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Supplementary Materials: The Photochemistry of $Fe_2(S_2C_3H_6)(CO)_6(\mu\text{-}CO)$ and Its Oxidized form, Two Simple [FeFe]-Hydrogenase CO-Inhibited Models. A DFT and TDDFT Investigation

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Table S1. Mulliken population analysis (in percentage) of $^2a^+$**-CO** FMOs.

		−2	−1	SOMO	LUMO	+1	+2	+3	+4	+5	+6	+7	+8	+9	+10	+11	
α		101	102	103	104	105	106	107	108	109	110	111	112	113	114	115	
μCO		3	9	10	8	6	8	5	15	5	6	7	4	2	10	10	
2Fe		23	32	36	22	22	24	18	19	18	15	17	17	16	16	17	
2S		25	15	13	21	24	17	8	9	6	5	6	5	5	4	5	
2CO	cis	10	6	17	8	5	20	23	6	21	21	19	9	9	25	24	
	/2	5	3	9	4	2	10	11	3	11	11	10	5	4	12	12	
4CO	trans	25	24	14	30	31	20	33	40	40	44	43	59	55	34	28	
	/4	6	6	3	7	8	5	8	10	10	11	11	15	14	8	7	
pdt		15.2	14.9	9.7	12	12	11	14	11	10	9	8	6	13	12	17	
			−1	SOMO	LUMO	+1	+2	+3	+4	+5	+6	+7	+8	+9	+10	+11	+12
β			101	102	103	104	105	106	107	108	109	110	111	112	113	114	115
μCO			7	9	10	8	4	7	6	14	6	5	7	4	2	8	6
2Fe			31	34	36	22	26	22	18	19	19	16	17	17	16	15	5
2S			15	14	13	19	18	17	8	9	7	5	6	5	5	5	11
2CO	cis		5	6	17	9	5	25	21	6	17	23	21	9	9	29	7
	/2		3	3	9	5	2	12	11	3	8	11	10	4	5	14	4
4CO	trans		28	24	14	29	36	19	34	40	42	45	41	57	55	32	58
	/4		7	6	4	7	9	5	9	10	10	11	10	14	14	8	14
pdt			14	14	10	3	11	11	13	11	11	7	8	8	13	11	14

Table 2. MO eigenvalues (Eigen, in Hartree) for **^{1}a-CO** and **^{1}a**. The **^{1}a** HOMO interacting with the free CO LUMO (eigenvalue at the same level of theory is -0.0799 Hartree) rises its eigenvalue from -0.22310 Hartree to -0.18258 Hartree. .

^{1}a-CO			**^{1}a**		
n	**occ**	**Eigen**	**n**	**occ**	**Eigen**
110		-0.07319	103		-0.06845
109		-0.07786	102		-0.06914
108		-0.07852	101		-0.07055
107		-0.09036	100		-0.08188
106		-0.11062	99		-0.11026
105		-0.11650	98		-0.11349
104		-0.12663	97		-0.13039
103	2	-0.18258	96	2	-0.22310
102	2	-0.23702	95	2	-0.23256
101	2	-0.24033	94	2	-0.23291
100	2	-0.24481	93	2	-0.23985
99	2	-0.25057	92	2	-0.24004
98	2	-0.25222	91	2	-0.24802
97	2	-0.25359	90	2	-0.25021

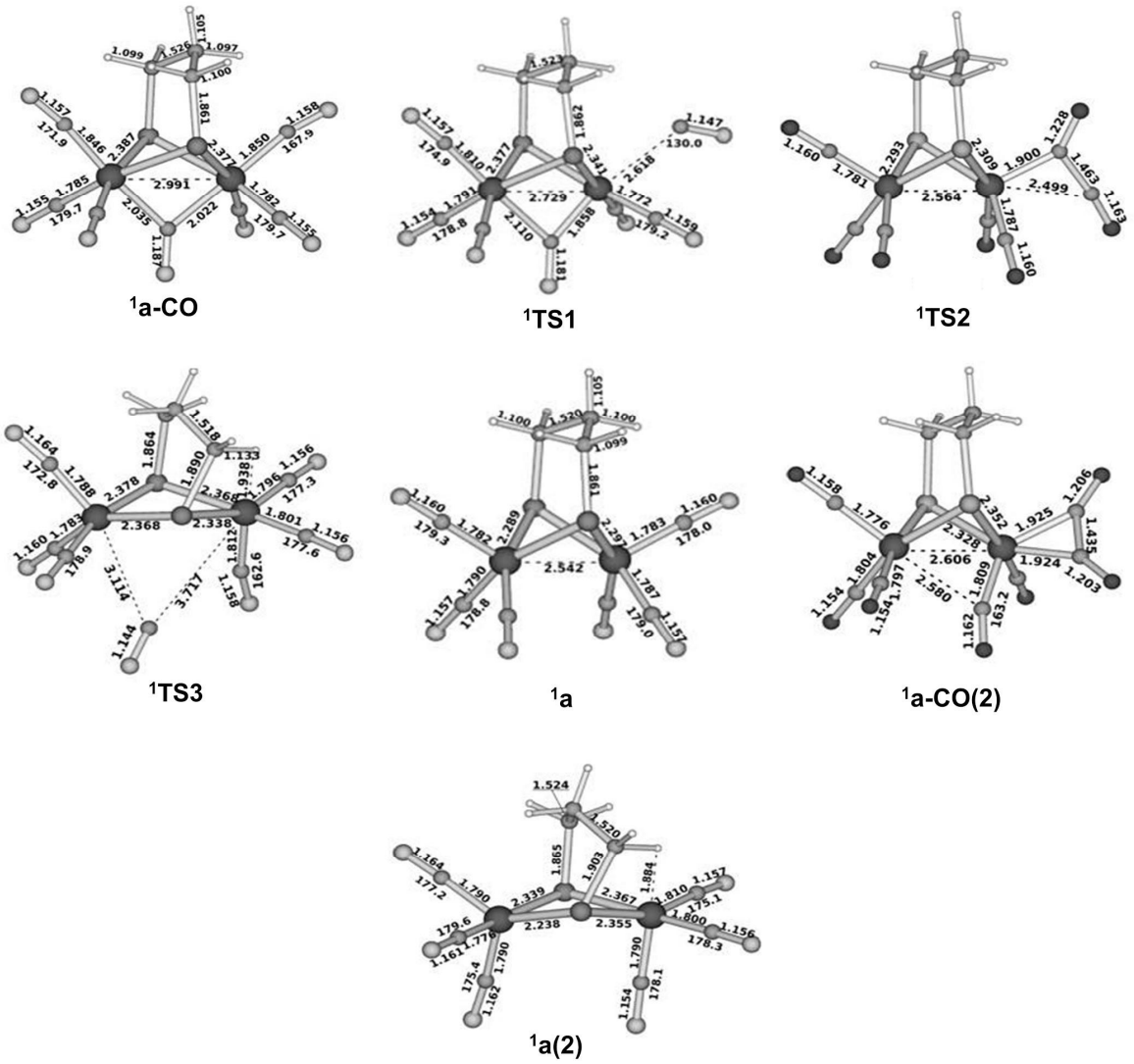

Figure S1. Optimized structures and geometrical parameters of minima and transition states involved in CO dissociation from **^{1}a-CO.** Distances are in Å and angles in degrees.

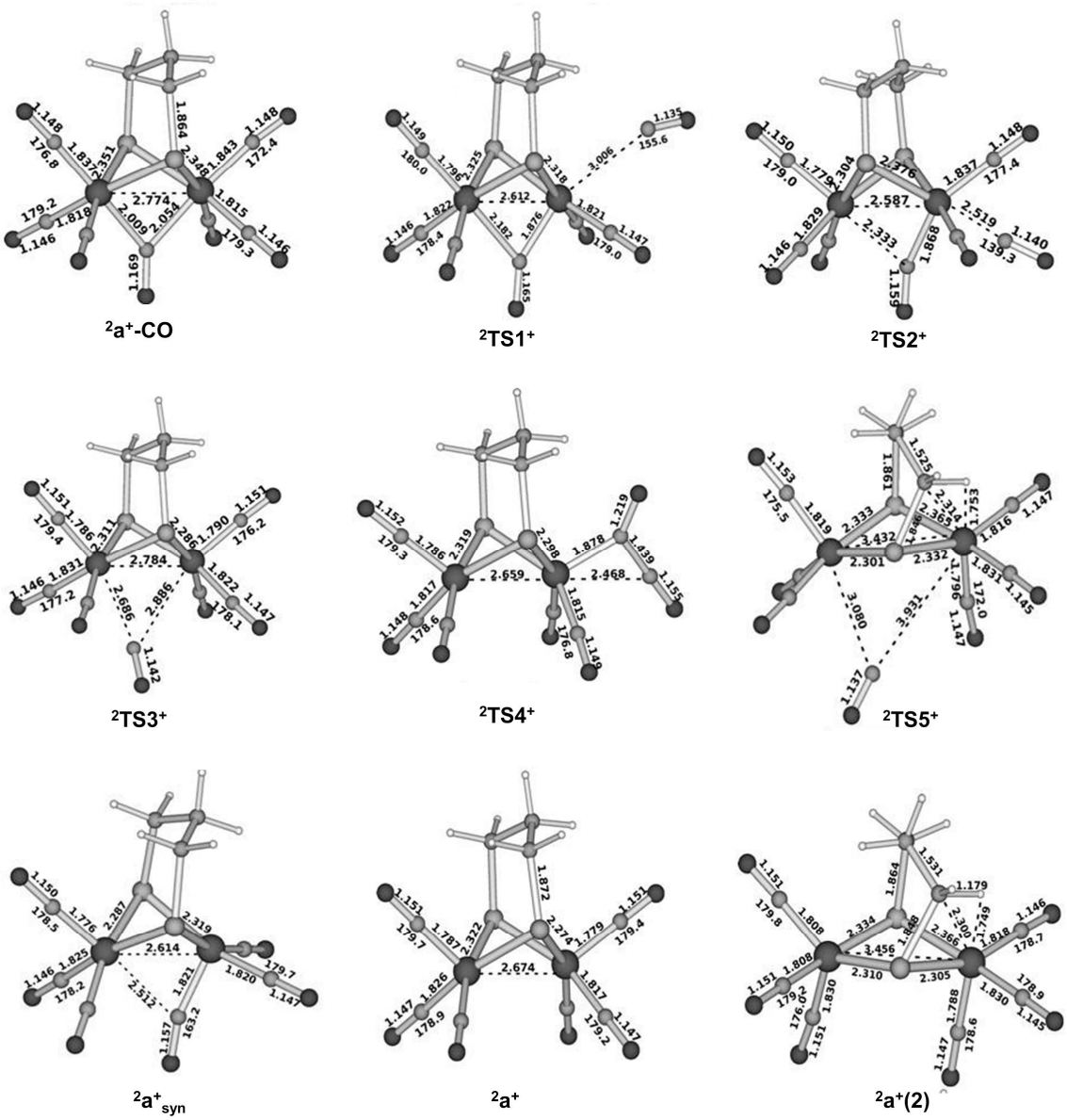

Figure S2. Optimized structures and geometrical parameters of minima and transition states involved in CO dissociation from **^{2}a$^+$-CO.** Distances are in Å and angles in degrees.

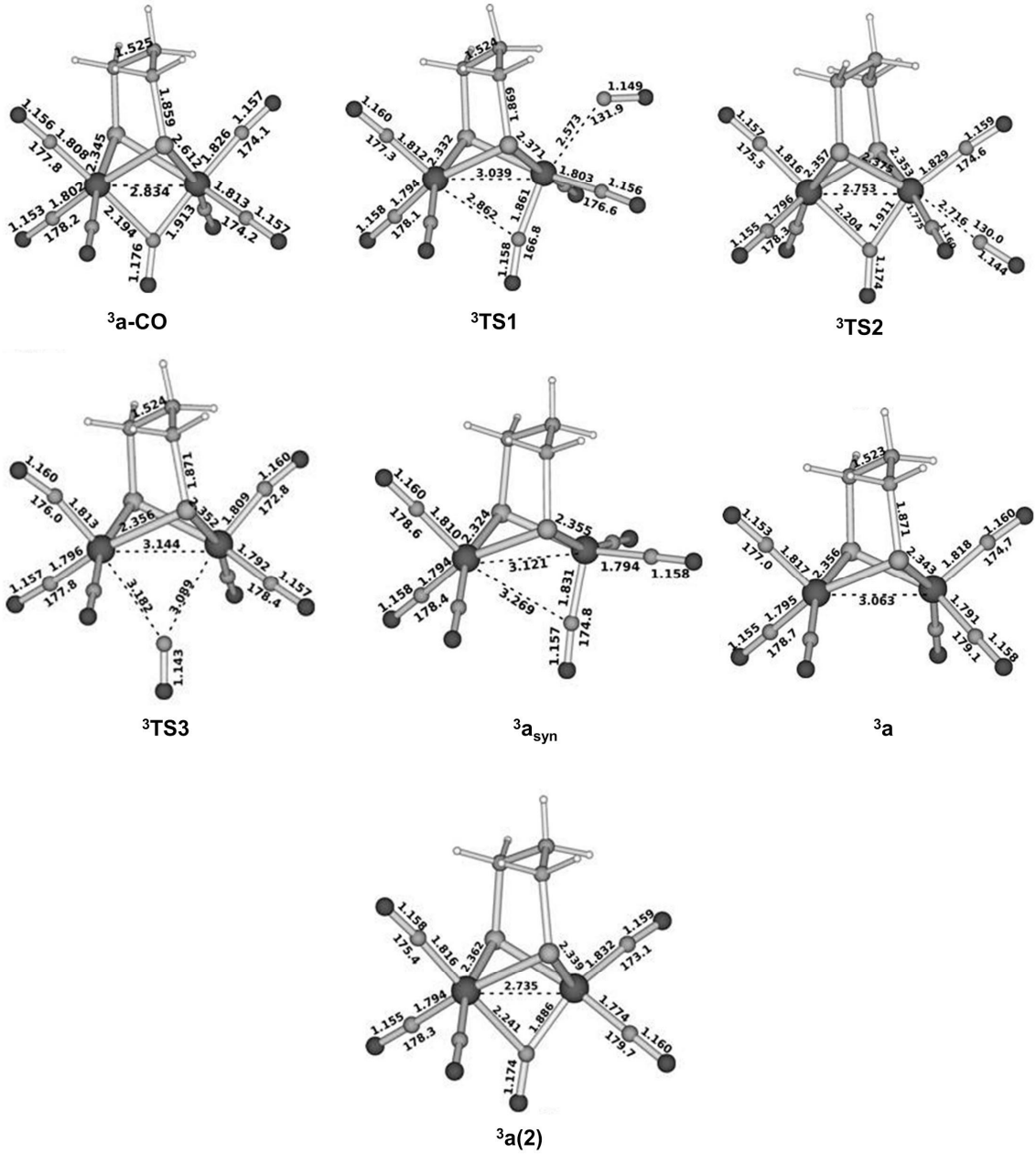

Figure S3. Optimized structures and geometrical parameters of minima and transition states involved in CO dissociation from **^{3}a-CO.** Distances are in Å and angles in degrees.

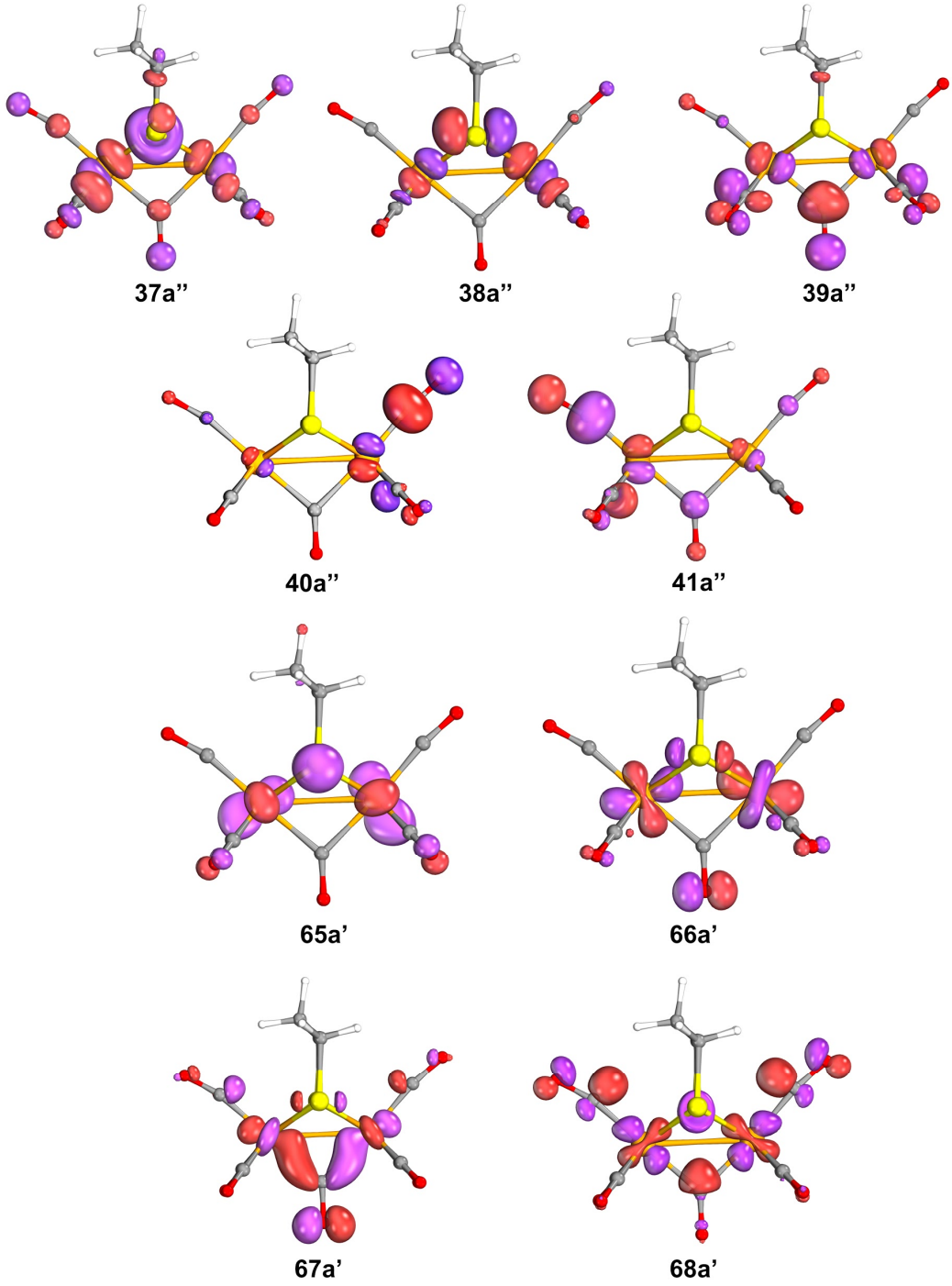

Figure S4. Isosurfaces (0.05 a.u) of 1a-CO MOs involved in the discussed electronic transitions.

Coordinates (xyz) of selected structures.

^{1}a-CO

C	-1.717554	2.422086	-1.318767
O	-2.258892	2.972767	-2.177573
Fe	-0.876923	1.567050	0.000000
C	0.525037	2.773916	0.000000
O	1.223355	3.697262	0.000000
S	-0.066616	-0.024747	1.583104
C	1.748089	-0.326515	1.303189
C	2.362337	0.175711	0.000000
C	1.748089	-0.326515	-1.303189
S	-0.066616	-0.024747	-1.583104
Fe	-1.177487	-1.409792	0.000000
C	0.054120	-2.782241	0.000000
O	0.699058	-3.742964	0.000000
C	-1.717554	2.422086	1.318767
O	-2.258892	2.972767	2.177573
C	-2.159886	-2.115816	-1.312110
O	-2.801697	-2.572022	-2.156934
C	-2.159886	-2.115816	1.312110
O	-2.801697	-2.572022	2.156934
H	2.370691	1.273292	0.000000
H	3.423166	-0.133272	0.000000
H	1.882656	-1.412550	1.413572
H	2.247213	0.159414	2.153096
H	2.247213	0.159414	-2.153096
H	1.882656	-1.412550	-1.413572
C	-2.390991	0.207030	0.000000
O	-3.572006	0.328117	0.000000

^{2}a^{+}-CO

C	-1.610432	2.341502	-1.337983
O	-2.129982	2.915625	-2.182959
Fe	-0.772017	1.446021	0.000000
C	0.593983	2.683711	0.000000
O	1.334511	3.560837	0.000000
S	0.108741	-0.045441	1.585224
C	1.927160	-0.337907	1.301645
C	2.540961	0.162292	0.000000
C	1.927160	-0.337907	-1.301645
S	0.108741	-0.045441	-1.585224
Fe	-1.079630	-1.311271	0.000000
C	0.111490	-2.709170	0.000000
O	0.805930	-3.622910	0.000000
C	-1.610432	2.341502	1.337983
O	-2.129982	2.915625	2.182959
C	-2.055327	-2.058731	-1.338843
O	-2.659669	-2.540754	-2.184677
C	-2.055327	-2.058731	1.338843
O	-2.659669	-2.540754	2.184677
H	2.569046	1.259062	0.000000
H	3.597605	-0.157050	0.000000
H	2.069098	-1.419601	1.435840
H	2.402622	0.163282	2.155976
H	2.402622	0.163282	-2.155976
H	2.069098	-1.419601	-1.435840
C	-2.404433	0.199358	0.000000
O	-3.564251	0.343477	0.000000

^{3}a-CO

C	-1.819138	2.377071	-1.406053
O	-2.350059	3.001413	-2.222482
Fe	-1.050682	1.528317	0.000000

C	0.348105	2.702225	0.000000
O	1.153868	3.532314	0.000000
S	0.083807	-0.160096	1.638490
C	1.885229	-0.470393	1.299281
C	2.462784	0.082503	0.000000
C	1.885229	-0.470393	-1.299281
S	0.083807	-0.160096	-1.638490
Fe	-1.145196	-1.301692	0.000000
C	-0.030352	-2.723099	0.000000
O	0.640063	-3.664785	0.000000
C	-1.819138	2.377071	1.406053
O	-2.350059	3.001413	2.222482
C	-2.158043	-1.954672	-1.340000
O	-2.782761	-2.405282	-2.198490
C	-2.158043	-1.954672	1.340000
O	-2.782761	-2.405282	2.198490
H	2.388596	1.177941	0.000000
H	3.543546	-0.151268	0.000000
H	2.044333	-1.555982	1.375702
H	2.396795	-0.006907	2.154660
H	2.396795	-0.006907	-2.154660
H	2.044333	-1.555982	-1.375702
C	-2.570472	0.365476	0.000000
O	-3.743760	0.291323	0.000000

$^{2}a^{+}$-CO $1^{2}A''$

C	-1.759593	2.271068	-1.462777
O	-2.226010	2.890667	-2.307894
Fe	-1.058888	1.382200	0.000000
C	0.302105	2.599369	0.000000
O	1.079330	3.443405	0.000000
S	0.147500	-0.230953	1.602579
C	1.971690	-0.424907	1.294534
C	2.542194	0.135673	0.000000
C	1.971690	-0.424907	-1.294534
S	0.147500	-0.230953	-1.602579
Fe	-1.080210	-1.291201	0.000000
C	-0.033416	-2.717957	0.000000
O	0.668204	-3.628910	0.000000
C	-1.759593	2.271068	1.462777
O	-2.226010	2.890667	2.307894
C	-2.149508	-1.953955	-1.338878
O	-2.789871	-2.403434	-2.175049
C	-2.149508	-1.953955	1.338878
O	-2.789871	-2.403434	2.175049
H	2.462856	1.230046	0.000000
H	3.623920	-0.085288	0.000000
H	2.177281	-1.499163	1.405582
H	2.424387	0.079234	2.159744
H	2.424387	0.079234	-2.159744
H	2.177281	-1.499163	-1.405582
C	-2.673080	0.454876	0.000000
O	-3.820828	0.296126	0.000000