Supplementary Information for

Can single reference density functional theory methods describe spin state crossing for 3d transition metal carbon monoxide association?

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Computational details

Details of the SA-CASSCF/MRCI+Q calculation are provided in this section. The electronic states $^{2S+1}\Lambda$ for each system, which taken for state-averaging, are presented in Table S1. Here, $2S+1$ and Λ denote the spin multiplicity and the projection of the total orbital angular momentum onto the molecular axis, respectively. For non-zero orbital angular momentum terms (e.g., $\Lambda = \Pi,\ \Delta,\ \Phi,\ \Gamma$ etc.), both counterparts of opposite signs are included in these state-averaged calculations.

Table S1. The electronic states $^{2S+1}\Lambda$ included in the SA-CASSCF calculations for the transition metal atoms (TM) and their carbonyl complexes (TMCO). For each TM species, the leading number indicates the total number of electronic states.

TM	Atom	Carbonyl complex
Sc	19: ^4F, ^4D, ^4P, 1 ^4S, 2 ^4S, ^2F, 1 ^2D, 2 ^2D, ^2P, 1 ^2S, 2 ^2S, 3 ^2S	10: $^4\Phi$, $^4\Pi$, $^4\Sigma^-$, $^2\Delta$, $^2\Pi$, $^2\Sigma^-$
Ti	18: ^5F, ^5D, ^5P, 1 ^5S, 2 ^5S, ^3F, 1 ^3D, 2 ^3D, ^3P, 1 ^3S, 2 ^3S	18: $^5\Phi$, $^5\Delta$, $^5\Pi$, $^3\Gamma$, $^3\Phi$, 1 $^3\Delta$, 2 $^3\Delta$, $^3\Pi$, 1 $^3\Sigma^-$, 2 $^3\Sigma^-$
V	17: ^6D, ^6P, 1 ^6S, 2 ^6S, ^4F, 1 ^4D, 2 ^4D, ^4P, 1 ^4S, 2 ^4S, 3 ^4S	–
Cr	14: ^7S, ^5G, ^5F, 1 ^5D, 2 ^5D, ^5P, 1 ^5S, 2 ^5S, 3 ^5S	–
Mn	18: ^6D, ^6P, 1 ^6S, 2 ^6S, ^4G ^4F, 1 ^4D, 2 ^4D, ^4P, 1 ^4S, 2 ^4S	–
Fe	20: 1 ^5D, 2 ^5D, ^5P, 1 ^5S, 2 ^5S, 3 ^5S, ^3H, ^3G, ^3F, ^3D, ^3P, ^3S	14: $^5\Phi$, $^5\Delta$, $^5\Pi$, $^5\Sigma^-$, $^3\Phi$, $^3\Delta$, $^3\Pi$, $^3\Sigma^-$
Co	27: ^4F, 1 ^4D, 2 ^4D, 1 ^4P, 2 ^4P, 1 ^4S, 2 ^4S, 3 ^4S, ^2G, ^2F, 1 ^2D, 2 ^2D, 1 ^2P, 2 ^2P, 1 ^2S, 2 ^2S	15: $^4\Phi$, $^4\Delta$, $^4\Pi$, 1 $^4\Sigma^-$, 2 $^4\Sigma^-$, $^2\Phi$, 1 $^2\Delta$, 2 $^2\Delta$, $^2\Pi$, $^2\Sigma^-$
Ni	17: ^3F, 1 ^3D, 2 ^3D, ^3P, 1 ^3S, 2 ^3S, ^1F, ^1D, ^1P, ^1S	11: $^3\Delta$, $^3\Pi$, $^3\Sigma^-$, $^1\Delta$, $^1\Pi$, 1 $^1\Sigma^+$, 2 $^1\Sigma^+$,
Cu	4: ^2P, ^2D, 1 ^2S, 2 ^2S	–

Atomic and binding energies

Table S2: Calculated relative spin state energies for the Sc atom, and the Sc-CO binding energy for the lowest energy spin states. The binding energy is calculated relative to Sc (^{2}D) + CO.

	PBE	TPSSh	PBE0	HSE06	B3LYP	MN15	B2PLYP	CCSD(T)	MRCI+Q	Exp
Sc ^{2}D (s^2d^1)	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Sc ^{4}F (s^1d^2)	0.48	0.40	0.56	0.59	0.75	1.40	1.10	1.58	1.63	1.44
ScCO $^{2}\Pi$	-0.82	-0.68	-0.46	-0.43	-0.25	-0.35	0.01	0.25		
ScCO $^{4}\Sigma^{-}$	-1.37	-1.16	-0.97	-0.94	-0.67	-0.43	-0.27	0.02		

Table S3: Calculated relative spin state energies for the Ti atom, and the Ti-CO binding energy for the lowest energy spin states. The binding energy is calculated relative to Ti (^{3}F) + CO.

	PBE	TPSSh	PBE0	HSE06	B3LYP	MN15	B2PLYP	CCSD(T)	MRCI+Q	Exp
Ti ^{3}F (s^2d^2)	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Ti ^{5}F (s^1d^3)	-0.40	-0.07	-0.05	-0.24	0.01	0.43	0.34	0.85	0.89	0.83
TiCO $^{3}\Delta$	-1.58	-1.00	-0.75	-0.95	-0.72	-0.54	-0.19	0.21		
TiCO $^{5}\Delta$	-2.14	-1.54	-1.36	-1.55	-1.22	-0.99	-0.77	-0.32		

Table S4: Calculated relative spin state energies for the V atom, and the V-CO binding energy for the lowest energy spin states. The binding energy is calculated relative to V (^{4}F) + CO.

	PBE	TPSSh	PBE0	HSE06	B3LYP	MN15	B2PLYP	CCSD(T)	MRCI+Q	Exp
V ^{4}F (s^2d^3)	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
V ^{6}D (s^1d^4)	-0.86	-0.60	-0.58	-0.59	-0.22	-0.37	0.10	0.38	0.17	0.28
VCO $^{4}\Delta$	-1.75	-1.22	-0.87	-0.88	-0.60	-0.65	-0.07	0.14		
VCO $^{6}\Sigma$	-2.49	-1.90	-1.64	-1.64	-1.22	-1.66	-0.71	-0.38		

Table S5: Calculated relative spin state energies for the Cr atom, and the Cr-CO binding energy for the lowest energy spin states. The binding energy is calculated relative to Cr (^{7}S) + CO.

	PBE	TPSSh	PBE0	HSE06	B3LYP	MN15	B2PLYP	CCSD(T)	MRCI+Q	Exp
Cr^{5}D (s^{2}d^4)	2.06	1.18	1.81	1.81	1.39	2.27	2.59	0.99	1.19	0.99
Cr ^{5}S (s^{1}d^5)	1.23	1.21	1.14	1.19	0.79	0.78	0.68	0.45	0.84	0.94
Cr ^{7}S (s^{1}d^5)	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
CrCO $^5\Sigma$	-0.25	0.23	0.38	0.39	0.17	0.07	0.20	0.29		
CrCO $^7\Sigma$	-0.46	-0.35	-0.18	-0.18	-0.16	-0.24	-0.11	-0.05		

Table S6: Calculated relative spin state energies for the Mn atom, and the Mn-CO binding energy for the lowest energy spin states. The binding energy is calculated relative to Mn (^{6}S) + CO.

	PBE	TPSSh	PBE0	HSE06	B3LYP	MN15	B2PLYP	CCSD(T)	MRCI+Q	Exp
Mn ^{6}D (s^{1}d^6)	0.85	1.01	1.37	1.34	1.38	1.23	1.77	2.30	2.46	2.16
Mn ^{6}S (s^{2}d^5)	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
MnCO $^4\Pi$	-0.81	0.22	0.62	0.63	0.62	0.45	1.14	1.32		
MnCO $^6\Pi$	-0.53	-0.24	0.13	0.11	0.39	0.24	0.84	0.98		

Table S7: Calculated relative spin state energies for the Fe atom, and the Fe-CO binding energy for the lowest energy spin states. The binding energy is calculated relative to Fe (^{5}D) + CO.

	PBE	TPSSh	PBE0	HSE0	B3LYP	MN15	B2PLYP	CCSD(T)	MRCI+Q	Exp
Fe ^{3}F (s^{1}d^7)	0.99	0.96	1.04	1.06	0.95	0.81	1.13	1.48	1.71	1.55
Fe ^{5}F (s^{1}d^7)	0.39	0.35	0.50	0.49	0.52	0.36	0.73	1.10	0.56	0.95
Fe ^{5}D (s^{2}d^6)	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
FeCO $^3\Sigma$	-1.55	-0.91	-0.58	-0.58	-0.57	-0.99	-0.43	0.06	-0.66	-0.46
FeCO $^5\Sigma$	-1.23	-1.02	-0.71	-0.71	-0.48	-0.69	-0.43	0.01	-0.66	

Table S8: Calculated relative spin state energies for the Co atom, and the Co-CO binding energy for the lowest energy spin states. The binding energy is calculated relative to Co (^{4}F) + CO.

	PBE	TPSSh	PBE0	HSE0	B3LYP	MN15	B2PLYP	CCSD(T)	MRCI+Q	Exp
Co ^{2}F(s^{1}d^8)	0.40	0.39	0.39	0.36	0.28	0.41	0.28	0.68	0.43	0.92
Co ^{4}F (s^{1}d^8)	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
CoCO $^2\Delta$	-2.15	-1.42	-1.01	-1.01	-1.05	-1.29	-0.98	-0.54	-1.31	
CoCO $^4\Delta$	-1.26	-1.04	-0.83	-0.83	-0.67	-0.61	-0.79	-0.34	-0.98	

Table S9: Calculated relative spin state energies for the Ni atom, and the Ni-CO binding energy for the lowest energy spin states. The binding energy is calculated relative to Ni (^{3}F) + CO.

	PBE	TPSSh	PBE0	HSE0	B3LYP	MN15	B2PLYP	CCSD(T)	MRCI+Q	Exp
Ni ^{1}S (d^{10})	0.89	1.30	1.61	1.63	1.70	1.28	1.22	1.70	1.30	1.80
Ni ^{1}D (s^{1}d^9)	0.18	0.18	0.16	0.16	0.13	0.12	0.12	0.13	0.25	0.33
Ni ^{3}F (s^{1}d^9)	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
NiCO $^1\Sigma$	-2.66	-1.95	-1.41	-1.41	-1.43	-1.72	-2.55	-0.93	-1.62	-1.76
NiCO $^3\Pi$	-0.09	-0.83	-0.57	-0.60	-0.45	-0.55	-0.63	-0.46	-0.51	

Table S10: Calculated relative spin state energies for the Cu atom, and the Cu-CO binding energy for the lowest energy spin states. The binding energy is calculated relative to Cu (^{2}S) + CO.

	PBE	TPSSh	PBE0	HSE0	B3LYP	MN15	B2PLYP	CCSD(T)	MRCI+Q	Exp
Cu ^{2}D (s^{2}d^9)	2.24	1.98	1.81	1.77	1.76	2.30	1.96	1.68	2.26	1.49
Cu ^{2}S (s^{1}d^{10})	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
CuCO $^2\Delta$	-0.68	-0.49	-0.31	-0.32	-0.20	-0.26	-0.32	-0.19		

Association potential energy curve

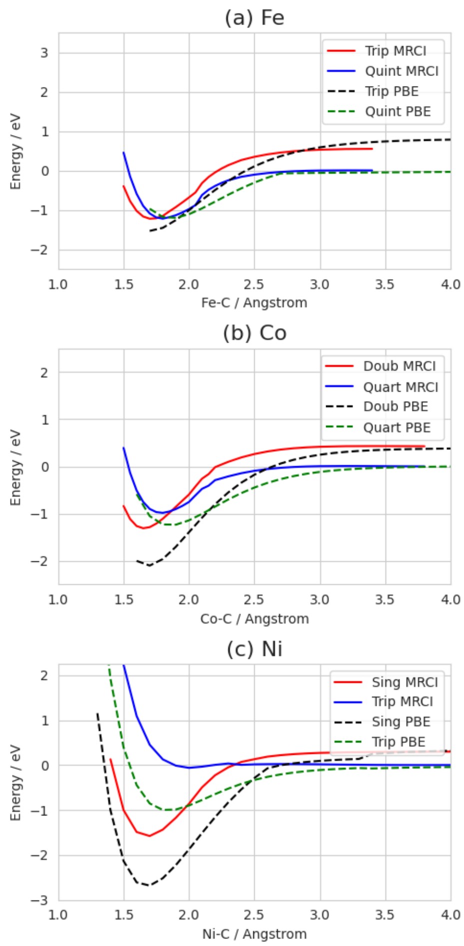

Figure S1 Potential energy curve for the TM-CO collinear association calculated by PBE DFT functionals and the MRCI+Q methods for (a) Fe, (b) Co, and (c) Ni. The solid lines represent the results for MRCI+Q, while the dotted ones represent the DFT results. Red and blue colors represent the low and high spin states for MRCI+Q while black and green colors represent the low and high spin states for DFT.

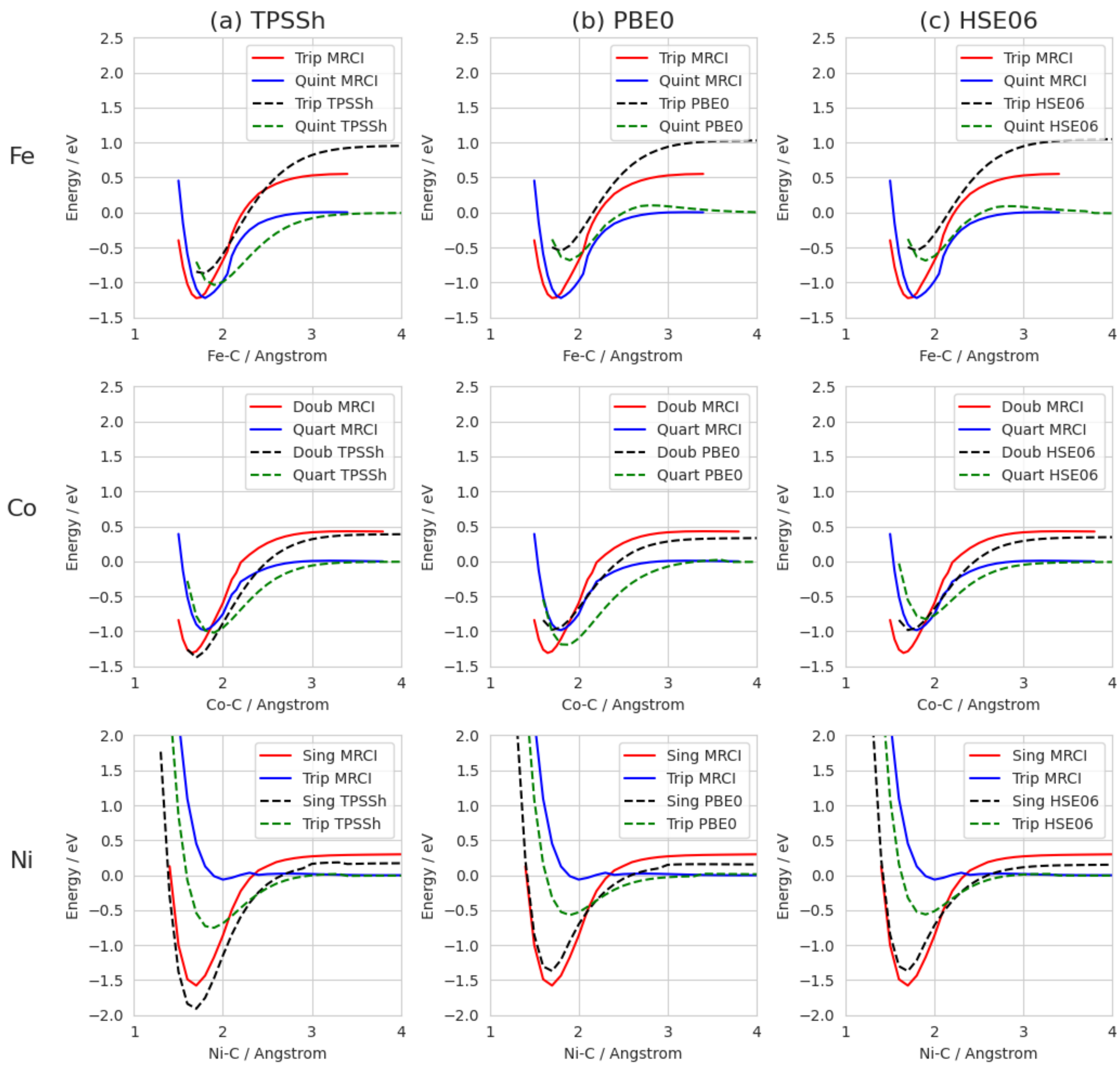

Figure S2 Potential energy curve for the TM-CO collinear association calculated by (a) TPSSh (b) PBE0, and (c) HSE06 DFT functionals and the MRCI+Q methods. The solid lines represent the results for MRCI+Q, while the dotted ones represent the DFT results. Red and blue colors represent the low and high spin states for MRCI+Q while black and green colors represent the low and high spin states for DFT.

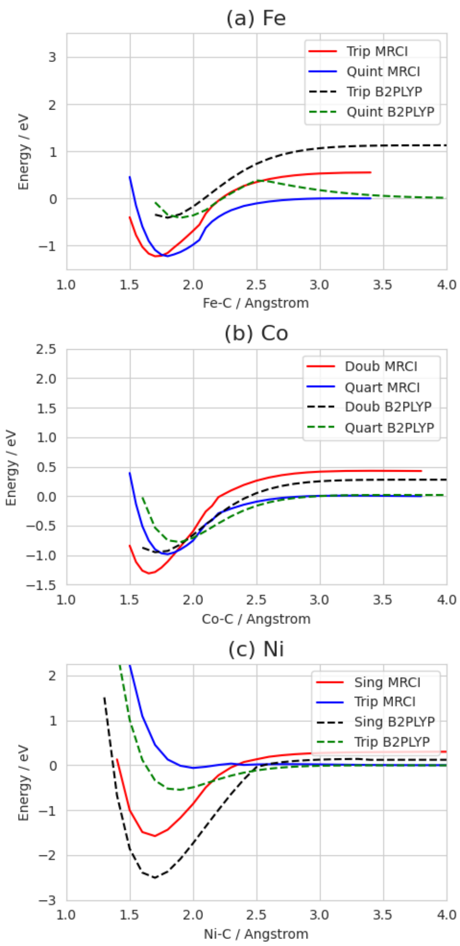

Figure S3 Potential energy curve for the TM-CO collinear association calculated by B2PLYP DFT functional and the MRCI+Q methods for (a) Fe, (b) Co, and (c) Ni. The solid lines represent the results for MRCI+Q, while the dotted ones represent the DFT results. Red and blue colors represent the low and high spin states for MRCI+Q while black and green colors represent the low and high spin states for DFT.

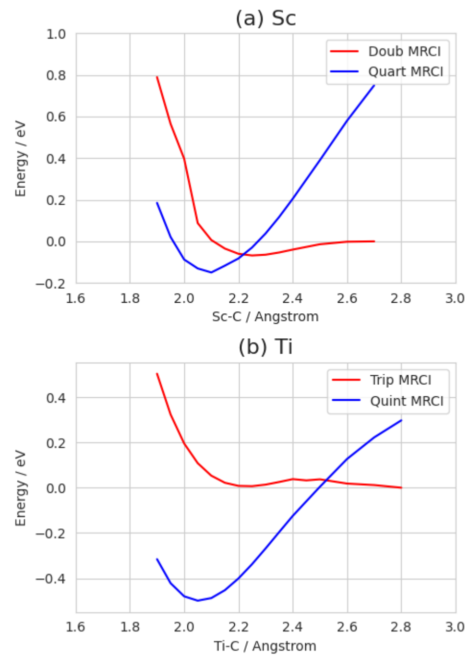

Figure S4 Potential energy curve for the TM-CO collinear association calculated by MRCI+Q method for (a) Sc and (b) Ti. The solid lines represent the results for MRCI+Q. Red and blue colors represent the low and high spin states for MRCI+Q.

Density functional dependence

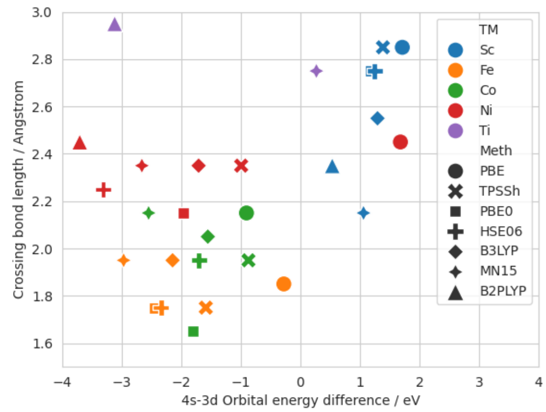

Figure S5 Relationship between 4s-3d orbital splitting and the spin state crossing bond length for Sc, Fe, Co, Ni, and Ti calculated by various DFT methods.

Basis set dependence

Table S11: Calculated B3LYP basis set dependence of relative spin state energies for the Sc atom, and the Sc-CO binding energy for the lowest energy spin states. The binding energy is calculated relative to Sc (^2D) + CO.

	aug-cc-pVTZ	6-31+G(d,p)	LANL2DZ	SDD
Sc ^2D (s^2d^1)	0.00	0.00	0.00	0.00
Sc ^4F (s^1d^2)	0.75	0.82	0.51	0.92
ScCO $^2\Pi$	-0.25	-0.25	-0.71	-0.38
ScCO $^4\Sigma^-$	-0.67	-0.68	-0.89	-0.55

Table S12: Calculated B3LYP basis set dependence of relative spin state energies for the Ti atom, and the Ti-CO binding energy for the lowest energy spin states. The binding energy is calculated relative to Ti (^5F) + CO.

	aug-cc-pVTZ	6-31+G(d,p)	LANL2DZ	SDD
Ti ^3F (s^2d^2)	0.00	0.00	0.00	0.00
Ti ^5F (s^1d^3)	0.01	0.05	0.25	0.40
TiCO $^3\Delta$	-0.72	-0.73	-0.79	-0.42
TiCO $^5\Delta$	-1.22	-1.24	-1.22	-0.85

Table S13: Calculated B3LYP basis set dependence of relative spin state energies for the V atom, and the V-CO binding energy for the lowest energy spin states. The binding energy is calculated relative to V (^4F) + CO.

	aug-cc-pVTZ	6-31+G(d,p)	LANL2DZ	SDD
V ^4F (s^2d^3)	0.22	0.16	0.25	0.02
V ^6D (s^1d^4)	0.00	0.00	0.00	0.00
VCO $^4\Delta$	-0.40	-0.46	-0.42	-0.40
VCO $^6\Sigma$	-1.00	-1.05	--0.43	-0.42

Table S14: Calculated B3LYP basis set dependence of relative spin state energies for the Cr atom, and the Cr-CO binding energy for the lowest energy spin states. The binding energy is calculated relative to Cr (^7S) + CO.

	aug-cc-pVTZ	6-31+G(d,p)	LANL2DZ	SDD
Cr ^5D (s^2d^4)	1.39	1.32	1.75	1.14
Cr ^5S (s^1d^5)	0.79	0.79	0.74	0.82
Cr ^7S (s^1d^5)	0.00	0.00	0.00	0.00
CrCO $^5\Sigma$	0.17	0.13	0.22	0.22
CrCO $^7\Sigma$	<u>-0.16</u>	<u>-0.19</u>	<u>-0.13</u>	<u>-0.15</u>

Table S15: Calculated B3LYP basis set dependence of relative spin state energies for the Mn atom, and the Mn-CO binding energy for the lowest energy spin states. The binding energy is calculated relative to Mn (^6S) + CO.

	aug-cc-pVTZ	6-31+G(d,p)	LANL2DZ	SDD
Mn ^6D (s^1d^6)	1.38	1.46	1.43	1.65
Mn ^6S (s^2d^5)	0.00	0.00	0.00	0.00
MnCO $^4\Pi$	0.62	0.61	2.90	3.02
MnCO $^6\Pi$	<u>0.39</u>	<u>0.40</u>	<u>-0.01</u>	<u>-0.02</u>

Table S16: Calculated B3LYP basis set dependence of relative spin state energies for the Fe atom, and the Fe-CO binding energy for the lowest energy spin states. The binding energy is calculated relative to Fe (^5D) + CO.

	aug-cc-pVTZ	6-31+G(d,p)	LANL2DZ	SDD
Fe ^3F (s^1d^7)	0.95	1.00	0.71	0.73
Fe ^5F (s^1d^7)	0.52	0.57	0.30	0.28
Fe ^5D (s^2d^6)	0.00	0.00	0.00	0.00
FeCO $^3\Sigma$	<u>-0.57</u>	<u>-0.60</u>	<u>-0.86</u>	<u>-0.79</u>
FeCO $^5\Sigma$	-0.48	-0.49	-0.71	-0.73

Table S17: Calculated B3LYP basis set dependence of relative spin state energies for the Co atom, and the Co-CO binding energy for the lowest energy spin states. The binding energy is calculated relative to Co (^4F) + CO.

	aug-cc-pVTZ	6-31+G(d,p)	LANL2DZ	SDD
Co $^2F(s^1d^8)$	0.28	0.28	0.27	0.61
Co ^4F (s^1d^8)	0.40	0.38	0.03	031
CoCO $^2\Delta$	0.00	0.00	0.00	0.00
CoCO $^4\Delta$	-1.05	-1.11	-0.91	-0.52

Table S18: Calculated B3LYP basis set dependence of relative spin state energies for the Ni atom, and the Ni-CO binding energy for the lowest energy spin states. The binding energy is calculated relative to Ni (^3F) + CO.

	aug-cc-pVTZ	6-31+G(d,p)	LANL2DZ	SDD
Ni ^1S (d^{10})	1.70	1.36	1.55	1.63
Ni ^1D (s^1d^9)	0.13	0.13	0.16	0.20
Ni ^3F (s^1d^9)	0.00	0.00	0.00	0.00
NiCO $^1\Sigma$	-1.43	-1.51	-1.34	-1.20
NiCO $^3\Pi$	-0.45	-0.49	0.56	0.53

Table S19: Calculated B3LYP basis set dependence of relative spin state energies for the Cu atom, and the Cu-CO binding energy for the lowest energy spin states. The binding energy is calculated relative to Cu (^2S) + CO.

	aug-cc-pVTZ	6-31+G(d,p)	LANL2DZ	SDD
Cu ^2D (s^2d^9)	1.76	1.79	2.09	1.40
Cu ^2S (s^1d^{10})	0.00	0.00	0.00	0.00
CuCO $^2\Delta$	-0.20	-0.20	-0.12	-0.13