

Electronic Supplementary Information

On the ground and excited electronic states of LaCO and AcCO

Isuru R. Ariyaratna

Physics and Chemistry of Materials (T-1), Los Alamos National Laboratory, Los Alamos, NM 87545, USA

Email: isuru@lanl.gov

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Table S1. Dissociation energy of LaCO($1^4\Sigma^-$) calculated with various density functional approximations (DFA) with respect to La($4F$)+CO($X^1\Sigma^+$) fragments (D_e , kcal/mol) and the % DFT D_e error with respect to the QZ-CCSD(T) D_e (i.e., 27.12 kcal/mol). CCSD(T) D_e obtained with respect to the same La($4F$)+CO($X^1\Sigma^+$) fragments.

Family of functional	DFA	D_e	% DFT error
GGA	BP86	41.91	54.5
	BLYP	37.56	38.5
	PBE	42.81	57.9
MGGA	TPSS	39.00	43.8
	MN15-L	37.37	37.8
global GGA Hybrid	B3LYP	33.38	23.1
	B3P86	37.48	38.2
	B3PW91	35.06	29.3
	PBE0	35.62	31.3
MGGA Hybrid	TPSSh	36.41	34.2
	M06	38.47	41.9
	M06-2X	37.15	37.0
	MN15	33.21	22.5
RSH	LRC- ω PBE	31.10	14.7
	CAM-B3LYP	31.85	17.4
	ω B97X	32.69	20.6

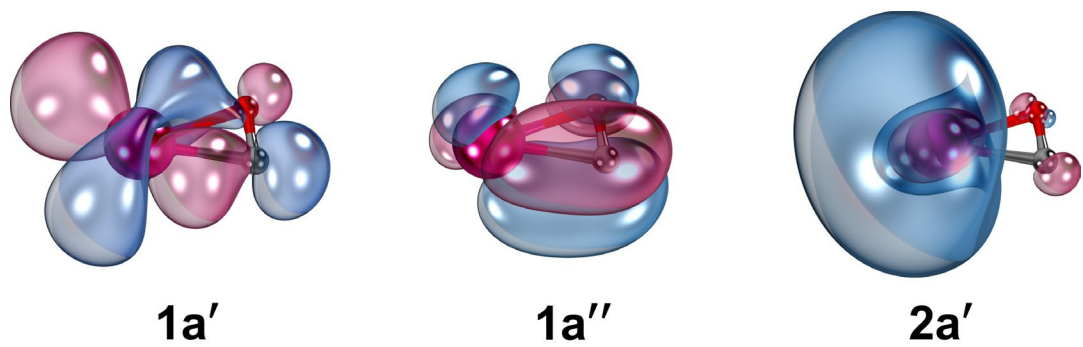


Figure S1. The singly-occupied molecular orbitals of $\text{La}(\eta^2\text{-CO})$ (${}^4\text{A}''$).

Table S2. Ionization energy of LaCO($1^4\Sigma^-$) calculated with various density functional approximations (DFA) (IE, eV) and the % DFT error with respect to the QZ-CCSD(T) IE (i.e., 5.316 eV).

Family of functional	DFA	IE	% DFT error
GGA	BP86	5.672	6.7
	BLYP	5.456	2.6
	PBE	5.556	4.5
MGGA	TPSS	5.332	0.3
	MN15-L	5.127	-3.6
global GGA Hybrid	B3LYP	5.507	3.6
	B3P86	6.025	13.3
	B3PW91	5.473	3.0
	PBE0	5.415	1.9
MGGA Hybrid	TPSSh	5.290	-0.5
	M06	5.070	-4.6
	M06-2X	5.371	1.0
	MN15	5.063	-4.8
RSH	LRC- ω PBE	5.138	-3.3
	CAM-B3LYP	5.365	0.9
	ω B97X	4.932	-7.2

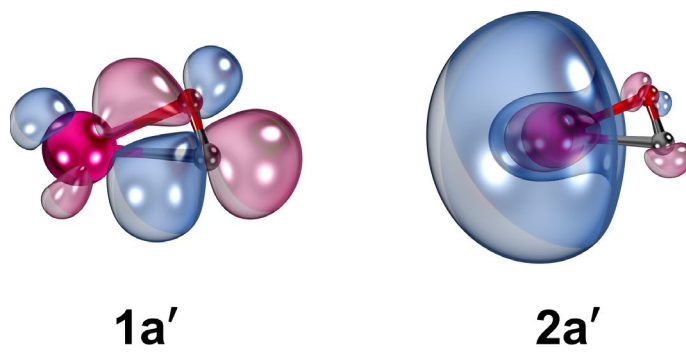


Figure S2. The singly-occupied $1a'$ and doubly-occupied $2a'$ molecular orbitals of $\text{Ac}(\eta^2\text{-CO})$ (${}^2A'$).

Table S3. Cartesian coordinates of the transition states lie in between $\text{LaCO} \rightarrow \text{La}(\eta^2\text{-CO})$ and $\text{AcCO} \rightarrow \text{Ac}(\eta^2\text{-CO})$ reactions at the DFT/B3LYP level.

TS [$\text{LaCO} \rightarrow \text{La}(\eta^2\text{-CO})$]				TS [$\text{AcCO} \rightarrow \text{Ac}(\eta^2\text{-CO})$]			
La	0.000000	0.515841	0.000000	Ac	-0.000000	0.404422	0.000000
C	0.588159	-1.760702	-0.000000	C	0.582714	-2.240353	0.000000
O	-0.441119	-2.354839	0.000000	O	-0.437035	-2.818926	-0.000000

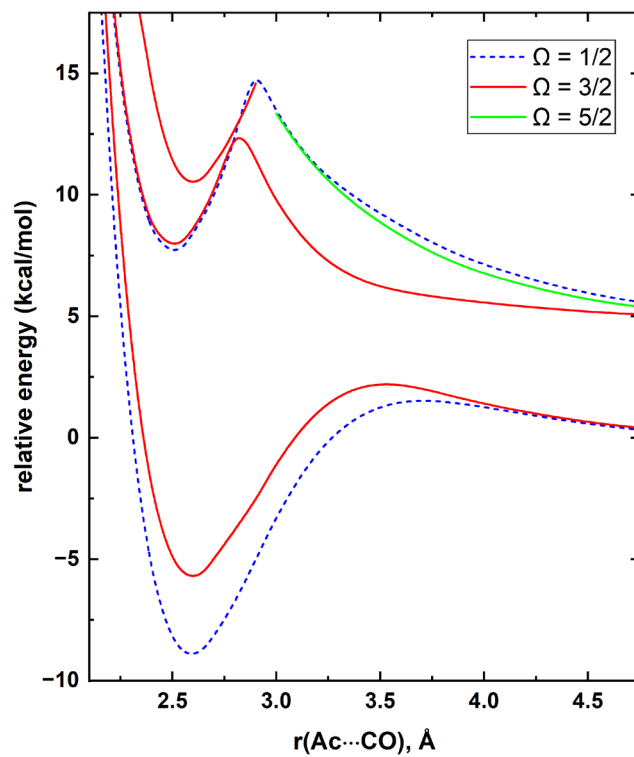


Figure S3. Select MRCI spin-orbit coupling curves of AcCO as a function of Ac...CO distance [$r(\text{Ac}\cdots\text{CO})$, Å]. The relative energies are referenced to the lowest energy spin-orbit curve of $\text{Ac}(^2\text{D})+\text{CO}(X^1\Sigma^+)$ at the dissociation limit, which is set to 0 kcal/mol. At each scan the C–O length is kept fixed to the 1.159 Å. The $\Omega = 1/2$, $\Omega = 3/2$, and $\Omega = 5/2$ curves are shown in blue, red, and green, respectively.