e)	exptl ($\omega_e x_e$)
OH $^2\Pi$	R_{O-H}	0.978	0.971	0.971[b]	3686	3735.2[b]	82.8[b]
OH^- $^1\Sigma^+$	R_{O-H}	0.969	0.967	0.970[c]	3718	(3700)	
CrOH $^6A'$	R_{Cr-O}	1.838	1.835		628		
	R_{O-H}	0.964	0.959		3833		
	∠CrOH	121.31	121.9		608		
CrF $^6\Sigma^+$	R_{Cr-F}	1.808	1.796	1.784[d]	632	664.1[d]	4.2[d]
CrO $^5\Pi$	R_{Cr-O}	1.622		1.618[e]	864	898.5[e]	6.7[e]

[a] Roman numerals indicates the computational approach taken. [b] Reference 43. [c] Huber, K. P.; Herzberg, G. *Constants of Diatomic Molecules*; Van Nostrand Reinholdt: New York, 1979. [d] Reference 42. [e] Reference 38.

TABLE 4: Computed First Ionization Potentials[a] of CrOH, $^5A' \leftarrow {}^6A'$, and Cr, $^6S \leftarrow {}^7S$

	IP(CrOH)		IP(Cr 4s)	
approach	I	II	I	II
HF	6.81	6.84	5.90	5.90
relativity	0.09	0.09	0.11	0.11
vSD	0.45	0.42	0.50	0.52
vT	0.00		0.04	
cSDT	0.16	0.21	0.18	0.16
vΔBasis	0.03	0.02	0.03	0.02
sum	7.54	7.57	6.76	6.71
exptl	7.5−7.9		6.76[b]	

[a] All energies in eV. [b] Moore, C. E. Atomic Energy Levels. *Natl. Bur. Stand.* **1983**, 467.

effects for the ground state. The lowest quartet states are found approximately 1.1 eV above the ground state.

Among the title molecules the lowest energy separation between ground and first excited state is found for chromium hydroxide. If this separation is taken to be 0.74 eV, the contribution from the first excited state to the enthalpy of CrOH amounts to 1 kJ/mol at a temperature of 2000 K. Thus, within the error bars accepted in this work, the electronic partition function may be approximated by the degeneracy of the ground state for CrO, CrF, and CrOH.

As pointed out in the Introduction, some of the experiments carried out for CrOH are designed to measure the bond strength of $CrOH^+$ rather than that of the neutral molecule. To proceed, an accurate value of the ionization potential of CrOH is therefore warranted. The highest occupied molecular orbital in CrOH is mainly of Cr 4s character, albeit somewhat hybridized with $3d_\sigma$ and $4p_\sigma$ in order to reduce repulsion to the ligand. In the first ionization step of chromium hydroxide, the single electron occupying this orbital is removed to produce the ground $^5A'$ state of $CrOH^+$. The metal−ligand bond is reduced by 0.07 Å, and ∠CrOH opens up by 12° upon ionization, as optimized at the ACPF level of accuracy. In Table 4, the various contributions to the energy of the adiabatic ionization process are reported and compared to counterparts for the ionization of 4s in atomic chromium. Close agreement is revealed between the two ionization processes, and also between the two computational models applied. The atomic ionization potential is well-known experimentally, and this value is reproduced by the calculations. This lends credibility to the computed value for IP(CrOH), which is placed at an energy of 7.54 and 7.57 eV by the two computational approaches used. We believe that the most accurate estimate is obtained in approach I, and we expect 7.54 eV to be within 0.05 eV of the true adiabatic ionization potential of CrOH. Experimentally, two different studies[9,7] derive lower bounds for IP(CrOH) at 6.9 and 7.5 eV and upper bounds at 7.9 and 8.1 eV, respectively. Taken together, the ionization potential is confined to the interval [7.5,7.9] eV, which agrees well with computed value. However, the computed value of IP(CrOH) is given with substantially lower error bars.

3.2. Vibrational Degrees of Freedom. In Table 3, structural parameters and vibrational frequencies are reported for CrX, X = OH, F, and O, as well as for the hydroxyl radical and anion, as obtained in this work. For the diatomic molecules, experimental results are available for comparison. Very good agreement is obtained between the theoretical methods, and between theory and experiment, with respect to bond lengths. The largest difference is found for chromium fluoride, where approach I (approach II) leads to a bond length too long by 0.024 Å (0.012 Å) compared to experiment. For CrOH, the agreement between geometry parameters obtained by approach I and II is better, and it is likely that the presented molecular constants for CrOH are accurate to within 0.01 Å and 2°.

Turning to the vibrational spectra, the computed harmonic frequencies are seen to underestimate the experimental frequencies slightly. The difference is the largest for the hydroxyl radical, which, however, displays a large anharmonic correction of $\omega_e x_e = 82.8$ cm^{-1}.[43] The zero-point vibrational energy (ZPVE) is determined as $G(0) = {}^1/_2\omega_0$, where $\omega_0 = \omega_e - {}^1/_2\omega_e\chi_e$. Very similar estimates of the ZPVE are therefore obtained whether the experimental values are used, or the computed harmonic frequency with anharmonicity neglected.

The contribution from anharmonicity is negligible for CrF and CrO, and the computed harmonic frequencies are underestimated by some 4.5% relative to experimental values. This observation is used to correct the estimate of the Cr−OH stretching frequency in CrOH, by adding 4.5% to its computed value. On the other hand, the CrO−H frequency is employed without corrections when computing thermodynamic quantities. This may be regarded as an ad hoc procedure for inclusion of anharmonicity. Hence, when computing thermodynamic properties, experimental frequencies are employed where available (OH, CrO, and CrF), and the following computed frequencies are used for CrOH: 608 cm^{-1}, 656 cm^{-1}(scaled), and 3833 cm^{-1}.

3.3. Bond Dissociation Energies of Chromium Hydroxide and Chromium Fluoride. By definition, the bond dissociation energy D_0(Cr−X) is the energy required to form neutral, ground state fragments Cr(g) and X(g) from CrX(g) in its ground state, at 0 K and all partial pressures maintained at 1 atm. In Table 5, the computed energies of these reactions are broken down into a number of terms for X = OH and F. The upper four rows report on a conventional theoretical description; essentially a size-consistent valence configuration interaction calculation including singly and doubly excited determinants, with relativistic and vibrational corrections added. The subsequent three rows in the table describe a refined treatment: inclusion of triple excitations in the valence CI, correlation of the chromium 3s3p

TABLE 5: Decomposition of D_0(CrX), X = OH and F, as Computed by Dissociating into Neutral Fragments, along with Electron Affinities of the Corresponding Ligands[a]

	D_0(CrOH)		EA(OH)		D_0(CrF)		EA(F)	
approach	I	II	I	II	I	II	I	II
HF	2.15	2.18	−0.27	−0.13	3.35	3.37	1.18	1.31
relativity	0.15	0.15	−0.01	−0.01	0.15	0.15	−0.01	−0.01
ZPVE	−0.09	−0.09			−0.04	−0.04		
vSD	1.16	1.20	1.68	1.62	1.24	1.29	1.85	1.76
vT	0.15		0.14		0.13		0.13	
cSDT	−0.05	0.13			−0.08	0.10		
vΔBasis	0.16	0.08	0.18	0.08	0.16	0.07	0.14	0.09
sum	3.64	3.64	1.72	1.57	4.91	4.93	3.28	3.15
exptl	3.86		1.829[b]		5.42		3.401[c]	

[a] All energies in eV. [b] Celotta, R. J.; Bennet, R. A.; Hall, J. L. *J. Chem. Phys.* **1974**, *60*, 1740. [c] Lide, D. R., Ed. *CRC Handbook of Chemistry and Physics*, 76th ed.; CRC Press: Boca Raton, 1995.

TABLE 6: Decomposition of D_0(CrX),[a] X = OH and F, as Computed[b] by Dissociating into Ions, along with the Ionization Potential of Chromium

	D_0(CrOH)		D_0(CrF)		IP(Cr 3d)	
approach	I	II	I	II	I	II
HF	2.87[b]	2.85[b]	4.21[b]	4.17[b]	6.91	7.00
relativity	−0.01	−0.01	−0.01	−0.01	−0.17	−0.17
ZPVE	−0.09	−0.09	−0.04	−0.04		
vSD	0.60	0.69	0.51	0.64	1.11	1.12
vT	0.08		0.06		0.06	
cSDT	0.18	0.26	0.15	0.24	0.24	0.14
vΔBasis	0.01	0.02	0.05	0.01	0.03	0.03
sum	3.64	3.73	4.93	5.01	8.18	8.11
exptl	3.86		5.42		8.29[c]	

[a] All energies in eV. [b] Adjusted to the neutral asymptote by subtracting the experimental values of IP(Cr 3d) − EA(X) = 6.46 and 4.89 eV for X = OH and F, respectively. [c] Moore, C. E. Atomic Energy Levels. *Natl. Bur. Stand.* **1983**, 467.

electrons, and increasing the one-particle bases to include up through g functions on Cr. The discussion will focus on the numbers obtained by approach I, with the comparison of the two theoretical approaches postponed to the end of this section.

The valence SDCI level of accuracy is sufficient to give a useful estimate of D_0 of the isoelectronic molecules CrOH and CrF. However, a refined treatment increases the estimates of the bond dissociation energies by 0.26 and 0.21 eV, respectively, which are considerable contributions when aiming for high accuracy. In fact, the magnitude of these corrections suggests that one must expect important contributions also from quadruply excited configurations, as well as from increasing the bases further. This anticipation is supported by the numbers presented in Table 5 for the electron affinities of OH($^2\Pi$) and F(^{2}P). For these species, the refined treatment cuts the difference between the computed and experimental electron affinity by 0.32 and 0.27 eV, leaving the computed electron affinities short by some 0.1 eV for both ligands.

The analogy between bond dissociation energies and electron affinities may be taken even further for the present systems. A close agreement is found for the numerical values of the individual terms in the refined model (vT and vΔBasis) between the bond dissociation energies of CrOH and CrF, on one hand, and electron affinities of the corresponding ligands on the other. This suggests that the higher order terms are necessary primarily to improve the description of the negatively charged ligands in the molecule.

When computing bond energies by quantum mechanical methods, it is, as pointed out by Bauschlicher et al.,[44] advantageous to choose a dissociation asymptote such that the resulting fragments correspond as closely as possible to the electronic structure of the molecule. Such a choice facilitates optimal cancelation between the errors made in describing the molecule in its equilibrium geometry and those made when describing the products of the dissociation reaction. To obtain the bond dissociation energy, the computed energy must be adjusted by an amount corresponding to the energy released upon relaxing the dissociation products to their neutral, ground states. In view of our experience from the neutral asymptote, a good choice may be to consider dissociation of CrX(g) into its constituent ions. This view is corroborated by performing a Mulliken analysis of the electron distribution in the title molecules. In the molecules considered here, chromium carries a positive charge of approximately $^1/_2$ e.[53] Furthermore, in the singly bound molecules, the metal may be described as a superposition of Cr(^{7}S; 4s^{1}3d^5) and Cr$^+$(^{6}D; 4s^{1}3d^4).[4] It is noteworthy that the ground state of the chromium cation (^{6}S; 3d^5) plays only a minor role in the molecules, the rationale being that population of d_σ, as required in ^{6}S, would introduce excessive repulsion to the negatively charged ligand.

In Table 6, bond energies are computed according to heterolytic dissociation, to Cr$^+$(^{6}D) and singly charged ligands; OH$^-$($^1\Sigma^+$) and F$^-$(^{1}S), for CrOH and CrF, respectively. The thus computed bond dissociation energies are resolved into its various electronic components, as done above for dissociation to neutral fragments. To obtain values of D_0(Cr−X), dissociation energies are adjusted to the neutral asymptote by subtracting the experimental energy required to ionize the d shell in chromium, IP(Cr 3d), and adding the electron affinity of the ligand in each case. First, it should be noted that the numbers making up estimates of D_0(Cr−X) in Table 6 are rather similar to the corresponding values in Table 5, computed by dissociating to neutral fragments. This is true with respect to the accuracy of the valence SDCI model, the importance of an extended treatment, and the resulting estimates of bond dissociation energies. As such, this is a disappointment, in that the extra

TABLE 7: Decomposition of D_0(CrX),[a] X = OH and F, as Computed[b] According to a Dissociative Electron Attachment Reaction

	D_0(CrOH)		D_0(CrF)	
approach	I	II	I	II
HF	4.24	4.13	5.58	5.46
relativity	0.16	0.16	0.16	0.16
ZPVE	−0.09	−0.09	−0.04	−0.04
vSD	−0.51	−0.42	−0.60	−0.47
vT	0.02		0.00	
cSDT	−0.05	0.13	−0.08	0.10
vΔBasis	−0.02	−0.01	0.03	−0.02
sum	3.74	3.90	5.04	5.19
exptl	3.86		5.42	

[a] All energies in eV. [b] Adjusted to the neutral asymptote by adding the experimental values of EA(X), as listed in Table 5.

TABLE 8: Decomposition of D_0(CrO)[a] As Computed According to a Dissociation to Different Asymptotes

	neutral	EA(O)	ionic[b]	DEA[c]
UHF	0.31	−0.57	0.98	2.35
Relativity	0.26	−0.01	0.09	0.26
ZPVE	−0.06		−0.06	−0.06
vSD	3.11	1.59	2.63	1.51
vT	0.52	0.12	0.47	0.40
cSDT	0.00		0.24	0.00
vΔBasis	0.25	0.19	0.09	0.06
sum	4.39	1.31	4.44	4.54
PCI-85	4.78	1.43	4.66	4.81
PCI-93	4.68	1.46	4.69	4.69
exptl	4.77	1.461[d]	4.77	4.77

[a] All energies in eV. [b] Adjusted to the neutral asymptote by subtracting the experimental values of IP(Cr 3d) − EA(O) = 6.83 eV. [c] Adjusted to the neutral asymptote by adding the experimental value of EA(O) [d] Lide, D. R., Ed. *CRC Handbook of Chemistry and Physics*, 76th ed.; CRC Press: Boca Raton, 1995.

cancelation of errors sought, has evidently not taken place. Also reported in Table 6 is the computed ionization potential of Cr 3d. The correspondence between each term in the refined description of IP(Cr 3d) on one hand, and D_0(Cr−OH) and D_0(CrF) on the other, is striking. This numerical coincidence suggests that in CrOH and CrF, chromium behaves as in its neutral ground state, rather than a positive cation. Furthermore, considering the error still present in the Cr 3d ionization potential even after an extended theoretical description, it is likely that the bond dissociation energies of CrOH and CrF are still underestimated.

Combining the findings from Tables 5 and 6, it seems as if chromium energetically behaves as the neutral atom, and at the same time the ligands behave as being singly negatively charged. Put differently, contrary to a fully ionic picture, it seems that both constituents in CrX have full energetic advantage of one of the electrons originating from chromium. Dissociation of such a molecule into neutral fragments would suffer from a poor description of the electron affinity of X in the molecule, whereas dissociation to singly charged fragments would suffer from deficiencies in the ionization potential of the metal. This is precisely what is found for the title molecules in this study. Furthermore, this analysis suggests that the optimal dissociation asymptote should retain the shared electron attached to both Cr^+ and the ligand. This is of course only possible if an extra electron is supplied, i.e., one should consider the process of dissociative electron attachment (DEA), viz.

$$CrX + e^- \rightarrow Cr(^7S) + X^- \qquad (1)$$

The energy of reaction 1 is given by D_0(Cr−X) − EA(X), and in Table 7 this relation has been used to compute the bond dissociation energy of CrOH and CrF, based on accurate calculations of the energy of the dissociative electron attachment process. This approach leads to significantly larger estimates of the bond energies both at the Hartree−Fock and valence singly and doubly excited CI level of accuracy than previously obtained when using asymptotes corresponding to homolytic and heterolytic dissociation. Moreover, application of the DEA reaction leads to very small correction terms; in fact, the contribution from extending the level of electron correlation and improving the bases drops to −0.05 eV in the corresponding estimates of D_0(Cr−OH) and D_0(Cr−F), using computational approach I. The magnitude of these corrections suggest that the contribution from extending the computational model further will be small.

At this point, corresponding results obtained by approach II will be considered. First, it is important to note that the use of different reference states in the two approaches, i.e., UHF vs RHF, precludes a term-by-term correspondence between approach I and II. Still, in Table 5, it appears that UCCSD(T) and MCPF leads to very similar estimates of the bond dissociation energy of CrOH and CrF. However, the description of the electron affinity of the ligands is clearly inferior in approach II, and this is likely to affect also the description of the bound molecules. When the dissociation is taken to a limit which involves a negatively charged ligand, presumably reducing the effect of a flaw in the description of EA(X), a notable discrepancy evolves between approach I and II with respect to the bond dissociation energies, making a maximum of 0.16 eV for CrOH when applying the DEA asymptote, see Tables 6 and 7. What then are the reasons for this discrepancy? Separate tests show that basis set differences can account for only 0.02 eV, and that the contribution from triply excited configurations amounts to another 0.02 eV in the bond dissociation energies as computed in approach I by means of the DEA asymptote. The correlation method used in approach II, MCPF, is usually found to perform intermediate between CCSD and CCSD(T), and usually close to the latter.[45] At the valence correlated level of accuracy, we expect the result obtained by the DEA asymptote in approach II to be close to what would have been obtained using a restricted reference state in the CCSD(T) expansion. A relevant observation is that the difference between a restricted and unrestricted description is accentuated in the DEA asymptote, since there is essentially no energy difference between UHF and RHF for chromium in its ground state nor for the singly charged ligands OH^- ($^1\Sigma^+$) and F^-(^1S). On the other hand, the bound molecules are stabilized by some 0.1 eV at the UHF level of accuracy compared to RHF. This does, however, not imply severe spin contamination for these systems. Rather on the contrary, the expectation value of S^2 deviates only by 0.007 and 0.005 au for CrOH and CrF, respectively, from their exact values at the UHF level of accuracy, to be further reduced when correlation is introduced in terms of CCSD. Separate test calculations for CrF, invoking restricted CCSD(T), show that the effect of spin restriction is in fact negligible. The important contribution to the difference between approach I and II may therefore be traced to an inadequacy of the MCPF method when it comes to computing core correlation effects.

Hence, our best estimates of D_0(Cr−OH) and D_0(Cr−F) are obtained by means of approach I and the DEA asymptote, and read 3.74 ± 0.10 and 5.04 ± 0.10 eV, respectively. The error bars are based on the convergence properties observed for approach I using the DEA asymptote, the magnitude of the basis set superposition error (see Computational Details), as well as an uncertainty of 0.03 eV in the estimate of relativistic effects. The value for chromium hydroxide agrees well with the most recent experimental estimate, by Gorokhov et al.[7] at 3.86 ±

0.15 eV. When our computed value of IP(CrOH) at 7.54 ± 0.05 eV is combined with experimental values of the bond dissociation energy in the chromium hydroxide cation, two further experimental estimates of D_0(Cr−OH) are obtained as 3.95 ± 0.23 and 4.00 ± 0.14 eV.

Our best value of D_0(Cr−F) is almost 0.4 eV lower than that obtained in the most recent experiment[12]at 5.42 ± 0.20 eV. Given the much closer agreement between theory and experiment for the isoelectronic molecule CrOH, there is little doubt that 5.42 eV is too high. The presently derived value of 5.04 eV is considered the most reliable estimate available for the bond dissociation energy of CrF.

Several empirical schemes have been suggested for relating bond energies of metal halides to those of the corresponding metal hydroxide. Krikorian[46] uses a proportionality relation, suggesting that the bond strength in a metal hydroxide is equal to 83% of the bond strength of the corresponding fluoride. The values derived here amounts to a proportionality of 74%, which serves to exemplify the accuracy to be expected from this kind of rules of thumb. Two research groups have suggested[7,47] that there is a constant difference in bond strength between a metal fluoride and the corresponding hydroxide. Here, this difference is determined to 1.30 eV in the case of chromium, to be compared with average values of 1.39 and 1.37 eV found for main group metals. The agreement is reasonable, given that Bauschlicher et al. found the "constant" to vary by 0.2 eV among alkali and alkali earth metals alone.[48]

3.4. Bond Dissociation Energy of Chromium Monoxide. The charge distribution in CrO is similar to that of CrF, in that chromium carries a positive charge of about half a unit according to Mulliken population analysis of the B3LYP/TZD1P wave function. On the other hand, the electron structure is considerably more complicated in the monoxide than in the fluoride, in that also doubly charged structures, involving Cr^{2+} ($4s^13d^3$), are represented in the wave function, in addition to neutral and singly charged structures. As such, CrO makes an interesting test case for the DEA asymptote for computing the bond dissociation energy. In Table 8, the resulting estimate of D_0(CrO) is decomposed into a number of contributions, as previously done for CrOH and CrF. It is important to note that the contribution from triple excitations, 0.40 eV, is a substantial part of final DEA-based estimate of D_0(CrO). This in sharp contrast to what was the case for the two singly bound molecules, for which the corresponding numbers read 0.01 and 0.00 eV, respectively. Furthermore, for chromium monoxide, the estimate of the bond energy is found to increase monotonously as the theoretical model is improved. Again, this is in contrast to the oscillating convergence seen for CrOH and CrF. Concluding, there is ample reason to believe that quadruple and higher excitations will contribute significantly to increase the estimated bond dissociation energy further from the present estimate of 4.54 eV. For comparison, the corresponding estimates obtained by dissociation to neutral and singly charged fragments read 4.39 and 4.44 eV, respectively.

The discussion above illustrates well the complexity of the chromium−oxygen double bond, and suggests that a converged description of this system is very expensive with present day computers and ab initio techniques. Hence, extrapolation procedures such as those suggested by Gordon and Truhlar,[49] as well as Siegbahn et al.[50] constitute attractive alternatives. The main idea is that by using standardized basis sets in conjunction with a high-quality correlation method, approximately the same fraction of the total correlation effects is recovered, independent of the system. In the present context, such an Ansatz implies that the computed correlation effects (CI_c) may be considered to make a fraction X_f of the total contribution from correlation to the exact bond dissociation energy, i.e., $CI_c = X_f\{D_{0,\text{exact}} - D_{0,\text{HF-limit}}\}$. Ideally, the parameter X_f should be based on data for a large number of systems related to the one of interest. Used in conjunction with ANO-M bases, Siegbahn obtain X_f = 81.4% for the MCPF method in a study of atomization of first row molecules. When applying this value of the scaling factor for the vSD numbers for CrOH and CrF as obtained in approach II, errors in the resulting bond dissociation energies decrease from about 0.3 eV to about 0.03 eV, illustrating the applicability of the extrapolation scheme to the present systems. From the trend in the data reported by Siegbahn, one may expect the corresponding factor for CCSD(T) to be some 2−5% higher than for MCPF, and we adopt a value of 85 ± 3% to be used with vSD+vT numbers in approach I. The extrapolation factor is highly dependent on the degree of basis set saturation, and Siegbahn obtained a value of 94.1% for CCSD(T) when used with ANO bases slightly extended compared to the ANO-L sets used in this study. Since the SEG-L sets are demonstrated to agree closely with ANO-L, a scaling factor of X_f = 93% is adopted for use with our most accurate CCSD(T) energies: vSD+vT+cSDT+vΔBasis.

From calculations on singly charged complexes between methylene and first-row transition metal ions, Siegbahn[51] determined the extrapolation coefficient in the PCI-X approach to 83 and 87% for MCPF and CCSD(T), respectively, in combination with bases of only DZP quality. Clearly, these numbers are high compared to those cited above for first-row molecules, and since they are based on significantly less data, they serve rather to illustrate the spread to expect between optimal scaling factor for various systems. In the study by Siegbahn, the deviation between experimental and extrapolated metal−ligand bond strengths reaches a maximum for $CrCH_2^+$ at a disappointing 0.30 eV. However, this poor performance may at least in part be ascribed to the use of RHF reference states, which implies that correlation effects of both dynamical and nondynamical origin are scaled on an equal footing. In the present work, this problem is reduced by using a UHF reference state.

Based on our most accurate energies, PCI-93 leads to a bond dissociation energy of chromium monoxide of D_0(CrO) = 4.69 ± 0.10 eV. The agreement with the most recent measurement, at 4.77 eV, is gratifying and suggests that the approach taken is justified. The error bars are based on a estimated uncertainty of ±2% in the extrapolation coefficient, in addition to estimates of BSSE and uncertainty in our estimate of relativistic effects. Numbers from the DEA asymptote are preferred when computing this final estimate, since correlation effects are the least for this approach. Extrapolation based on valence-correlated CCSD(T) energies, PCI-85 (±3%), gives a bond dissociation energy of 4.81 ± 0.12 eV, which agrees well with the more elaborate calculation.

3.5. Enthalpies of Formation. On the basis of the recommended bond dissociation energies, reported in the last section; computed and experimental vibration frequencies, enthalpies of formation, and temperature corrections to the enthalpy function are computed for the title molecules. The data are reported in Table 9, along with experimental data for gaseous OH, F, O, and Cr.

4. Conclusions

Accurate quantum chemical methods have been applied to the calculation of bond dissociation energies and enthalpies of formation of gaseous CrOH, CrF, and CrO. For the singly bound molecules the resulting values, D_0(Cr−OH) = 3.74 ±

TABLE 9: Enthalpies of Formation at 0 and 298 K($\Delta_f H^\circ_T$) and Temperature Corrections $H^\circ_{298K} - H^\circ_{0K}$ to the Enthalpy Function[a]

	$\Delta_f H^\circ_{298K}$	$H^\circ_{298K} - H^\circ_{0K}$	$\Delta_f H^\circ_{0K}$
Cr	397.5	6.2	395.4
OH	39.3	8.8	39.1
F	79.4	6.5	77.3
O	249.2	6.7	246.8
CrOH	71.7	10.7	73.7
CrF	−13.1	9.0	−13.6
CrO	190.1	8.8	189.7

[a] All quantities in kJ/mol.

0.10 eV and D_0(CrF) = 5.04 ± 0.10 eV, constitute the most accurate thermodynamical data available for these compounds. The high accuracy has been realized through the use of an asymptote which is analogous to electron attachment induced dissociation, leading to high degree of cancelation of errors in the calculation of bond strengths for ionic systems. For chromium monoxide, the presently derived value of D_0(CrO) = 4.69 ± 0.10 eV verifies the latest experimental estimates of the bond strength.

The present work represents the first study of gaseous CrOH by theoretical methods, and the electronic ground and lowest excited state are determined for the neutral and singly ionized molecule. The ionization potential of CrOH is computed to 7.54 ± 0.05 eV.

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