Supporting Information

for

Vibrational Analysis of the Model Complex (μ-edt)[Fe(CO)$_3$]$_2$ and Comparison to Iron-only Hydrogenase: The Activation Scale of Hydrogenase Model Systems

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Table S1. Manually adjusted force constants in the QCC-NCA simulation of (μ-edt)[Fe(CO)$_3$]$_2$, starting from the B3LYP/TZVP-calculated force field.

Coordinate[a]	Force constant[b]	
	Redong	QCC-NCA
Fe(1)-S(3)	0.591586	0.521586
Fe(2)-S(3)	0.592404	0.522404
Fe(1)-S(4)	0.591597	0.521597
Fe(1)-S(4)	0.592437	0.522437
S(3)-C(20)	1.85367	1.73367
S(4)-C(17)	1.85376	1.73376
C(8)-Fe(1)-C(9)	0.459841	0.325841
C(6)-Fe(2)-C(7)	0.459954	0.325954
C(9)-Fe(1)-C(10)	0.266437	0.125437
C(8)-Fe(1)-C(10)	0.266475	0.125475
C(5)-Fe(2)-C(7)	0.267512	0.126512
C(5)-Fe(2)-C(6)	0.267380	0.126380
Fe(1)-S(3)-C(20)	0.370261	0.380261
Fe(1)-S(4)-C(17)	0.370314	0.380314
Fe(2)-S(3)-C(20)	0.366590	0.376590
Fe(2)-S(3)-C(17)	0.366526	0.376526
S(3)-C(20)-C(17)	0.461224	0.671224
S(4)-C(17)-C(20)	0.461233	0.671233
C(9)-Fe(1)-S(3)	0.283571	0.305571
C(8)-Fe(1)-S(4)	0.283577	0.305577
C(7)-Fe(2)-S(3)	0.292616	0.314616
C(6)-Fe(2)-S(4)	0.292680	0.314680

[a]Atom numbers are shown in Figure 2. [b]The units for the force constants of stretching and linear bending are mdyn/Å and mdyn·Å, respectively.

Table S2. Cartesian coordinates [Å] for the DFT optimized geometry of (μ-edt)[Fe(CO)$_3$]$_2$ using B3LYP/TZVP.

Fe	1.26230900	-0.17491200	0.00002500
Fe	-1.26245100	-0.17467900	-0.00012900
S	-0.00003900	1.03969700	1.48548600
S	0.00010800	1.03958800	-1.48565700
C	-2.80750500	0.75012800	0.00002200
C	-1.63198200	-1.36820500	-1.30677200
C	-1.63183500	-1.36799700	1.30673900
C	1.63180600	-1.36842900	-1.30664200
C	1.63192400	-1.36815900	1.30690800
C	2.80729100	0.74999000	-0.00015600
O	-3.78776397	1.33687148	0.00011780
O	-1.86526950	-2.12168629	-2.13166484
O	-1.86503010	-2.12134829	2.13177532
O	1.86507147	-2.12190279	-2.13154800
O	1.86526351	-2.12146086	2.13194875
O	3.78751628	1.33680093	-0.00027084
C	0.00007600	2.74545500	-0.76290700
H	0.88120200	3.24536000	-1.16400400
H	-0.88156100	3.24496300	-1.16336400
C	0.00061400	2.74552800	0.76262300
H	-0.88033400	3.24577900	1.16367600
H	0.88243300	3.24472800	1.16306100
X	-2.86302270	0.65753816	-0.99413337
X	-2.29692774	1.60315542	-0.10793672
X	-1.40431266	-2.11836326	-0.68594251
X	-0.67993866	-1.33055461	-1.61040984
X	-1.52894460	-0.64810851	1.99316025
X	-0.65835340	-1.58262495	1.38591236
X	1.96847888	-2.01433028	-0.62146837
X	2.55097906	-0.98505552	-1.39689536
X	2.32601429	-0.74967691	1.67530801
X	2.32217019	-1.79458806	0.72234110
X	2.29406360	1.60730715	0.03990572
X	2.78662739	0.78431152	-0.99935320

Note: X represents anchor atoms for the definition of linear bending internal coordinates.

Table S3. Cartesian coordinates [Å] for the DFT optimized geometry of (μ-edt)[Fe(CO)$_3$]$_2$ using BP86/TZVP.

Fe	1.26985700	-0.16670900	-0.00060400
Fe	-1.26986400	-0.16668600	0.00059500
S	0.00071000	1.01812800	1.47530200
S	-0.00069600	1.01811100	-1.47532400
C	-2.80156600	0.74834300	0.00063600
C	-1.65972100	-1.34970200	-1.28367400
C	-1.65866900	-1.34965500	1.28528500
C	1.65864300	-1.34972200	-1.28526100
C	1.65973200	-1.34967700	1.28370400
C	2.80155300	0.74832800	-0.00066900
O	-3.79896800	1.33931400	-0.00054300
O	-1.92865200	-2.11671000	-2.10751500
O	-1.92692400	-2.11664000	2.10936000
O	1.92689500	-2.11673400	-2.10931200
O	1.92868800	-2.11664200	2.10757800
O	3.79892800	1.33934500	0.00052900
C	-0.00048500	2.73927200	-0.76176500
H	0.88985400	3.23369700	-1.17446900
H	-0.89155200	3.23337800	-1.17327400
C	0.00053200	2.73928100	0.76172500
H	-0.88979900	3.23372500	1.17442400
H	0.89160800	3.23337600	1.17322800

Table S4. Comparison of experimental and calculated (B3LYP and BP86 with basis set TZVP) vibrational frequencies of (μ-edt)[Fe(CO)$_3$]$_2$, focusing on the ν(C=O) and ν(Fe-CO)/δ(Fe-C=O) energy regions.

	Experimental [cm^{-1}]		Calculated (DFT) [cm^{-1}] [c]	
Mode	IR [a] (^{12}CO/^{13}CO)	rR [b] (^{12}CO/^{13}CO)	B3LYP/TZVP	BP86/TZVP
ν(C=O)	2078(2077)/2030	2070 / 2023	2153	2063
ν(C=O)	2038(2037)/1991	2005 / 1959	2105	2028
ν(C=O)	2008(1998)/1962	1979 / 1934	2095	2002
ν(C=O)	1995/1950	1968 / 1924	2083	1988
ν(C=O)	not observed	1964 / 1919	2076	1985
ν(C=O)	1985/1940	1961 / 1917	2072	1979
ν(Fe-CO) + δ(Fe-C=O)		630 / 615	636	637
ν(Fe-CO) + δ(Fe-C=O)		592 / 579	601	609
ν(Fe-CO) + δ(Fe-C=O)		572 / 562	578	588
ν(Fe-CO) + δ(Fe-C=O)		565 / 556	571	584
δ(Fe-C=O)		528 / 519	526	521
ν(Fe-CO) + δ(Fe-C=O)		503 / 495	507	525
ν(Fe-CO) + δ(Fe-C=O)		494 / 485	496	500
ν(Fe-CO) + δ(Fe-C=O)		483 / 474	481	501
ν(Fe-CO) + δ(Fe-C=O)		470 / 462	471	496
ν(Fe-CO) + δ(Fe-C=O)		463 / 452	454	464
ν(Fe-CO) + δ(Fe-C=O)		456 / 444	448	453
ν(Fe-CO) + δ(Fe-C=O)		454 / 442	446	446
ν(Fe-CO) + δ(Fe-C=O)		447 / 435	440	445
δ(Fe-C=O)		419 / 406	416	413
δ(Fe-C=O)		416 / 403	410	407

[a] Vibrational IR energies were obtained in hexane and acetonitrile (in parenthesis). [b] From resonance Raman measurements on a saturated solution in acetonitrile. [c] DFT calculations.

Figure S1. Diffuse reflectance Fourier transform infrared spectra of solid (μ-edt)[Fe(CO)$_3$]$_2$ and (μ-edt)[Fe(^{13}CO)$_3$]$_2$.

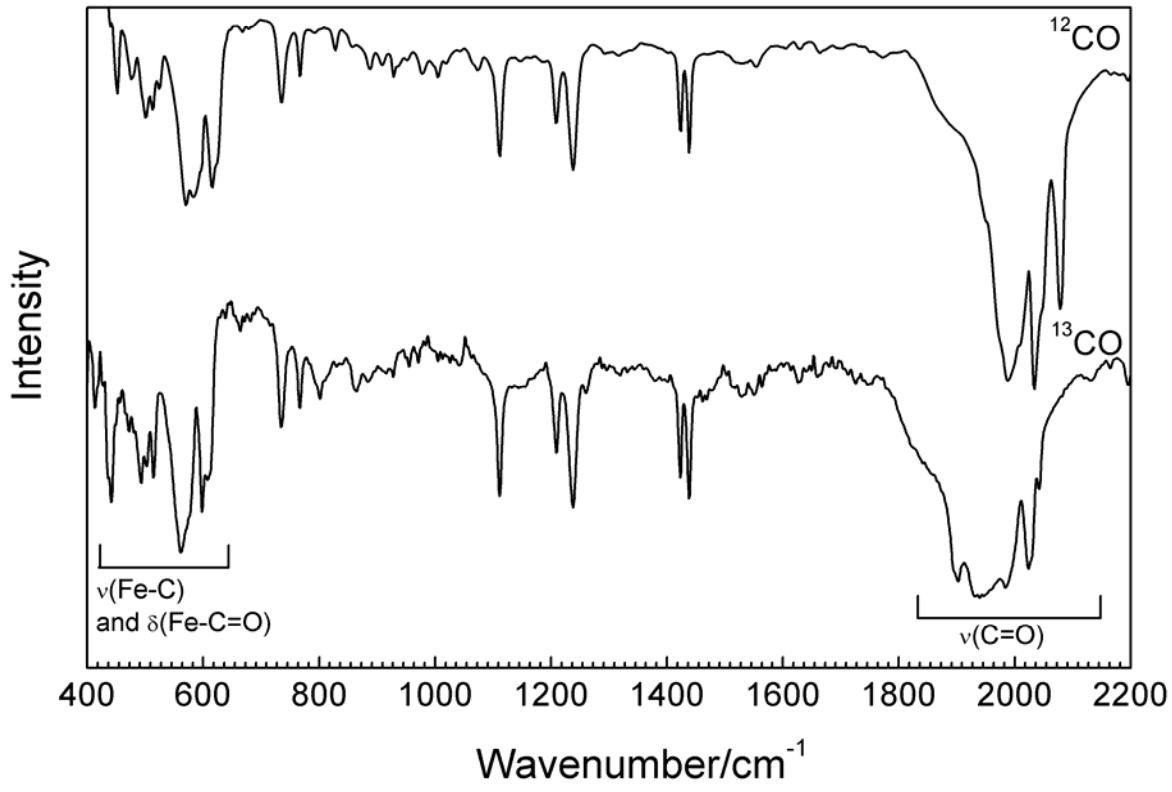

Figure S2. Comparison of experimental (in hexane, solid line) and B3LYP/TZVP calculated (column bar) IR spectra of (μ-edt)[Fe(CO)$_3$]$_2$.

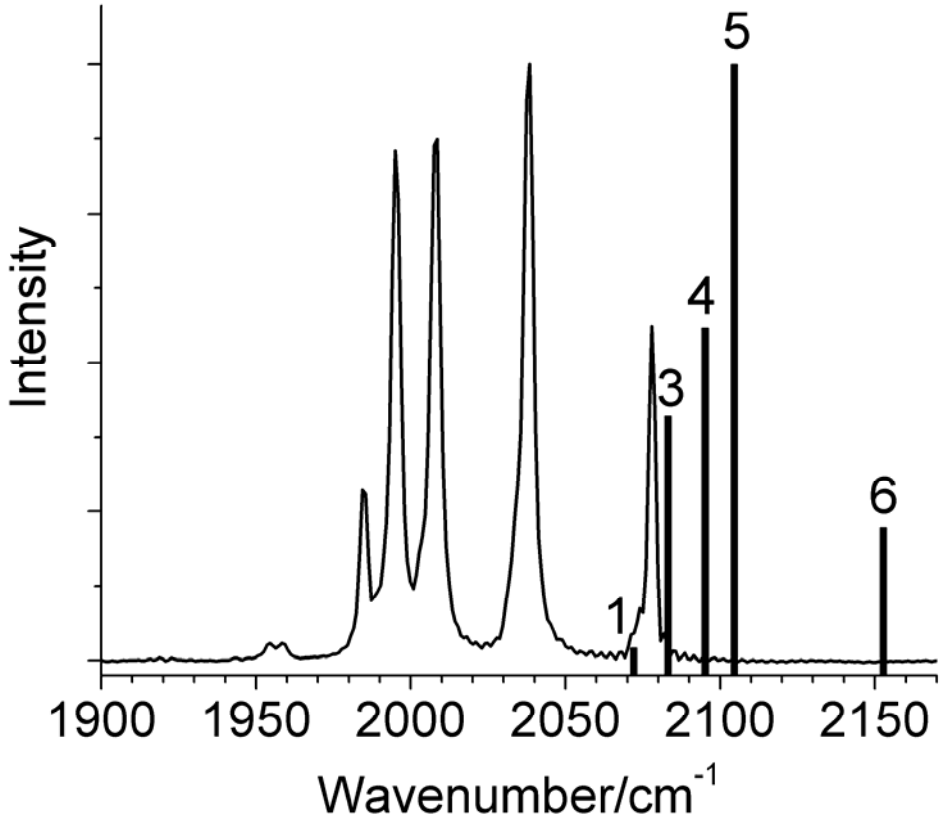

Figure S3. Comparison of experimental (in hexane, solid line) and BP86/TZVP calculated (column bar) IR spectra of (μ-edt)[Fe(CO)$_3$]$_2$.

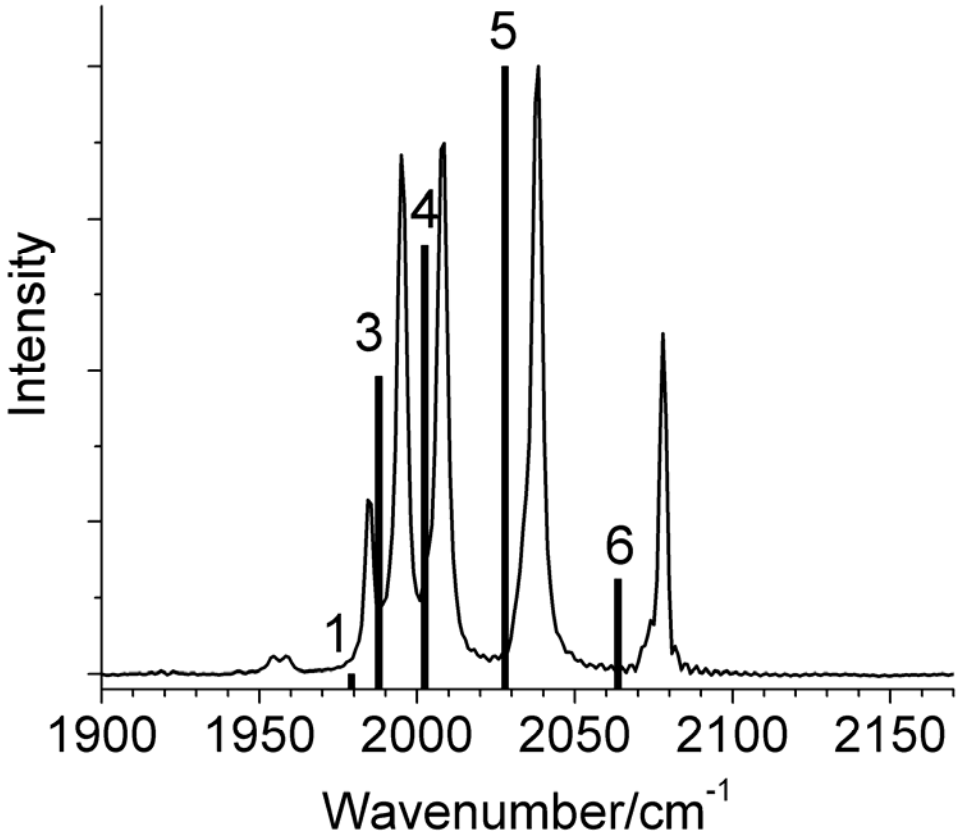

Figure S4. Overlay of the BP86/TZVP calculated (column bars) and experimental (solid lines) Raman spectra of (μ-edt)[Fe(CO)$_3$]$_2$ in acetonitrile in the A) ν(Fe-CO)/δ(Fe-C=O) and B) ν(C=O) regions. The DFT-calculated modes are labeled according to the corresponding experimental modes (refer to Figure 5 and Table S4).