Theoretical study of the first transition row oxides and sulfides

Charles W. Bauschlicher, Jr., Phillippe Maitre*
NASA Ames Research Center, Moffett Field, CA 94035, USA

Summary. The first transition row oxides and sulfides are studied using several different levels of theory. The calculations show the bonding mechanism in the sulfides and oxides to be very similar. For the oxides, accurate experimental data allow the theoretical methods to be calibrated. The same level of theory is used to study the sulfides where there is far less experimental information. For ScO through MnO and CuO the coupled cluster singles and doubles technique including a perturbational estimate of the connected triple excitations [CCSD(T)] yields spectroscopic constants (r_e, ω_e, and D_0) in good agreement with experiment. The triple excitations are found to be very important in achieving this accuracy. For FeO to NiO, the self-consistent-field (SCF) approach yields π orbitals that are localized on the metal or oxygen. This appears to cause problems for the single reference techniques; this is discussed in detail for NiO. The complete-active-space SCF/internally contracted averaged coupled pair functional approach (CASSCF/ICACPF) works well for FeO to NiO. The calculation of accurate dipole moments is found to be very difficult.

1. Introduction

The transition metal oxides are very interesting systems (see the review by Merer [1]). The early transition metal oxides, ScO to CrO, have been observed in stellar spectra. This arises because of the large binding energies for the early transition metal oxides and large oxygen abundance. In fact, TiO and VO can dominate the spectra of M-type stars if they are metal-rich, which can arise from recycled supernova material. The spectra of the transition metal oxides can be very complicated because of the large number of excited states arising from the open-shell $3d$ electrons. The spectra is further complicated by numerous perturbations between states and large nuclear spins and magnetic moments. In spite of these problems,

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* *Current address*: Department of Chemistry, University of California, Santa Barbara, CA 93106, USA

much progress has been made experimentally on understanding these systems. For example, the ground states of the first transition row oxides are now known [1]. Far less is known about the valence isoelectronic transition metal sulfides.

Metal–oxygen and metal–sulfur bonds are also of interest in explaining bulk metal properties. For example, most metal surfaces are in fact metal oxides and, hence, the resistance to erosion in harsh environments is determined more by the stability of the metal-oxide surface than the bulk metal. Sulfur segregation to internal metal interfaces has been implicated in changing the mechanical properties. Thus there is interest in the nature of metal–oxygen and metal–sulfur bonds to explain bulk properties at an atomistic level.

Previous work [2–7] has shown that metal oxides are difficult to describe accurately. For example, the dissociation energy of CuO is significantly too small if a single reference configuration interaction singles and doubles (CISD) approach is used [2]. Unlike the alkali oxides, this problem cannot be circumvented by dissociating to the ionic limit because both ionic and covalent contributions to the CuO bond are important. The coupled-pair functional (CPF) approach [8] significantly improves the computed result, resulting in a binding energy in good agreement with experiment. However, in the case of the early metal oxides, the CPF or modified CPF [9] (MCPF) levels of theory yield dissociation energies that are significantly too small [7]. The very large binding energies for the early oxides has been explained in terms of oxygen donation [7, 10, 11] into the empty metal $3d\pi$ orbitals. The importance of this effect has been demonstrated for the second transition row metals by a plot [11] of the MO and MCH_2 binding energies versus transition metal atom atomic number; while the MO and MCH_2 binding energies are similar on the right side of the row, the oxides are much larger on the left side of the row. In addition to problems with computing accurate binding energies, it has been found that it is very difficult to compute the dipole moments of metal oxides [3, 5]. For NiO it has been found that while high levels of theory yield the correct delocalized Ni $3d$–O $2p$ π bonding and π^* anti-bonding molecular orbitals picture, lower levels of theory yield to localized Ni $3d$ and O $2p$ orbitals [4, 12]. This difference in the zeroth-order description of NiO could result in significant problems for even the most accurate single reference based approaches.

In this manuscript we report on a study of the ground states of the transition metal oxides and sulfides. We focus on the calculation of r_e, ω_e, D_0, and μ, as there are accurate experimental data available for comparison for many of the metal oxides. On the basis of these comparisons we are able to address what level of theory is required to compute accurately the spectroscopic constants. We also compare the bonding in the oxides and sulfides.

2. Methods

Two basis sets are used in this work, which we denote as small and large. The small metal basis sets are derived from the $(14s\ 9p\ 5d)$ sets optimized by Wachters [13]. For V to Cu the sp set is contracted to $[8s\ 4p]$ using contraction number 3. For Sc and Ti, the p contraction is changed to $(3\ 3\ 1\ 1\ 1)$ to allow the $3p$ orbital to be correlated. The d space is contracted $(3\ 1\ 1)$. Two p functions to describe the $4p$ orbital are added; these are the functions optimized by Wachters multiplied by 1.5. The diffuse d function of Hay [14] is added, as is a $(3f)/[2f]$ polarization set. The f functions are a three-term fit to a $4f$ Slater function, which varies from 1.6 for Sc

to 4.8 for Cu, in steps of 0.4. The small O and S basis sets are the augmented-correlation-consistent polarized valence triple zeta (aug-cc-pVTZ) basis sets of Dunning and co-workers [15] with the diffuse f function deleted. The large metal basis sets are atomic natural orbital [16] contractions of the large primitive sets optimized by Partridge [17]. Diffuse and polarization functions are added [18]. For V to Cu, the final basis sets are of the form $[6 + 1s\, 5 + 1p\, 4d\, 3f\, 2g]$. For Sc and Ti, the basis sets are modified to allow $3s3p$ correlation, namely the basis set is contracted $[3 + 5s\, 2 + 6p\, 1 + 5d\, 3 + 1'f\, 2g]$, where the $1'$ for the f contraction is to indicate that the uncontracted function is not the most diffuse, but rather the second tightest function, which is used to describe $3s3p$ correlation. The large O and S basis sets are the aug-cc-pV quadruple zeta (aug-cc-pVQZ) sets of Dunning and co-workers [15] with the diffuse g function deleted.

The orbitals are optimized using either the self-consistent-field (SCF) or complete active space SCF (CASSCF) approaches. When the orbitals are optimized using the SCF approach, more extensive correlation is added using either the MCPF method [9] or the coupled-cluster singles and doubles approach [19] including a perturbational estimate of the triple excitations [20] [denoted CCSD (T)]. CCSD (T) calculations are performed using spin-restricted and spin-unrestricted Hartree–Fock (UHF) reference wave functions. For NiO, we also perform the UCCSD calculation using Brueckner orbitals. This approach is commonly called Brueckner doubles [21], and denoted BD. The metal $3d$ and $4s$ electrons, the O $2s$ and $2p$, and the S $3s$ and $3p$ electrons are correlated; except for Sc and Ti, where the $3s$ and $3p$ electrons are correlated as well, because of a mixing of these inner-shell metal orbitals and the O or S orbitals. The geometry is optimized at all levels of energy theory using the small basis set. The effect of basis set saturation on the dissociation energy is computed by repeating the MCPF calculation using the large basis set. Test calculations, where the CCSD (T) calculations were performed using the large basis set, confirm the use of the MCPF level of theory to compute basis set saturation correction.

MnO, FeX, CoX, and NiX are treated using the CASSCF approach. In these calculations, the metal $3d$, $4s$, and $4p\sigma$ orbitals and the O or S p orbitals are active. The metal $4p\sigma$ orbital is added to accurately describe the $4s4p$ hybridization. For NiO, the δ orbitals are made inactive because their occupation number is essentially two. For MnO, NiO, and NiS, all configurations in the CASSCF calculation are used as references in the subsequent averaged CPF [22] (ACPF) calculations. For the remaining systems, reference selection is required; an occupation is included in the reference list if any of its component determinants have a coefficient with absolute value greater than 0.01 at any r values near r_e. The same number of electrons are correlate as in the MCPF and CCSD(T) calculations. Internal contraction [23] (IC) is used to keep the ACPF expansions tractable. Only the large basis sets are used in the ICACPF calculations.

The dissociation energy is computed relative to ground state atoms, even if the molecular wave function does not dissociate to this limit. Note for Ni we use $^3D(3d^9\,4s^1)$ even though the $^3F(3d^8\,4s^2)$ state is lower at all levels of theory used in this work. The r_e and ω_e values are computed using a parabolic fit in $1/r$. The dipole moments are computed as expectation values for the ICMRCI calculations and using a finite field ($\pm\, 0.005$ a.u.) for the UCCSD(T) calculations. The MCPF and CASSCF/MRCI calculations are carried out using the SWEDEN package [24] interfaced into SEWARD [25], while the RCCSD(T) calculations are performed

using TITAN [26] for the closed-shell systems and the program developed by Scuseria [27] for the open-shell systems. The UCCSD(T) and BD(T) calculations are performed using Gaussian 92 [28]. The CASSCF/ICACPF calculations are performed using MOLPRO [23, 29].

3. Overview of the bonding

In this section we give an overview of the bonding. To aid in this discussion we have summarized the experimental spectroscopic constants [1, 30–39] in Table 1. The bonding can be considered as arising from two neutral atoms or from singly charged ions. The populations and dipole moments suggest that the bonding is best described as being halfway between these two limits. The bonding arises from the interaction of the metal valence $3d$ and $4s$ orbitals and the oxygen (sulfur) $2p(3p)$

Table 1. Comparison and theoretical and experimental spectroscopic parameters for the ground states of the first transition row metal oxides and sulfides. The ScO to CoD D_0 values are taken from Merer [1]; the remaining values are taken from Huber and Herzberg [30] unless otherwise noted

	$r_e(a_0)$		$\omega_e(cm^{-1})$		$D_0(eV)$	
	Theory	Expt.	Theory	Expt.	Theory	Expt.
ScO $^2\Sigma^+$	3.174	3.153[a]	971	965[a]	6.90	7.01 ± 0.12
TiO $^3\Delta$	3.077	3.062	1014	1009	6.84	6.92 ± 0.10
VO $^4\Sigma^-$	3.027	3.003	1028	1011	6.26	6.44 ± 0.20
CrO $^5\Pi$	3.087	3.052	888	898	4.30	4.41 ± 0.30
MnO $^6\Sigma^+$	3.146	3.110[b]	794	840	3.56	3.83 ± 0.08
FeO $^5\Delta$	3.041	3.054[c]	885	880[d]	3.65	4.17 ± 0.08
CoO $^4\Delta$	3.063	3.078[e]	909	853[d]	3.64	3.94 ± 0.14
NiO $^3\Sigma^-$	3.073	3.075[f]	850	838[d]	3.75	3.87 ± 0.03[g]
CuO $^2\Pi$	3.347	3.258	572	640	2.66	2.85 ± 0.15[h]
ScS $^2\Sigma^+$	4.073	4.035[i]	563	565	4.81	4.92
TiS $^3\Delta^+$	3.937	3.935	575	558	4.58	4.75
VS $^4\Sigma^-$	3.933		521		4.08	4.62
CrS $^5\Pi$	4.022		435		3.05	3.37
MnS $^6\Sigma^+$	3.988	3.905[j]	467	491[j]	2.76	2.85
FeS $^5\Delta$	3.827		521		2.80	3.31
CoS $^4\Delta$	3.742		537		2.94	3.39
NiS $^3\Sigma^-$	3.743		636		3.40	3.53
CuS $^2\Pi$	3.981	3.876	385	415	2.71	2.80

[a] For ScO the experimental values correspond to r_0 and $\Delta G_{1/2}$
[b] Ref. [31]
[c] Ref. [32]
[d] Ref. [33]
[e] Ref. [34]
[f] Ref. [35]
[g] Ref. [36]
[h] Ref. [37]
[i] Ref. [38]
[j] Ref. [39]

orbitals. The metal σ orbitals undergo sp and $sd\sigma$ hybridization; these orbitals interact with the oxygen (sulfur) $2p(3p)$ orbital to form bonding and anti-bonding orbitals. The metal orbitals also give rise to a non-bonding σ orbital. The $3d\pi$ and $2p\pi(3p\pi)$ orbitals can also form bonding and antibonding orbitals. Since oxygen and sulfur have no occupied δ orbitals, the metal $3d\delta$ orbital is nonbonding. The order of the stability of the orbitals is therefore expected to be: σ bond $< \pi$ bond $< \sigma$ and δ non-bonding $< \pi$ anti-bonding $< \sigma$ anti-bonding. The filling order is complicated by the fact that the $3d$–$3d$ exchange energy is larger than the energy separation between different kinds of orbitals. Thus it can be better to add an electron to a π^* orbital than to add a second electron to a nonbonding orbital. The filling order is also complicated by the mixing of the metal occupations, for example $3d^n 4s^2$ and $3d^{n+1} 4s^1$ for the neutral metal. Thus we consider the bonding in each system.

We first consider the ground state starting with ScO and proceeding to the right. The ground state of Sc is $^2D(3d^1 4s^2)$. In the covalent limit, the bonding is derived from Sc $3d\pi^1 4s^2$ + O $2p\sigma^1 2p\pi^3$. The Sc $4s$ and $3d\sigma$ orbitals form two $sd\sigma$ hybrids, one of which is polarized along the z axis and bonds to the O $2p\sigma$ and the other is polarized in the plane perpendicular to the bonding axis. A second bond is formed between the Sc $3d\pi$ and O $2p\pi$ orbitals. These bonds are polarized toward the O. There is some backdonation of the doubly occupied oxygen $2p\pi$ orbital into the empty Sc $3d\pi$ orbital. Thus the system has some triple bond character and a large (about 7 eV) D_0 value. This leads to a $^2\Sigma^+$ ground state. We note that $sd\sigma$ hybridization occurs instead of sp hybridization because it is important that the σ and π bonds have the same optimal distance. That is, the $3d\pi$–$2p\pi$ bond constrains the σ bond to be an sd hybrid instead of an sp hybrid. Some mixing in of the $3d^2 4s^1$ Sc occupation occurs when the $sd\sigma$ hybridization occurs.

Ti and V have $^3F(3d^2 4s^2)$ and $^4F(3d^3 4s^2)$ ground states and the bonding is similar to that in ScO, with the "extra" $3d$ electrons occupying the $3d\delta$ orbital, leading to $^3\Delta$ and $^4\Sigma^-$ ground states for TiO and VO, respectively. Because the extra electrons are added to orbitals that do not affect the bonding, the binding energies of ScO, TiO, and VO are all larger than 6.0 eV (see Table 1). The bonding changes somewhat for CrO, because the next electron goes into the empty $3d\pi$ orbital instead of the nonbonding $3d\delta$ orbital, resulting in a $^5\Pi$ ground state. The very large $3d$–$3d$ exchange energy makes it favorable to add the electron to the $3d\pi$ orbital even though it eliminates the backdonation. This dramatically reduces the O lone pair to metal donation and results in a significant (2 eV) reduction in the binding energy and a decrease in the vibrational frequency. Thus the bonding changes from having significant triple bond character to being a double bond for CrO.

If the bonding in MnO was the same as in ScO to CrO, then the additional electron would be added to the nonbonding $sd\sigma$ hybrid orbital. The energy required to polarize two electrons away from the O and loss of $3d$–$3d$ exchange energy means that this mechanism is not the most favorable. The alternative is to transfer one Mn $4s$ electron to the O $2p\pi$ orbital and form a bond between the Mn $sd\sigma$ hybrid and the O $2p\sigma$ orbitals. This leads to a $^6\Sigma^+$ ground state. This view is too simple as there is some mixing of the $3d\pi$ and O $2p\pi$ orbitals, that is π and π^* orbitals are formed. However due to the large $3d$–$3d$ exchange energy, the open shell π^* orbital is mostly Mn in character. The covalent π bond means that there is some contribution to the bonding from the excited Mn $^6D(3d^6 4s^1)$ state, where bonds are formed between a Mn $sd\sigma$ hybrid orbital and O $2p\sigma$ orbital and between the Mn $3d\pi$ and O $2p\pi$ orbitals. These bonds are polarized toward the oxygen.

The ground state of FeO can be viewed as arising from that in MnO by adding the extra electron to the non-bonding $3d\delta$ orbital, resulting in a $^5\Delta$ ground state. CoO adds the extra electron to the non-bonding $sd\sigma$ orbital, leading to a $^4\Delta$ ground state. We should note that adding the extra electron to the $3d\delta$ orbital leads to the low-lying $^4\Sigma^-$ state. It might initially seem odd that it is favorable to add the electron to the $sd\sigma$ hybrid orbital instead of the $3d\delta$ orbital. However, the $^4\Sigma^-$ state is derived from 40% ^4F and 60% $^4P(3d^8\ 4s^1)$, while the $^4\Delta$ state is mostly derived from the energetically more favorable $3d^7\ 4s^2$ occupation [40]. As expected the extra electron in NiO is added to the $3d\delta$ orbital leading to a $^3\Sigma^-$ ground state. In addition to the σ bond, FeO to NiO (and to some extent MnO) all have a $\pi^4\pi^{*2}$ occupation that can be viewed as a single π bond arising from $3d\pi^3 + 2p\pi^3$. Thus these systems are best described as having a double bond.

For CuO, the extra electron is added to what would be the π^* orbital for MnO to NiO. The bonding arising from $\pi^4\pi^{*3}$ is sufficiently weak, that the orbitals localize and are better described as $3d\pi^42p\pi^3$. Thus the bonding is best described as a single bond in CuO. As has been discussed previously [2], the highest levels of theory show that there is some multiple bond character, but it is clear that the bonding in CuO is different from that in the other first transition row metal oxides.

The binding energies are consistent with this discussion; for ScO to VO where there is triple bond character the binding energies are greater than 6 eV. For CrO to NiO, where there is a double bond, the binding energies are between 3.8 and 4.4 eV. For CuO, where there is basically a single bond, the binding energy is 2.86 ± 0.15 eV. We find essentially the same bonding mechanism for the sulfides. Thus the ground states of sulfides and oxides are the same. There is a similar trend in the binding energies, however, the metal–sulfur bond is weaker than the metal–oxide bond so the difference in binding energies between ScS and CuS is much smaller than for the oxides. These trends are discussed in more detail in the discussion section.

4. Calibration calculations

We first consider ScO–MnO and CuO as these systems are well described by the single reference based techniques. The results are summarized in Table 2. The effect of relativity, computed using first-order perturbation theory [41] and denoted $+ R$, is to contract the bond length; this is consistent with the contraction of the metal $4s$ orbital, which contributes to the $sd\sigma$ orbital involved in the σ bond. This effect is largest for Cu, where the $4s$ atomic contraction is the largest. The effects of relativity on D_0 can either increase or decrease the bond energy. This appears to be due to changes in the $4s$ occupation as well as a contraction of the metal orbitals due to the metal positive charge.

Improving the basis set decreases the r_e values and increases the D_0 values. The basis set effect on D_0 is relatively large for ScO and TiO, and decreases to a very small effect for CuO. It is probably not surprising that the basis set effect is much smaller for CuO where there is only a single bond than for ScO and TiO where there is a triple bond.

The MCPF results fall between those obtained at the CCSD and CCSD(T) levels of theory, as has been found in many other cases. The triple excitations are required for accurate results. In all cases the effect of triple excitations is larger than the effect of improving the basis set. Excluding CuO, which has only a single bond, the difference between the MCPF and CCSD(T) levels of theory is much larger

Table 2. Comparison of level of treatment for the ground states of the oxides. All calculations use the small basis except for the MCPF (big) calculation and the ICACPF

	MCPF	MCPF + R	MCPF (big)	RCCSD	RCCSD(T)	UCCSD	UCCSD(T)	ICACPF
ScO $^2\Sigma^+$								
r_e	3.173	3.172	3.154	3.141	3.174	3.141	3.173	
D_0	6.38	6.34	6.58	6.16	6.71	6.15	6.70	
ω_e	952	956	950	1021	971	1020	973	
TiO $^3\Delta$								
r_e	3.083	3.079	3.076	3.037	3.077	3.039	3.065	
D_0	6.29	6.24	6.48	5.95	6.64	5.95	6.61	
ω_e	992	1000	977	1070	1014	1082	1080	
VO $^4\Sigma^-$								
r_e	3.020	3.020	3.020	2.979	3.027	3.005	2.988	
D_0	5.66	5.69	5.70	5.33	6.13	5.34	5.91	
ω_e	999	1006	993	1071	1028	1043	974	
CrO $^5\Pi$								
r_e	3.090	3.076	3.078	3.079	3.087	3.046	3.063	
D_0	3.80	4.02	3.91	3.42	4.20	3.51	4.06	
ω_e	1291	1310	1227	920	888	904	865	
MnO $^6\Sigma^+$								
r_e	3.125	3.105	3.118	3.145	3.146	3.161	3.134	3.118
D_0	3.14	3.11	3.27	2.90	3.43	2.92	3.29	3.37
ω_e	735	729	753	791	794	737	779	792
CuO $^2\Pi$								
r_e	3.343	3.279	3.334	3.386	3.347	3.386	3.347	
D_0	2.61	2.69	2.63	2.42	2.63	2.41	2.63	
ω_e	582	588	585	577	572	582	578	

than the effect of improving the basis set. Thus the small D_0 values computed using the MCPF approach previously [7] for transition metal oxides was mostly a result of level of correlation treatment. The SDCI + Q results of Dolg et al. [6] are too small for the same reason.

For ScO, TiO, and CuO there are only very small differences between RCCSD and UCCSD results. The inclusion of triples has a significant effect on the computed spectroscopic constants, especially on the D_0 values; the RCCSD(T) and UCCSD(T) results are also in good agreement, as are the UCCSD and RCCSD results. The biggest difference is for the TiO ω_e value, where part of the difference (up to 30 cm^{-1}) probably arises from using a only parabolic fit to 3 points near r_e. For VO, CrO, and MnO, where the SCF yields a poorer description of the systems, there are differences between the RCCSD and UCCSD results. Even larger differences occur for the RCCSD(T) and UCCSD(T) results, see for example the D_0 values. The difference between the RCCSD(T) and UCCSD(T) results is not related to the magnitude of the triples, which is actually larger for ScO and TiO than for CrO or MnO. It appears that the difference between RCCSD(T) and UCCSD(T) results increases with the spin multiplicity. For these systems the large $3d$–$3d$ exchange energy leads to a bias against the formation of metal $3d$-oxygen $2p$ bonds in the SCF calculations. Apparently this basis is somewhat different in the RHF and UHF calculations, which results in some differences in the CCSD treatments.

For MnO we also used the CASSCF/ICACPF approach in the large basis set. The RCCSD(T) and UCCSD(T) D_0 values, after adding the MCPF basis set correction, are 3.56 and 3.42 eV, respectively. The UCCSD(T) approach agrees better with the ICACPF for both D_0 and r_e. However, all three r_e values are very similar. A comparison with experiment (Table 1) shows that the RCCSD(T) D_0 value is in better agreement with experiment. A similar conclusion is reached for VO and CrO. Thus for D_0 the RCCSD(T) results appear to be somewhat superior to the UCCSD(T) results, but overall there is good agreement between the RCCSD(T) and UCCSD(T) results.

Only the restricted coupled cluster approach is used for the analogous sulfides – see Table 3. The results parallel those for the oxides. The basis set effects are small for CuS with only a single bond. The basis set effect is generally smaller than the effect of higher levels of correlation treatment. The MCPF results are between the RCCSD and RCCSD(T) results. All of these observations are the same as for the analogous oxides. Thus the computational requirements for the sulfides are similar to those for the oxides. We compare the bonding in the oxides and sulfides in more detail below.

For FeO to NiO the single reference based techniques did not work as well as they did for ScO–MnO and CuO. The problems encountered for NiO were typical of all three systems and therefore we consider NiO in detail. As noted above the ground state of NiO is $^3\Sigma^-$ with a $\pi^4\pi^{*2}$ occupation. The CASSCF or ICACPF natural orbitals show that the π orbital is a Ni $3d$–O $2p\pi$ bonding orbital, while the π^* orbital is the antibonding combination of the same atomic orbitals. However, at the SCF level of theory the occupation is still $\pi^4\pi'^2$, but the π and π' orbitals are localized on either Ni or O and three different localized solutions are found. $C_{\infty v}$ symmetry is retained in two solutions. In the first the π orbitals are the oxygen $2p\pi$ orbitals and the π' orbitals are the Ni $3d$ orbitals. This solution corresponds to Ni$^+$ $(3d^8 4s^1)$ forming a σ bond with O$^-$. In the second solution with $C_{\infty v}$ symmetry, the character of the π orbitals is reversed. This solution is high in

Table 3. Comparison of level of theory for the sulfides

	MCPF	MCPF + R	MCPF (big)	RCCSD	RCCSD(T)
ScS $^2\Sigma^+$					
r_e	4.083	4.079	4.063	4.042	4.073
D_0	4.41	4.37	4.60	4.15	4.62
ω_e	553	555	546	590	563
TiS $^3\Delta$					
r_e	3.944	3.939	3.936	3.949	3.936
D_0	4.18	4.14	4.40	3.83	4.36
ω_e	725	738	663	587	577
VS $^4\Sigma^-$					
r_e	3.928	3.917	3.911	3.928	3.933
D_0	3.71	3.66	3.77	3.51	4.02
ω_e	521	520	527	530	521
CrS $^5\Pi$					
r_e	3.921	3.911	3.901	3.974	4.022
D_0	2.42	2.57	2.58	2.37	2.89
ω_e	517	516	515	476	435
MnS $^6\Sigma^+$					
r_e	3.988	3.977	4.029	3.991	3.988
D_0	2.35	2.29	2.52	2.26	2.56
ω_e	454	453	467	468	467
CuS $^2\Pi$					
r_e	3.990	3.929	3.965	4.020	3.981
D_0	2.61	2.67	2.66	2.49	2.65
ω_e	386	406	383	383	385

energy and is not discussed further. The solution without $C_{\infty v}$ symmetry has the occupation

$$\pi_x(3d)^2 \, \pi_y(2p)^2 \, \pi'_x(2p)^1 \, \pi'_y(3d)^1.$$

This solution corresponds to a $3d\pi^3$ and O $2p\pi^3$ occupation. We use solution one (with symmetry) and solution three (without symmetry) as starting points for our MCPF and CCSD calculations, which are summarized in Table 4. The MCPF calculations in the small basis set show a very large difference between using the SCF solutions with and without symmetry; the D_0 values differ by 0.35 eV and the ω_e values by 257 cm^{-1}. In the large basis set the MCPF results are almost independent of which SCF starting point is used. However, the results are in poor agreement with experiment. The effect of triples for the RCCSD approach without symmetry is very large; the D_0 increases by more than an eV. In the large basis set at the RCCSD level of theory there is a significant difference between the results whether the starting wave function has $C_{\infty v}$ symmetry or not. This is the same as the MCPF or RCCSD results in the small basis set, but different from the MCPF in the large basis set. The UCCSD results are somewhat less sensitive to the symmetry of the reference wave function. Note that for the RCCSD and MCPF approaches, the D_0 values derived from the reference wave function with $C_{\infty v}$ symmetry are larger than those results without symmetry, whereas the opposite is true for the

Table 4. The summary of results for NiO as a function of level of theory. Reference wave functions both with and without $C_{\infty v}$ symmetry are used

	$r_e(a_0)$		$D_0(eV)$		$\omega_e(cm^{-1})$	
	With	Without	With	Without	With	Without
Expt	3.075		3.87		839	
MCPF	3.041	3.101	3.76	3.41	956	699
MCPF (large basis)	3.118	3.103	3.42	3.42	756	762
RCCSD		3.115		2.58		683
RCCSD (T)		3.066		3.65		900
RCCSD (T) (large basis)	3.122	3.061	3.93	3.67	874	900
UCCSD	3.073	3.068	2.97	3.16	879	868
UCCSD (T)	3.109	3.085	3.48	3.64	808	872
BD		3.060		2.83		844
BD (T)		3.087		3.62		834
ICACPF	3.077		3.75		850	

UCCSD approach. We note that the BD results are very similar to those obtained with the UCCSD approach.

The ICACPF results agree with experiment as well as any of the other approaches. The CASSCF reference wave function has $C_{\infty v}$ symmetry. While the UCCSD(T) and BD(T) results without symmetry are in reasonable agreement with experiment, it is somewhat disconcerting to use a reference wave function with the wrong spatial symmetry and with orbitals that do not show significant bonding in the π space. Therefore we treat FeO to NiO and FeS to NiS with the CASSCF/ICACPF approach.

5. Dipole moments

It is well known that it is difficult to compute the dipole moment of transition metal containing systems; see for example the studies [3, 5] of TiO, CrO, and FeO. In Table 5, we summarize the dipole moment of the oxides along with some relevant prior calculations [3, 5–7, 42] and the available experimental results [2, 43–48].

As has been previously noted, the MCPF dipole moments are in poor agreement with experiment [2, 5]; the best result is for TiO, where the error is only 0.34 D and the worst results is for CrO, where the error is 1.62 D. We note that the current MCPF results for ScO and VO are very similar to the previous [7] CPF results. Excluding TiO, the UCCSD(T) results are superior to the MCPF, with the worst UCCSD(T) error being only 0.56 D. The best agreement between the UCCSD(T) and MCPF is for CuO, which is the system that is best described by a single reference. However, even for this simple system the MCPF and UCCSD(T) results are outside the experimental error bars [48]. It would be desirable to have a new experimental determination of this dipole moment with smaller error bars as it would serve as a good calibration for theory.

For FeO we find the current ICACPF result to be significantly smaller than the previous [5] ACPF results. In addition to internal contraction, the current calculations have a smaller threshold for reference selection and a superior basis set. The two sets of ACPF results bracket experiment. The large difference between

Table 5. Comparison of selected dipole moments (D) as a function of level of theory

	Present work				CI + Q[a]	Other[b]	Expt.
	MCPF	UCCSD	UCCSD(T)	ICACPF			
ScO	3.25	4.27	3.91		3.60	2.96 (CI)[c], 3.22 (CPF)[d]	4.55[e]
TiO	2.62	3.79	3.52		3.07	5.11 (CI)[f], 3.38 (I)[g], 3.44 (A)[g]	2.96 ± 0.05[h]
VO	2.47	3.27	3.60		3.09	2.50 (CPF)[d]	3.355 ± 0.014[i]
CrO	2.26	4.05	3.89		5.08	3.17 (M)[i], 3.66 (I)[j], 3.99 (F)[j]	3.88 ± 0.13[j]
MnO	4.14	4.95	4.99	3.44	7.32		
FeO				4.17	7.48	5.48 (A)[d] 5.86 (F)[d], 5.20 (I)[d]	4.7 ± 0.2[k]
CoO				3.46	7.28		
NiO				3.91	6.72		
CuO	5.01	5.35	5.11		6.00		4.45 ± 0.3[l]

[a] Ref. [6]

[b] CI indicates an SDCI calculation, M indicates an MRCI calculation, I indicates an interative natural orbital MRCI calculation, A indicates an ACPF calculation and F indicates that a finite field MRCI + Q approach was used

[c] Ref. [42]

[d] Ref. [7]

[e] Ref. [43]

[f] Ref. [44]

[g] Ref. [5]

[h] Ref. [45]

[i] Ref. [46]

[j] Ref. [3]

[k] Ref. [47]

[l] Ref. [48]

two different ACPF calculations shows how difficult it is to compute the dipole moments. On the basis of the FeO results, we expect that the ICACPF results for CoO and NiO are also somewhat too small. This is also supported by the difference between the UCCSD(T) and ICACPF results for MnO.

The results obtained by Dolg et al. [6] using a single and double configuration interaction calculation including the Davidson correction (SDCI + Q) approach in conjunction with an effective core potential were in better agreement with experiment than the MCPF results for ScO–VO. This is somewhat unexpected since the MCPF should better account for the effect of higher excitations than the + Q correction. The CrO, FeO, and CuO results show that the SDCI + Q approach is not uniformly accurate for the transition metal oxides. We conclude that at the present time there is no simple way to accurately compute the dipole moments of transition metal oxides.

6. Results and discussion

The population analyses and dipole moments are summarized in Tables 6 and 7. The net metal charges are very similar for the oxides, showing a range of + 0.46 to + 0.61, and for the sulfides, showing a range of + 0.18 to + 0.37. Some of this difference in oxide and sulfide populations is due to metal $4s$ and $4p$ populations. Since these orbitals are rather diffuse, they are subject to population artifacts, so while the trends between the different metals are expected to be accurate, the differences between the oxides and sulfides are only qualitative. However, the $3d$ populations are expected to be more accurate as this is a relatively contracted orbital. Since some of the difference between the oxides and sulfides arise from the $3d$ populations, we conclude that the sulfides are slightly less ionic than the oxides which is expected based on the relative electronegativity of S and O. The population analysis shows a larger participation of the $3d\sigma$ orbital than of the $4s$ orbital to

Table 6. Mulliken populations and dipole moments for the ground states of first transition-row metal oxides. For FeO, CoO, and NiO the results are obtained at the ICACPF level using the large basis set. For the remaining systems, the results are obtained at the MCPF level of theory using small basis set

	ScO $^2\Sigma^+$	TiO $^3\Delta$	VO $^4\Sigma^-$	CrO $^5\Pi$	MnO $^6\Sigma^+$	FeO $^5\Delta$	CoO $^4\Delta$	NiO $^3\Sigma^-$	CuO $^2\Pi$
$4s$	0.81	0.75	0.73	0.74	0.68	0.56	1.05	0.88	0.60
$4p$	0.13	0.11	0.15	0.25	0.36	0.29	0.25	0.19	0.18
$3d$	1.41	2.55	3.57	4.49	5.32	6.55	7.19	8.40	9.69
Net	0.60	0.55	0.52	0.49	0.61	0.58	0.46	0.48	0.51
Dipole (a.u.)	1.28	1.03	0.97	0.89	1.63	1.64	1.36	1.54	1.97
σ	1.51	1.51	1.52	1.60	1.72	1.70	2.61	2.55	2.46
$4s$	0.81	0.75	0.73	0.74	0.68	0.56	1.05	0.88	0.60
$4p\sigma$	0.12	0.10	0.09	0.08	0.06	0.05	0.08	0.05	0.06
$3d\sigma$	0.58	0.65	0.70	0.78	0.98	1.09	1.48	1.62	1.80
π	0.81	0.90	0.98	1.89	2.65	2.72	2.90	2.95	4.02
$4p\pi$	0.02	0.02	0.06	0.17	0.30	0.24	0.17	0.14	0.11
$3d\pi$	0.79	0.88	0.92	1.72	2.35	2.48	2.74	2.81	3.91
δ	0.04	1.02	1.96	1.99	2.00	2.99	2.98	3.97	3.98

Table 7. Mulliken populations and dipole moments for the ground states of first transition-row metal sulfides. For FeS, CoS, and NiS the results are obtained at the ICACPF level using the large basis set. For the remaining systems, the results are obtained at the MCPF level of theory using small basis set

	ScS $^2\Sigma^+$	TiS $^3\Delta$	VS $^4\Sigma^-$	CrS $^5\Pi$	MnS $^6\Sigma^+$	FeS $^5\Delta$	CoS $^4\Delta$	NiS $^3\Sigma^-$	CuS $^2\Pi$
$4s$	0.94	0.91	0.75	0.79	0.93	0.85	1.06	0.82	0.79
$4p$	0.19	0.13	0.20	0.31	0.45	0.41	0.39	0.26	0.25
$3d$	1.46	2.67	3.77	4.66	5.33	6.36	7.32	8.60	9.72
Net	0.37	0.25	0.25	0.22	0.28	0.34	0.19	0.28	0.18
Dipole (a.u.)	1.82	1.61	2.10	1.93	2.32	2.17	2.03	1.84	1.88
σ	1.66	1.71	1.77	1.87	2.08	2.03	2.97	2.74	2.78
$4s$	0.94	0.91	0.75	0.79	0.93	0.85	1.07	0.82	0.79
$4p\sigma$	0.12	0.05	0.06	0.08	0.09	0.09	0.11	0.08	0.12
$3d\sigma$	0.60	0.75	0.96	1.00	1.06	1.09	1.81	1.84	1.87
π	0.90	0.98	1.01	1.90	2.62	2.61	2.81	2.96	4.04
$4p\pi$	0.07	0.08	0.14	0.23	0.35	0.32	0.28	0.18	0.13
$3d\pi$	0.83	0.90	0.87	1.67	2.27	2.28	2.53	2.78	3.91
δ	0.04	1.02	1.94	1.99	2.00	2.98	2.98	3.98	3.98

the bond in the oxide relative to that in the sulfide. This probably arises because the $3d\sigma$ orbital has a better overlap with the compact oxygen $2p$ orbitals than the more diffuse sulfur $3p$ orbital. The $3d$ populations also show mixing of the metal occupations with different $3d$ occupations. The dipole moments, like the populations, show that the bonding in these systems is not ionic but a mixture of ionic and covalent. The dipole moments for the sulfides tend to be larger than for the oxides because of the longer bond length. However, as noted above, these MCPF dipole moments are only of qualitative accuracy and this is about the limit of the conclusions that can be drawn from the computed dipole moments.

In Table 1 we summarize our best spectroscopic constants along with the available experimental results for comparison. The Fe–Ni results are for the ICACPF level of theory using the large basis set, while the remaining results are from the RCCSD(T) level in the small basis set. The D_0 values include a correction for basis set saturation, which is computed as the difference in the MCPF results with the large and small basis set.

Overall the computed r_e values are in reasonable agreement with experiment. Although the RCCSD(T) bond lengths are slightly long, an inspection of Tables 2 and 3 show that this is a result of basis set limitations and relativistic effects. Somewhat surprisingly the ICACPF bond lengths are too short. Since relativistic effects are expected to shorten the bond length slightly, it appears that the choice of active space is slightly biased in favor of describing the bonding, although this does not show up in the dissociation energies, which are too small, as are those computed using the RCCSD(T) level. On the basis of a comparison of our results with experiment, the computed r_e values for VS, CrS, FeS, CoS, and NiS, where there are no experimental results, are probably accurate to 0.005 a_0 and certainly accurate to $0.010a_0$.

The computed ω_e values are in reasonable agreement with experiment. The largest errors are for MnO, CoO, and CuO. In light of the small binding energy for MnO, the small computed frequency is not unexpected. The accuracy of the values for CoO and CuO are somewhat disappointing. We expect the same accuracy for

VS, CrS, FeS, CoS, and NiS thus computed values should be a reasonable estimate for these frequencies.

Most of the computed dissociation energies are in reasonable agreement with experiment. For the oxides, it appears that adding 0.1 eV and assigning an uncertainty of $\pm$ 0.1 eV results in an overlapping of most of the computed and experimental D_0 values. The only exception is FeO where the theoretical upper bound of 3.85 eV is still significantly smaller than the experimental lower bound of 4.09 eV. It should be noted that for the oxides of Mn and Co, which are on either side of Fe, the theoretical and experimental ranges just overlap. It therefore appears that the middle of the transition row is the most difficult to describe accurately. This is expected because the loss of $3d$–$3d$ exchange energy with bond formation is the largest for these systems and therefore it is difficult to accurately balance the bonding against the loss of exchange.

On the basis of the oxide values it is probably safe to assume an uncertainty of about 0.1 eV for the experimental sulfide D_0 values. Even with this assumption, the agreement between theory and experiment is not as good as for the oxides. The theoretical results for FeS, and CoS are significantly smaller than experiment. Somewhat surprisingly the MnS result is in very good agreement with experiment, whereas the theoretical value was expected to be smaller than experiment. It is also surprising to find that the computed VS value is significantly smaller than experiment. However, theory and experiment show a large reduction in D_0 between TiO and VO, as theory finds between TiS and VS. Thus the calculations suggest that the experimental value for the VS dissociation energy is probably too large.

7. Conclusions

The bonding in the oxides and sulfides are very similar. The oxides are used to calibrate the level of theory required to study these systems. Application of this level of theory to the sulfides should yield reasonable estimates for the spectroscopic constants for the unknown sulfides. The calculation of dipole moments is very difficult with even the CCSD(T) results being in only acceptable agreement with experiment.

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