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Electronic structures of 5d transition metal monoxides by density functional theory

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Abstract Bond distances, vibrational frequencies, electron affinities, ionization potentials, and dissociation energies of the diatomic 5d transition metal (except La) monoxides and their positively and negatively charged ions were studied by use of density functional methods B3LYP, BLYP, B3PW91, BPW91, B3P86, BP86, MPW1PW91, PBE1PBE, and SVWN. Our calculation shows that for each individual species, the calculated properties are quite sensitive to the method used. Compared with hybrid density functional method B3PW91 (B3P86), pure density functional method BPW91 (BP86) gives longer bond distance (lower vibrational frequency) from HfO to PtO for neutral species, HfO⁺ to IrO⁺ for cationic species, and HfO⁻ to AuO⁻ for anionic species. While for B3LYP and BLYP, the trend was observed for cationic species from HfO⁺ to IrO⁺ and anionic species from HfO⁻ to AuO⁻ (except TaO⁻), but not for neutrals. Pure density function methods BLYP, BPW91, and BP86 give larger dissociation energy compared with hybrid density functional methods B3LYP, B3PW91, and B3P86. SVWN in most cases gives the smallest bond distance, while BLYP gives the largest value. MPW1PW91 and PBE1PBE show the same performance in predicting the spectroscopic constants. In addition, 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 which differs by ± 1 .

Keywords 5d metal monoxide · Density functional theory · Spectroscopic constants · Ionization potential · Electron affinity

1 Introduction

Transition-metal oxides are very important technological materials. Recently, there is a considerable interest in the electrical, magnetic, and catalytic properties on such systems. The strength of the metal–oxygen bond in these systems leads to the importance of transition-metal oxides in many research fields, such as astrophysics, catalysis, and high temperature chemistry. The structures and properties of transition-metal oxides have been the subject of numerous investigations [1–4]. The interaction between transition metal and oxygen is, therefore, of fundamental importance.

Transition-metal oxides are theoretically one of the most interesting electronic systems because transition metal possesses unfilled d orbitals and therefore can form various spin configurations in a limited energy region. The open shell nature of the molecules containing transitional-metal atoms leads to large numbers of low-lying configurations and electronic states. This also leads to considerable difficulties in the computational study of their electronic structure and bonding as results may vary with the method applied [5–13].

Transition-metal monoxides have been studied both experimentally and theoretically. For instance, non-local, density functional calculations have been performed by Bridgeman and Rothery [2] on the ground and low-lying excited states of the 3d transition metal monoxide. Periodic trends in properties such as bond lengths, bond energies, vibrational force constants, and dipole moments were examined. Analysis of the electronic structures of the molecules reveals the d-orbital splitting to be $d\pi > d\sigma > d\delta$ and shows the non-bonding role of the $d\sigma$ and $d\delta$ functions. Gutsev et al. [3] calculated the structure and properties of the 3d-metal monocarbides and monoxides by density functional theory (DFT) and analyzed some similarities and differences between them by the natural bond orbital scheme. Siegbahn [4]

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discussed the properties (including bond lengths and bond energies) of the 4d transition metal monoxides by CCSD (coupled-cluster singles and doubles perturbatively method) and CCSD(T) (coupled-cluster singles and doubles with triple excitations added perturbatively method). However, for 5d metal monoxides, the studies are scarce. The individual studies include the study of diatomic molecule HgO by ab initio four-component Hartree–Fock–Dirac method [14]. For AuO, more studies were available. For instance, theoretical study include DFT study by Legge et al. [15], while experimental study was conducted by photoelectron spectroscopy on AuO⁻ [16]. The electron affinity of AuO was determined to be 2.374 ± 0.007 eV [16]. A summary of the previous AuO studies can be seen from the DFT study on AuX (X=O, S, Se, Te) by one of the present authors [17]. In addition, experimental studies were also available on TaO [18,19].

Density functional theory is now widely used to determine structures and reaction energy diagrams for a wide variety of molecules. Compared to high-level ab initio molecular orbital theories, DFT has the advantage of applicability anywhere in the periodic table and inherent computational efficiency. This makes it particularly effective for those molecules involving heavy metal elements. On the other hand, till now, many density functional methods have been developed during the past decades [20]. It is known that each density functional method is different from the others on theoretical aspect. Therefore, it is necessary and meaningful to test these density functional methods when applied on different systems, especially for systems containing transition metals because different density functional methods may produce quite different properties for a given system. In this study, we have examined the ground state of the 5d transition metal (except La) and their charged ions by use of diverse density functional methods. The results are compared with experimental data and previous theoretical results. The performance among different density functional methods is also compared. We hope this work could stimulate more researches on the diatomic monoxides of transition metals and provide reference in choosing the reliable density functional methods in future study.

2 Computational methods

All geometry optimizations were performed using the Gaussian98 suite of programs [21]. Equilibrium geometries, vibrational frequencies, electron affinities (EA), ionization potentials (IP), and dissociation energies were determined for the studied clusters by using nine different exchange-correlation functionals, i.e., B3LYP, BLYP, B3PW91, BPW91, B3P86, BP86, SVWN, MPW1PW91, and PBE1PBE [22–34]. For these density functional methods, the correlation functional is from either Lee, Yang and Parr (LYP) [22], Perdew–Wang 1991 (PW91) [23], or Perdew 86 [24]. While the exchange functional is from either Becke’s three-parameter HF/DFT hybrid exchange functional (B3) [25], pure DFT exchange functional of 1988(B) [26], a modification of the half-and-half HF/DFT hybrid method (BH)

[27], Perdew–Wang 1991 (PW91) [23], or Barone’s modified PW91 (MPW1) [28]. PBE1PBE is the GGA exchange–correlation functionals of Perdew et al. [29,30]. SVWN is the older local-spin-density approximation (LSDA) which utilizes the 1980 correlation functional of Vosko et al. [31] along with Slater exchange functional [32–34]. The basis set used for 5d elements is Stuttgart/Dresden effective core potentials (ECPs), SDD [35]. For oxygen, all-electron basis set 6–311+G(d) was used as in this study. The valence electrons considered are $5s^2 5p^6 5d^n 6s^2$ for $n=2–10$ from Hf to Hg. To avoid trapping at local minima of the potential energy surface, different initial geometries (bond distances) were adopted. The calculated dissociation energies were corrected by the zero-point vibrational energies. The dissociation energy was computed as the difference in the total energies E_{tot} of the diatomic TMO ($M = 5d$ element) and its constituent atoms. e.g., for neutral species, it is $D_e(\text{TMO}) = E_{\text{tot}}(\text{TM}) + E_{\text{tot}}(\text{O}) - E_{\text{tot}}(\text{TMO})$.

3 Results and discussion

The calculated results were listed in Tables 1, 2, 3, and 4. Because of the spin polarization, the molecules were first calculated by use of B3LYP and BLYP at various spin multiplicities in order to find the structure with the lowest energy for each molecule (including the charged species). The calculated results are listed in Table 1 (for detailed data see the supplementary material, Tables S1 and S2). From the supplementary material, it is seen that the calculated square of total spin is quite close to its eigenvalues $s(s+1)$, indicating that the spin contamination is minor. Table 2 lists the bond distances, vibrational frequencies, EA, IP, and dissociation energies from the lowest spin multiplicity of the neutral molecules at various density functional methods, B3LYP, BLYP, B3PW91, BPW91, B3P86, BP86, SVWN, MPW1PW91, and PBE1PBE. Table 3 lists the bond distances and vibrational frequencies of the charged species. Table 4 lists the ground state occupations of the neutral and charged 5d metal monoxides.

It is seen that for some species, extremely low-lying excited states were found. For instance, for anion TaO⁻, the lowest conformer at B3LYP level is from triplet state, while singlet state is only 0.02 eV higher than triplet state (Table 1). At BLYP level (Table 1), opposite to B3LYP, singlet state is the lowest, while triplet state is only 0.04 eV higher than singlet state. This means for TaO⁻, it is difficult to determine which state (triplet or singlet) is the ground state. The same behavior also happened in neutral OsO between B3LYP and BLYP (Table 1). Therefore, both further experimental and advanced theoretical studies are necessary to solve the discrepancy. Glancing at Table 1, it was found that within the energy cutoff 0.2 eV, this phenomena (low-lying state) is not unusual because they are also found in neutral OsO, cationic OsO⁺, anionic WO⁻ and ReO⁻ at both B3LYP and BLYP levels, and cationic HgO⁺, anionic AuO⁻ at B3LYP level. However, in the following paper, we will still use term

Table 1 Calculated relative energies ΔE (eV) at various spin multiplicities for each diatomic monoxide of 5d transition metal at B3LYP and BLYP level

	HfO		WO		OsO		PtO		HgO	
	B3LYP	BLYP	B3LYP	BLYP	B3LYP	BLYP	B3LYP	BLYP	B3LYP	BLYP
Neutral										
1	0.00	0.00	0.00	0.00	0.63	0.37	1.25	1.17	0.62	0.33
3	0.93	0.97	0.62	0.35	0.19	0.00	0.00	0.00	0.00	0.00
5	4.70	5.20	1.51	1.69	0.00	0.01	2.07	1.64		
7	9.09	9.62	3.73	3.18	1.65	1.82				
9	18.64	19.25	5.68	6.50						
Cation										
2	0.00	0.00	1.54	1.43	0.95	0.36	0.49	1.09	0.00	0.00
4	2.95	3.26	0.00	0.00	0.21	0.03	0.00	0.00	0.19	0.44
6	6.78	7.38	5.52	2.84	0.00	0.00	1.89	2.95		
8	15.06	15.74	5.86	4.72	4.31	4.51				
10			12.4	11.39						
Anion										
2	0.99	0.80	0.18	0.11	0.74	0.60	0.00	0.00	0.00	0.00
4	0.00	0.00	0.37	0.25	0.00	0.00	0.35	0.40		
6	3.74	4.01	0.00	0.00	1.28	1.44				
8	8.79	8.82	3.15	3.52						
TaO										
Neutral										
2	0.00	0.00	1.14	0.52	0.60	0.44	0.00	0.00		
4	1.46	1.55	1.89	1.79	0.00	0.00	1.27	1.15		
6	4.54	4.99	0.00	0.00	1.51	1.69				
8	7.99	8.74	3.78	4.21						
10	17.70	18.29								
Cation										
1	0.91	1.33	0.22	0.68	1.44	1.07	1.97	1.69		
3	0.00	0.00	0.00	0.00	0.57	0.34	0.00	0.00		
5	3.67	4.30	1.08	0.37	0.00	0.00	2.35	2.31		
7	6.37	7.05	2.00	2.46	3.04	3.23				
9	13.89	14.66	2.25	3.11						
Anion										
1	0.02	0.00	0.93	0.76	1.02	0.95	0.00	0.00		
3	0.00	0.04	0.20	0.12	0.00	0.00	0.14	0.36		
5	0.88	1.45	0.00	0.00	0.72	0.89				
7	4.22	4.61	0.14	0.33						
9	8.89	9.31								

“ground state” for the structure with the lowest energy, but care should be taken that the term is only tentative for those possessing the low-lying excited state(s) as mentioned above.

Since both experimental and theoretical data were rare for charged species, we will mainly focus our discussion on neutral species. Charged species will be mentioned when necessary.

From Table 4, it is seen that compared with 3d metal monoxides (Table 7 in Ref.[3]), the bonding patterns of 5d metal monoxides are different for most species.

HfO. $^1\Sigma^+$ is the ground state for the neutral species, indicating a double bond. The calculated bond distances (Table 2) are from 1.746 Å at PBE1PBE and MPW1PW91 levels to 1.773 Å at BLYP level. The calculated vibrational frequencies are from 909.9 cm^{-1} at BLYP to 964.6 cm^{-1} at MPW1PW91. Comparing with the other methods, B3P86 (8.027 eV) has the best performance in reproducing the experimental dissociation energy 8.19 eV [36].

TaO. $^2\Delta$ is the ground state for the neutral species, in agreement with experimental observation [19]. The calculated bond distances from all the methods are around 1.70 Å, close to experimental value 1.6875 Å [37]. SVWN (1.704 Å) and PBE1PBE (1.704 Å) have the best performance in reproducing the experimental value (1.6875 Å) [37]. The calculated vibrational frequencies are from 968.7 cm^{-1} at BLYP to 1,031.3 cm^{-1} at PBE1PBE, comparable to experimental value 1,028.9 cm^{-1} [19]. PBE1PBE (8.535 eV) has the best performance in reproducing the experimental IP 8.61 eV [18]. For the dissociation energy, BP86 (8.152 eV) is the best compared with the experimental value 8.2 eV [36].

As mentioned earlier, for anionic species TaO^- , singlet state has the lowest energy at BLYP, while for the other DFT methods, triplet state ($^3\Sigma^-$) is the ground state.

WO. $^1\Sigma^+$ is the ground state for the neutral species. The calculated bond distances are the smallest compared with its neutral partners. They change in a narrow range from

Table 2 Calculated bond distances d (Å), vibrational frequencies ω (cm^{-1}), dissociation energies D_e (eV), ionization potentials IP (eV), and electron affinities EA (eV) of neutral MO at ground state

		HfO	TaO	WO	ReO	OsO	IrO	PtO	AuO	HgO	
	S	1	2	1	6	5	4	3	2	3	
d	B3LYP	1.757	1.715	1.672	1.768	1.746	1.752	1.766	1.941	2.317	
	BLYP	1.773	1.713	1.689	1.786	1.704 ^a	1.772	1.784	1.927	2.313	
	B3PW91	1.750	1.708	1.665	1.757	1.735	1.742	1.755	1.927	2.280	
	BPW91	1.763	1.721	1.679	1.771	1.752	1.759	1.769	1.910	2.272	
	B3P86	1.748	1.706	1.664	1.756	1.734	1.740	1.753	1.919	2.259	
	BP86	1.764	1.722	1.680	1.773	1.753	1.759	1.768	1.905	2.260	
	MPW1PW91	1.746	1.704	1.661	1.753	1.731	1.738	1.752	1.932	2.280	
	PBE1PBE	1.746	1.704	1.661	1.753	1.731	1.737	1.752	1.930	2.277	
	SVWN	1.747	1.705	1.664	1.751	1.673 ^a	1.715	1.739	1.853	2.156	
	Expt.			1.6875 ^{b,c}	1.666 ^b	1.702 ^b	1.712 ^b		1.7273 ^b	1.912 ^d	2.03 ^e
	Theor.									1.907 ^f	
										1.946 ^g	
										1.831 ^h	
									1.864 ⁱ		
									1.9 ^j		
ω	B3LYP	946.4	1000.2	1072.1	883.8	904.4	877.9	796.2	511.0	241.1	
	BLYP	909.9	968.7	1026.8	846.0	960.6 ^a	838.0	838.0	536.5	260.3	
	B3PW91	956.4	1021.9	1087.9	899.4	922.0	893.3	814.4	527.2	256.4	
	BPW91	923.9	985.3	1047.4	869.4	884.6	859.1	795.3	560.1	277.9	
	B3P86	960.7	1025.6	1091.4	903.7	925.6	898.8	820.9	540.7	275.2	
	BP86	923.5	985.0	1046.9	868.3	884.4	861.5	799.4	571.0	289.1	
	MPW1PW91	964.6	1031.2	1100.1	906.8	930.8	903.0	819.9	523.0	250.2	
	PBE1PBE	963.7	1031.3	1099.9	906.8	930.8	904.1	818.4	525.0	253.0	
	SVWN	954.7	1020.3	1084.9	907.8	1032.8 ^a	931.6	851.0	669.7	365.0	
	Expt.		1028.9 ^c								
	Theor.								497 ^g		
									695 ^h		
									632 ⁱ		
								532.1 ^j			
D_e	B3LYP	7.853	7.952	5.684	5.787	4.958	4.433	3.528	1.794	0.328	
	BLYP	8.378	7.971	6.504	6.362	6.121 ^a	5.182	4.292	2.264	0.508	
	B3PW91	7.811	7.353	4.877	5.770	4.943	4.382	3.545	1.758	0.305	
	BPW91	8.358	7.969	5.551	6.362	5.396	5.144	4.332	2.230	0.485	
	B3P86	8.027	7.538	5.300	5.957	5.138	4.574	3.720	1.909	0.392	
	BP86	8.532	8.152	6.074	6.517	5.493	5.330	4.489	2.377	0.562	
	MPW1PW91	7.643	7.160	4.606	5.629	4.760	4.177	3.341	1.653	0.271	
	PBE1PBE	7.716	7.198	4.719	5.730	4.618	4.348	3.153	1.717	0.315	
	SVWN	9.965	10.917	7.547	7.790	9.153 ^a	6.604	5.734	3.316	1.078	
	Expt.	8.19 ^k	8.2 ^k	6.8 ^k			3.64 ^k	3.82 ^k	2.33 ^k		
	Theor.								2.26 ^b		
									1.92 ^l		
									1.52 ^g		
								2.81 ^h			
								2.84 ⁱ			
								2.04 ^m , 1.96 ^m			
								1.60 ^m , 1.50 ^m			
IP	B3LYP	7.876	7.921	7.128	9.716	8.996	9.420	10.712	10.015	9.962	
	BLYP	7.757	7.841	8.996	9.454	8.938 ^a	9.420	9.869	9.958	9.796	
	B3PW91	8.404	7.713	8.655	10.630	9.214	9.272	10.725	9.947	9.873	
	BPW91	7.662	7.663	8.695	9.909	9.086	9.347	9.915	9.996	9.805	
	B3P86	9.015	8.337	9.329	11.105	9.779	9.902	11.346	10.574	10.442	
	BP86	7.869	7.909	8.998	9.924	9.197	9.558	10.087	10.162	9.935	
	MPW1PW91	8.351	7.670	8.550	10.684	9.208	9.195	10.609	9.865	9.838	
	PBE1PBE	8.195	7.668	8.535	10.647	9.169	9.171	11.310	9.829	9.798	
	SVWN	8.431	8.545	9.811	10.356	9.804 ^a	10.291	10.742	10.810	13.084	
	Expt.		8.61 ⁿ								
	Theor.								9.82 ^l		

Table 2 (Contd.)

	<i>S</i>	HfO 1	TaO 2	WO 1	ReO 6	OsO 5	IrO 4	PtO 3	AuO 2	HgO 3
EA	B3LYP	0.687	1.299	1.094	0.755	2.145	2.234	2.116	2.198	2.165
	BLYP	0.896	0.502	0.770	0.765	2.129 ^a	2.209	2.024	2.309	2.236
	B3PW91	0.387	0.695	1.640	0.572	1.943	2.203	2.204	2.098	2.065
	BPW91	0.434	0.654	1.520	0.643	1.991	2.280	2.022	2.301	2.233
	B3P86	0.342	1.198	2.031	1.190	2.551	2.791	2.610	2.703	2.685
	BP86	0.480	0.747	1.415	0.872	2.226	2.443	2.188	2.480	2.436
	MPW1PW91	0.365	0.701	1.718	0.504	1.884	2.145	1.485	1.986	1.987
	PBE1PBE	0.350	0.675	1.659	0.476	1.877	2.117	1.224	1.966	1.973
	SVWN	0.341	1.116	1.587	1.392	2.759 ^a	3.098	2.726	3.179	3.247
	Expt.								2.374±0.007 ^f	2.298±0.347 ^e
Theor.								2.26 ^f	2.36 ^l	

^aThe spin multiplicity of the lowest structure is $S=3$ for neutral OsO at BLYP level

^bRef. 36

^cRef. 19

^dRef. 37

^eRef. 14

^fRef. 16. Theoretical study at the CCSD(T) level. For the basis set, Stuttgart small core energy consistent relativistic pseudopotentials are used for Au and augmented-cc-pVTZ for O. The bond distance for AuO (1.907 Å) is the average if the two spin-orbital states $^2\Pi_{1/2}$ and $^2\Pi_{3/2}$

^gRef. 38. Theoretical study at the CISD/SC level

^hRef. 40. Theoretical study by the Becke-Perdew (BP) functional

ⁱRef. 40. Theoretical study by the ZORA method

^jRef. 39. Theoretical study at the BPW91 level. For basis set, LANL2DZ for Au, 6-311+G(d) for O

^kRef. 35

^lRef. 41. Theoretical study at the B3PW91/LANL-E level

^mRef. 15. DFT studies with LANL2DZ basis set. The value 2.04 eV is from BLYP, 1.96 eV from BPW91, 1.60 eV from B3LYP, and 1.50 eV from B3PW91

ⁿRef. 18

S is the spin multiplicity

1.661 Å at PBE1PBE and SVWN to 1.689 Å at BLYP, close to experimental value 1.666 Å [37]. Our calculated frequency from 1,026.8 cm⁻¹ at BLYP to 1,100.1 cm⁻¹ at MPW1PW91 is larger than the values of the other neutral species. The calculated dissociation energy indicates that BLYP (6.504 eV) is the best compared with experimental value 6.8 eV [36].

ReO. $^6\Sigma^+$ is the ground state for neutral species. The bond distances are from 1.751 Å at SVWN to 1.786 Å at BLYP, a little larger than the experimental value 1.702 Å [37]. The calculated vibrational frequencies change in a narrow range from 846.0 cm⁻¹ at BLYP to 907.8 cm⁻¹ at SVWN.

OsO. Although $^5\Sigma^+(16\sigma^2 9\pi^2 4\delta^2)$ has the lowest energy at B3LYP, it is seen from Table 1 that triplet state ($^3\Phi$ with electronic configuration $16\sigma^2 9\pi^1 4\delta^3$, or $^3\Sigma^-$ with electronic configuration $16\sigma^2 9\pi^2 4\delta^2$) is only 0.19 eV higher than $^5\Sigma^+$. However, from Table 1 we note that at BLYP level, triplet state ($^3\Phi$) and quintet state are nearly isoenergetic, with triplet state slightly favored (0.01 eV lower than quintet state). This suggests that further study is necessary to solve the discrepancy. Comparing with the other methods, BLYP (1.704 Å) has the best performance in reproducing the experimental result 1.712 Å [37]. The vibrational frequencies change in a narrow range from 884.4 cm⁻¹ at BP86 to

1,032.8 cm⁻¹ at SVWN. All of the nine methods give similar results for IP and EA.

IrO. $^4\Sigma^-$ is the ground state. The bond distances change from 1.715 Å at SVWN to 1.772 Å at BLYP. The frequency is from 838.0 cm⁻¹ at BLYP to 931.6 cm⁻¹ at SVWN. Compared with experiment [36], all DFT methods overestimate the dissociation energy significantly.

PtO. $^3\Sigma^-$ is the ground state for the neutral species. The calculated bond distance is from 1.739 Å at SVWN to 1.784 Å at BLYP. Compared with the experimental value 1.7273 Å [37], the calculated bond distances are slight larger, for instance, by 0.0117 Å at SVWN. The frequency is from 795.3 cm⁻¹ to at BPW91 874.3 cm⁻¹ at BLYP.

AuO. This is the most studied molecule among the title molecules. $^2\Pi$ is the lowest conformer for the neutral species. For the bond distance, DFT calculations show a scattering from 1.853 Å at SVWN to 1.941 Å at B3LYP. BPW91 (1.910 Å) is the best in reproducing the experimental value (1.912 Å) [38], followed by BP86 (1.905 Å), and B3P86 (1.919 Å). Our results are also in agreement with previous theoretical study at CCSD(T) (1.907 Å) [16], CISD/SC (1.946 Å) [39], BPW91 (1.9 Å) [40], and ZORA (1.864 Å) [41] and better

Table 3 Calculated bond distances d (Å) and vibrational frequencies ω (cm^{-1}) of cationic and anion MO at ground state

	S	HfO ⁺ 2	TaO ⁺ 3	WO ⁺ 4	ReO ⁺ 3	OsO ⁺ 4	IrO ⁺ 5	PtO ⁺ 4	AuO ⁺ 3	HgO ⁺ 2
d	B3LYP	1.727	1.693	1.660	1.686	1.758 ^a	1.757	1.855	1.970	2.061
	BLYP	1.745	1.711	1.735	1.706	1.778 ^a	1.774	1.787	1.928	2.066
	B3PW91	1.729	1.686	1.709	1.682	1.672	1.744	1.843	1.957	2.046
	BPW91	1.735	1.702	1.724	1.695	1.687	1.758	1.771	1.910	2.045
	B3P86	1.728	1.685	1.707	1.680	1.670	1.742	1.838	1.941	2.034
	BP86	1.736	1.702	1.725	1.696	1.688	1.759	1.770	1.903	2.039
	MPW1PW91	1.726	1.683	1.706	1.677	1.670	1.741	1.848	1.981	2.052
	PBE1PBE	1.725	1.682	1.705	1.677	1.669	1.740	1.845	1.976	2.047
	SVWN	1.720	1.686	1.705	1.678	1.668	1.734	1.741	1.846	1.972
	Theor.								1.981 ^c	
	ω	B3LYP	994.2	1043.9	1074.7	1019.0	878.6 ^a	838.1	636.1	400.0
BLYP		950.4	997.9	937.2	968.8	842.8 ^a	815.3	751.3	496.2	444.8
B3PW91		968.2	1054.3	982.9	1039.1	997.1	858.2	648.6	405.2	432.4
BPW91		966.6	1014.3	951.9	990.5	978.3	840.4	773.4	516.7	455.3
B3P86		972.0	1059.4	989.8	1043.3	1008.9	864.6	662.2	433.5	450.1
BP86		965.2	1014.3	953.3	989.1	980.0	841.7	778.5	534.7	460.8
MPW1PW91		977.0	1064.1	986.3	1049.5	982.3	861.3	630.4	363.5	408.7
PBE1PBE		977.4	1065.2	987.4	1050.8	987.0	862.9	634.4	370.5	417.3
SVWN		997.0	1050.4	995.7	1031.6	1031.7	890.4	832.7	644.3	507.6
Theor.										
d		S	HfO ⁻ 4	TaO ⁻ 3	WO ⁻ 6	ReO ⁻ 5	OsO ⁻ 4	IrO ⁻ 3	PtO ⁻ 2	AuO ⁻ 1
	B3LYP	1.809	1.766	1.782	1.768	1.759	1.739	1.816	1.916	2.199
	BLYP	1.825	1.764 ^b	1.798	1.783	1.777	1.759	1.834	1.930	2.162
	B3PW91	1.800	1.756	1.772	1.756	1.749	1.730	1.805	1.901	2.159
	BPW91	1.812	1.769	1.784	1.767	1.763	1.746	1.819	1.910	2.119
	B3P86	1.799	1.756	1.771	1.756	1.748	1.728	1.802	1.897	2.145
	BP86	1.813	1.770	1.785	1.769	1.763	1.746	1.818	1.908	2.115
	MPW1PW91	1.796	1.753	1.769	1.753	1.746	1.725	1.802	1.898	2.170
	PBE1PBE	1.795	1.752	1.768	1.752	1.745	1.724	1.800	1.896	2.165
	SVWN	1.792	1.735 ^b	1.763	1.747	1.741	1.722	1.788	1.866	2.027
	Theor.								1.899 ^d	
ω	B3LYP	826.0	873.6	816.4	834.2	877.2	895.1	750.5	578.5	286.1
	BLYP	796.4	893.0 ^b	792.3	807.9	839.2	850.1	725.3	559.6	336.1
	B3PW91	838.7	888.3	830.2	850.6	892.0	910.6	766.8	603.5	307.6
	BPW91	816.1	864.1	812.3	830.8	860.4	871.3	746.9	592.0	363.3
	B3P86	841.2	889.9	833.2	853.9	896.9	915.5	772.6	611.6	321.7
	BP86	813.8	863.8	811.5	830.0	861.2	873.2	750.2	597.0	371.7
	MPW1PW91	845.8	894.9	835.0	855.8	900.6	920.6	768.8	608.4	297.0
	PBE1PBE	845.8	895.6	835.3	855.5	900.8	921.5	771.2	609.8	299.1
	SVWN	845.3	944.5 ^b	847.8	869.2	902.8	920.4	800.1	675.1	453.8
	Theor.								1.910 ^c	

^aThe spin multiplicity of the lowest structure is $S=6$ for cationic OsO⁺ at B3LYP and BLYP levels

^bThe spin multiplicity of the lowest structure is $S=1$ for anionic TaO⁻ at BLYP level

^cRef. 41. Theoretical study at the B3PW91/LANL-E level

^dRef. 16

^eRef. 16. Theoretical study at the CCSD(T) level. For the basis set, Stuttgart small core energy consistent relativistic pseudopotentials are used for Au and augmented-cc-pVTZ for O

S is the spin multiplicity

than those from Becke-Perdew (BP) (1.831 Å) [41]. The calculated vibrational frequencies change from 523.0 cm^{-1} at MPW1PW91 to 669.7 cm^{-1} at SVWN, comparable to ZORA method result 632 cm^{-1} [41] and BPW91 (LANL2DZ for Au, 6-311+G(d) for O) result 532.1 cm^{-1} [40], but larger than CISD/SC (configuration interaction with single and double excitations corrected by size-consistency effects) result 497 cm^{-1} [39], smaller than the BP result 695 cm^{-1} [41]. For EA, our calculated values are from 1.966 eV at PBE1PBE to 3.179 eV at SVWN, in which BLYP (2.309 eV) and BPW91

(2.301 eV) have the best performance in reproducing the experimental value 2.347 eV [16] and the previous theoretical studies at CCSD(T) (2.26 eV) [16] and B3PW91 (2.36 eV) [42]. SVWN has the worst performance. The calculated IP is from 9.829 eV at PBE1PBE to 10.810 eV at SVWN, in fair agreement with the previous theoretical value 9.82 eV at B3PW91 [42], in particular for our PBE1PBE value (9.829 eV) and MPW1PW91 value (9.865 eV). For neutral species, its dissociation energy is the lowest except HgO. Our calculated results are from 1.653 eV at MPW1PW91 to 3.316 eV

Table 4 Ground state or lowest state in energy occupations of the neutral and charged 5 dmetal monoxides

Neutral			Cation			Anion		
State	Electronic configuration		State	Electronic configuration		State	Electronic configuration	
HfO	$^1\Sigma^+$	$16\sigma^2$	HfO ⁺	$^2\Sigma^+$	$16\sigma^1$	HfO ⁻	$^4\Sigma^-$	$16\sigma^14\delta^2$
TaO	$^2\Delta$	$16\sigma^24\delta^1$	TaO ⁺	$^3\Delta$	$16\sigma^14\delta^1$	TaO ⁻	$^3\Sigma^-$	$16\sigma^24\delta^2$
WO	$^1\Sigma^+$	$16\sigma^24\delta^2$	WO ⁺	$^4\Sigma^-$	$16\sigma^14\delta^2$	WO ⁻	$^6\Sigma^-$	$16\sigma^19\pi^24\delta^2$
ReO	$^6\Sigma^+$	$16\sigma^19\pi^24\delta^2$	ReO ⁺	$^3\Sigma^-$	$16\sigma^24\delta^2$	ReO ⁻	$^5\Sigma^-$	$16\sigma^29\pi^24\delta^2$
OsO	$^5\Sigma^+$	$16\sigma^29\pi^24\delta^2$	OsO ⁺	$^4\Delta$	$16\sigma^19\pi^14\delta^3$	OsO ⁻	$^4\Delta$	$16\sigma^29\pi^24\delta^3$
IrO	$^4\Sigma^-$	$16\sigma^19\pi^24\delta^4$	IrO ⁺	$^5\Delta$	$16\sigma^19\pi^24\delta^3$	IrO ⁻	$^3\Sigma^-$	$16\sigma^29\pi^24\delta^4$
PtO	$^3\Sigma^-$	$16\sigma^29\pi^24\delta^4$	PtO ⁺	$^4\Sigma^-$	$16\sigma^19\pi^24\delta^4$	PtO ⁻	$^2\Pi$	$16\sigma^29\pi^34\delta^4$
AuO	$^2\Pi$	$16\sigma^29\pi^34\delta^4$	AuO ⁺	$^3\Sigma^-$	$16\sigma^29\pi^24\delta^4$	AuO ⁻	$^1\Sigma^+$	$16\sigma^29\pi^44\delta^4$
HgO	$^3\Pi$	$16\sigma^29\pi^34\delta^417\sigma^1$	HgO ⁺	$^2\Pi$	$16\sigma^29\pi^34\delta^4$	HgO ⁻	$^2\Sigma^+$	$16\sigma^29\pi^44\delta^417\sigma^1$

at SVWN, in which BLYP (2.264 eV) performs the best in reproducing the experimental data 2.26 eV [37] and 2.33 eV [36], followed by BPW91 (2.230 eV) and BP86 (2.377 eV). This indicates that pure density functional methods are superior to hybrid density functional methods (B3LYP, B3PW91, and B3P86) in predicting the dissociation energy in AuO. For AuO⁻, our calculated bond distance is from 1.866 Å at SVWN to 1.930 Å at BLYP, in fair agreement with the experimental value (1.899 Å) [16] and a previous theoretical study at CCSD(T) (1.888 Å) [16] and B3PW91 (1.910 Å) [42]. For AuO⁺, the calculated bond distance shown in Table 3 is comparable to the previous theoretical value 1.981 Å [42], in particular for MPW1PW91 (1.981 Å) and PBE1PBE (1.976 Å) methods.

HgO. Hg is a unique element compared with the other transition metals because it has a closed-shell ($5d^{10}6s^2$). From Table 1, it is seen that $^3\Pi$ is the ground state for neutral species. From Table 2, it can be seen that neutral HgO has the smallest dissociation energy compared with both other neutral species (Table 2) and its charged partner HgO⁺ and HgO⁻. The neutral HgO (anionic HgO⁻) has the lowest frequency compared with the other neutral (anionic) species. The calculated bond distance for neutral species is from 2.156 Å at SVWN level to 2.317 Å at B3LYP level, larger than the experimental value 2.03 Å [14]. The larger difference in bond distance between our calculation and experiment may be the insufficient (large core) of basis set SDD. For the EA, DFT calculation show a scattering from 1.973 eV at PBE1PBE to 3.247 eV at SVWN, in which BLYP (2.236 eV) gives better performance in reproducing the experimental data 2.298 eV [14], followed by BPW91 (2.233 eV). The calculated IP is from 9.796 eV at BLYP to 13.084 eV at SVWN.

3.1 Bonding analysis and general trends

The calculated ground state electron configuration is listed in Table 4. The spin multiplicity is not regular compared with 3d metal monoxides [3]. The calculated dipole moments at B3LYP level from HfO to HgO are 3.82D, 3.14D, 2.63D, 4.03D, 3.71D, 3.11D, 3.01D, 3.61D, and 2.12D, and at BLYP

level they are 3.59D, 2.89D, 2.35D, 3.63D, 3.34D, 3.34D, 2.75D, 2.65D, 3.28D, and 2.20D. These calculated dipole moments suggest that the bonding patterns are complex for these systems which involve covalent, ionic, and dative components. For instance, if the bonding is purely ionic, the dipole moment of HfO would be 8.36D, but it is only 3.82D (B3LYP) and 3.59D (BLYP) which show that other components of the bonding are dominant. Therefore, besides ionic component, covalent bonds are formed between the metal 5d orbitals and O 2p orbitals. This is also true for other species. In fact, the bonding for the title molecules mainly arises from interactions between metal d and s orbitals and silicon 3p orbital. The metal σ orbital undergoes sd_σ hybridization and interacts with silicon $3p_\sigma$ orbital to form bonding, nonbonding and antibonding orbitals. The metal $3d_\pi$ orbitals interact with silicon $3p_\pi$ orbitals to give bonding and antibonding orbitals. The metal $3d_\delta$ orbitals are nonbonding because there are no corresponding orbitals in silicon. Although the expected order of stability is σ bond > π bond > σ and δ nonbonding > π antibonding > σ antibonding, the filling order is complicated due to the fact that d-d exchange energy is larger than the energy separation between different orbitals and the mixings of the metal s^2d^n and s^1d^{n+1} asymptotes.

From Tables 2 and 3, we noticed that compared with hybrid density functional method B3PW91 (B3P86), pure density functional method BPW91 (BP86) gives longer bond distance (lower vibrational frequency) from HfO to PtO for neutral species, HfO⁺ to IrO⁺ for cationic species and HfO⁻ to AuO⁻ for anionic species. While for B3LYP and BLYP, the trend was observed for cationic species from HfO⁺ to IrO⁺ and anionic species from HfO⁻ to AuO⁻ (except TaO⁻), but not for neutrals. For the dissociation energy, pure density function methods BLYP, BPW91, and BP86 give larger values compared with hybrid density functional methods B3LYP, B3PW91, and B3P86 (Table 2). SVWN gives the largest dissociation energy compared with the other methods. For most of the species, hybrid density functional methods give larger IP compared with pure density functional methods. In addition, for most species (including neutral and charged species), BLYP gives the longest bond distance compared with other density functional methods (except TaO⁻, HgO⁻, PtO⁺,

AuO⁺, TaO, OsO, AuO, and HgO), while SVWN gives the shortest bond distance (except HgO⁻, TaO⁺, ReO⁺, HfO, TaO, and WO). On the other hand, MPW1PW91 and PBE1PBE show the same performance in predicting the studied quantities. Useful empirical criteria that one can rely on to obtain the ground state of a species and its ions are the spin multiplicities of a neutral and its single charged ions which differs by ± 1 .

4 Conclusions

Different density function methods are used to study the bond distances, vibrational frequencies, dissociation energies, EA, and IP of the diatomic 5d transition metal (except La) monoxides and their positively and negatively charged ions. The main conclusions are:

1. For some species, such as neutral OsO, cationic OsO⁺, anionic TaO⁻, WO⁻, and ReO⁻ at both B3LYP and BLYP levels, and cationic HgO⁺, anionic AuO⁻ at B3LYP level, low-lying states which are the competitive candidate for the ground state were found. In this case, both further experimental study and advanced theoretical study are necessary to help finding the true ground state.
2. Useful empirical criteria that one can rely on to obtain the ground state of a species and its ions are the spin multiplicities of a neutral and its single charged ions which differs by ± 1 . For 5d metal monoxides we only found WO⁺, ReO⁺, and HfO⁻, WO⁻, which are exceptions to this criteria.
3. Compared with hybrid density functional method B3PW91 (B3P86), pure density functional method BPW91 (BP86) gives longer bond distance (lower vibrational frequency) from HfO to PtO for neutral species, HfO⁺ to IrO⁺ for cationic species and HfO⁻ to AuO⁻ for anionic species. While for B3LYP and BLYP, the trend was observed for cationic species from HfO⁺ to IrO⁺ and anionic species from HfO⁻ to AuO⁻ (except TaO⁻), but not for neutrals. For the dissociation energy, pure density function methods BLYP, BPW91, and BP86 give larger values compared with hybrid density functional methods B3LYP, B3PW91, and B3P86 (Table 2). SVWN gives the largest dissociation energy compared with the other methods. For most species, BLYP gives the largest value (except TaO⁻, HgO, PtO⁺, AuO⁺, TaO, OsO, AuO, and HgO), SVWN gives the smallest value (except HgO⁻, TaO⁺, ReO⁺, HfO, TaO, and WO).
4. MPW1PW91 and PBE1PBE show the same performance in predicting the spectroscopic constants (i.e., bond distance, vibrational frequency and dissociation energy), EA, and IP.
5. For neutral species, the calculated frequency increases from HfO to WO, then decreases from OsO to HgO. The dissociation energy decreases from TaO to HgO (except for a rise at ReO).

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