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Similarities and differences in the structure of 3*d*-metal monocarbides and monoxides

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Abstract. The structure and properties of the monocarbides ScC, TiC, VC, CrC, MnC, FeC, CoC, NiC, CuC, ZnC and their negatively and positively charged ions together with 3*d*-metal monoxide cations are calculated by density functional theory (DFT) and hybrid DFT methods. In addition to the spectroscopic constants, the computed properties include the electron affinities, ionization energies, and dissociation energies. These results along with our previous results for the neutral and negatively charged 3*d*-metal monoxides allow a detailed comparison of similarity and differences in the bonding of the metal oxides and carbides. These results are compared with results obtained using other theoretical approaches and with experiment. Chemical bonding, analyzed using the natural bond orbital scheme, was found to be rather different in the 3*d*-metal monocarbides and monoxides.

Keywords: 3*d*-metal monoxide – 3*d*-metal monocarbide – Density functional theory – Electron affinity – Ionization energy

1 Introduction

Transition-metal carbides and oxides are very important technological materials and their structure and properties have been the subject of numerous investigations [1–3]. However, the structure of the simplest gas-phase 3*d*-metal monocarbides and their ions seems to be not well understood. For ScC, an upper limit for the dissociation energy was obtained [4] to be $D_0^\circ(\mathrm{ScC}) \leq 440 \pm 21$ kJ mol^{-1}. Electron spin resonance measurements have predicted the ground state of VC [5] and CoC [6] to be $^2\Delta$ and $^2\Sigma$, respectively. For CoC, laser-induced fluorescence studies [7, 8] have been used to determine the $^2\Sigma^+$ ground state r_e and ω_e values. Iron monocarbide has received the most attention [9–14] among all the monocarbides and spectroscopic parameters of its ground $^3\Delta$ state and several excited states were derived from experimental data. Experimental data are available [15–18] for the $M^+ + \mathrm{C}$ dissociation energies of ScC$^+$, TiC$^+$, VC$^+$, FeC$^+$, and CoC$^+$. Laser photodetachment spectra were obtained(LS Wang, personal communication) for CoC$^-$ and NiC$^-$.

Theoretical studies of 3*d*-metal monocarbides were performed at different levels of theory including density functional theory (DFT) and hybrid DFT methods for ScC [19, 20], TiC [21–23], VC [24, 25], CrC [26, 27], FeC [28–31], NiC [32–35], CuC [36], ZnC [37], ScC$^+$, TiC$^+$ [38], and CrC$^+$ [39]. We are unaware of any computational studies for the 3*d*-metal monocarbide anions. A comparison of the ground-state spin multiplicities, bond lengths, and vibrational frequencies of neutral 3*d*-metal carbides obtained by different methods was published recently [20]. As is quite common for transition-metal compounds, the results of calculations depend strongly on the method and basis set used.

Unlike the carbides, the gas-phase 3*d*-metal monoxides along with their positively and negatively charged ions have received more attention and the structure of at least their ground states is known. Reliable experimental data are available on the bond lengths [40–44], vibrational frequencies [40, 45, 46], dissociation energies [47–52], and dipole moments [53–58] of all the neutral 3*d*-metal monoxides except dipole moments of MnO, CoO, NiO, and ZnO. Photodetachment spectra have been obtained for all the 3d-metal monoxide anions [59–74] and some spectroscopic parameters of the anions were derived from the spectra along with the electron affinities of the neutral monoxides. For the 3*d*-metal monoxide cations, the dissociation energies have been measured [75, 76].

On the theoretical side, the structure of the neutral 3*d*-metal monoxides has been calculated by a number of

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methods (see Refs [77–81] and references therein). The structure of the monoxide anions was calculated [81] by DFT and hybrid DFT methods, while that of the monoxide cations was calculated recently [82] by ab initio, DFT, and hybrid DFT methods.

Excluding CrO^-, computational and experimental studies are in agreement for the assignment of the ground states of the neutral 3*d*-metal monoxides and their ions. CrO^- is a difficult case as there are two very close states [62, 63], separated by only 0.096±0.050 eV. Lineberger et al. [62] tentatively assigned the ground state of CrO^- to be $^4\Pi$, while on the basis of DFT calculations, Gutsev et al. [63] assigned it as $^6\Sigma^+$. Our recent-high level computations [83], which reproduce the experimental separation between the two lowest states of CrO^-, show that the ground state is $^4\Pi$.

The aim of the present work is fourfold:

1. To evaluate the performance of DFT methods with a generalized gradient approximation for the exchange–correlation potential.
2. To compare the pure DFT results to those obtained using the hybrid B3LYP method.
3. To compare the trends in the series of neutral as well as negatively and positively charged 3*d*-metal monocarbides and monoxides.
4. To gain insight into the similarities and differences in the chemical bonding of the metal monocarbides and monoxides.

2 Computational details

The (15s11p6d1f)/[10s7p4d1f] basis due to Wachters [84], Hay [85], and Raghavachari and Trucks [86] referred as to 6-311+G* in the Gaussian98 software [87] is used for the 3*d*-metal atoms and the conventional [88] 6-311+G* basis sets are used for carbon and oxygen. Computations are performed using two different pure DFT functionals [the exchange–correlation potentials are combinations of Becke's exchange [89] and Perdew and Wang's correlation [90] (BPW91) and Becke's exchange [89] with Lee, Yang, and Parr's correlation [91] (BLYP)] and using the popular hybrid [92, 93] B3LYP method.

The zero-point energy (ZPE) is taken as half the computed ω_e value without any scaling. The electron affinities (EA) and ionization energies (IE) reported in this work are adiabatic values, that is, each state is at its equilibrium bond length. Dissociation energies are computed as the differences in total energies of a diatomic and the corresponding constituent atomic species corrected for the ZPE of the diatomic. No constraints are imposed in the atomic calculations; thus, the metal configuration can be a mixture of the $3d^{n+1}4s^1$ and $3d^n4s^2$ states.

The geometry was optimized for each possible spin multiplicity until further increasing the spin multiplicity would result in a state whose total energy is above the energy of the lowest asymptote. Different starting geometries and/or orbitals were used to find the ground state. Useful empirical criteria that one has obtained the ground states of a species and its ions are the spin multiplicities of a neutral and its single charged ions differ by ±1, and the change in the bond length due to attachment or detachment of an electron is relatively small. For 3*d*-metal monocarbides and monoxides we did not find any contradiction to these guidelines. For some states, where π orbitals have not been resolved by symmetry, their assignment as Π states was supported by the results of population analyses performed within the conventional Mulliken [94] or natural atomic orbitals (NAO) [95,96] schemes. The calculations were performed using Gaussian98 [87].

3 3*d*-metal atoms and their ions

Since the total energies of atoms and their ions are required to compute the dissociation energies, it is appropriate to take a closer look at their ground-state occupations. The 3*d* and 4*s* populations computed at the BPW91 level are given in Table 1 as representatives. A more detailed discussion of the DFT description of neutral 3*d*-metal atoms and their anions is given elsewhere [97]. All the 3*d*-metal atoms possess $3d^n4s^2$ electronic ground-state occupations except Cr, Ni, and Cu, which have $3d^{n+1}4s^1$ ground-state occupations. As shown in Table 1, the BPW91 method favors $3d^{n+1}4s^1$ occupations with some admixture of $3d^n4s^2$ configurations for all the atoms except Sc, Mn, and Zn. The admixture is rather large for the Fe atom. Excluding Sc, there is much less mixing of the $3d^n$ and $3d^{n+1}$ occupations for the cations and anions. Our computed EA and IE values together with experimental data [98,99] are presented in Table 1. Overall, the agreement between theory and experiment is reasonable, which might seem surprising considering that for some atoms the BPW91 approach yields the wrong ground state, for example, Ti, where BPW91 yields a $3d^34s^1$ ground state which is actually 0.81 eV above the $3d^24s^2$ occupation.

The BPW91 EA values of C and O, 1.54 and 1.63 eV, respectively, are larger than the experimental values [98] of 1.26 and 1.46 eV. The computed IEs of C and O are 11.56 and 14.04 eV, respectively, which are also larger than the experimental values [100] of 11.26 and 13.61 eV. Actually, the errors in the IE and EA values for C and O are similar to those found for the 3*d*-metal atoms.

4 Structure and properties

Our ground-state spectroscopic constants for the neutral oxides and carbides are summarised in Tables 2 and 3. The results of recent CASSCF/MRCI (for carbides) and CCSD(T) (for oxides) calculations are also included along with experimental data. The spectroscopic constants for the ground states obtained at lower levels of theory may be found elsewhere [20].

Our assignment of the ground states of VC, CrC, FeC, and NiC is the same for all functionals used here and agrees with the MRCI assignment. For FeC and NiC, theory is in accord with the experimental assignment. For ScC and TiC, our results do not agree with the MRCI results. For ScC, the MRCI approach [20] yields a $^2\Pi$ ground state, with the $^2\Sigma^+$ state 2518 cm^{-1} higher in energy. The BPW91 shows the opposite order and places $^2\Pi$ (r_e = 1.895 Å, ω_e = 684 cm^{-1}) above $^2\Sigma^+$ (r_e = 1.758 Å, ω_e = 854 cm^{-1}) by 1872 cm^{-1}. The BLYP provides similar results, while the B3LYP favors the $^2\Pi$ (r_e = 1.904 Å, ω_e = 698 cm^{-1}) as the ground state, but the difference in total energy with $^2\Sigma^+$ (r_e = 1.753 Å, ω_e = 861 cm^{-1}) is only 55 cm^{-1}. Bond lengths of ScC obtained for both states in BPW91, BLYP and B3LYP calculations are close to each other, but are significantly different from those obtained in the MRCI computations [20],

Table 1. The natural atomic orbital (NAO) populations of the BPW91 ground state for the 3*d*-metal atoms and their ions

	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Neutral										
Multiplicity	2	5	6	7	6	5	4	3	2	1
$3d$	1.2	3.0	4.0	5.0	5.1	6.6	7.9	8.9	10.0	10.0
$4s$	1.8	1.0	1.0	1.0	1.9	1.4	1.1	1.1	1.0	2.0
$\Delta_{sd}(X)$ Exp.(eV)[a]	1.43	0.81	0.25	−1.0	2.15	0.87	0.42	−0.03	−1.49	...
EA BPW91 (eV)	0.19	0.43	0.35	0.29	−0.38[b]	0.61	0.90	1.04	1.16	−0.99[b]
Exp.[c]	0.19	0.08	0.53	0.67	≤0.0	0.16	0.66	1.16	1.23	≤0.0
IE BPW91(eV)	6.16	6.54	6.96	7.29	7.07	7.83	7.86	8.02	8.12	9.35
Exp.[d]	6.56	6.83	6.74	6.77	7.44	7.90	7.86	7.64	7.73	9.39
Anion										
Multiplicity	3	4	5	6	7	4	3	2	1	2
$3d$	1.7	3.0	4.0	5.0	5.0	7.0	8.0	9.0	10.0	10.0
$4s$	2.0	2.0	2.0	1.9	2.0	2.0	2.0	2.0	2.0	2.0
$4p$	0.0	0.0	0.0	0.1	1.0	0.0	0.0	0.0	0.0	1.0
$5s$	0.3	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Cation										
Multiplicity	3	4	5	6	7	4	3	2	1	2
$3d$	1.5	3.0	4.0	5.0	5.0	7.0	8.0	9.0	10.0	10.0
$4s$	0.5	0.0	0.0	0.0	1.0	0.0	0.0	0.0	0.0	1.0

[a] $\Delta_{sd} = E_{total}(3d^{n+1}4s^1) - E_{total}(3d^n4s^2)$. Negative values indicate $3d^{n+1}4s^1$ is the ground-state configuration. The lowest excited configuration of Zn is $3d^{10}4s^14p^1$

[b] Indicates that the system will not attach an extra electron

[c] From Ref. [98]

[d] From Ref. [99]

Table 2. Spectroscopic constants of neutral ground-state monocarbides

		ScC $^2\Sigma^+$	TiC $^1\Sigma^+$	VC $^2\Delta$	CrC $^3\Sigma^-$	MnC $^4\Sigma^-$	FeC $^3\Delta$	CoC $^2\Sigma^+$	NiC $^1\Sigma^+$	CuC $^2\Pi$	ZnC $^3\Sigma^-$
r_e	BPW91	1.756	1.637	1.598	1.591	1.606	1.566	1.542	1.631	1.811	1.971
(Å)	BLYP	1.779	1.651	1.612	1.602	1.608	1.574	1.552	1.640	1.823	1.998
	B3LYP	1.753	1.609	1.587	1.636	1.699	1.621	1.527	1.621	1.843	2.011
	MRCI[a]	1.823	1.790	1.645	1.676	...	1.585	...	1.631	...	...
	Exp.	...	...	...	...	...	1.596[b]	1.561[c]	1.631[d]	...	...
ω_e	BPW91	853	921	1006	938	831	949	1050	914	628	478
(cm^{-1})	BLYP	821	869	962	907	839	940	1027	897	613	439
	B3LYP	861	967	946	638	542	606	700	930	585	430
	MRCI[b]	759	592	733	675	...	859	...	875	...	...
	Exp.	...	...	...	...	...	863[e]	934[f]	...	...	...
μ	BPW91	6.51	5.92	5.77	5.55	2.75	2.38	2.16	1.91	2.44	2.98
(D)	BLYP	6.30	5.30	5.59	5.32	2.80	2.41	2.14	1.77	2.28	2.88
	B3LYP	6.86	5.97	6.02	5.74	3.00	2.70	2.35	2.20	2.75	2.98
	MRCI[b]	5.94	2.16	...	6.84	...	1.86	...	2.36	...	...
D_0	BPW91	4.02[g]	4.57	4.39	3.50	4.65	4.88	4.57	4.39	2.54	1.37
(eV)	BLYP	3.72	4.62	4.60	3.80	4.38	4.80	4.53	4.41	2.59	1.17
	B3LYP	3.08	4.10	3.72	2.80	3.07	3.78	3.11	3.06	2.04	1.00
	MRCI[h]	2.48	2.61	2.88	3.86	...	2.77	...	2.70	...	...

[a] ScC [20], the lowest excited state is $^2\Pi$, by 0.31 eV; TiC [23], the lowest excited state is $^3\Sigma^+$, by 0.16 eV; VC [25], CrC [27], FeC [31], NiC [35]

[b] See Ref. [10]

[c] See Ref. [7]

[d] Brugh, DJ and Morse MD, as cited in Ref. [35]

[e] See Ref. [12]

[f] See Ref. [7]

[g] Experimental value [4] D_0^0(ScC)≤ 4.56 ± 0.22 eV

[h] MRCI: ScC [20], TiC [23], VC [25], CrC [27], FeC [31], NiC [35]

namely, $^2\Pi$ (r_e = 1.988 Å, ω_e = 607 cm^{-1}) and $^2\Sigma^+$ (r_e = 1.823 Å, ω_e = 759 cm^{-1}). The leading electronic configurations of the $^2\Sigma^+$ and $^2\Pi$ states are $8\sigma^13\pi^4$ and $8\sigma^23\pi^3$, respectively.

For TiC, there are also two closely spaced lowest-energy states $^1\Sigma^+$ ($8\sigma^23\pi^4$) and $^3\Sigma^+$ ($9\sigma^18\sigma^13\pi^4$). Both CASSCF/CCI [21] and recent CASSCF/MRCI [23] computations have placed $^1\Sigma^+$ above $^3\Sigma^+$ by 780 and 1250 cm^{-1}, respectively. All our computations performed at the BPW91, BLYP, and B3LYP levels favor $^1\Sigma^+$ as the ground state, placing $^3\Sigma^+$ higher by 887, 645, and 242 cm^{-1}, respectively. While the DFT and MRCI approaches are in reasonable agreement for the $^3\Sigma^+$ r_e and ω_e values, there are surprising differences between the DFT and MRCI approaches for the $^1\Sigma^+$ r_e and ω_e values. Note that the $^1\Sigma^+$ state corresponds to the (2) $^1\Sigma^+$ excited

Table 3. Comparison of results of BPW91, BLYP, B3LYP, and CCSD(T) calculations with experimental data for the neutral ground-state 3*d*-metal monoxides

	Method	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 $^1\Sigma^+$
r_e	BPW91	1.665	1.618	1.586	1.611	1.628	1.608	1.637	1.639	1.734	1.714
(Å)	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	1.632	1.767	1.719
	Theory[a]	1.679	1.628	1.602	1.633	1.665	1.609	1.621	1.626	1.771	1.719
	Exp.[b]	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
(cm^{-1})	BLYP	953	993	1002	903	876	881	878	808	630	707
	B3LYP	999	1045	1044	870	868	897	832	851	581	720
	Theory[a]	971	1014	1028	888	794	885	909	850	572	731
	Exp.[c]	971	1009	1011	898	840	880	853	838	640	769
μ	BPW91	3.58	3.37	3.35	3.64	4.36	4.37	4.07	4.06	4.38	5.46
(D)	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	4.74	4.72	5.80
	Theory[a]	3.91	3.79	3.60	3.89	4.99	4.17	3.46	3.91	5.11	5.37[d]
	Exp.[e]	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
(eV)	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	3.56	2.68	1.17
	Theory[a]	6.90	6.84	6.26	4.30	3.56	3.65	3.64	3.75	2.66	1.63
	Exp.[f]	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] Results of CCSD(T) calculations are from Ref. [77], except for those for ZnO, which are from Ref. [78]

[b] Experimental data are from Ref. [40], except for MnO [41], FeO [42], CoO [43], and NiO [44]

[c] Experimental frequencies are from Ref. [40], except for FeO, NiO, and CoO (see Ref. [45]) and ZnO [46]

[d] The QCISD(T)/6-311 + G(2d,2f) value from Ref. [79]

[e] Experimental dipole moments: ScO [53]; TiO [54]; VO [55]; CrO [56]; FeO [57]; CuO [58]

[f] Experimental D_0 are from Ref. [47] except for ScO [48], TiO [49], CrO [50], NiO [51], CuO [51], and ZnO [52]

state in the MRCI calculations [23]. We suspect that the DFT approaches have incorrectly ordered the two lowest states for ScC and TiC as has been found [83] for some other transition-metal-containing species. However, an experimental determination of the ground states of ScC and TiC would be ideal.

As shown in Table 2, the discrepancies between the BPW91, BLYP, and experimental r_e values for FeC, CoC, and NiC are the largest for FeC. The B3LYP predicts the same r_es for FeC and NiC and underestimates the r_e of CoC. Experimental frequencies appear to be measured only for FeC and CoC. Both BPW91 and BLYP frequencies of these species are overestimated by as much as 100 cm^{-1}, while the B3LYP underestimates them by around 250 cm^{-1}.

Unlike the carbides, no significant discrepancies between post-Hartree–Fock, DFT, and hybrid DFT results have been found [81] for 3*d*-metal oxides, and the BPW91 results agree better with the experimental values of r_e and ω_e (the average deviations with respect to experiment are $\Delta r_e = 0.008$ Å and $\Delta\omega_e = 16.5$ cm^{-1}), while both CCSD(T) and B3LYP provide the smallest average deviations with respect to experiment in D_0 (0.23 and 0.19 eV, respectively). Both BPW91 and BLYP D_0 discrepancies are higher (0.79 and 0.70 eV, respectively), which has to be partly related with difficulties of pure DFT methods in describing the ground states of the 3*d*-metal atoms as stated in the previous section.

5 Charged species

The results of our BPW91, BLYP, and B3LYP computations are presented in Tables 4 and 5 along with the MRCI results and experimental dissociation energies for the monocarbide and monoxide cations, respectively. No experimental data seem to be available on the bond lengths or vibrational frequencies in both series. As for the 3*d*-metal monocarbide cations, the results of the MRCI calculations for ScC^+ and TiC^+ have recently been reported [38]. There is no controversy about the assignment of the ground states ($^3\Pi$ and $^2\Sigma^+$, respectively) of these cations. The ground state of the CrC^+ is assigned as $^4\Sigma^-$ according to the results of the BPW91 and B3LYP computations, while the BLYP level shows the lowest state to be $^2\Delta$. The differences in $E_{tot}(^2\Delta)$–$E_{tot}(^4\Sigma^-)$ are rather small: 0.058 eV (BPW91), –0.033 eV (BLYP), and 0.16 eV (B3LYP). Therefore, further studies are required to reliably assign the ground state of this cation.

The differences between bond lengths and vibrational frequencies of the monocarbide cations computed at the DFT, B3LYP, and MRCI levels are smaller than those found for the corresponding neutral parents. The same holds for the monoxide cations where MRCI computations [82] have produced essentially the same bond lengths and vibrational frequencies as those computed at the BPW91 level for all the species except MnO^+ and CuO^+.

Table 4. Spectroscopic constants of ground-state monocarbide cations

	State	ScC^{+a} $^3\Pi$	TiC^{+a} $^2\Sigma^+$	VC^+ $^3\Delta$	CrC^+ $^4\Sigma^-$	MnC^+ $^3\Sigma^-$	FeC^+ $^2\Delta$	CoC^+ $^1\Sigma^+$	NiC^+ $^2\Sigma^+$	CuC^+ $^3\Pi$	ZnC^+ $^2\Pi$
r_e	BPW91	1.846	1.647	1.620	1.609	1.564	1.529	1.508	1.616	1.822	2.090
(Å)	BLYP	1.862	1.660	1.633	1.622	1.569	1.538	1.518	1.627	1.838	2.115
	B3LYP	1.841	1.633	1.609	1.636	1.637	1.572	1.482	1.616	1.872	2.115
ω_e	BPW91	787	979	1008	962	905	1027	1109	919	578	429
(cm^{-1})	BLYP	762	948	977	941	907	1010	1082	895	560	406
	B3LYP	775	986	989	743	606	623	1162	802	509	413
D_0	BPW91	3.75	4.37	3.99	2.83	3.96	4.86	4.45	4.05	2.02	1.86
(eV)	BLYP	3.62	4.22	4.04	3.02	4.19	4.84	4.43	4.09	2.06	2.00
	B3LYP	3.26	3.76	3.13	1.95	2.89	3.48	2.76	2.67	1.58	1.67
	Exp.[b]	3.34	4.05	3.95	...	...	4.08	3.90[c]	...	...	...
		±0.06	±0.24	±0.04	...	...	±0.30	±0.30	...	...	...

[a] MRCI ground-state data [38] are ScC^+ $^3\Pi$, $r_e = 1.908$, $\omega_e = 709$ and TiC^+ $^2\Sigma^+$, $r_e = 1.696$, $\omega_e = 859$

[b] Experimental D_o: ScC^+ [16], TiC^+ [16], VC^+[15], FeC^+ [17], CoC^+ [17]

[c] Another experimental D_o of CoC^+ is 3.58 ± 0.30 [18]

Table 5. Spectroscopic constants of ground-state monoxide cations

	State	ScO^+ $^1\Sigma^+$	TiO^+ $^2\Delta$	VO^+ $^3\Sigma^-$	CrO^+ $^4\Sigma^-$	MnO^+ $^5\Pi$	FeO^+ $^6\Sigma^+$	CoO^+ $^5\Delta$	NiO^+ $^4\Sigma^-$	CuO^+ $^3\Sigma^-$	ZnO^+ $^2\Pi$
r_e	BPW91	1.622	1.579	1.547	1.571	1.638	1.638	1.633	1.630	1.777	1.824
(Å)	BLYP	1.635	1.592	1.558	1.581	1.645	1.652	1.647	1.643	1.783	1.832
	B3LYP	1.612	1.570	1.537	1.592	1.730	1.641	1.640	1.645	1.811	1.818
	MRCI[a]	1.649	1.607	1.566	1.614	1.814	1.646	1.632	1.612	1.678	1.799
ω_e	BPW91	1041	1089	1108	929	724	847	821	799	553	575
(cm^{-1})	BLYP	1019	1063	1083	920	732	825	801	779	571	560
	B3LYP	1074	1122	1138	764	639	819	760	688	487	590
	MRCI[a]	...	...	...	856	801	845	833	859	802	...
D_0	BPW91	7.42	7.16	6.37	3.93	3.29	4.14	3.68	3.23	1.74	1.69
(eV)	BLYP	7.49	7.23	6.55	4.28	3.62	4.19	3.83	3.36	1.90	1.82
	B3LYP	6.93	6.72	5.60	3.00	2.69	3.23	2.79	2.24	1.27	1.51
	MRCI[a]	6.56	6.30	5.85	3.07	1.95	3.03	3.26	2.41	0.76	1.36
	Exp.[b]	7.14	6.88	5.81	3.72	2.95	3.53	3.32	2.74	1.62	1.65
		±0.11	±0.07	±0.17	±0.12	±0.13	±0.06	±0.06	±0.07	±0.15	±0.12

[a] MRCI data from Ref. [82]

[b] Experimental D_0 are from Refs. [75, 76]

There is rather close agreement between the results obtained for the monoxide cations at the DFT and B3LYP levels except MnO^+, where the B3LYP predicts somewhat larger r_e. The MnO^+ cation appears to present a difficult case [101] for pure DFT methods since there is a $^5\Sigma^+$ state which is close to the ground $^5\Pi$ state. While CASSCF/IC-MRCI, CASSCF/IC-ACPF, and B3LYP methods do predict [101] the gap of around 2000 cm^{-1} between these two states, the pure DFT methods decrease the gap to 50–200 cm^{-1}.

The largest deviations, neglecting experimental error bars, in dissociation energies are 0.61 eV (BPW91, FeO^+), 0.74 eV (BLYP, VO^+), 0.72 eV (B3LYP, CrO^+), and 1.00 eV (MRCI, MnO^+). On average, the BPW91 provides an error in the dissociation energies of the monoxide cations of 0.33 eV, BLYP – 0.49 eV, B3LYP – 0.33 eV, and MRCI – 0.44 eV. As a matter of fact, the B3LYP error in the D_0 of the monoxide cations is larger than that of the neutral monoxides. In contrast, the pure DFT method shows an essential reduction of the error. The latter appears to be due to a better description of electronic configurations of the 3*d*-metal ions as stated in Sect. 3.

Large discrepancies between the BPW91 and BLYP (which provide rather similar r_es and ω_es), and B3LYP results for the center of the series CrC^+, MnC^+, and FeC^+ are found (see Table 4). Thus for FeC^+, the B3LYP ω_e is reduced by as much as 400 cm^{-1}, and the B3LYP D_0 is smaller than the experimental value by 1.19 eV, which is larger than the errors obtained at the BPW91 (0.78 eV) and BLYP (0.76 eV) levels. As shown below, the spin polarization in CrC, MnC, and FeC is largest in the monocarbide and monoxide series and we suspect that this is a reason for the poorer performance of the B3LYP for the monocarbides with respect to the monoxides, which posess a smaller spin polarization.

There are no prior computational data for the 3*d*-metal monocarbide anions. The results of our

Table 6. Spectroscopic constants of ground-state monocarbide and monoxide anions computed at the BPW91 level

	ScC^-	TiC^-	VC^-	CrC^-	MnC^-	FeC^-	CoC^-	NiC^-	CuC^-	ZnC^-
State	$^1\Sigma^+$	$^2\Sigma^+$	$^3\Delta$	$^4\Sigma^-$	$^3\Sigma^-$	$^2\Delta$	$^1\Sigma^+$	$^2\Pi$	$^3\Sigma^-$	$^4\Sigma^-$
r_e(Å)	1.819	1.681	1.642	1.643	1.618	1.584	1.564	1.650	1.824	2.061
ω_e(cm^{-1})	782	866	917	813	839	937	1028	850	575	395
D_0(eV)	3.50	4.24	4.18	3.43	4.03	4.45	4.33	4.05	2.75	1.22
	ScO^-	TiO^-	VO^-	CrO^-	MnO^-	FeO^-	CoO^-	NiO^-	CuO^-	ZnO^-
State	$^1\Sigma^+$	$^2\Delta$	$^3\Sigma^-$	$^4\Pi$	$^5\Sigma^+$	$^4\Delta$	$^3\Sigma^-$	$^2\Pi$	$^1\Sigma^+$	$^2\Sigma^+$
r_e[a]	1.697	1.644	1.609	1.629	1.655	1.632	1.616	1.655	1.705	1.776
ω_e[b]	916	963	970	879	836	849	822	780	701	629
D_0	7.20	6.98	6.21	4.17	4.78	4.90	4.37	4.27	3.19	2.28

[a] Experimental data CuO^- = 1.670(10)Å [72]

[b] Experimental data: CrO^- = 885(80) [62]; MnO^- = 820(40) [64]; FeO^- = 740(20) [68]; CuO^- = 739(25) cm^{-1} [72]

BPW91 calculations on the MC^- and MO^- anions are presented in Table 6. It is interesting to note that CrC^- and ZnC^- both possess quartet states, even though Cr atom has a ^7S ground state and Zn has a ^1S ground state. The behavior of the ground-state spin multiplicies is rather different in the two series beginning with Cr.

Because of overall better agreement with experiment obtained at the BPW91 level, we chose to analyze bonding patterns in neutral and charged monocarbide and monoxide series using the results of the BPW91 natural bond orbital (NBO) analysis. The valence molecular orbital configurations of all the species considered are presented in Table 7. Comparison shows that most isoelectronic carbides and oxides have different electronic occupation, see, for example, CuC and CoO, NiC and FeO, and CoC and MnO.

The trend in the spin multiplicity for the monocarbide cation series is not as regular as that of the monoxide cations. Such differences in the spin multiplicity behavior may be related to the fact that, except for ScC^+ and ZnC^+, ionization involves detachment of a 8σ or 9σ electron, while no such "σ preference" is observed for the monoxides.

6 Electron affinities

The experimental electron affinities of all the 3*d*-zmonoxides, CoC, and NiC were obtained from photoelectron spectra (LS Wang, personal communication, [59–74]) and are presented in Table 8 together with the results of our BPW91 calculations. The electron affinities of the monocarbides are reasonably similar, falling in the range 0.92–1.75 eV. The differences between the theoretical EA values of the corresponding monocarbide and monoxide species are rather small; excluding Zn, the differences are less than 0.5 eV. Agreement with experiment at the beginning of the monoxide series is not as good as at the end of the series. We should note that Schaefer et al. [102] obtained a better value for the TiO EA value using the BP86 level of theory with a

Table 7. Ground-state occupations of the neutral and charged 3*d* metal monocarbides and monoxides

	Neutral			Anion			Cation	
	State	Electronic config.		State	Electronic config.		State	Electronic config.
ScC	$^2\Sigma^+$	$8\sigma^1 3\pi^4$	ScC^-	$^1\Sigma^+$	$8\sigma^2 3\pi^4$	ScC^+	$^3\Pi$	$8\sigma^1 3\pi^3$
TiC	$^1\Sigma^+$	$8\sigma^2 3\pi^4$	TiC^-	$^2\Sigma^+$	$9\sigma^1 3\pi^4$	TiC^+	$^2\Sigma^+$	$8\sigma^1 3\pi^4$
VC	$^2\Delta$	$8\sigma^2 3\pi^4 \delta^1$	VC^-	$^3\Delta$	$9\sigma^1 3\pi^4 \delta^1$	VC^+	$^3\Delta$	$8\sigma^1 3\pi^4 \delta^1$
CrC	$^3\Sigma^-$	$8\sigma^2 3\pi^4 \delta^2$	CrC^-	$^4\Sigma^-$	$9\sigma^1 3\pi^4 \delta^2$	CrC^+	$^4\Sigma^-$	$8\sigma^1 3\pi^4 \delta^2$
MnC	$^4\Sigma^-$	$9\sigma^1 3\pi^4 \delta^2$	MnC^-	$^3\Sigma^-$	$9\sigma^2 3\pi^4 \delta^2$	MnC^+	$^3\Sigma^-$	$8\sigma^2 3\pi^4 \delta^2$
FeC	$^3\Delta$	$9\sigma^1 3\pi^4 \delta^3$	FeC^-	$^2\Delta$	$9\sigma^2 3\pi^4 \delta^3$	FeC^+	$^2\Delta$	$8\sigma^2 3\pi^4 \delta^3$
CoC	$^2\Sigma^+$	$9\sigma^1 3\pi^4 \delta^4$	CoC^-	$^1\Sigma^+$	$9\sigma^2 3\pi^4 \delta^4$	CoC^+	$^1\Sigma^+$	$8\sigma^2 3\pi^4 \delta^4$
NiC	$^1\Sigma^+$	$9\sigma^2 3\pi^4 \delta^4$	NiC^-	$^2\Pi$	$9\sigma^2 4\pi^1 \delta^4$	NiC^+	$^2\Sigma^+$	$9\sigma^1 3\pi^4 \delta^4$
CuC	$^2\Pi$	$9\sigma^2 4\pi^1 \delta^4$	CuC^-	$^3\Sigma^-$	$9\sigma^2 4\pi^2 \delta^4$	CuC^+	$^3\Pi$	$9\sigma^1 4\pi^1 \delta^4$
ZnC	$^3\Sigma^-$	$9\sigma^2 4\pi^2 \delta^4$	ZnC^-	$^4\Sigma^-$	$10\sigma^1 4\pi^2 \delta^4$	ZnC^+	$^2\Pi$	$9\sigma^2 4\pi^1 \delta^4$
ScO	$^2\Sigma^+$	$9\sigma^1 3\pi^4$	ScO^-	$^1\Sigma^+$	$9\sigma^2 3\pi^4$	ScO^+	$^1\Sigma^+$	$8\sigma^2 3\pi^4$
TiO	$^3\Delta$	$9\sigma^1 3\pi^4 \delta^1$	TiO^-	$^2\Delta$	$9\sigma^2 3\pi^4 \delta^1$	TiO^+	$^2\Delta$	$8\sigma^2 3\pi^4 \delta^1$
VO	$^4\Sigma^-$	$9\sigma^1 3\pi^4 \delta^2$	VO^-	$^3\Sigma^-$	$9\sigma^2 3\pi^4 \delta^2$	VO^+	$^3\Sigma^-$	$8\sigma^2 3\pi^4 \delta^2$
CrO	$^5\Pi$	$9\sigma^1 4\pi^1 \delta^2$	CrO^-	$^4\Pi$	$9\sigma^2 4\pi^1 \delta^2$	CrO^+	$^4\Sigma^-$	$9\sigma^1 3\pi^4 \delta^2$
MnO	$^6\Sigma^+$	$9\sigma^1 4\pi^2 \delta^2$	MnO^-	$^5\Sigma^+$	$9\sigma^2 4\pi^2 \delta^2$	MnO^+	$^5\Pi$	$9\sigma^1 4\pi^1 \delta^2$
FeO	$^5\Delta$	$9\sigma^1 4\pi^2 \delta^3$	FeO^-	$^4\Delta$	$9\sigma^2 4\pi^2 \delta^3$	FeO^+	$^6\Sigma^+$	$9\sigma^1 4\pi^2 \delta^2$
CoO	$^4\Delta$	$9\sigma^2 4\pi^2 \delta^3$	CoO^-	$^3\Sigma^-$	$9\sigma^2 4\pi^2 \delta^4$	CoO^+	$^5\Delta$	$9\sigma^1 4\pi^2 \delta^3$
NiO	$^3\Sigma^-$	$9\sigma^2 4\pi^2 \delta^4$	NiO^-	$^2\Pi$	$9\sigma^2 4\pi^3 \delta^4$	NiO^+	$^4\Sigma^-$	$9\sigma^1 4\pi^2 \delta^4$
CuO	$^2\Pi$	$9\sigma^2 4\pi^3 \delta^4$	CuO^-	$^1\Sigma^+$	$9\sigma^2 4\pi^4 \delta^4$	CuO^+	$^3\Sigma^-$	$9\sigma^2 4\pi^2 \delta^4$
ZnO	$^1\Sigma^+$	$9\sigma^2 4\pi^4 \delta^4$	ZnO^-	$^2\Sigma^+$	$10\sigma^1 4\pi^4 \delta^4$	ZnO^+	$^2\Pi$	$9\sigma^2 4\pi^3 \delta^4$

somewhat different basis set. There appears to be only one experimental measurement of the ionization energies for $3d$-metal monocarbides; Morse and Brugh [11] have determined the IE of FeC to be 7.74±0.09 eV, which is in good agreement with our theoretical value of 7.85 eV (see Table 8).

7 Analysis of the bonding

The bonding in these systems is quite complex, involving covalent, ionic, and dative components. In addition, the metal atom can have a $3d^n$ or $3d^{n+1}$ occupation and C can undergo *sp* hybridization. Using the NBO analysis and NAO populations, which are summarized in Tables 9 and 10, we discuss the main features of the bonding. In the tables we give the number of α and β bonds and the number of α and β lone spin orbitals.

ScC to CrC are perhaps best viewed as starting from M^+ $(3d^{n+1})$ and C^- (s^2p^3), where the metal $4s$ electron is donated to the C $2p\sigma$ orbital. This could also be viewed as an extreme dative bonding where almost the entire $4s$ is donated to the bonding orbital. If the bonding was purely ionic, the dipole moment of TiC would be 7.86 D, but it is 5.92 D, which shows that there are other components of the bonding. For these systems, in addition to the ionic component, covalent bonds are formed between the metal $3d$ orbitals and the carbon $2p$ orbitals. In ScC, where Sc has two d electrons, two two-electron π bonds are formed in addition to a one-electron σ bond, leading to a $^2\Sigma^+$ state, which is the ground state at the DFT level. If the Sc d occupation is $d\sigma^1 d\pi^1$ (or actually a mixture of $d\sigma^1 d\pi^1$ and $4s^1 d\pi^1$), a $^2\Pi$ state would be formed, which, as noted earlier, is the ground state at the MRCI level.

For TiC, the $3d^3$ occupation of Ti^+ leads to the formation of three two-electron bonds and a $^1\Sigma^+$ ground state at the DFT level. From a covalent point of view, Ti $(3d\sigma^1 3d\pi^2 4s^1)$ can form three two-electron bonds with an *sp* hybridized carbon, leading to a $^3\Sigma^+$ state. The open-shell orbitals are a C *sp* hybrid pointing away from the metal and Ti hybrid orbital polarized away from the carbon. MRCI calculations show that the ground state is actually $^3\Sigma^+$.

Relative to the $^1\Sigma^+$ state of TiC, VC adds the "extra" electron to the nonbonding $3d\delta$ orbital, yielding a $^2\Delta$ state. In CrC, the extra electron adds to the other component of the $3d\delta$ orbital yielding a $^3\Sigma^-$ ground state.

While the bonding in these four species is similar, there is some variation in the dissociation energy. Clearly there should be an increase from ScC to TiC since the number of bonds grows from 2.5 to 3. The decrease from TiC to CrC we attributed to the increasing loss of metal d–d exchange energy as the bonds are formed. The weaker bonding can be seen in the spin polarization, where the α density is more localized on the Cr $3d$ orbitals and the β density on the carbon.

Table 8. Adiabatic electron affinities (EA_{ad}) and ionization energies (IE) of the ground-state $3d$-metal monocarbides and monoxides

	ScC	TiC	VC	CrC	MnC	FeC	CoC	NiC	CuC	ZnC
EA_{ad}, (eV)	1.02	1.20	1.33	1.46	0.92	1.10	1.28[a]	1.19[a]	1.75	1.36
IE, (eV)	6.43	6.74	7.36	7.96	7.75	7.85[b]	7.99	8.36	8.65	8.86
	ScO	TiO	VO	CrO	MnO	FeO	CoO	NiO	CuO	ZnO
EA_{ad}	1.07	0.94	0.81	1.17	1.04	1.26	1.35	1.29	1.73	2.19
Exp.[c]	1.35	1.30	1.229	1.221	1.375	1.492	1.45	1.46	1.777	2.088
	±0.02	±0.03	±0.008	±0.006	±0.01	±0.03	±0.01	±0.02	±0.006	±0.01
IE	6.34	6.52	7.48	8.18	9.08	8.87	8.72	9.29	9.41	9.30

[a] Experimental values (LS Wang, personal communication) are 1.04 ± 0.04 eV(CoC) and 1.00 ± 0.04 eV(NiC)

[b] Experimental value [11] is 7.74 ± 0.09 eV

[c] Experimental EA_{ad} s: ScO [59], TiO [60], VO [61], CrO [62], MnO [64], FeO [65], CoO [70], NiO [71], CuO [72], ZnO [74]

Table 9. NAO population analysis of the carbide neutrals

	ScC	TiC	VC	CrC	MnC	FeC	CoC	NiC	CuC	ZnC
$3d$	1.94	3.04	4.28	5.43	5.90	7.12	8.33	8.98	9.69	9.97
$4s$	0.16	0.13	0.16	0.16	0.84	0.78	0.70	1.04	0.99	1.31
$4p$	0.03	0.04	0.03	0.02	0.02	0.01	0.01	0.01	0.02	0.08
M(net)	+0.87	+0.79	+0.53	+0.39	+0.24	+0.09	−0.04	−0.3	+0.30	+0.64
M(net)[a]	+0.43	+0.42	+0.34	+0.26	0.00	−0.05	−0.06	−0.10	−0.14	+0.24
$2s$	1.84	1.93	1.91	1.89	1.92	1.91	1.90	1.92	1.95	1.97
$2p$	3.06	2.88	2.65	2.52	2.32	2.17	2.04	2.03	2.32	2.65
Spin M[b]	0.4	0.0	1.4	2.9	4.0	2.6	0.9	0.0	0.0	0.0
Spin C	0.6	0.0	−0.4	−0.9	−1.0	−0.6	0.1	0.0	1.0	2.0
α bonds	3	3	3	3	3	3	3	3	1	1
β bonds	2	3	3	3	3	3	3	3	1	1
α lone spin orbitals	1	1	2	3	4	4	4	4	7	8
β lone spin orbitals	1	1	1	1	1	2	3	4	6	6

[a] Mulliken net charge on the metal

[b] The $\alpha - \beta$ population

Table 10. NAO population analysis of the oxide neutrals

	ScO	TiO	VO	CrO	MnO	FeO	CoO	NiO	CuO	ZnO
$3d$	1.12	2.35	3.52	4.52	5.43	6.65	7.49	8.73	9.68	9.94
$4s$	0.91	0.88	0.57	0.72	0.63	0.51	0.81	0.62	0.55	0.78
$4p$	0.03	0.03	0.14	0.08	0.09	0.07	0.03	0.02	0.03	0.12
M(net)	+0.94	+0.74	+0.77	+0.68	+0.85	+0.77	+0.67	+0.63	+0.74	+1.16
M(net)[a]	+0.42	+0.36	+0.31	+0.36	+0.42	+0.40	+0.33	+0.31	+0.26	+0.38
$2s$	1.94	1.93	1.94	1.94	1.95	1.95	1.95	1.96	1.97	1.98
$2p$	4.98	4.79	4.82	4.73	4.89	4.80	4.70	4.64	4.75	5.16
Spin M[b]	1.1	2.2	3.3	4.3	4.7	3.5	2.2	1.0	0.1	0.0
Spin O	−0.1	−0.2	−0.3	−0.3	0.3	0.5	0.8	1.0	0.9	0.0
α bonds	3	3	3	2	1	1	1	1	1	1
β bonds	3	3	3	3	3	3	3	3	2	1
α lone spin orbitals	2	3	4	6	8	8	8	8	8	8
β lone spin orbitals	1	1	1	1	1	2	3	4	6	8

[a] Mulliken net charge on the metal

[b] The $\alpha - \beta$ population

For MnC, the extra electron adds to a nonbonding σ orbital, which contains significant $4s$ character. The spin polarization is even larger than for CrC, but surprisingly the BPW91 yields a larger D_0 for MnC than CrC; this could be an artifact of the BPW91 approach, as it predicts MnO is more strongly bound than CrO, but experiment has CrO more strongly bound than MnO by about 1 eV. The Mulliken population shows a significant decrease in the metal-to-carbon donation, which is consistent with the reduction in the dipole moment. It is a bit surprising that the NAO population shows such a small reduction in metal-to-carbon donation for MnC relative to CrC.

For FeC and CoC, the electrons add to the nonbonding $3d\delta$ orbital, leading to $^3\Delta$ and $^2\Sigma^+$ ground states, respectively. For NiC, the extra electron adds to the open-shell σ nonbonding orbital, yielding a $^1\Sigma^+$ ground state. Since the additional electrons for FeC to NiC are all adding into open-shell nonbonding orbitals, it is not surprising that their properties are relatively similar. For CuC, the next electron must add to an antibonding orbital. In addition, the closed $3d^{10}$ occupation is very stable. Thus there is significant change in the bonding at CuC. The NBO analysis shows only one two-electron σ bond between the Cu $4s$ and the C $2p\sigma$ orbital. The open-shell π orbital is localized on the C. The large decrease in D_0 at CuC is consistent with the loss of the π bonds.

The bonding changes again in ZnC, since Zn is a closed shell. For this system, the Zn $4s$ electrons donate to C to form a dative σ bond. The two-open shell orbital are localized on the carbon. This bonding mechanism is even weaker than that in CuC.

The bonding in ScO is probably best viewed as arising from Sc^+ ($3d\sigma^1 4s^1$) and O^- ($2p\sigma^1 2p\pi^4$). The $4s$ electron polarizes away from the O and a covalent σ bond and two dative $O2p\pi \rightarrow Sc$ bonds form. Thus, ScO has some triple bond character and a large D_0. The dative bonds reduce the dipole moment relative to that in ScC. In TiO and VO, the extra electrons add to the nonbonding $3d\delta$ orbital, and as a result the dissociation energies and dipole moments are similar for ScO to VO. At CrO, the next electron must add to an antibonding orbital, and the NBO analysis shows one less $\alpha\pi$ bond than for VO, and there is a large reduction in the dissociation energy relative to ScO to VO.

In MnO, the other π bond is lost. Experimentally there is a large reduction in the D_0 of MnO relative to CrO, but the BPW91 does not show a reduction in the D_0 even though MnO has fewer bonds than CrO. However, both BLYP and B3LYP yield an MnO D_0 smaller than in CrO. For FeO, CoO, and NiO, the extra electrons add to the nonbonding orbitals $3d\delta$, 9σ, and $3d\delta$, respectively. Since the electrons are adding to nonbonding orbitals, it is not surprising that the properties of these species are rather similar. At CuO, the next electron must add to the antibonding orbital, and a π bond of β spin is lost, see Table 10. For ZnO, the other component of the π bond is also lost. With the loss of one and two bonds of β spin, it is not surprising that there is a significant drop in the D_0 values of CuO and ZnO relative to NiO.

For the carbide anions, excluding ScC and ZnC, the extra electron adds into an essentially $4s$-like orbital that is polarized away from the carbon; see the occupations in Table 7. For ScC^- the electron adds to the σ bonding orbital, and hence ScC^- has a bond order of 3.0 instead of 2.5. For TiC^- to CoC^-, the electron adds to a nonbonding σ orbital that is either empty or singly occupied. Thus the anions have a bond order of 3.0 like the neutral species, and so the bonding remains similar to that discussed for the neutrals, but there is more metal donation to the carbon. For NiC^-, relative to NiC, the electron adds to the antibonding 4π orbital and the bond order drops to 2.5. The bonding in CuC^- is the same as in ZnC. In ZnC^-, there is a weak single σ bond arising between a Zn $4s4p$ hybrid and the $2p\sigma$ orbital of C^- ($2p^3$).

For ScO to FeO, the anions are formed by adding the extra electron to the non-bonding open-shell σ orbital. For CoO, the anion is formed by adding an electron to the nonbonding $3d\delta$ orbital. Thus, the anion spin multiplicity is reduced by 1 relative to the neutral species, but overall the bonding remains similar to that discussed for the neutrals. For NiO, the anion is formed by adding an electron to the π antibonding orbital, thus NiO^- has half a bond less than NiO; note the increase in r_e and the decrease in ω_e for NiO^- relative to CoO^-. The bonding

Table 11. NAO population analysis of the carbide and oxide cations

	ScC^+	TiC^+	VC^+	CrC^+	MnC^+	FeC^+	CoC^+	NiC^+	CuC^+	ZnC^+
$3d$	1.55	2.76	3.94	5.06	6.01	7.18	8.31	8.97	9.72	9.98
$4s$	0.05	0.05	0.05	0.04	0.08	0.06	0.05	0.37	0.33	1.07
M(net)	+1.42	+1.21	+1.03	+0.91	+0.92	+0.77	+0.64	+0.65	+0.92	+0.92
M(net)[a]	+1.09	+1.03	+0.92	+0.78	+0.71	+0.60	+0.54	+0.54	+0.51	+0.69
$2s$	1.86	1.80	1.80	1.81	1.92	1.94	1.95	1.93	1.90	1.99
$2p$	2.56	2.41	2.23	2.09	1.99	1.82	1.68	1.71	2.02	1.93
	ScO^+	TiO^+	VO^+	CrO^+	MnO^+	FeO^+	CoO^+	NiO^+	CuO^+	ZnO^+
$3d$	1.26	2.45	3.62	4.34	5.28	6.27	7.45	8.63	9.58	9.97
$4s$	0.01	0.01	0.01	0.39	0.31	0.27	0.19	0.13	0.22	0.52
M(net)	+1.76	+1.55	+1.37	+1.27	+1.39	+1.44	+1.34	+1.21	+1.17	+1.48
M(net)[a]	+1.21	+1.16	+1.11	+0.95	+1.00	+1.00	+0.96	+0.90	+0.78	+0.93
$2s$	1.96	1.96	1.95	1.95	1.97	1.97	1.98	1.98	1.99	1.99
$2p$	4.79	4.59	4.42	4.32	4.41	4.46	4.35	4.23	4.17	4.47

[a] Mulliken net charge on the metal

in CuO^- is similar to that discussed previously for ZnO. For ZnO^-, a σ bond forms between a $4s4p$ hybrid and the $2p\sigma$ orbital of O^- ($2p^5$).

It is difficult to view the bonding in the cations as the simple removal of an electron from the neutral species, therefore, we discuss the bonding in the cations in some detail. The populations are given in Table 11. Excluding Zn, the carbide cations are best viewed as arising from M^+ ($3d^{n+1}$). In ScC^+, the Sc^+ has a $3d\sigma^1 3d\pi^1$ occupation. The $3d\sigma$ donates to the empty C $2p\sigma$ orbital. The $3d\pi$ forms a two-electron bond with an open-shell $2p\pi$ orbital, while the other C $2p\pi$ electron donates to the empty $3d\pi$ orbital. The carbon orbitals undergo some *sp* hybridization to add some covalent character to the σ bond. In TiC^+, the C *sp* hybridization is more complete and three two-electron bonds are formed between C and Ti^+ $3d\sigma^1 3d\pi^2$. In VC^+ and CrC^+ the extra electrons add to the nonbonding $3d\delta$ orbital. In MnC^+, the carbon *sp* hybridization is less complete than for TiC^+ to CrC^+, as the Mn $d\sigma$ orbital is doubly occupied and donates to the empty C $2p\sigma$ orbitals. In FeC^+ and CoC^+, the extra electron adds to the nonbonding $3d\delta$ orbital. Thus, the bondings for MnC^+ to CoC^+ are relatively similar, although the large $4s$ to $3d$ promotion energy for Mn results in the MnO^+ D_0 being somewhat smaller than that of FeC^+ and CoC^+.

For NiC^+ the extra electron adds to the σ nonbonding orbital. This orbital has some $4s$ character, and thus NiC^+ is the first carbide cation with an appreciable $4s$ population. The bonding in CuC^+ arises for the donation of C $2p\sigma$ electrons to the empty $4s$. Given that the covalent bonding is lost, it is not surprising that CuC^+ is much more weakly bound than the carbide cations that precede it. The bonding in ZnC^+ is similar to that in CuC discussed earlier.

Relative to the neutrals, ScO^+, TiO^+, and VO^+ are all formed by the loss of an electron from the nonbonding metal σ orbital. CrO^+ is formed by the loss of the π^* electron; thus, CrO^+ has a bond order of 3.0, whereas CrO has a bond order of 2.5. However, because of the large loss of *d–d* exchange energy when the bonds are formed, CrO^+ is less strongly bound than ScO^+ to VO^+ despite all having three two-electron bonds.

The bonding in MnO^+ is similar to that in CrO. That is, relative to CrO^+ an electron can add to either the σ or π antibonding orbital, yielding $^5\Sigma^+$ and $^5\Pi$ states, respectively. These states have a bond order of 2.5. At the BPW91 level these two states are virtually degenerate.

The formation of FeO^+ arises from the loss of the nonbonding $3d\delta$ in the neutral species, while CoO^+ and NiO^+ represent the loss of the nonbonding σ electron; thus, the bondings in FeO^+, CoO^+, and NiO^+ all have similarities with the neutral species. The bonding in CuO^+ is weak, as promotion to Cu^+ $3d^9 4s^1$ requires significant energy. The weak bonding is probably best viewed as arising from O ($2p\sigma^2 2p\pi^4$) donation to the Cu. In ZnO^+, the Zn $4s$ electron forms a bond with the $2p\sigma$ electron of O. The open-shell is a $2p\pi$ orbital localized on C; thus, the bonding in ZnO^+ is similar to that in CuO.

8 Conclusions

A systematic study of the $3d$-metal monocarbides and monoxides shows the overall good agreement of the results obtained using the BPW91, BLYP, and hybrid B3LYP methods. The computed r_e, ω_e, EA, and IE values are generally in good agreement with experiment, while the computed dipole moments and D_0 values are in reasonable agreement with experiment. For the monoxides D_o is better for the B3LYP, but pure DFT functionals do better for CrC, MC, FeC, and their cations. These species possess the largest spin polarization among the $3d$-metal monocarbides and monoxides, which appears to be the reason for a worse description at the B3LYP level where the exchange contains Hartree–Fock contributions. While we find some similarities in the $3d$-metal monocarbides and monoxides, there are many more differences; this is true for both the neutrals and the ions. The NAO and NBO analyses appear to be very useful in understanding the trends in chemical bonding of the neutral and charged species and the behavior of the dipole moment when moving along the neutral series. The chemical bonding in $3d$-metal monocarbides and monoxides is very complex, with covalent, ionic, and dative contributions.

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