Electronic Structures of MCO (M = Nb, Ta, Rh, Ir, Pd, Pt) Molecules by Density Functional Theory

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Equilibrium geometries, vibrational frequencies, and dissociation energies of the transition metal carbonyls MCO (M = Nb, Ta, Rh, Ir, Pd, Pt) were studied by use of diverse density functional methods B3LYP, BLYP, B3P86, B3PW91, BHLYP, BP86, and PBE1PBE. It was found that the ground electronic state is $^6\Sigma^+$ for NbCO and TaCO, $^2\Sigma^+$ for RhCO, $^2\Delta$ for IrCO, and $^1\Sigma^+$ for PdCO and PtCO, in agreement with previous theoretical studies. The calculated properties are highly dependent on the functionals employed, in particular for the dissociation energy. For most of the molecules, the predicted bond distance is in agreement with experiments and previous theoretical results. BHLYP is the worst method in reproducing the experimental results compared with the other density functional methods for the title molecules.

I. Introduction

In recent years, the interaction of carbon monoxide with transition metals has attracted particular interest.[1−15] This is because, first, metal carbonyls are important in many processes including catalysis, organometallic synthesis and decomposition, and modeling of metal surface/carbonyl interaction. Second, there is a fundamental desire to understand the nature of bonding between various transition metals and ligands. Third, carbon monoxide has long been used as a probe for surface characterizations. Its vibrational properties reflect the metal−CO strength and the influence of the direct environment. An excellent review concerning transition metal carbonyls was given by Andrews and co-workers.[6]

The metal−CO system was extensively studied both experimentally[1,2,4−8] and theoretically,[1−6,9−15] in particular for PdCO[3,4,6,8,15] and PtCO.[3,4,6,7,12,13] A good summary of the geometries from the various theoretical studies on PdCO and PtCO can be found in refs 8 and 7, respectively. Experimentally, geometries of PdCO were given by Fourier transform microwave (FTMW) spectroscopy,[8] i.e., $R_{\mathrm{Pd-C}} = 1.844$ Å and $R_{\mathrm{C-O}} = 1.138$ Å. Similarly, the geometries of PtCO by FTMW[7] are $R_{\mathrm{Pd-C}} = 1.760$ Å and $R_{\mathrm{C-O}} = 1.148$ Å. The determined CO stretching vibrational frequencies by laser ablation and matrix isolation spectroscopy are 2056.4 cm^{-1} for PdCO[4] and 2065.5 cm^{-1} for PtCO.[4] Meanwhile, density functional theory (DFT) studies at the B3LYP level were also conducted on PdCO[4] and PtCO,[4] and agreement with experimental results was achieved. For RhCO[2] and IrCO,[2] the experimentally determined CO stretching vibrational frequencies by laser ablation and matrix isolation spectroscopy are 2022.5 and 2024.5 cm^{-1}, respectively, in agreement with previous DFT results at the B3LYP and BP86 levels.[4] Similarly, for NbCO[1] and TaCO,[1] the experimentally determined CO stretching vibrational frequencies are 1932.0 and 1865.2 cm^{-1}, respectively, in agreement with previous DFT results at the B3LYP and BP86 levels.[1] Besides the DFT results, the potential energy surfaces for the low-lying excited states of NbCO,[9] TaCO,[10] RhCO,[11] IrCO,[11] and PtCO[12] were also studied by use of the complete active space multiconfiguration self-consistent field (CASMCSCF) and multireference singles + doubles configuration interaction (MRSDCI) by Balasubramanian and co-workers. It is found that CASMCSCF and MRSDCI give longer M−C bond distances compared with both experiments and previous DFT calculations.

DFT 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 requires less computational time and storage memory. On the other hand, many density functional methods have been developed during the past decade. It is known that these density functional methods are different from theoretical aspects. Therefore, it is necessary to test these density functional methods when applied on different systems, especially for systems containing transition metals because different density function methods may produce quite different properties for a given system.[16] In this study, the great availability of accurate experimental data coupled with the advances in density functional theory motivated us to examine the ground state of the MCO molecules by use of diverse density functional methods. The results are compared with experiments and previous theoretical studies. The performance among different density functional methods is compared. We hope this work could stimulate more research on transition metals with different ligands and provide a reference in choosing the reliable density functional method in future studies.

II. Computational Methods

All geometry optimizations were performed using the Gaussian 98 suite of programs.[17] Equilibrium geometries and dissociation energies were determined for the studied molecules by using seven different exchange−correlation functionals, denoted as B3LYP, BLYP, B3P86, B3PW91, BHLYP, BP86, and PBE1PBE.[18−24] For these density functional methods, the

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TABLE 1: Calculated Bond Distances R (Å), Vibrational Frequencies $\omega_1-\omega_4$ (cm^{-1}), and Relative Stability ΔE (eV) of MCO Molecules at the B3LYP Level for Various Spin Multiplicities S[a]

	S	R_{M-C}	R_{C-O}	ω_1	ω_2	ω_3	ω_4	ΔE
NbCO	2	1.918	1.178	382.5	382.5	524.2	1871.8	1.11
	4	2.014	1.176	323.4	342.4	449.4	1862.6	0.33
	6	2.087	1.154	301.6	301.6	405.1	1990.7	0.00
	8	2.368	1.216	−1872.3	−1872.3	200.9	1549.1	7.20
TaCO	2	1.962	1.181	348.1	380.8	494.3	1840.0	2.66
	4	2.046	1.161	285.4	318.3	418.7	1949.4	1.42
	6	2.050	1.160	312.6	312.6	418.9	1958.2	0.00
	8	2.319	1.226	205.8	307.7	307.7	1482.6	7.30
RhCO	2	1.818	1.153	339.0	339.0	509.4	2043.2	0.00
	4	6.327	1.128	4.5	18.1	18.2	2211.7	1.86
	6	2.315	1.161	140.7	183.4	248.7	1875.8	5.83
	8	1.982	1.324	117.9	117.9	413.5	1109.1	10.5
IrCO	2	1.787	1.153	428.6	428.6	598.7	2082.2	0.00
	4	2.118	1.133	−304.5	−259.6	253.2	2137.7	2.20
	6	2.252	1.166	138.5	187.6	283.7	1871.2	5.51
	8	2.027	1.232	208.3	208.3	436.2	1091.5	9.86
PdCO	1	1.878	1.142	242.3	242.3	443.5	2111.5	0.00
	3	2.068	1.130	−439.4	−439.4	243.7	2167.8	2.30
	5	2.121	1.177	136.7	207.0	327.2	1828.1	6.90
PtCO	1	1.795	1.147	392.4	392.4	565.0	2118.1	0.00
	3	1.975	1.138	−281.8	−281.8	348.0	2118.7	1.93
	5	2.133	1.174	176.8	210.7	316.7	1849.4	6.17
	7	1.904	3.007	43.8	72.7	72.7	625.3	11.4

[a] R_{M-C} indicates the bond distance between transition metal M and carbon. R_{C-O} indicates the bond distance between carbon and oxygen. The same notations were also used in Table 2.

correlation functional is from either Lee, Yang, and Parr (LYP),[18] Perdew 86 (P86),[19] or Perdew-Wang 1991 (PW91),[20] while the exchange functional is from either Becke's three-parameter HF/DFT hybrid exchange functional (B3),[21] the pure DFT exchange functional of 1988 (B),[22] or a modification of the half-and-half HF/DFT hybrid method (BH).[23] PBE1PBE is the GGA exchange−correlation functionals of Perdew, Burke, and Ernzerhof.[24] For oxygen and carbon atoms, 6-311+G(d) is used. For transition metals, basis set CEP-121G (relativistic compact effective potential)[25] is used, in which the dependence of spin−orbit effects was averaged out. The valence electrons considered for transition metals are $4s^24p^64d^45s^1$ for Nb, $5s^25p^65d^36s^2$ for Ta, $4s^24p^64d^85s^1$ for Rh, $5s^25p^65d^76s^2$ for Ir, $4s^24p^64d^{10}5s^0$ for Pd, and $5s^25p^65d^96s^1$ for Pt. To avoid trapping at local minima of the potential energy surface, different initial structures (bond distance) are used, but only the results from the global minimum are presented. The calculated dissociation energies were corrected by the zero-point vibrational energies.

From both experimental[1−2,4−8] and previous theoretical[1−6,9−15] studies, it is known that linear chain is the ground-state geometry for the title molecules. Therefore, in this study, the geometry is restricted to the linear chain. On the other hand, from previous theoretical study on NbCO[1] and TaCO,[1] we know that the inserted conformer CMO and side-bonded conformer M[CO] (M = Nb, Ta) have higher energy than carbonyl MCO. Therefore, in this study, only carbonyl MCO was considered.

III. Results and Discussion

The calculated results are listed in Tables 1 and 2. Because of the spin polarization of transition metals, the molecules were first calculated by use of B3LYP at various spin multiplicities in order to locate the most stable (ground state) spin state for each molecule. The results are listed in Table 1. After obtaining the ground spin state at B3LYP for each molecule, the bond distances, vibrational frequency, and dissociation energy from these most stable spin multiplicities for molecules MCO (M = Nb, Ta, Rh, Ir, Pd, Pt) at various density functional methods, B3LYP, BLYP, B3P86, B3PW91, BHLYP, BP86, and PBE1PBE, were calculated and are summarized in Table 2.

From Table 1, it is seen that the ground electronic state for NbCO and TaCO is $^6\Sigma^+$. For NbCO, the second lowest conformer is at spin multiplicity 4, which is 0.33 eV higher than the ground state. For TaCO, the second lowest state at spin multiplicity 4 is 1.42 eV higher than the ground electronic state $^6\Sigma^+$. Doublet is the ground state for RhCO ($^2\Sigma^+$) and IrCO ($^2\Delta$ at BLYP and BP86; for the remaining density functionals, the electronic state cannot be determined). For PdCO and PtCO, singlet ($^1\Sigma^+$) gives the global minimum; other conformers are much higher in energy than the ground state. It is also seen (Table 1) that negative frequencies are found at triplet of PdCO, PtCO and at spin multiplicity 4 of IrCO, indicating that these conformers are saddle points. Since in this calculation, only linear chain, which is the most stable geometry for the ground state, is considered for both the ground state and excited states, these obtained negative vibrational frequencies may indicate that linear chain is not the most stable shape for the excited states. This was confirmed by a recent study on PdCO[3] and PtCO,[3] in which it was found that the bent geometry is more favorable for the excited states.

NbCO. The ground electronic state is $^6\Sigma^+$, in agreement with previous studies.[1,9] The calculated Nb−C bond distance (Table 2) is from 2.069 Å at B3P86 to 2.103 Å at BHLYP, in agreement with DFT study at BP86/LANL2DZ (2.064 Å)[1] and at B3LYP/LANL2DZ (2.080 Å).[1] These calculated bond distances at DFT levels (including ours and those in ref 1) for Nb−C are smaller than those at CASMCSCF (2.168 Å)[9] and MRSDCI (2.124 Å).[9] For the C−O bond, our calculated value is from 1.135 Å at BHLYP to 1.170 Å at BLYP, comparable to the results at B3LYP/LANL2DZ (1.168 Å),[1] CASMCSCF (1.139 Å),[9] and MRSDCI (1.146 Å)[9] but smaller than the result at BP86/LANL2DZ (1.182 Å).[1] The Nb−C−O bending mode (ω_1, ω_2, doubly degenerate) in NbCO has vibrational frequencies from 291.4 cm^{-1} at BLYP to 311.3 cm^{-1} at PBE1PBE, varying in a narrow range. The Nb−C strectching vibrational frequency (ω_3) is from 384.3 cm^{-1} at BHLYP to 420.9 cm^{-1} at B3P86. For the C−O stretching mode (ω_4), the calculated vibrational frequency is from 1891.9 cm^{-1} at BLYP to 2034.4 cm^{-1} at PBE1PBE, in which BLYP (1891.9 cm^{-1}) and BP86 (1918.9 cm^{-1}) give the best performance compared with the experimental value 1932.0 cm^{-1} [1] and previous DFT result 1916.2 cm^{-1} at BP86/LANL2DZ;[1] other functionals in this study overestimate the experimental value. On the other hand, our predicted vibrational frequencies and experimental value (1932.0 cm^{-1})[1] are smaller than theoretical study at CASMCSCF (2133 cm^{-1})[9] and MRSDCI (2135 cm^{-1})[9] by more than 100 cm^{-1}. This was attributed to the reason that not enough C and O orbitals were included in the active space at CASMCSCF and MRSDCI to accurately describe the C−O stretch as commented by Andrews and co-workers.[1] From Table 2, it is also seen that our calculated dissociation energy is from 1.78 eV at B3LYP to 2.34 eV at BHLYP, much higher than the values obtained at CASMCSCF (0.389 eV)[9] and MRSDCI (0.968 or 1.11 eV).[9] This indicates that further study is necessary for the accurate evaluation of dissociation energy.

TaCO. For this molecule, spin multiplicity at 6 gives the ground state ($^6\Sigma^+$) (Table 1). This is in agreement with previous studies at the BP86/LANL2DZ[1] and CASMCSCF levels[10] but contradicts the results at B3LYP/LANL2DZ[1] and MRSDCI[10] in which spin multiplicity at 4 ($^4\Delta$) gives the global minimum. On the other hand, previous DFT study at BP86/LANL2DZ

TABLE 2: Ground State Bond Distances R (Å), Vibrational Frequencies $\omega_1-\omega_4$ (cm^{-1}), and Dissociation Energies D_e (eV) for MCO (M = Nb, Ta, Rh, Ir, Pd, Pt) from Various Density Functional Methods; Results from Previous Theoretical Studies (DFT, CASMCSCF, and MRSDCI) and Experiments Are Listed for Comparison

		B3LYP	BLYP	B3P86	B3PW91	BHLYP	BP86	PBE1PBE	DFT	DFT	CASMCSCF[h]	MRSDCI[i]	expt
NbCO	R_{M-C}	2.087	2.089	2.069	2.075	2.103	2.071	2.071	2.064[b]	2.080[c]	2.168[j]	2.124[j]	
	R_{C-O}	1.154	1.170	1.152	1.152	1.135	1.169	1.150	1.182	1.168	1.139	1.146	
	ω_1	301.6	291.4	310.3	309.1	308.6	299.9	311.3					
	ω_2	301.6	291.4	310.3	309.1	308.6	299.9	311.3					
	ω_3	405.1	405.2	420.9	415.1	384.3	420.3	418.3					
	ω_4	1990.7	1891.9	2016.3	2014.5	2104.8	1918.9	2034.4	1916.2		2133	2135	1932.0[n]
	D_e[a]	1.78	2.30	2.23	2.22	2.34	1.85	2.25			0.389	0.968(1.11)	
TaCO	R_{M-C}	2.050	2.056	2.035	2.041	2.052	2.042	2.036	2.012[b]	2.022[c]	2.142[k]	2.063[k]	
	R_{C-O}	1.160	1.176	1.158	1.158	1.143	1.174	1.156	1.184	1.170	1.128	1.143	
	ω_1	312.6	298.8	322.2	321.8	325.5	308.1	325.0					
	ω_2	312.6	298.8	322.2	321.8	325.5	308.1	325.0					
	ω_3	418.9	413.9	432.5	427.6	413.9	427.3	431.8					
	ω_4	1958.2	1867.1	1989.2	1987.4	2055.3	1899.2	2006.0	1893.3				1865.2[n]
	D_e	1.10	1.02	1.46	1.49	0.42	1.64	1.50			1.076	0.929(1.075)	
RhCO	R_{M-C}	1.818	1.839	1.797	1.800	1.853	1.789	1.800	1.824[d]	1.822[e]	1.871[l]	1.839[l]	
	R_{C-O}	1.153	1.164	1.153	1.153	1.133	1.171	1.151	1.173	1.177	1.128	1.146	
	ω_1	339.0	309.5	350.1	348.9	325.6	351.4	347.5					
	ω_2	339.0	310.2	350.1	348.9	325.6	352.1	347.5					
	ω_3	509.4	508.9	534.4	530.6	464.1	550.5	529.3					
	ω_4	2043.2	1983.1	2061.7	2056.9	2171.3	1957.9	2078.8	1999.6	2004.7	2107	2127	2022.5[o]
	D_e	1.83	2.31	2.12	1.98	1.36	2.55	1.96			1.24	0.87(1.19)	
IrCO	R_{M-C}	1.787	1.791	1.774	1.775	1.792	1.800	1.773	1.769[d]	1.768[e]	1.825[l]	1.772[l]	
	R_{C-O}	1.153	1.169	1.152	1.153	1.135	1.169	1.151	1.179	1.183	1.163	1.161	
	ω_1	428.6	416.2	434.1	433.9	438.3	422.2	435.4					
	ω_2	428.6	416.2	434.1	433.9	438.3	422.2	435.4					
	ω_3	598.7	593.9	617.3	615.1	590.8	611.8	618.8					
	ω_4	2082.2	1987.9	2017.1	2102.7	2192.2	2012.7	2123.4	2011.3	2022.0	2023	2074	2024.5[o]
	D_e	2.55	2.90	2.80	2.67	1.92	3.16	2.70			1.45	2.13(2.04)	
PdCO	R_{M-C}	1.878	1.869	1.856	1.859	1.909	1.847	1.858	1.873[f]	1.873[g]			1.884[p]
	R_{C-O}	1.142	1.158	1.142	1.143	1.125	1.159	1.141	1.140	1.143			1.138[p]
	ω_1	242.3	245.5	251.4	249.9	234.3	256.6	247.8	249	242.4			
	ω_2	242.3	245.5	251.4	249.9	234.3	256.6	247.8	249	242.4			
	ω_3	443.5	456.3	468.7	464.7	407.6	481.9	465.1	449	445.3			
	ω_4	2111.5	2006.1	2129.0	2123.8	2237.9	2023.6	2145.9	2114	2112.9			2056.4[q]
	D_e	1.64	1.95	1.85	1.76	1.18	2.20	1.78		1.79			
PtCO	R_{M-C}	1.795	1.795	1.780	1.782	1.806	1.780	1.780	1.780[f]	1.781[g]	1.904[m]	1.900[m]	1.760[r]
	R_{C-O}	1.147	1.163	1.146	1.147	1.130	1.162	1.145	1.146	1.148	1.151	1.147	1.148[r]
	ω_1	392.4	385.9	400.5	400.0	396.4	394.2	400.8	407	404.7			
	ω_2	392.4	385.9	400.5	400.0	396.4	394.2	400.8	407	404.7			
	ω_3	565.0	565.8	586.1	584.0	545.6	586.9	586.2	585	590.3			
	ω_4	2118.1	2018.9	2141.4	2137.1	2230.1	2042.7	2157.7	2114	2121.4			2065.5[q]
	D_e	2.66	2.95	2.99	2.88	2.10	3.31	2.90	3.15	2.89	1.89	1.86	

[a] The dissociation energies refer to the reactions MCO → M + CO. [b] Reference 1. Density functional theory at BP86/LANL2DZ. Basis set LANL2DZ indicates the D95* basis set for C and O atoms and the Los Alamos effective core potential (ECP) plus DZ for Nb and Ta atoms. [c] Reference 1. Density functional theory at B3LYP/LANL2DZ. [d] Reference 2. Density functional theory at the BP86 level. For the basis set, 6-31+G(d) is used for C and O atoms, and LANL2DZ is used for Rh and Ir atoms. [e] Reference 2. Density functional theory at BP86/LANL2DZ. [f] Reference 3. Density functional theory at the B3LYP level. For the basis set, 6-311+G(2d) is used for C and O atoms, and LANL2DZ is used for Pd and Pt atoms. [g] Reference 4. Density functional theory at the B3LYP level. For the basis set, 6-311+G(d) is used for C and O atoms, and LANL2DZ is used for Pd and Pt atoms. [h] CASMCSCF indicates the complete active space multiconfiguration self-consistent field. [i] MRSDCI indicates multireference singles + doubles configuration interaction. Values in parentheses are the Davidson corrected (MRSDCI+Q) energies. [j] Reference 9. [k] Reference 10. [l] Reference 11. [m] Reference 12. [n] Reference 1. Laser ablation and matrix isolation spectroscopy. [o] References 2 and 5. Laser ablation and matrix isolation spectroscopy. [p] Reference 8. Fourier transform microwave spectroscopy. [q] Reference 4. Laser ablation and matrix isolation spectroscopy. [r] Reference 7. Fourier transform microwave spectroscopy.

predicted that the spin multiplicity at 6 ($^6\Sigma^+$) is only marginally more stable than the spin multiplicity at 4 ($^4\Delta$) by 1.7 kcal/mol.[1] At B3LYP/LANL2DZ, $^6\Sigma^+$ is only 3.7 kcal/mol higher than $^4\Delta$.[1] These results indicate that $^6\Sigma^+$ and $^4\Delta$ are competitive candidates for the ground state at the BP86(B3LYP)/LANL2DZ level(s). In our calculation, nonetheless, it can be seen that spin multiplicity 4 is 1.42 eV higher than spin multiplicity 6 at the current basis set, i.e., CEP-121G for Ta and 6-311+G(d) for C and O atoms. Therefore, except B3LYP, calculations are done only for spin multiplicity at 6 for other functionals as listed in Table 2.

The calculated Ta−C bond distance is from 2.035 Å at B3P86 to 2.056 Å at BLYP, comparable to the value 2.012 Å at BP86/LANL2DZ,[1] 2.022 Å at B3LYP/LANL2DZ,[2] and 2.063 Å at MRSDCI[10] but smaller than the value 2.142 Å at the CASMCSCF level. The C−O bond distance is from 1.143 Å at BHLYP to 1.176 Å at BLYP, in agreement with previous theoretical study at BP86/LANL2DZ (1.184 Å),[1] B3LYP/LANL2DZ (1.170 Å),[1] and MRSDCI (1.143 Å)[10] but larger than the value 1.128 Å at the CASMCSCF level.[10] The calculated Ta−C−O bending and Ta−C stretching modes in TaCO have a higher vibrational frequency than the corresponding value for NbCO (Table 2). At BLYP (1867.1 cm^{-1}) and BP86 (1899.2 cm^{-1}), the calculated C−O stretching vibrational frequency is close to the experimental value[1] 1865.2 cm^{-1} and the previous theoretical result at BP86/LANL2DZ (1893.3 cm^{-1}).[1] Other functionals overestimate the experimental value by at least 93.0 cm^{-1} (at the B3LYP level). The calculated dissociation energy at the B3LYP

(1.10 eV) and BLYP (1.02 eV) levels is close to the previous theoretical study at CASMCSCF (1.076 eV)[10] and MRSDCI (0.968 or 1.075 eV).[10] Other functionals (Table 2) either underestimate (BHLYP, 0.42 eV) or overestimate (B3P86, 1.46 eV; B3PW91, 1.49 eV; BP86, 1.64 eV; PBE1PBE, 1.50 eV) the values at the CASMCSCF and/or MRSDCI levels.[10]

RhCO. The ground electronic state is $^2\Sigma^+$, in agreement with previous study at the DFT level[2] but different from the study at the CASMCSCF and MRSDCI levels ($^2\Delta$).[11] The calculated Rh−C bond distance is from 1.789 Å at BP86 to 1.853 Å at BHLYP, close to the results at BP86 with the general basis set (6-31+G(d) for C and O, LANL2DZ for Rh) (1.824 Å),[2] BP86/LANL2DZ(1.822 Å),[2] and MRSDCI (1.839 Å)[11] but smaller than the result at CASMCSCF (1.871 Å).[11] For C−O bond distance, a similar trend as in Rh−C is also observed, except that the C−O bond distance is shorter at CASMCSCF (1.128 Å)[11] compared with other methods (Table 2). The calculated vibrational frequency varies in a wide range from 1957.9 cm^{-1} at BP86 to 2171.3 cm^{-1} at the BHLYP level. Compared with the experimental value 2022.5 cm^{-1},[2,5] the calculated values change from an absolute error of −64.6 cm^{-1} at BP86 to 128.8 cm^{-1} at BHLYP, in which B3LYP (by an absolute error of 20.7 cm^{-1}) gives the best performance. Previous theoretical studies at CASMCSCF (2107 cm^{-1})[11] and MRSDCI (2127 cm^{-1})[11] overestimate the experimental result. For the calculated dissociation energy, only BHLYP (1.36 eV) gives best agreement with previous theoretical results at CASMCSCF (1.24 eV)[11] and MRSDCI (0.87 or 1.19 eV).[11] Other functionals have higher dissociation energies, even doubled at the BP86 level (2.55 eV).

IrCO. For BLYP and BP86, the determined ground electronic state is $^2\Delta$, in agreement with previous studies.[2,11] For the remaining density functionals, i.e., B3LYP, B3P86, B3PW91, BHLYP, and PBE1PBE, it is not possible to determine which electronic state at doublet is the ground electronic state.

The calculated Ir−C bond distances at various density functionals (from 1.773 Å at PBE1PBE to 1.800 Å at BP86) vary in a narrow range, in agreement with previous theoretical results at BP86 with the general basis set (6-31+G(d) for C and O, LANL2DZ for Rh) (1.769 Å),[2] BP86/LANL2DZ (1.768 Å),[2] and MRSDCI (1.772 Å)[11] but slightly smaller than the result at CASMCSCF (1.825 Å).[11] The variation in calculated C−O bond distances is a little larger, from 1.135 Å at BHLYP to 1.169 Å at the BLYP and BP86 levels. These values are slightly smaller than previous DFT results (1.179 and 1.183 Å)[2] and results at CASMCSCF (1.163 Å)[11] and MRSDCI (1.161 Å).[11] The Ir−C−O bending and Ir−C stretching modes have a higher vibrational frequency compared with the corresponding values in RhCO (see Table 2). For the C−O stretching mode, only B3P86 (2017.1 cm^{-1}) and BP86 (2012.7 cm^{-1}) give the best vibrational frequency compared with the experimental value 2024.5 cm^{-1}.[2] Other density functionals either underestimate (BLYP) or overestimate (B3LYP, B3PW91, BHLYP, and PBE1PBE) the experimental value. For the dissociation energy, only BHLYP (1.92 eV) has a value close to the results at CASMCSCF (1.45 eV)[11] and MRSDCI (2.13 or 2.04 eV).[11] Other density functionals produce higher values.

PdCO. The ground electronic state is $^1\Sigma^+$, in agreement with previous studies.[3,4] PdCO is one of the most extensively studied systems both theoretically and experimentally. For a summary of the theoretical study, see ref 8. In experimental study,[8] the observed Pd−C bond distance is 1.884 Å, and the C−O bond distance is 1.138 Å. These values are in good agreement with our calculation for the Pd−C bond distance which varies from 1.856 Å at B3P86 to 1.909 Å at BHLYP and the C−O bond distance which varies from 1.125 Å at BHLYP to 1.159 Å at BP86 (Table 2). In addition, agreement with previous DFT calculation at the B3LYP level is also observed, i.e., 1.873 Å for Pd−C, 1.140 Å for C−O (6-311+G(2d) basis set for C and O, LANL2DZ for Pd);[3] 1.873 Å for Pd−C, 1.143 Å for C−O (6-311+G(d) basis set for C and O, LANL2DZ for Pd).[4] Our calculated Pd−C−O bending mode from 234.3 cm^{-1} at BHLYP to 256.6 cm^{-1} at BP86 and Pd−C stretching mode from 407.6 cm^{-1} at BHLYP to 481.9 cm^{-1} at BP86 are in agreement with previous DFT calculation at the B3LYP level, i.e., 249 cm^{-1} [3] and 242.4 cm^{-1} [4] for the bending mode and 449 cm^{-1} [3] and 445.3 cm^{-1} [4] for the Pd−C stretching mode, respectively. For the C−O stretching mode, our calculation at BP86 (2023.6 cm^{-1}) gives the best performance compared with the experimental value 2056.4 cm^{-1},[4] followed by BLYP (2006.1 cm^{-1}) and B3LYP (2111.5 cm^{-1}). BHLYP produces the worst result (2237.9 cm^{-1}). For the calculated dissociation energy, except BHLYP (1.18 eV), our results which vary from 1.69 eV at B3LYP to 2.20 eV at BP86 are in fair agreement with previous DFT calculation at the B3LYP level, 1.79 eV.[4] However, from Table 2, we can see that our results (bond distance, vibrational frequency, and dissociation energy) at B3LYP are quite similar to the results of ref 4 (11th column in Table 2) for PdCO. This is not surprising because the same DFT method (B3LYP) and basis set for C and O (6-311+G(d)) are used; the only difference is the basis set for the metal: we use CEP-121G for Pd, while ref 4 uses LANL2DZ. This results in a little larger difference in the dissociation energy (1.64 eV in our case, 1.79 eV in ref 4). This is also observed in PtCO (Table 2).

PtCO. The ground electronic state is $^1\Sigma^+$, in agreement with previous studies.[3,4,12] Similar to PdCO, many theoretical studies are available for PtCO (see ref 7 for a summary of the previous theoretical studies). The calculated Pt−C and C−O bond distances are close to the experimental values 1.760 Å for Pt−C[7] and 1.148 Å for C−O[7] and previous theoretical results[3,4] (Table 2). However, the predicted Pt−C bond distance tends to be large at CASMCSCF (1.904 Å)[12] and MRSDCI (1.900 Å)[12] compared with our results, previous DFT calculations,[3,4] and experiment.[7] The calculated vibrational frequencies for the Pt−C−O bending and Pt−C stretching modes are in agreement with previous DFT calculations[3,4] (Table 2). But they are much larger than the corresponding modes in PdCO (Table 2). PdCO gives the lowest bending mode among the molecules studied in this paper (Table 2). The experimental C−O stretching mode in PtCO (Table 2) is 2065.5 cm^{-1},[4] close to our result at the BP86 level (2042.7 cm^{-1}). As in PdCO, BHLYP has the worst performance in reproducing the C−O vibrational frequency (2230.1 cm^{-1}). Except BHLYP (2.10 eV), the calculated dissociation energy from 2.66 eV at B3LYP to 3.31 eV at the BP86 level is in agreement with previous theoretical results, 2.89[4] and 3.15 eV.[3] It is also seen that DFT calculations (including ours and those of refs 3 and 4) produce a larger dissociation energy compared with the calculations at CASMCSCF (1.89 eV)[12] and MRSDCI (1.86 eV).[12]

IV. Conclusions

The performance of different density functional methods, i.e., B3LYP, BLYP, B3P86, B3PW91, BHLYP, BP86, and PBE1PBE, was tested on the transition metal carbonyls MCO (M = Nb, Ta, Rh, Ir, Pd, Pt). For TaCO, the predicted spin multiplicity at ground state is 6 ($^6\Sigma^+$), in agreement with previous theoretical studies at the BP86/LANL2DZ and CASMCSCF levels but contradicting the results at B3LYP/LANL2DZ and MRSDCI in which spin multiplicity at 4 ($^4\Delta$) gives the global minimum. This suggests that further study with a higher level basis set is necessary to solve the discrepancy. The results also indicate that the calculated properties are highly sensitive to the density functionals used, in particular for the dissociation energy. For most of the molecules, the predicted bond distance is in general agreement with experiment and previous theoretical results. Compared with experiments, except at TaCO, B3LYP, B3P86, B3PW91, BHLYP, and PBE1PBE tend to give higher C−O vibrational frequency for the studied molecules, while the performance of BLYP and BP86 is the opposite. For all the studied molecules, BHLYP is the worst density functional in reproducing the experimental results compared with the other density functionals used in this study.

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