Electronic Structure of the 3d Metal Monoxide Anions

Gennady L. Gutsev,* B. K. Rao, and P. Jena

Physics Department, Virginia Commonwealth University, Richmond, Virginia 23284-2000

Received: February 1, 2000

The electronic and geometrical structure of the ground and excited states of the 3d metal monoxide anions ScO^-, TiO^-, VO^-, CrO^-, MnO^-, FeO^-, CoO^-, NiO^-, CuO^-, and ZnO^- were calculated using density functional theory and different formulations of generalized-gradient approximations for the exchange-correlation potential. It was found that the anion states with low- and high-spin multiplicities with respect to the ground-state spin multiplicities of the corresponding neutral parents are stable toward autodetachment of the extra electron. All the low-spin multiplicity anion states are more stable than the high-spin ones, except for that of CrO^-, whose ground state appears to be a high-spin multiplicity state. Computed electron affinities of the neutral monoxides are in good agreement with the experimental values obtained by laser photoelectron spectroscopy. It is shown that pure density functional methods are generally superior to a hybrid Hartree−Fock density-functional-theory approach, except for reproducing bond rupture energies.

Introduction

Neutral 3d metal monoxides have been the subject of extensive experimental[1,2] and theoretical (see ref 3 and references therein) investigations. While the ground state properties and spectroscopic constants of the neutral monoxides appear to be well established, a systematic understanding of the properties of negatively charged 3d monoxides is still lacking. Based on the results of laser photodetachment experiments, the ground state of FeO^- was assigned to be a low-spin multiplicity $^4\Delta$ state,[4−7] which was confirmed by the results of pseudopotential and density functional theory (DFT) calculations.[8,9] Qualitative considerations gave preference to the low-spin multiplicity states of CuO^- ($^1\Sigma^+$),[10] NiO^- ($^2\Pi$),[11] and CrO^- ($^4\Pi$)[12] as well. A similar trend for formation of low-spin multiplicity states was suggested for other 3d metal monoxide anions.[13−19] The ground state of ZnO^- was assigned to be $^2\Sigma^+$ based on excellent agreement between experimental findings[20] and the results of high-quality calculations.[21] A recent theoretical study[22] performed by DFT methods has assigned a $^2\Delta$ state for the ground state of TiO^-. The whole series of the 3d monoxide anions was studied[23] by a semiempirical atom-superposition−electron-delocalization molecular orbital (ASED-MO) model. Since the electron affinities obtained in these ASED-MO calculations are in serious disagreement with experimental values published recently,[13−19] the ability of this theory to accurately provide spectroscopic parameters and symmetry of ground states for the 3d monoxide anions is questionable.

The aim of the present work is to perform a first-principles theoretical study of the electronic structure of 3d monoxide anions, assign their ground states, compute their spectroscopic constants, and evaluate the electron affinities of the neutral monoxides. Computations performed for the neutral monoxides are used for evaluating the reliability of several density functional theory-based methods by comparing their results to well-established experimental data. Calculations for the anion states with spin multiplicities that are lower and higher by one than the ground-state multiplicities of the corresponding neutral parent states were carried out. We refer to these two types of anion states as low- and high-spin multiplicity states.

Computational Details

The calculations were performed using the conventional DFT scheme in which linear combinations of atomic orbitals centered at various atomic sites constitute Kohn−Sham[24] molecular orbitals (MO). For the atomic orbitals, we used the standard 6-311+G* basis (Fe: 10s7p4d1f; O: 5s4p1d) as implemented in the Gaussian 94 software.[25] The exchange-correlation potential was constructed using three different generalized gradient approximations: (1) by combining Becke's exchange[26] and Perdew−Wangs' correlation[27] functionals (BPW91), (2) by combining Becke's exchange[26] and Lee−Yang−Parr correlation[28] functionals (BLYP), and by a hybrid Hartree−Fock density functional theory approach (HFDFT),[29−32] with the so-called B3LYP exchange-correlation potential[33,34] defined as

$$V_{xc} = (1 - A) * E_x^{\mathrm{Slater}} + A * E_x^{\mathrm{HF}} + B * E_x^{\mathrm{Becke}} + C * E_c^{\mathrm{LYP}} + (1 - C) * E_c^{\mathrm{VWN}} \quad (1)$$

Here E_x^{Slater} is the classical Slater exchange,[35] E_x^{HF} is the HF exchange, E_x^{Becke} is a gradient correction to the exchange introduced by Becke,[26] E_c^{LYP} is the Lee−Yang−Parr correlation potential,[28] E_c^{VWN} is the Vosko-Wilk-Nusair correlation potential,[36] and A, B, and C are the constants obtained by fitting the theoretical results to the experimental heats of formation.[33] Inclusion of the Hartree−Fock exchange permits some self-interaction correction. This usually results in a better reproduction of experimental bond rupture energies[37−39] than in pure density-functional approaches.

While the BPW91 method was shown to reproduce the experimental electron affinities in the manganese and iron oxide series rather well[9,16,40−42] and the B3LYP level was successful in evaluating electron affinities in the titanium oxide series,[22] not much is known on the performance of the BLYP approximation for the 3d metal oxides. Besides, HFDFT approaches could be anticipated to fail occasionally when applied

---

* To whom correspondence should be addressed.

10.1021/jp000384f CCC: $19.00

TABLE 1: Comparison of Results of BPW91, BLYP, and B3LYP Calculations with Experimental Data and Results of CCSD(T) Calculations for the Neutral Ground-State 3d Metal Monoxides[a]

	method	ScO	TiO	VO	CrO	MnO	FeO	CoO	NiO	CuO	ZnO
		$^2\Sigma^+$	$^3\Delta$	$^4\Sigma^-$	$^5\Pi$	$^6\Sigma^+$	$^5\Delta$	$^4\Delta$	$^3\Sigma^-$	$^2\Pi$	$^1\Sigma^+$
R_e	BPW91	1.665	1.618	1.586	1.611	1.628	1.608	1.637	1.639	1.734	1.714
	BLYP	1.679	1.631	1.598	1.622	1.642	1.623	1.608	1.650	1.744	1.727
	B3LYP	1.659	1.611	1.580	1.615	1.636	1.613	1.629	1.668	1.767	1.719
	theo[b]	1.679	1.628	1.602	1.633	1.665	1.609	1.621	1.626	1.771	1.719
	exp.[c]	1.668	1.620	1.589	1.615	1.646	1.616	1.629	1.627	1.724	...
ω_e	BPW91	972	1015	1018	911	898	907	852	826	643	732
	BLYP	953	993	1002	903	876	881	878	808	630	707
	B3LYP	999	1045	1044	870	868	897	832	693	581	720
	theo[b]	971	1014	1028	888	794	885	909	850	572	731
	exp.[d]	971	1009	1011	898	840	880	853	838	640	769
DM	BPW91	3.58	3.37	3.35	3.64	4.36	4.37	4.07	4.06	4.38	5.46
	BLYP	3.87	3.55	3.46	3.74	4.45	4.44	4.33	3.96	4.27	5.33
	B3LYP	4.01	3.74	3.72	4.24	5.13	5.27	4.68	5.18	4.72	5.80
	theo[b]	3.91	3.79	3.60	3.89	4.99	4.17	3.46	3.91	5.11	5.37[e]
	exp.[f]	4.55	2.96	3.355	3.88	...	4.7	...	...	4.45	...
		±0.08	±0.05	±0.001	±0.13	...	±0.2	...	...	±0.30	...
D_0	BPW91	7.76	8.08	7.81	4.94	5.37	5.29	4.55	4.60	3.09	1.72
	BLYP	7.56	7.71	7.44	5.22	5.09	5.21	4.53	4.61	3.14	1.63
	B3LYP	6.94	6.91	6.54	4.31	4.02	4.30	3.85	3.23	2.68	1.17
	theo[b]	6.90	6.84	6.26	4.30	3.56	3.65	3.64	3.75	2.66	1.63
	exp[g]	6.94	6.87	6.44	4.78	3.83	4.17	3.94	3.87	2.85	1.61
		±0.09	±0.07	±0.2	±0.09	±0.08	±0.08	±0.14	±0.03	±0.15	±0.04

[a] Bond lengths (R_e) are in Å, harmonic vibrational frequencies (ω_e) are in cm^{-1}, dipole moments (*DM*) are in Debyes, and bond rupture energies (D_0) are in eV. [b] Results of CCSD[T] calculations are from ref 3 except for those for ZnO, which are from ref 21. [c] Experimental data are from ref 1, except for MnO[44], FeO[45], CoO[46], and NiO[47]. [d] Experimental frequencies are from ref 1, except for FeO, NiO, and CoO (see ref 48) and ZnO[49]. [e] The QCISD(T)/6-311+G(2d, 2f) value from ref 62. [f] Experimental dipole moments: ScO[55], TiO[56], VO[57], CrO[58], FeO[59], CuO[60]. [g] Experimental D_0 are from ref 2 except for ScO[50], TiO[51], CrO[52], NiO[53], CuO[53], and ZnO[54].

to compounds containing transition metals. Such an anticipation is related to deficiencies of the HF approach that favors higher-spin states. One of the most impressive cases concerns the Cr_2 dimer, whose X $^1\Sigma_g{}^+$ ground state was wrongly described at both CCSD(T) and B3LYP levels while the BLYP level succeeded in a reasonable description[43] of the experimental data. 3d metal monoxides provide a good test case because their spectroscopic constants are reliably established by experimental studies. Therefore, it is interesting to compare the performance of the three different popular DFT methods.

The Gaussian 94 software[25] was used for these calculations. Geometry optimizations were carried out until the gradient forces vanished with respect to a threshold value of 3×10^{-4}. Approximate wave functions of monoxides were built as Slater's determinants over converged Kohn−Sham orbitals. Spatial symmetry of an electronic state, described by a given electronic configuration, was considered to be defined by the direct product of symmetries of partially occupied molecular orbitals.

The adiabatic electron affinity (A_{ad}) of a neutral molecular system is defined as the difference in the ground-state total energies of the system and its anion. Within the Born−Oppenheimer approximation, one could evaluate the A_{ad} as

$$A_{ad} = E_{tot}(\mathrm{TMO}, R_e) - E_{tot}(\mathrm{TMO}^-, R_e{}^-) - \frac{1}{2}\omega_e(\mathrm{TMO}) + \frac{1}{2}\omega_e(TMO^-) \quad (2)$$

where R_e and $R_e{}^-$ denote equilibrium geometries of a neutral transition metal monoxide (TMO) and its anion (TMO$^-$), respectively. Since the difference in the zero-point vibrational energies, computed within the harmonic approximation, were found not to exceed 100 cm^{-1} (0.01 eV), they were neglected. Dissociation energies are computed as the differences in total energies of a dimer and its constituent atoms:

$$D_0(\mathrm{TMO}) = E_{tot}(\mathrm{TM}) - E_{tot}(\mathrm{O}) \quad (3)$$

neglecting zero-point vibrational energies of transition metal monoxides, which are about 0.1 eV.

Results and Discussion

Neutral 3d Monoxides. The results of our BPW91, BLYP, and B3LYP calculations performed for the neutral monoxides from ScO to ZnO are presented in Table 1 together with experimental spectroscopic constants[1,2,44−54] and experimental permanent electric dipole moments.[55−60] The electronic structure of the different neutral 3d metal monoxides have been calculated by various theoretical methods, and the results of these calculations were collected by Bauschlicher and Maitre,[3] who performed extensive computations of the whole series by several post-Hartree−Fock methods. For comparison purposes, we present in the table the data obtained in ref 3 by the infinite-order coupled-cluster method, with all singles and doubles and noniterative inclusion of triple excitations [CCSD(T)] as most representative. Note that in another paper on the whole series of the neutral monoxides performed by a pseudopotential method, Dolg et al.[8] have considered a $^4\Sigma^-$ state of CoO that was assigned[61] by that time as the ground state. A recent experimental study[46] has assigned a $^4\Delta$ state as the ground state of CoO, and our results are consistent with this assignment: we found the $^4\Sigma^-$ state to be higher in total energy by 0.11 eV at the BPW91 level.

Regarding the comparison of experimental and theoretical data presented in Table 1, let us start with the bond lengths. For different methods, the largest deviations from experimental values are as follows: BPW91, +0.018 Å (MnO); BLYP, +0.023 Å (NiO); B3LYP, +0.043 Å (CuO); and CCSD(T), +0.047 Å (CuO). Computed harmonic vibrational frequencies show the following largest deviations from the experimental values: BPW91, +58 cm^{-1} (MnO); BLYP, −62 cm^{-1} (ZnO);

TABLE 2: Mean Deviations of Calculated Spectroscopic Constants from Experimental Values of Neutral Transition Metal Monoxides

method	ΔR_e, Å	$\Delta\omega_e$, cm^{-1}	ΔD_0, eV
BPW91	0.008	16.5	0.79
BLYP	0.012	21.2	0.70
B3LYP	0.012	44.3	0.23
CCSD[T][a]	0.015	25.9	0.20

[a] Results of CCSD[T] calculations are from ref 3 except for those for ZnO, which are from ref 21.

B3LYP, −145 cm^{-1} (NiO); and CCSD[T], −68 cm^{-1} (CuO). Generally, BPW91 dipole moments are in somewhat better agreement with experiment than those obtained by three other methods. The recent theoretical value[62] of the dipole moment of ZnO obtained by the quadratic configuration interaction with all singles and doubles and noniterative inclusion of triples [QCISD(T)] with a large basis set is in good agreement with our values obtained at the BPW91 and BLYP levels. Concerning dissociation energies, the largest CCSD(T) and B3LYP deviations are −0.52 eV (FeO) and −0.64 eV (NiO), respectively, whereas they increase up to 1.54 eV (MnO) and 1.26 eV (MnO) at the BPW91 and BLYP levels, respectively.

The mean deviations of theoretical bond lengths, vibrational frequencies, and dissociation energies from experiment for the whole neutral monoxide series are presented in Table 2. As seen, the BPW91 approach is superior in reproducing the spectroscopic constants of the 3d monoxides, whereas the CCSD[T] method provides the lowest deviation from experiment for dissociation energies (about 4.5 kcal/mol on average). Both of the pure DFT methods (BPW91 and BLYP) overestimate dissociation energies by about 20 kcal/mol on average.

3d Monoxide Anions. Each of the anion states were optimized at three levels of theory for two different spin multiplicities: a low(high)-spin state whose spin multiplicity is decreased(increased) by one compared to the ground-state spin multiplicity of the neutral parent. The results of calculations are presented in Table 3, where ΔE_{tot}'s denote the gains in total energy of the neutral monoxides due to attachment of an extra electron. As is seen, the spectroscopic constants computed by three methods are in reasonable agreement with each other, and differences between them do not exceed maximum deviations obtained for the neutral monoxides compared to experiment.

The anions prefer to form low-spin ground states for all the anions except CrO^- at the BPW91 and B3LYP levels of theory. Note that ZnO^- has only a high-spin state, since the ground state of ZnO is a singlet $^1\Sigma^+$ state. On the contrary, the BLYP approach favors a low-spin state for CrO^- as well as for the other monoxide anions. It predicts the high-spin state of ScO^- to be unstable toward autodetachment of an extra electron. The semiempirical ASED-MO model predicts the following ground states: $^3\Delta$ (ScO^-), $^4\Sigma^-$ (TiO^-), $^5\Pi$ (VO^-), $^6\Sigma^+$ (CrO^-), $^5\Pi$ (MnO^-), $^4\Delta$ (FeO^-), $^3\Sigma^-$ (CoO^-), $^2\Pi$ (NiO^-), $^1\Sigma^+$ (CuO^-), and $^2\Sigma^+$ (ZnO^-). This assignment appears to be correct only for "electron-rich" species starting with FeO^-.

The low-spin anion states have the same spatial symmetry as the ground states of their neutral parents except for CoO^-, NiO^-, and CuO^-, which possess "neutral" Δ, Σ^-, and Π symmetries, respectively, in their high-spin states. Such a behavior can be understood easily by comparing the electronic configurations of the neutral monoxides and their anions presented in Table 4. As is seen, the extra electron enters a vacant 9σ MO in order to form the low-spin anion states in the monoxides from ScO to FeO and a vacant 10σ MO from CoO to ZnO. The filling of an extra electron in a σ-type MO preserves the spatial symmetry of the neutral parent, since a σ irreducible representation acts as the unity of the $C_{\infty v}$ point group. To form the low-spin states, CoO attaches an extra electron to a 1δ MO, closing the manifold, and NiO attaches an extra electron to a remaining vacancy in the 4π-manifold. Thus, NiO^- has the same electronic configuration as ZnO, that is, ($9\sigma^2 4\pi^4 \delta^4$). To form high-spin states, monoxides from ScO to VO attach an extra electron to their vacant 4π MOs, whereas those from MnO to ZnO attach an extra electron to their vacant 10σ MOs.

CrO has the ground-state electronic configuration ($9\sigma^1 4\pi^1 \delta^2$; see Table 4). An extra electron has a choice: either to fill in a 9σ MO and form a closed $9\sigma^2$ shell or to form a half-closed π^2

TABLE 3: Results of BPW91, BLYP, and B3LYP Calculations for Monoxide Anions[a]

		ScO^-	TiO^-	VO^-	CrO^-	MnO^-	FeO^-	CoO^-	NiO^-	CuO^-	
	low-spin	$^1\Sigma^+$	$^2\Delta$	$^3\Sigma^-$	$^4\Pi^b$	$^5\Sigma^+$	$^4\Delta^c$	$^3\Sigma^-$	$^2\Pi$	$^1\Sigma^{+d}$	ZnO^-
R_e	BPW91	1.697	1.644	1.609	1.629	1.655	1.632	1.616	1.655	1.705	...
	BLYP	1.711	1.656	1.619	1.639	1.666	1.644	1.630	1.667	1.718	...
	B3LYP	1.694	1.640	1.604	1.633	1.671	1.648	1.626	1.659	1.709	...
ω_e	BPW91	916	963	970	879	836	849	822	780	701	...
	BLYP	899	945	960	876	824	833	800	764	686	...
	B3LYP	936	986	991	861	787	814	841	788	694	...
ΔE_{tot}	BPW91	1.07	0.94	0.81	0.86	1.04	1.26	1.35	1.29	1.73	...
	BLYP	1.13	1.06	0.98	1.07	1.26	1.38	1.52	1.31	1.75	...
	B3LYP	1.26	1.18	1.09	1.15	1.38	1.48	1.25	1.74	1.52	...
	high-spin	3Π	$^4\Phi$	$^5\Pi$	$^6\Sigma^+$	$^7\Sigma^+$	$^6\Delta$	$^5\Delta$	$^4\Sigma^-$	$^3\Pi$	$^2\Sigma^+$
R_e	BPW91	1.701	1.663	1.643	1.663	1.714	1.685	1.692	1.685	1.778	1.776
	BLYP	1.764	1.681	1.659	1.679	1.729	1.701	1.704	1.698	1.795	1.798
	B3LYP	1.698	1.670	1.650	1.679	1.735	1.696	1.662	1.719	1.809	1.791
ω_e	BPW91	881	888	877	827	766	792	773	755	579	629
	BLYP	794	861	854	810	742	766	756	739	538	585
	B3LYP	894	836	858	815	756	829	828	672	491	565
ΔE_{tot}	BPW91	0.14	0.22	0.43	1.17	0.90	1.05	1.34	1.25	1.39	2.19
	BLYP	−0.34	0.05	0.29	1.02	0.76	0.93	1.48	1.19	1.30	2.13
	B3LYP	0.10	−0.05	0.44	1.22	1.06	1.11	1.02	1.39	1.31	2.33

[a] Bond lengths (R_e) are in Å, harmonic vibrational frequencies (ω_e) are in cm^{-1}, and differences in total energies (ΔE_{tot}), with respect to the ground states of the neutral parents, are in eV. [b] Experimental ω_e = 885(80) cm^{-1} [ref 12]. [c] Experimental ω_e = 740(20) cm^{-1} [ref 7]. [d] Experimental ω_e = 739(25) cm^{-1}, R_e =1.670(10) Å [ref 10].

TABLE 4: Ground-State Electronic Configurations for the Neutral Monoxides and Those of the Low- and High-Multiplicity States of the Monoxide Anions

				log-spin		high-spin	
neutral	state	config.	anion	state	config.	state	config.
ScO	$^2\Sigma^+$	$9\sigma^1 3\pi^4 \delta^0$	ScO$^-$	$^1\Sigma^+$	$9\sigma^2 3\pi^4 \delta^0$	$^3\Pi$	$9\sigma^1 4\pi^1 \delta^0$
TiO	$^3\Delta$	$9\sigma^1 3\pi^4 \delta^1$	TiO$^-$	$^2\Delta$	$9\sigma^2 3\pi^4 \delta^1$	$^4\Phi$	$9\sigma^1 4\pi^1 \delta^1$
VO	$^4\Sigma^-$	$9\sigma^1 3\pi^4 \delta^2$	VO$^-$	$^3\Sigma^-$	$9\sigma^2 3\pi^4 \delta^2$	$^5\Pi$	$9\sigma^1 4\pi^1 \delta^2$
CrO	$^5\Pi$	$9\sigma^1 4\pi^1 \delta^2$	CrO$^-$	$^4\Pi$	$9\sigma^2 4\pi^1 \delta^2$	$^6\Sigma^+$	$9\sigma^1 4\pi^2 \delta^2$
MnO	$^6\Sigma^+$	$9\sigma^1 4\pi^2 \delta^2$	MnO$^-$	$^5\Sigma^+$	$9\sigma^2 4\pi^2 \delta^2$	$^7\Sigma^+$	$10\sigma^1 9\sigma^1 4\pi^2 \delta^2$
FeO	$^5\Delta$	$9\sigma^1 4\pi^2 \delta^3$	FeO$^-$	$^4\Delta$	$9\sigma^2 4\pi^2 \delta^3$	$^6\Delta$	$10\sigma^1 9\sigma^1 4\pi^2 \delta^3$
CoO[a]	$^4\Delta$	$9\sigma^2 4\pi^2 \delta^3$	CoO$^-$	$^3\Sigma^-$	$9\sigma^2 4\pi^2 \delta^4$	$^5\Delta$	$10\sigma^1 9\sigma^2 4\pi^2 \delta^3$
NiO	$^3\Sigma^-$	$9\sigma^2 4\pi^2 \delta^4$	NiO$^-$	$^2\Pi$	$9\sigma^2 4\pi^3 \delta^4$	$^4\Sigma^-$	$10\sigma^1 9\sigma^2 4\pi^2 \delta^4$
CuO	$^2\Pi$	$9\sigma^2 4\pi^3 \delta^4$	CuO$^-$	$^1\Sigma^+$	$9\sigma^2 4\pi^4 \delta^4$	$^3\Pi$	$10\sigma^1 9\sigma^2 4\pi^3 \delta^4$
ZnO	$^1\Sigma^+$	$9\sigma^2 4\pi^4 \delta^4$	ZnO$^-$	...	...	$^2\Sigma^+$	$10\sigma^1 9\sigma^2 4\pi^4 \delta^4$

[a] The energy splitting between $^4\Delta$ and $^4\Sigma^-$ states of CoO is 0.11 eV.

shell in addition to the half-closed $1\delta^2$ shell. The BPW91 approach favors the high-spin multiplicity state of the CrO$^-$ anion, as does the hybrid B3LYP approach. On the contrary, the BLYP method prefers a low-spin ground state for the anion.

Lineberger et al.[12] have assigned a $^4\Pi$ state as the ground of the CrO$^-$ anion, based on the similarity of the Cr$^-$ and CrO$^-$ photoelectron spectra. They also found that a tentatively assigned $^3\Pi$ state of CrO is displaced from the ground $^5\Pi$ state by 8600(40) cm^{-1}, which is in nice accord with the BPW91 value of 8360 cm^{-1} obtained from the difference in total energies of the ground and $^3\Sigma^-$ triplet states. If the ground state of the CrO$^-$ anion were high-spin, then one could not observe a triplet neutral state, and, instead, a peak corresponding to a neutral state with the multiplicity of seven could be observed. However, the lowest septet state of the neutral CrO is above the ground state by 16200 cm^{-1} according to the results of BPW91 computations. Thus, one may conclude that the BLYP level provides a correct low-spin assignment for the CrO$^-$ anion. On the other hand, one could assert that the BLYP level underestimates the total energies of high-spin multiplicity states of the anions. For example, the BLYP calculations provide 0.5 eV energy between the low- and high-multiplicity states of MnO$^-$, whereas these states appear to be nearly degenerate in total energy according to laser photodetachment data.[16] On the other hand, the experimental[11] $^2\Pi - {}^4\Sigma^-$ splitting for the NiO$^-$ anion is 0.112(4) eV, which is in perfect agreement with the BLYP value of 0.12 eV, whereas the BPW91 value of 0.04 eV is somewhat underestimated. The B3LYP level provides an overestimated value of 0.35 eV (see Table 3).

Charge and Spin Densities. Charges and spin densities (or magnetic moments) on atoms were computed using the conventional Mulliken population analysis. Table 5 presents charges and magnetic moments for neutral monoxides as well as for the low- and high-spin multiplicity states of the anions computed at the BPW91 level of theory. As is seen, charges on atoms in the neutral series are nearly the same. Spin coupling is slightly antiferromagnetic in ScO, TiO, VO, and CrO, whereas oxygen carries an unpaired electron in CoO, NiO, and CuO coupled ferromagnetically to the spin of metal atoms. CuO is the most interesting case: an unpaired electron of its $^2\Pi$ state is localized almost entirely at the oxygen site.

Upon attachment of an extra electron, charges on oxygen atoms grow by 0.2−0.3 *e* in both low- and high-spin multiplicity states of the anions, which means that the extra electron is localized mainly at metal sites. Oxygen remains to be weakly antiferromagnetic in ScO$^-$, TiO$^-$, VO$^-$, and CrO$^-$ in both their low- and high- spin multiplicity states. Magnetic moments are reduced by roughly one in low-spin multiplicity states of the anions MnO$^-$ and FeO$^-$, whereas they are reduced by only half in CoO$^-$ and NiO$^-$ with respect to the magnetic moment values in the corresponding neutral ground states. In the high-spin multiplicity states of the anions, the magnetic moments on metal atoms are increased almost exactly by one.

Electron Affinities. We compare electron affinities calculated at the three levels of theory with experimental data in Table 6. Mean deviations of computed electron affinities from experi-

TABLE 5: Magnetic Moments (μ_A in Bohr magneton) and Charges on Atoms (Q_A, in *e*) Computed at the BPW91/6-311+G* Level for the Ground States of the Neutral Monoxides and Low- and High-Spin States of Their Anions

neutral	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 $^2\Pi$	ZnO $^1\Sigma^+$
μ_M	1.05	2.18	3.33	4.25	4.74	3.50	2.15	1.00	0.08	0.0
μ_O	−0.05	−0.18	−0.33	−0.25	0.26	0.50	0.85	1.00	0.92	0.0
Q_M	0.42	0.36	0.31	0.36	0.42	0.40	0.33	0.31	0.26	0.38
Q_O	−0.42	−0.36	−0.31	−0.36	−0.42	−0.40	−0.33	−0.31	−0.26	−0.38
low-spin	ScO$^-$ $^1\Sigma^+$	TiO$^-$ $^2\Delta$	VO$^-$ $^3\Sigma^-$	CrO$^-$ $^4\Pi$	MnO$^-$ $^5\Sigma^+$	FeO$^-$ $^4\Delta$	CoO$^-$ $^3\Sigma^-$	NiO$^-$ $^2\Pi$	CuO$^-$ $^1\Sigma^+$	ZnO$^-$ ...
μ_M	0.0	1.19	2.28	3.23	3.85	2.66	1.49	0.55	0.0	...
μ_O	0.0	−0.19	−0.28	−0.23	0.15	0.34	0.51	0.45	0.0	...
Q_M	−0.44	−0.44	−0.46	−0.40	−0.33	−0.33	−0.33	−0.32	−0.33	...
Q_O	−0.56	−0.56	−0.44	−0.60	−0.67	−0.67	−0.67	−0.68	−0.67	...
high-spin	$^3\Pi$	$^4\Phi$	$^5\Pi$	$^6\Sigma^+$	$^7\Sigma^+$	$^6\Delta$	$^5\Delta$	$^4\Sigma^-$	$^3\Pi$	$^2\Sigma^+$
μ_M	2.04	3.13	4.23	5.11	5.72	4.48	3.11	2.01	1.05	0.62
μ_O	−0.04	−0.13	−0.23	−0.11	0.28	0.52	0.89	0.99	0.95	0.38
Q_M	−0.42	−0.42	−0.40	−0.31	−0.28	−0.29	−0.39	−0.40	−0.45	−0.29
Q_O	−0.58	−0.58	−0.60	−0.69	−0.72	−0.71	−0.61	−0.60	−0.55	−0.71

TABLE 6: Comparison of Theoretical and Experimental Electron Affinities (in eV) of 3d Metal Monoxides

	ScO	TiO	VO	CrO	MnO	FeO	CoO	NiO	CuO	ZnO
BPW91	1.07	0.94	0.81	1.17	1.04	1.26	1.35	1.29	1.73	2.19
BLYP	1.13	1.06	0.98	1.07	1.26	1.38	1.52	1.31	1.75	2.13
B3LYP	1.26	1.18	1.09	1.22	1.38	1.48	1.25	1.74	1.52	2.33
exp.[a]	1.35 ±0.02	1.30 ±0.03	1.229 ±0.008	1.221 ±0.006	1.375 ±0.01	1.492 ±0.03	1.45 ±0.01	1.46 ±0.02	1.777 ±0.006	2.088 ±0.01

[a] ScO[13], TiO[14], VO[15], CrO[12], MnO[16], FeO[4], CoO[17], NiO[18], CuO[10], ZnO[20].

mental values (neglecting experimental error bars) are 0.22, 0.14, and 0.11 eV at the BPW91, BLYP, and B3LYP levels of theory, respectively. The BPW91 method underestimates the A_{ad} values at the beginning of the series (ScO, TiO, VO, and MnO), whereas B3LYP overestimates the A_{ad}'s of CoO and CuO while underestimating the A_{ad} of the intermediate NiO.

The B3LYP level provides the smallest average error with respect to experimental values of the A_{ad}'s. However, the B3LYP results depend strongly on the choice of a guess wave function. As a matter of fact, optimizations can lead to higher-lying states, especially at the end of the monoxide series. Since the experimental electron affinities are known, we tailored the convergence to proper values in several cases: FeO, CoO, and NiO. Such a strong dependence on the guess parameters makes B3LYP predictions unreliable. The B3LYP level of theory was found to fail when computing the electron affinity of the CN radical,[39] where the BPW91 approach provides a rather good estimate compared with well-known experimental data.[64] B3LYP also failed to predict the singlet state of ZnO as the ground-state,[21,62] having placed the triplet state lower in total energy by about 0.2 eV. Again, the BPW91 level predicts the correct order. However, the B3LYP approach could be useful when evaluating unknown dissociation energy in cases when other data are available for tailoring.

The BLYP approach, similar to the BPW91 one, underestimates the electron affinities of the 3d metal monoxides while slightly overestimating the A_{ad} of CoO compared to the experimental values. The BLYP level also underestimates the binding energies of the extra electron in high-spin multiplicity anion states. On the whole, one could recommend the BPW91 level as more reliable, despite its providing underestimated values for the A_{ad}'s of ScO, TiO, VO, and MnO. Because of controversial results obtained by different methods, a definitive assignment of the ground state for the CrO^- requires further investigations.

Summary

Our density functional theory calculations of the electronic and geometrical structure of 3d metal monoxides and their anions by three density functional theory (DFT)-based methods allow us to estimate the reliability of these methods and draw definite conclusions on the electronic structure of the anions. The pure DFT methods (BPW91 and BLYP) provide similar accuracy in the description of spectroscopic constants and electron affinities of the neutral 3d monoxides, whereas the results of B3LYP calculations show larger deviations from experiment. We have found that the anion states with spin multiplicities that are lower and higher by one than the spin multiplicity of the corresponding neutral parent ground states are stable toward autodetachment of an extra electron. We have assigned the ground states of the anions and computed the electron affinities of the neutral 3d monoxides. The latter are in good agreement with experimental data obtained recently from laser photodetachment experiments.

Acknowledgment. This work was supported in part by a grant to Virginia Commonwealth University by the Department of Energy (grant No. DE-FG02-96ER45579). We appreciate stimulating discussions with Professor L. S. Wang, and his providing us with his experimental data prior to publication.

References and Notes

(1) Huber, K. P.; Herzberg, G. *Constants of Diatomic Molecules*; Van Nostrand-Reinhold: New York, 1979.

(2) Merer, A. J. *Annu. Rev. Phys. Chem*. **1989**, *40*, 407.

(3) Bauschlicher, C. W., Jr.; Maitre, P. *Theor. Chim. Acta* **1995**, *90*, 189.

(4) Engelking, P. C.; Lineberger, W. C. *J. Chem. Phys*. **1977**, *66*, 5054.

(5) Andersen, T.; Lykke, K. R.; Neumark, D. M.; Lineberger, W. C. *J. Chem. Phys*. **1987**, *86*, 1858.

(6) Fan, J.; Wang, L. S. *J. Chem. Phys*. **1995**, *102*, 8714.

(7) Drechsler, G.; Boesl, U.; Bäβmann, C.; Schlag, E. W. *J. Chem. Phys*. **1997**, *107*, 2284.

(8) Dolg, M.; Wedig, U.; Stoll, H.; Preuss, H.; *J. Chem. Phys*. **1987**, *86*, 2123.

(9) Gutsev, G. L.; Khanna, S. N.; Rao, B. K.; Jena, P. *J. Phys. Chem*. **1999**, *103*, 5812.

(10) Polak, M. L.; Gilles, M. K.; Ho, J.; Lineberger, W. C. *J. Phys. Chem*. **1991**, *95*, 3460.

(11) Moravec, V. D.; Jarrold, C. C. *J. Chem. Phys* **1998**, *108*, 1804.

(12) Wenthold, P. G.; Gunion, R. F.; Lineberger, W. C. *Chem. Phys. Lett*. **1996**, *258*, 101.

(13) Wu, H.; Wang, L. S. *J. Phys. Chem. A* **1998**, *102*, 9129.

(14) Wu, H.; Wang, L. S. *J. Chem. Phys*. **1997**, *107*, 8221.

(15) Wu, H.; Wang, L. S. *J. Chem. Phys*. **1998**, *108*, 5310.

(16) Gutsev, G. L.; Rao, B. K.; Jena, P.; Li, X.; Wang, L. S. *J. Chem. Phys*., accepted.

(17) Li, X.; Wang, L. S. *J. Chem. Phys*. **1999**, *111*, 8389.

(18) Wu, H.; Wang, L. S. *J. Chem. Phys*. **1997**, *107*, 16.

(19) Wu, H.; Desai, S. R.; Wang, L. S. *J. Phys. Chem. A* **1997**, *101*, 2103.

(20) Fancher, C. A.; de Clercq, H. L.; Thomas, O. C.; Robinson, D. W.; Bowen, K. H. *J. Chem. Phys*. **1998**, *109*, 8426.

(21) Bauschlicher, C. W.; Patridge, H. *J. Chem. Phys*. **1998**, *109*, 8430.

(22) Walsch, M. B.; King, R. A.; Schaefer, H. F., III. *J. Chem. Phys*. **1999**, *110*, 5224.

(23) Bakalbassis, E. G.; Stiakaki, M.-A. D.; Tsipis, A. C.; Tsipis, C. A. *Chem. Phys*. **1997**, *223*, 169.

(24) Kohn, W.; Sham, L. J. *Phys. Rev*. **1965**, *140*, A1133.

(25) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. *Gaussian 94, Revision B.1*; Gaussian, Inc.: Pittsburgh, PA, 1995.

(26) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098.

(27) Perdew, J. P.; Wang, Y. *Phys. Rev. B* **1991**, *45*, 13244.

(28) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.

(29) Clementi, E.; Chakravorty, S. J. *J. Chem. Phys*. **1990**, *93*, 2591.

(30) Gill, P. M. W.; Johnson, B. G.; Pople, J. A. *Int. J. Quantum Chem. Symp*. **1992**, *26*, 319.

(31) Oliphant, N.; Bartlett, R. J. *J. Chem. Phys*. **1994**, *100*, 6550.

(32) Sekino, H.; Oliphant, N.; Bartlett, R. J. *J. Chem. Phys*. **1994**, *101*, 7788.

(33) Becke, A. D. *J. Chem. Phys*. **1993**, *98*, 5648.

(34) Stevens, P. J.; Devlin, F. J.; Chablowski, C. F.; Frisch, M. J. *J. Phys. Chem*. **1994**, *98*, 11623.

(35) Slater, J. C. *Phys. Rev*. **1951**, *81*, 385.

(36) Vosko, S. H.; Wilk, L.; Nusair, M. *Can. J. Chem*. **1980**, *58*, 1200.

(37) Gill, P. M. W.; Johnson, B. G.; Pople, J. A. *Chem. Phys. Lett*. **1992**, *197*, 499.

(38) Bauschlicher, C. W., Jr. *Chem. Phys. Lett*. **1995**, *246*, 40.

(39) Gutsev, G. L.; Jena, P.; Bartlett, R. J. *J. Chem. Phys*. **1999**, *110*, 403.

(40) Gutsev, G. L.; Khanna, S. N.; Rao, B. K.; Jena, P. *Phys. Rev. A* **1999**, *59*, 3681.

(41) Gutsev, G. L.; Rao, B. K.; Jena, P.; Wang, X. B.; Wang, L. S. *Chem. Phys. Lett*. **1999**, *312*, 598.

(42) Gutsev, G. L.; Rao, B. K.; Jena, P. *J. Phys. Chem. A* **1999**, *103*, 10819.

(43) Bauschlicher, C. W.; Patridge, H. *Chem. Phys. Lett*. **1994**, *231*, 277.

(44) Gordon, R. M.; Merer, A. J. *Can. J. Phys*. **1980**, *58*, 642.

(45) Cheung, A. S. C.; Lee, N.; Lyyra, A. M.; Merer, A. J. *J. Mol. Spectrosc*. **1982**, *95*, 213.

(46) Ram, R. S.; Jarman, C. N.; Bernath, P. F. *J. Mol. Spectrosc*. **1993**, *160*, 574.

(47) Srdanov, V. I.; Harris, D. O. *J. Chem. Phys*. **1988**, *89*, 2748.

(48) Green, D. W.; Reedy, G. T.; Kay, J. G. *J. Mol. Spectrosc*. **1979**, *78*, 257.

(49) Chertihin, G. V.; Andrews, L. *J. Chem. Phys*. **1997**, *106*, 3457.

(50) Rostai, M.; Wahlbeck, P. G. *J. Chem. Thermodyn*. **1999**, *31*, 255.

(51) Naulin, C.; Hedgecock, I. M.; Costes, M. *Chem. Phys. Lett*. **1997**, *266*, 335.

(52) Kang, H.; Beauchamp, J. L. *J. Am. Chem. Soc*. **1986**, *108*, 5663.

(53) Watson, L. R.; Thiem, T. L.; Dressler, R. A.; Salter, R. H.; Murad, E. *J. Phys. Chem*. **1993**, *97*, 5577.

(54) Clemmer, D. E.; Dalleska, N. F.; Armentrout, P. B. *J. Chem. Phys*. **1991**, *95*, 7263.

(55) Shirley, J. E.; Scurlock, C.; Steimle, T. C. *J. Chem. Phys*. **1990**, *93*, 1568.

(56) Steimle, T. C.; Shirley, J. E. *J. Chem. Phys*. **1989**, *91*, 8000.

(57) Suenram, R. D.; Fraser, G. T.; Lovas, F. J.; Gillies, C. W. *J. Mol. Spectrosc*. **1991**, *148*, 114.

(58) Steimle, T. C.; Nachman, D. F.; Shirley, J. E.; Bauschlicher, C. W.; Langhoff, S. R. *J. Chem. Phys*. **1989**, *91*, 2049.

(59) Steimle, T. C.; Nachman, D. F.; Shirley, J. E.; Merer, A. J. *J. Chem. Phys*. **1989**, *90*, 5360.

(60) Steimle, T. C.; Nachman, D. F.; Fletcher, D. A. *J. Chem. Phys*. **1987**, *87*, 5670.

(61) DeVore, T. C.; Gallaher, T. N. *J. Chem. Phys*. **1979**, *71*, 474.

(62) Boldyrev, A. I.; Simons, J. *Mol. Phys*. **1997**, *92*, 365.

(63) Hotop, H.; Lineberger, W. C. *J. Phys. Chem. Ref. Data* **1985**, *14*, 731.

(64) Gutsev, G. L.; Rao, B. K.; Jena, P. *J. Chem. Phys*., to be submitted.