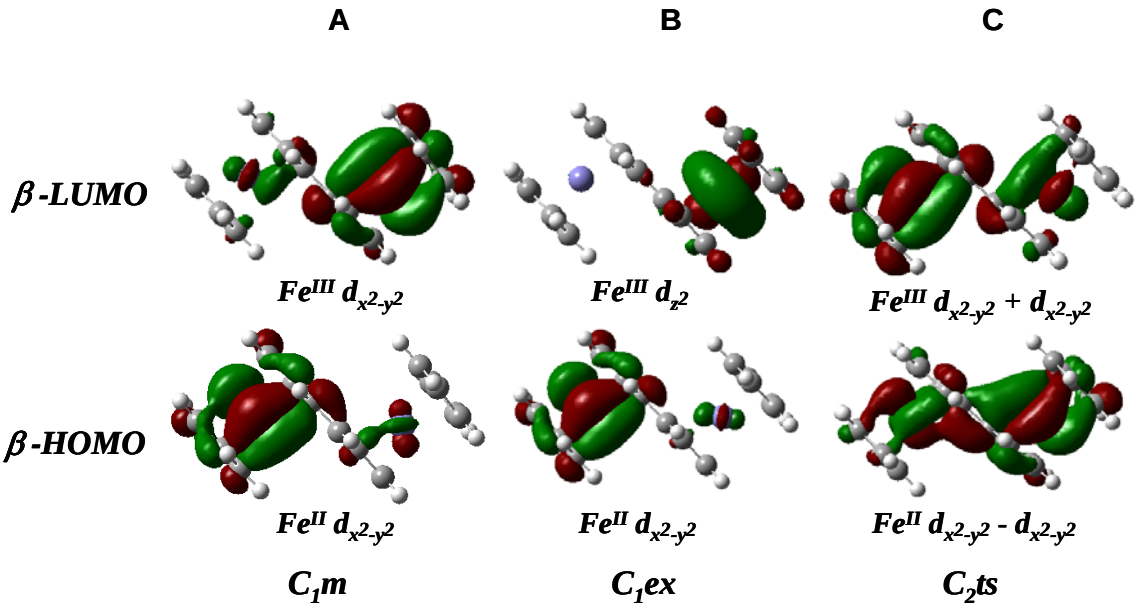
Supporting Information for:

Exploring the Ground and Excited State Potential Energy Landscapes of the Mixed-Valence Biferricenium Complex

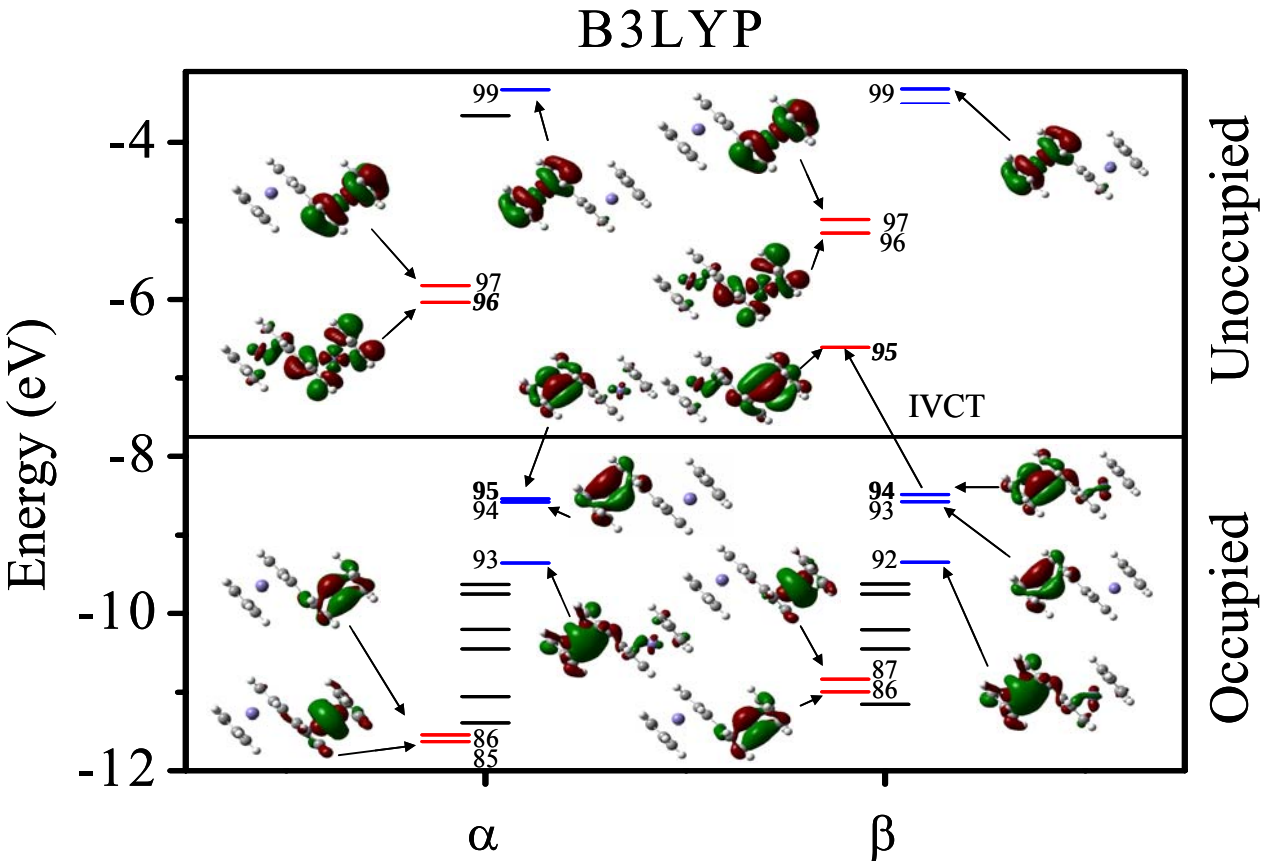
Ryan G. Hadt, Victor N. Nemykin,*

Department of Chemistry & Biochemistry, University of Minnesota Duluth, Duluth, MN 55812, USA

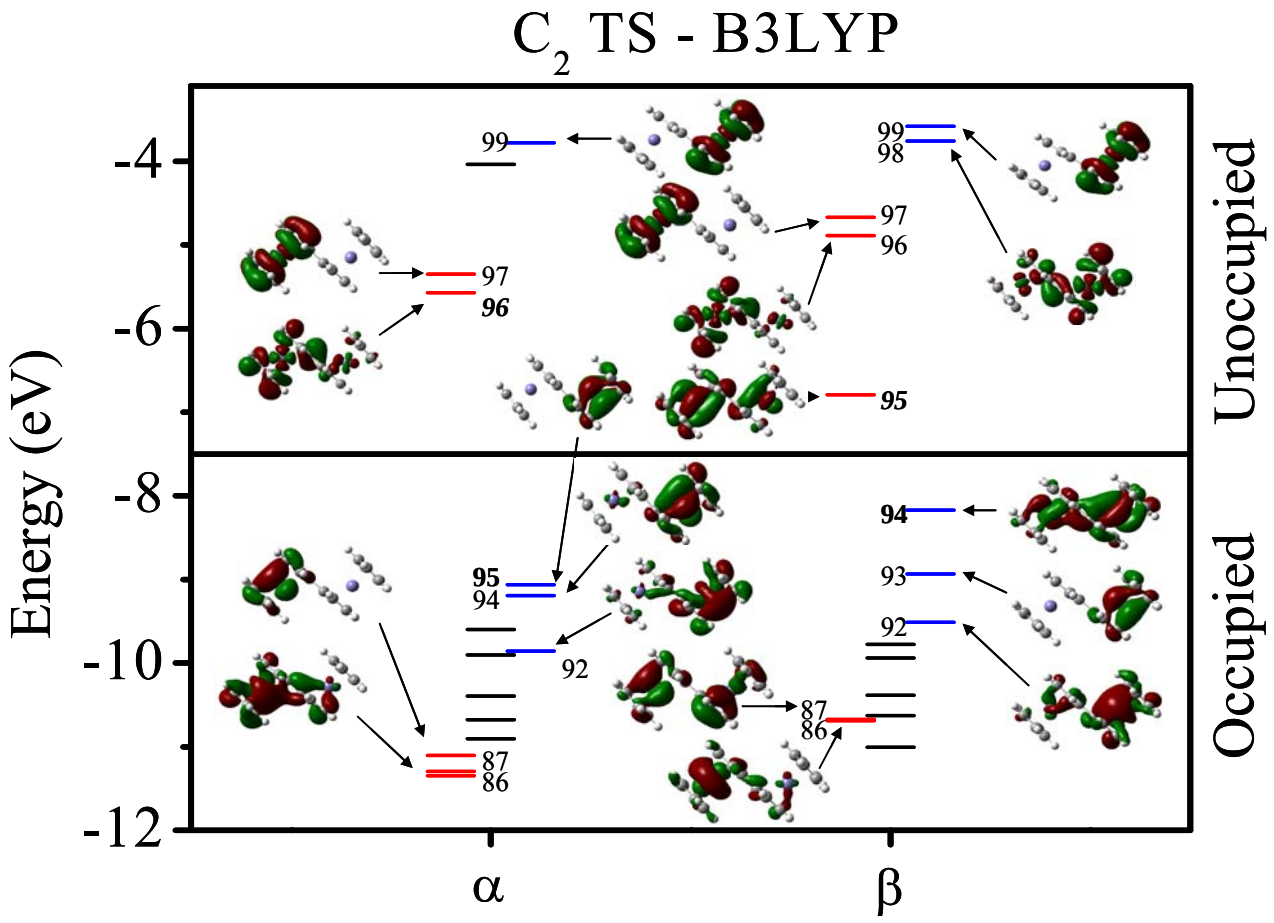
- author to whom correspondence should be addressed: vnemykin@d.umn.edu (VNN)



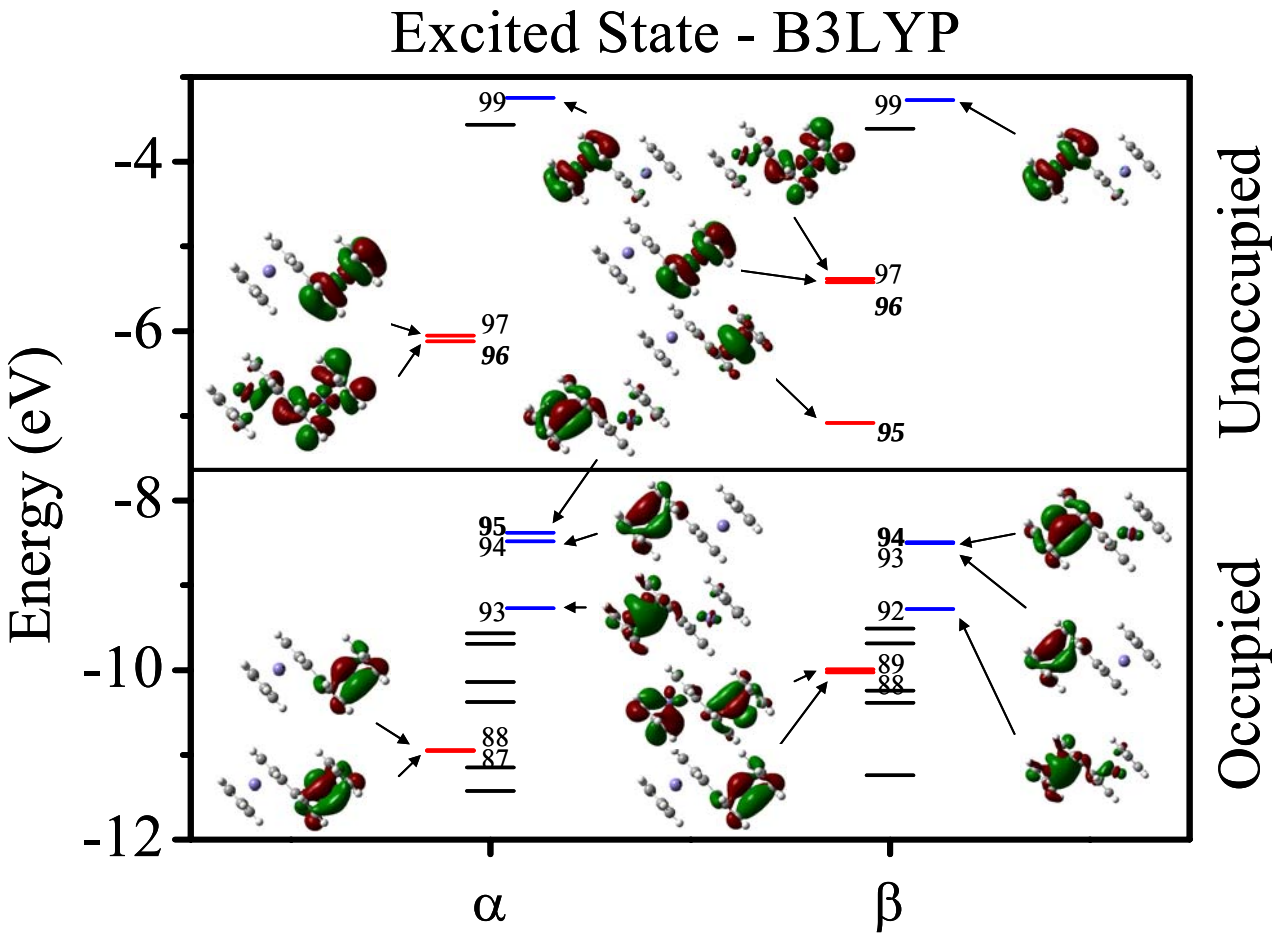
Supporting Information Figure 1. β HOMO and LUMO MOs for **C_1m** (**A**), **C_1ex** (**B**), and **C_2ts** (**C**) obtained using B3LYP exchange-correlation functional.



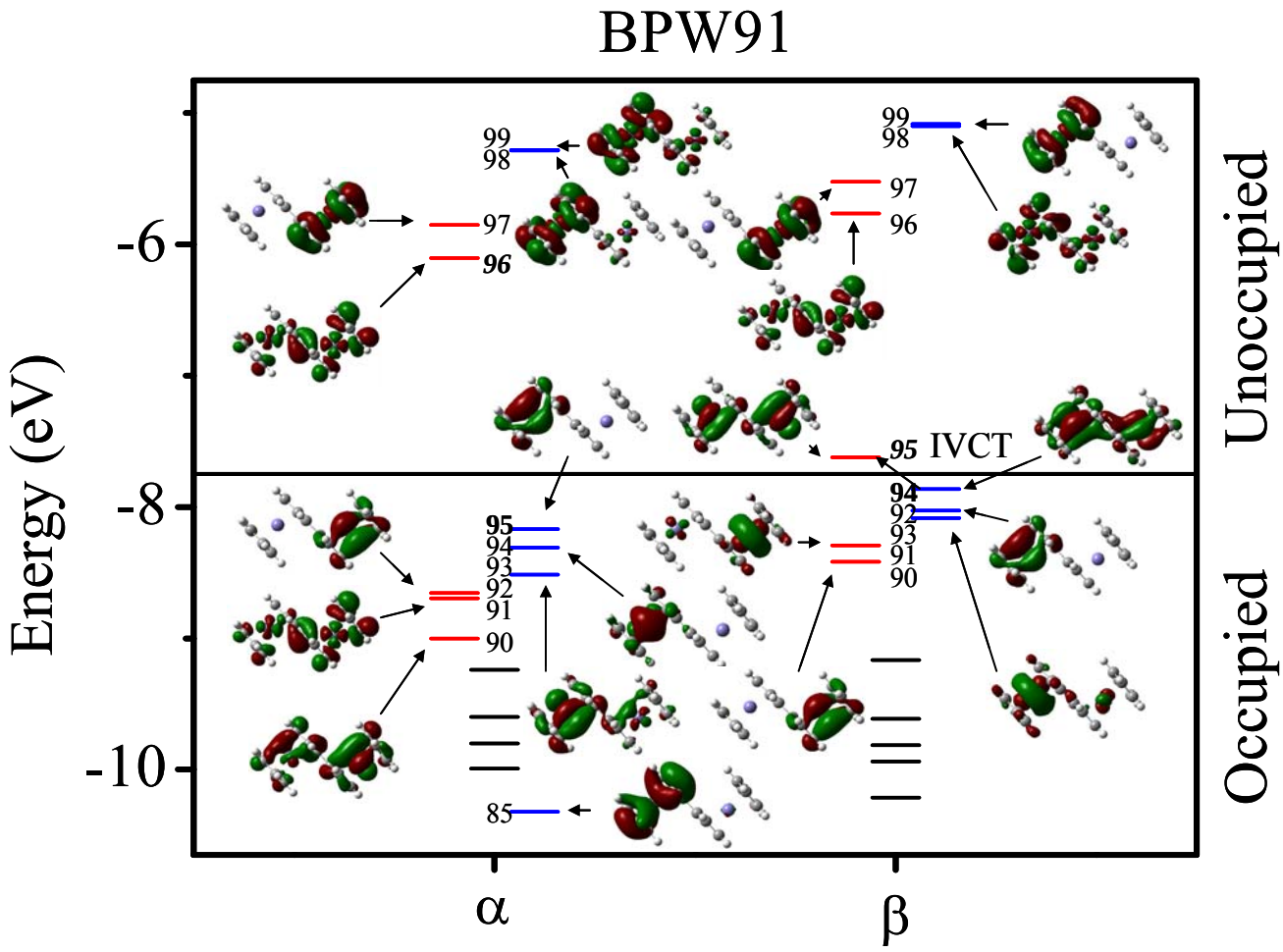
Supporting Information Figure 2. DFT predicted (B3LYP) molecular orbital diagram for **C_1m**.



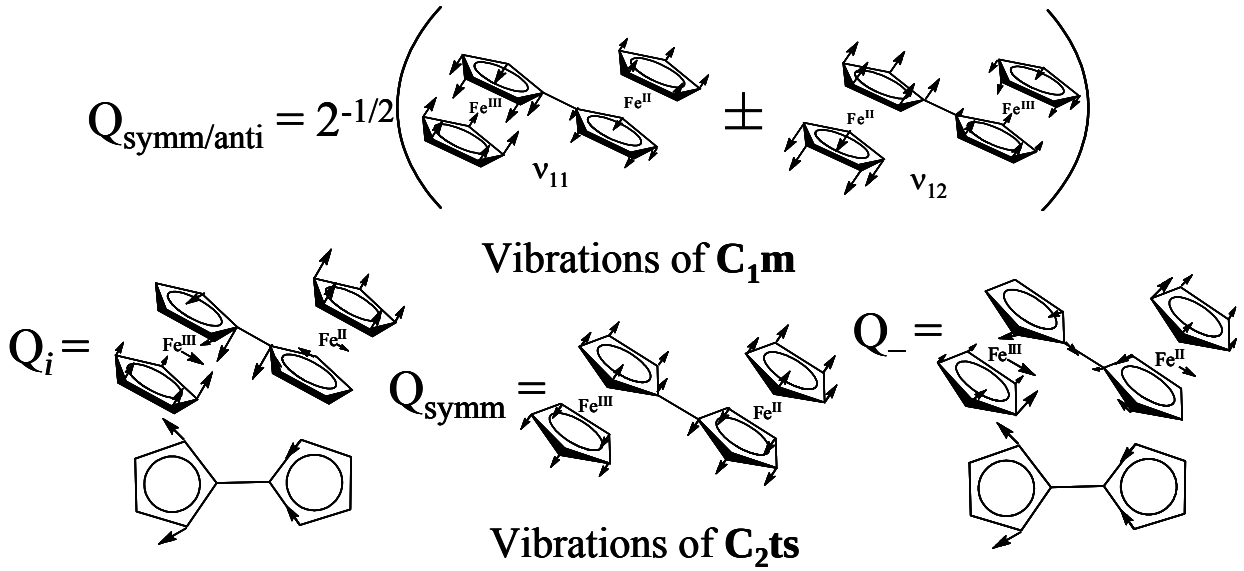
Supporting Information Figure 3. DFT predicted (B3LYP) molecular orbital diagram for **C_2ts.**



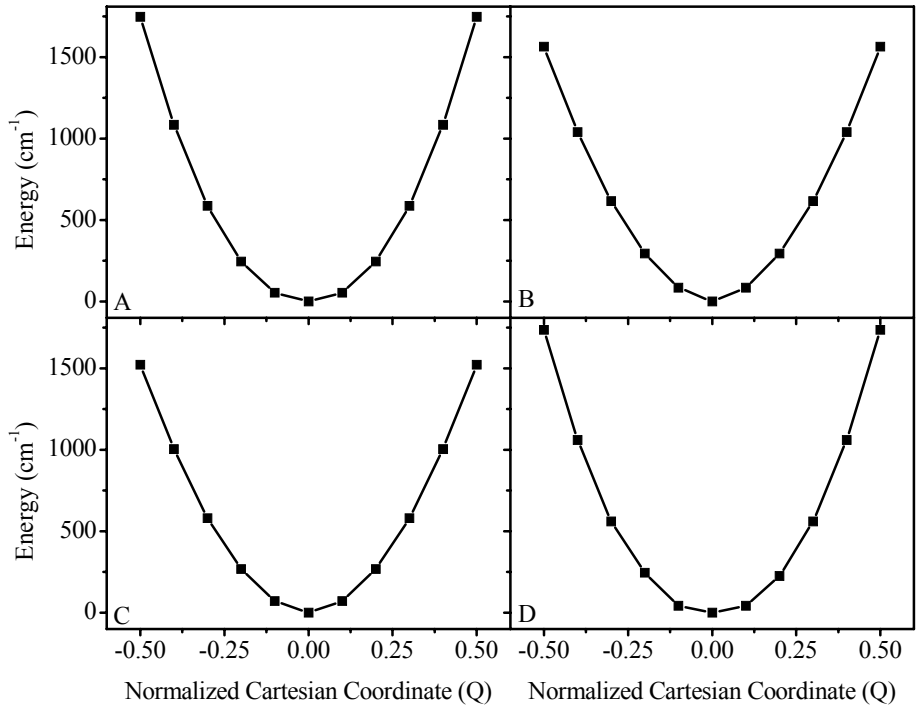
Supporting Information Figure 4. DFT predicted (B3LYP) molecular orbital diagram for **C_1ex.**



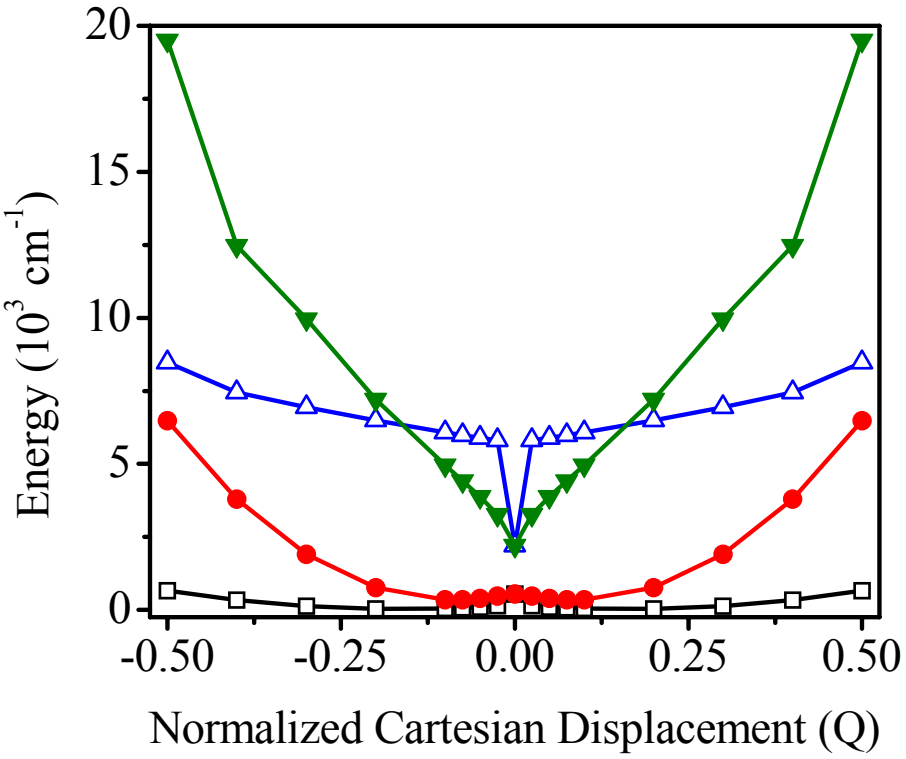
Supporting Information Figure 5. DFT predicted (BPW91) molecular orbital diagram for the **C_1m.**



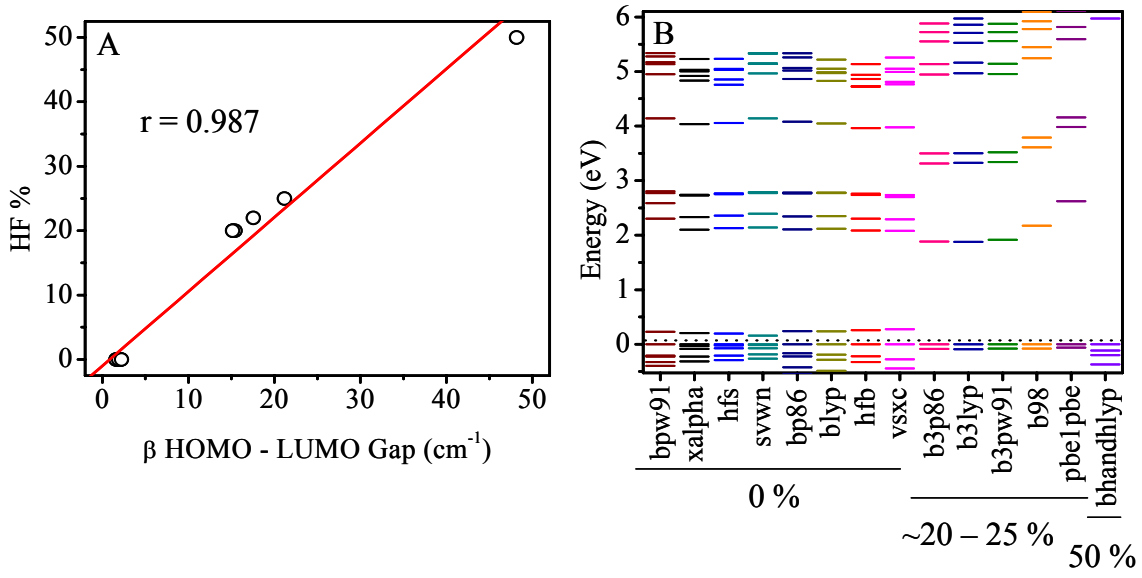
Supporting Information Figure 6. Important vibrations for both **C_1m** and **C_2ts**. Arrows indicated relative amplitude of vibration.



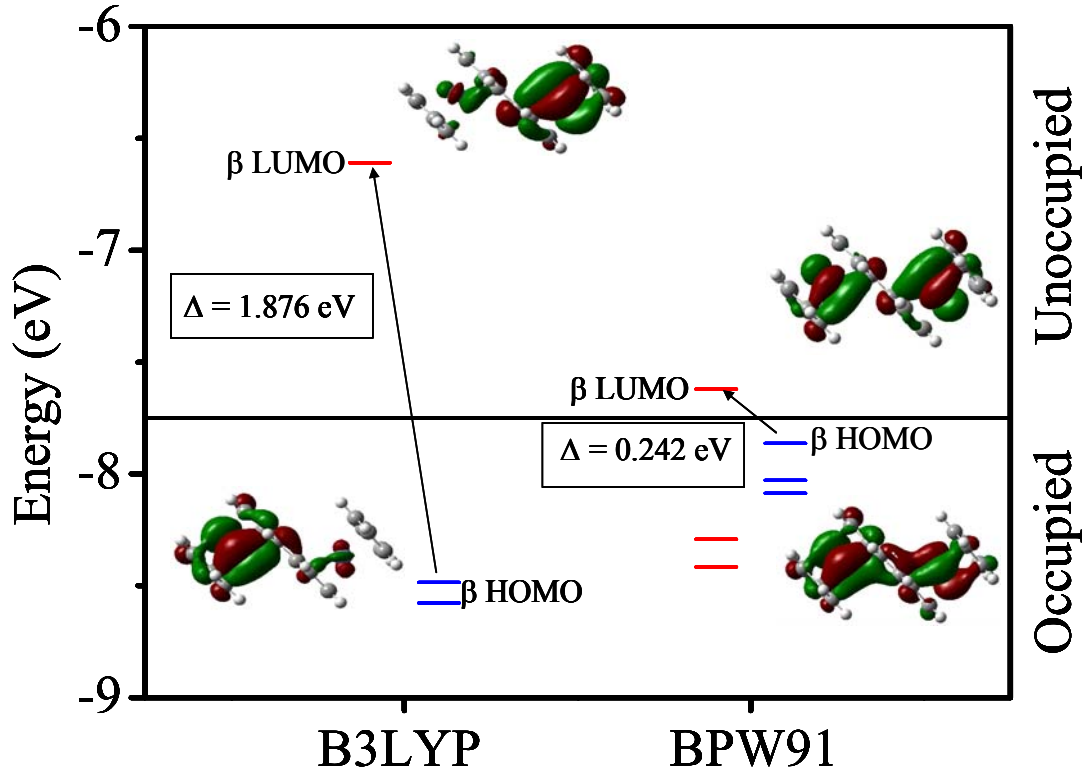
Supporting Information Figure 7. Important DFT (B3LYP) predicted PESs for the **C_1m** geometry: (A) ν_{11}; (B) ν_{12}; (C) Q_{symm} and (D) Q_{anti}.



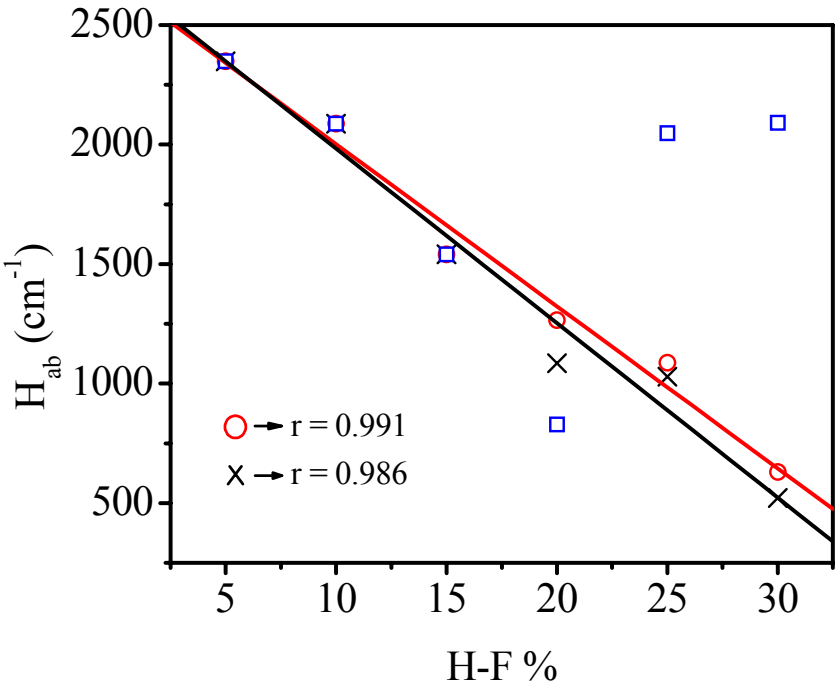
Supporting Information Figure 8. DFT and TDDFT predicted lower and upper adiabatic relaxed (black and blue) and rigid (red and green) PESs for the **BF**$^+$ cation.



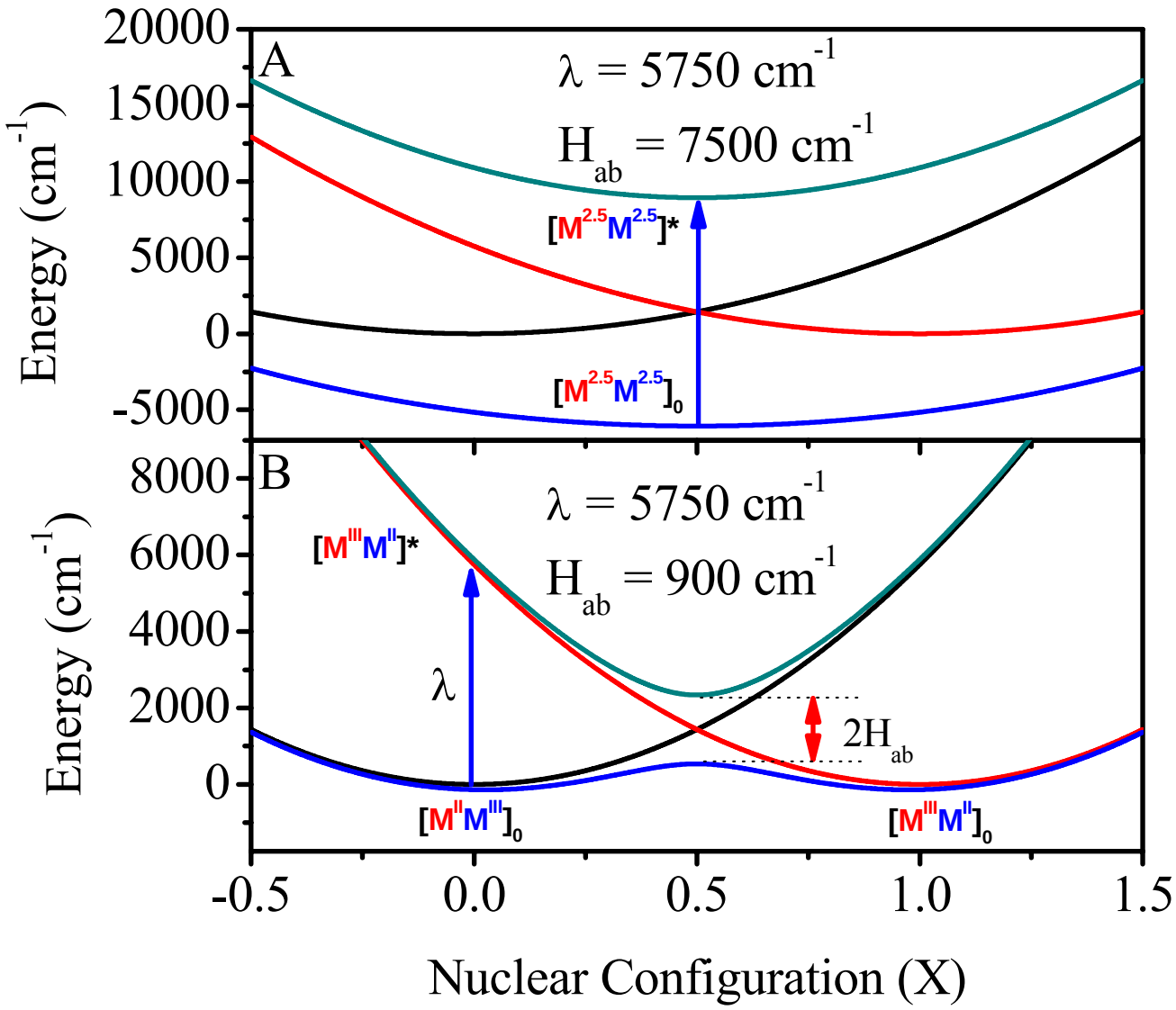
Supporting Information Figure 9. β HOMO-LUMO gap dependence: (A) correlation between Hartree-Fock percentage (B) partial MO diagram for 14 different exchange correlation functionals.



Supporting Information Figure 10. β HOMO-LUMO gap and MO plots for B3LYP and BPW91.



Supporting Information Figure 11. Linear dependence of Hab evaluated using Methods I (blue squares), IIA (black x's), and IIIB (red circles) for 5, 10, 15, 20, 25, and 30 % of Hartree-Fock exchange.



Supporting Information Figure 12. Class III (A) *versus* class II (B) PES profiles with various values of H_{ab}.

Supporting Information Table 1. Important structural parameters of **BF** and **BF**$^+$ (Å and degree) obtained via B3LYP optimization.

Symm.	Fe-Fe	$Fe^{2.5}$-C_i	Fe^{II}-C_i	Fe^{III}-C_i	C_i-C_i	$\theta_{Fe^{II}}$	$\theta_{Fe^{III}}$	r_1	r_2	r_3	r_4
					Neutral						
C_{2h}[a]	5.209		2.098		1.466	0.0		2.080	2.081	2.081	2.080
exp[b]	5.112		2.062		1.459	14.4		2.051	2.056	2.056	2.051
					Mixed-valent						
					Gas-Phase						
C_1m[a]	5.278		2.074	2.229	1.446	2.5	4.5	2.135	2.127	2.081	2.084
exp[c]	5.082		2.041	2.114	1.450	4.5	18.3	2.030	2.056	2.072	2.072
C_1[d]	5.274		2.074	2.227	1.445	0.1	22.4	2.133	2.130	2.081	2.084
C_1[e]	5.279		2.076	2.225	1.445	22.2	22.3	2.087	2.083	2.128	2.136
C_1ex	5.228		2.072	2.168	1.449	2.8	3.5	2.105	2.105	2.080	2.084
C_2ts	5.253	2.146			1.445	3.0	3.0	2.109	2.099	2.109	2.099
C_i	5.251	2.145			1.445	3.4	-3.4	2.110	2.098	2.098	2.110
C_{2h}[f]	5.250	2.145			1.445	0.0	0.0	2.109	2.098	2.098	2.109
C_{2h}[g]	5.252	2.144			1.445	0.0	0.0	2.112	2.099	2.099	2.112
					CH_2Cl_2						
C_1m	5.272		2.077	2.212	1.453	2.4	4.2	2.081	2.080	2.124	2.129
C_2ts	5.235	2.141			1.444	3.0	3.0	2.107	2.096	2.096	2.107
					CH_3CN						
C_1m	5.272		2.076	2.212	1.453	2.4	4.2	2.081	2.080	2.124	2.129
C_2ts	5.232	2.140			1.444	3.0	3.0	2.107	2.096	2.096	2.107

[a]Global minima; [b] CCDC code: BIFERO02; [c] CCDC code: FEKFUW; [d] single D_{5d} and single D_{5h} Cp conformations; [e]2 D_{5h} Cp conformations; [a]2 D_{5h} Cp conformations; [g]2 D_{5d} Cp conformations.

Supporting Information Table 2. DFT (B3LYP) predicted molecular orbitals with significant d character for the **C_1m** geometry (HOMO in bold and LUMO in bold and italics**)**.

α set							β set						
MO	Type	Energy (eV)	Fe^{III}	Fe^{II}	Cp^{III}	Cp^{II}	MO	Type	Energy (eV)	Fe^{III}	Fe^{II}	Cp^{III}	Cp^{II}
82	d_{x2-y2}	-12.369	68.6	0.9	23.4	7.1	82	cpd_{xz}	-11.938	24.1	2.9	53.5	17.5
83	cpd_{xz}	-12.236	58.8	0.6	36.4	4.1	83	cpd_{yz}	-11.818	32.1	0.0	67.6	0.2
84	cpd_{yz}	-12.196	43.4	0.0	56.4	0.2	86	d_{xy}	-10.998	78	0	21.7	0.3
85	d_{z2}	-11.630	92.3	0.1	6.6	0.9	87	d_{z2}	-10.834	91.7	0.1	7.5	0.7
86	d_{xy}	-11.543	81.7	0	17.8	0.5	88	cpd_{yz}	-10.451	0.1	25.7	0.9	73.3
89	cpd_{yz}	-10.451	0.1	25.8	1.1	73.0	89	cpd_{xz}	-10.205	3.1	26.7	13.4	56.9
90	cpd_{xz}	-10.204	3.1	26.4	14.0	56.5	92	d_{z2}	-9.346	1.5	80.1	4.5	13.9
93	d_{z2}	-9.357	1.6	80.4	4.2	13.8	93	d_{xy}	-8.576	0	73.3	0.5	26.1
94	d_{xy}	-8.582	0	73.5	0.5	25.9	**94**	**d_{x2-y2}**	**-8.485**	**1.8**	**61.3**	**3.6**	**33.3**
95	**d_{x2-y2}**	**-8.540**	**1.6**	**62.8**	**2.2**	**33.4**	***95***	***cpd_{x2-y2}***	***-6.609***	***49.2***	***3.1***	***44.3***	***3.4***
96	***cpd_{xz}***	***-6.036***	***38.5***	***3.8***	***53.1***	***4.6***	96	cpd_{xz}	-5.159	46.4	2.8	47.1	3.7
97	cpd_{yz}	-5.825	41.1	0.1	58	0.8	97	cpd_{yz}	-4.982	46.1	0.1	52.8	1
99	cpd_{yz}	-3.334	0.3	41.2	3.7	54.8	99	cpd_{yz}	-3.324	0.1	25.7	0.9	73.3

Supporting Information Table 3. DFT (B3LYP) predicted molecular orbitals with significant d character for the optimized **C_2ts** geometry (HOMO in bold and LUMO in bold and italics**)**.

α-set							β-set						
MO	Type	Energy (eV)	Fe^{III}	Fe^{II}	Cp^{III}	Cp^{II}	MO	Type	Energy (eV)	Fe^{III}	Fe^{II}	Cp^{III}	Cp^{II}
82	cpd_{xz}	-12.138	41.9	2.2	43.3	12.5	82	cpd_{xz}	-11.889	22.5	3.4	53.9	20.2
83	cpd_{yz}	-11.926	40.4	0.0	59.2	0.3	83	cpd_{yz}	-11.651	31.8	0.0	67.9	0.3
84	d_{x2-y2}	-11.783	75.5	0.2	23.2	1.0	86	d_{z2}	-10.686	87.9	0.9	8.0	3.2
86	cpd_{z2}	-11.296	67.1	2.1	21.2	9.6	87	d_{xy}	-10.672	60.8	5.7	17.0	16.5
87	d_{xy}	-11.102	79.1	0.0	20.4	0.5	88	cpd_{yz}	-10.625	25.3	17.6	10.7	46.4
89	cpd_{yz}	-10.676	0.6	28.1	4.8	66.4	89	cpd_{xz}	-10.383	6.0	27.8	13.5	52.7
90	cpd_{xz}	-10.394	2.3	27.9	14.4	55.4	92	d_{z2}	-9.511	2.8	73.3	6.4	17.5
92	d_{z2}	-9.856	1.2	67.1	5.5	26.3	93	d_{xy}	-8.935	0.0	72.7	0.3	27.0
94	d_{x2-y2}	-9.194	0.9	67.8	2.1	29.2	**94**	$\mathbf{d_{x2-y2} - d_{x2-y2}}$	**-8.172**	**9.6**	**46.5**	**12.2**	**31.7**
95	$\mathbf{d_{xy}}$	**-9.061**	**0.0**	**74.8**	**0.4**	**24.8**	***95***	$\boldsymbol{d_{x2-y2} + d_{x2-y2}}$	***-6.791***	***42.2***	***12.2***	***36.1***	***9.4***
96	$\boldsymbol{cpd_{xz}}$	***-5.570***	***40.5***	***3.7***	***50.2***	***5.5***	96	cpd_{xz}	-4.890	45.0	3.1	48.9	3.0
97	cpd_{yz}	-5.350	41.3	0.1	57.8	0.8	97	cpd_{yz}	-4.671	44.9	0.1	54.0	1.0
98	cpd_{xz}	-4.039	3.2	35.9	26.2	34.8	98	cpd_{xz}	-3.758	3.4	41.4	15.0	40.2
99	cpd_{yz}	-3.779	0.3	42.3	2.2	55.2	99	cpd_{yz}	-3.582	0.3	42.6	2.9	54.2

Supporting Information Table 4. DFT (B3LYP) predicted molecular orbitals with significant d character for the optimized **C_1ex** geometry (HOMO in bold and LUMO in bold and italics**)**.

α-set							β-set						
MO	Type	Energy (eV)	Fe^{III}	Fe^{II}	Cp^{III}	Cp^{II}	MO	Type	Energy (eV)	Fe^{III}	Fe^{II}	Cp^{III}	Cp^{II}
79	d_{z2}	-13.164	88.8	0.7	7.2	3.2	82	cpd_{yz}	-12.250	36.7	0.0	63	0.3
83	cpd_{yz}	-12.486	44.6	0.0	54.7	0.6	83	cpd_{xz}	-12.105	28.7	2.2	54.7	14.4
84	cpd_{xz}	-12.453	39.1	1.8	44.6	14.5	86	cpd_{yz}	-10.388	0.2	25.5	0.8	73.5
87	d_{xy}	-10.953	75.5	0.0	24	0.5	87	cpd_{xz}	-10.241	25.9	14.7	26.2	33.2
88	d_{x2-y2}	-10.945	73.7	0.1	25.9	0.3	88	d_{xy}	-10.029	69.2	0.1	30	0.7
89	cpd_{yz}	-10.376	0.1	25.3	1	73.6	89	cpd_{x2-y2}	-9.992	46.4	8.9	21	23.7
90	cpd_{xz}	-10.141	4.3	26.2	12.9	56.6	92	d_{z2}	-9.281	3.4	75.7	4.7	16.2
93	d_{z2}	-9.268	1.3	83.3	3.4	12	93	d_{xy}	-8.500	0	73.4	0.7	25.8
94	d_{xy}	-8.479	0.0	73.1	0.7	26.2	**94**	$\mathbf{d_{x2-y2}}$	**-8.493**	**1.4**	**63.7**	**1.6**	**33.3**
95	$\mathbf{d_{x2-y2}}$	**-8.379**	**2.0**	**60.9**	**2.6**	**34.4**	***95***	$\boldsymbol{d_{z2}}$	***-7.084***	***84.9***	***0.2***	***13.4***	***1.5***
96	$\boldsymbol{cpd_{xz}}$	***-6.122***	***36.4***	***4.0***	***55.1***	***4.5***	96	cpd_{xz}	-5.423	43.7	0.1	55.4	0.8
97	cpd_{yz}	-6.052	39.0	0.1	60.2	0.7	97	cpd_{yz}	-5.382	44.1	2.8	49.2	3.9
99	cpd_{yz}	-3.244	0.4	40.5	5.1	54.1	99	cpd_{yz}	-3.270	0.3	40.6	4.9	54.2

Supporting Information Table 5. DFT calculated (BPW91) quadrupole splittings, isomer shifts, and spin densities in various electric fields for the B3LYP optimized **C_1m** localized minimum geometry.

field (a.u.)	ΔE_q (mm/s)	η	δ (mm/s)	spin density
		Neutral (C_{2h})		
none	2.533	0.010	0.419	
exptl[a]	2.36		0.52	
		Average-Valence (**C_2ts**)		
none	1.512	0.606	0.410	0.601
	1.512	0.606	0.410	0.601
exptl[b]	1.130		0.505	
		Localized Mixed-Valence (**C_1m**)		
	Fe^{II} /Fe^{III}	Fe^{II} /Fe^{III}	Fe^{II} /Fe^{III}	Fe^{II} /Fe^{III}
none	1.622/1.281	0.494/0.427	0.382/0.438	0.457/0.758
0.0020	1.829/1.053	0.402/0.527	0.391/0.427	0.358/0.856
0.0025	1.880/0.999	0.382/0.556	0.393/0.424	0.334/0.879
0.0030	1.929/0.945	0.362/0.586	0.395/0.422	0.310/0.903
0.0035	1.978/0.894	0.342/0.617	0.397/0.419	0.285/0.926
0.0040	2.025/0.843	0.324/0.648	0.399/0.417	0.262/0.949
0.0045	2.071/0.795	0.305/0.678	0.401/0.414	0.238/0.971
0.0050	2.116/0.750	0.287/0.706	0.403/0.412	0.215/0.992
0.0055	2.159/0.707	0.270/0.729	0.405/0.409	0.193/1.013
0.0060	2.200/0.667	0.252/0.746	0.407/0.407	0.171/1.033
exptl[b]	2.141/0.288		0.510/0.518	

[a] ref. 48; [b] ref. 10.

Supporting Information Table 6. The calculated values of H_{ab}, the IVCT band, and oscillator strengths using various methods.

symm	HF %	imaginary freq (cm^{-1})	ΔE (cm^{-1})	IVCT (cm^{-1})	*f*	$H_{ab}{}^{k}$	$H_{ab}{}^{l}$	$H_{ab}{}^{m}$
			Gas-Phase					
C_2	5[a]			4700	0.0355	2350		
C_2	10[b]			4180	0.0577	2090		
C_2	15[c]			3080	0.0717	1540		
C_1	20[d]		538	6490	0.0046		1080	1260
C_2	20[d]	642 B		1660	0.0658	830		
C_1	25[e]		688	6870	0.0001		1030	1090
C_2	25[e]	23 B		4100	0.0070	2050		
C_1	30[f]		728	5000	0.0004		520	630
C_2	30[f]	26 B		4180	0.0015	2090		
C_1	21.98[g]		659	7570	0.0011		1230	1360
C_2	21.98[g]			3600	0.0303	1800		
C_1	25[h]		776	8850	0.0021		1440	1550
C_2	25[h]	22 B		4940	0.0227	2470		
			Solution					
$C_1{}^{i}$	20		672	9140	0.0011		1610	870
$C_2{}^{i}$	20			5920	0.0106	2970		
$C_1{}^{j}$	20		670	8910	0.0015		1560	670
$C_2{}^{j}$	20			6120	0.0106	3060		

[a] B3LYP-5; [b] B3LYP-10; [c] B3LYP-15; [d] B3LYP; [e] B3LYP-25; [f] B3LYP-30; [g]B98; [h]PBE1PBE; [i]CH_2Cl_2; [j]CH_3CN; [k]Method 1; [l]Method IIA; [m]Method IIB;

Supporting Information Table 7. Energetics results of various geometry optimizations of **BF$^+$** complex.

Symm.	HF %	ΔE [n] (cm^{-1})	ZPE (cm^{-1})	ΔE ZPE (cm^{-1}) [n]	Imaginary freqs (cm^{-1}), symmetry	Spin Density Fe^{III}/Fe^{II}
			Gas-phase			
C_1	20[a]	540	69990	360		1.27/0.02
	25[b]	690	70460	630		1.34/-0.01
	30[c]	730	70920	620		1.41/-0.02
	~22[d]	660	69790	540		1.30/0.01
	25[e]	780	70760	670		1.31/0.01
C_2	5[f]		70340			0.61/0.61
	10[g]		70400			0.63/0.63
	15[h]		70450			0.65/0.65
	20[a]		69810		642 B	0.98/0.34
	25[b]		70400		23 B	1.24/0.07
	30[c]		70810		26 B	1.30/0.06
	~22[d]		69670			1.16/0.14
	25[e]		70650		22 B	1.20/0.10
C_2	0[i]		67860			0.59/0.59
C_2	0[j]		68260			0.59/0.59
C_2	0[k]		68640			0.53/0.53
			PCM			
C_1[l]	20[a]	1560	69960	1380		1.28/0.00
C_2[l]	20[a]		69780		635 B	1.21/0.04
C_1[m]	20[a]	1420	69960	1240		1.28/0.00
C_2[m]	20[a]		69780		640 B	1.21/0.04

[a] B3LYP; [b] B3LYP-25; [b] B3LYP-30; [d] B98; [e]PBE1PBE; [f] B3LYP-5; [g] B3LYP-10; [h] B3LYP-15; [i] BP86; [j] BPW91; [k]LSDA; [l] CH_2Cl_2; [m] CH_3CN; [n] energy difference between C_2 (localized) and C_1 (delocalized) geometries at corresponding level of theory.

Supporting Information Table 8. DFT results (quadrupole splittings, electron densities on Fe, β-set HOMO-LUMO gaps, and spin densities) for 14 different exchange-correlation functionals using the B3LYP optimized $\mathbf{C_{1m}}$ geometry.

Functional (HF %)	ΔE_q (mm/s)	η	ρ	Δρ	β gap (cm^{-1})	spin density
	Fe^{II}/Fe^{III}	Fe^{II}/Fe^{III}	Fe^{II}/Fe^{III}			Fe^{II}/Fe^{III}
Xα (0)	1.63/1.30	0.56/0.44	11574.06/ 11573.88	0.18	1660	0.49/0.81
LSDA (0)	1.59/1.34	0.57/0.41	11560.17/ 11559.98	0.19	2100	0.45/0.70
HFS (0)	1.62/1.32	0.55/0.42	11559.02/ 11558.84	0.17	1570	0.48/0.78
HFB (0)	1.69/1.29	0.43/0.38	11615.70/ 11615.54	0.16	2100	0.48/0.82
BP86 (0)	1.62/1.29	0.49/0.41	11619.84/ 11619.66	0.18	1930	0.45/0.75
BPW91 (0)	1.62/1.28	0.49/0.43	11615.84/ 11615.66	0.18	1960	0.46/0.76
BLYP (0)	1.65/1.32	0.43/0.35	11615.48/ 11615.31	0.17	1900	0.45/0.74
VSXC (0)	1.69/1.27	0.40/0.32	11605.18/ 11605.00	0.18	2220	0.51/0.87
B3P86 (20)	3.12/0.56	0.18/0.70	11615.98/ 11616.02	-0.04	15200	0.02/1.28
B3PW91 (20)	2.12/0.55	0.18/0.72	11612.74/ 11612.78	-0.04	15420	0.01/1.30
B3LYP (20)	3.19/0.56	0.17/0.54	11612.45/ 11612.50	-0.06	15130	0.02/1.27
B98 (21.98)	3.29/0.58	0.16/0.47	11610.98/ 11611.03	-0.05	17550	0.00/1.30
PBE1PBE (25)	3.30/0.58	0.15/0.53	11616.68/ 11616.73	-0.04	21160	-0.01/1.36
BH&HLYP (50)	4.40/1.01	0.08/0.06	11618.69/ 11618.82	-0.13	48160	-0.01/1.55

Cartesian coordinates for the most important stationary points discussed in manuscript:

C_{2h} Neutral Gas Phase

Fe	-1.69025500	1.98173100	0.00000000
C	-0.00767300	1.58715100	1.15093300
C	-0.00489700	0.73285100	0.00000000
C	0.00767300	2.94241500	0.71248100
C	0.00767300	2.94241500	-0.71248100
H	-0.02572600	1.25912200	2.18028800
H	-0.00135000	3.81492100	1.35027500
H	-0.00135000	3.81492100	-1.35027500
C	-0.00767300	1.58715100	-1.15093300
H	-0.02572600	1.25912200	-2.18028800
C	-3.38653500	0.78108600	0.00000000
C	-3.38170300	1.61966700	1.15299000
C	-3.37321300	2.97617700	-0.71332600
C	-3.37321300	2.97617700	0.71332600
H	-3.36169100	-0.29928100	0.00000000
H	-3.36601200	1.28483000	2.18044800
H	-3.35074800	3.85019500	-1.34871800
H	-3.35074800	3.85019500	1.34871800
C	-3.38170300	1.61966700	-1.15299000
H	-3.36601200	1.28483000	-2.18044800
C	0.00489700	-0.73285100	0.00000000
C	0.00767300	-1.58715100	1.15093300
C	0.00767300	-1.58715100	-1.15093300
C	-0.00767300	-2.94241500	0.71248100
C	-0.00767300	-2.94241500	-0.71248100
Fe	1.69025500	-1.98173100	0.00000000
C	3.38170300	-1.61966700	1.15299000
C	3.37321300	-2.97617700	0.71332600
C	3.37321300	-2.97617700	-0.71332600
C	3.38170300	-1.61966700	-1.15299000
C	3.38653500	-0.78108600	0.00000000
H	3.36601200	-1.28483000	-2.18044800
H	3.35074800	-3.85019500	-1.34871800
H	3.35074800	-3.85019500	1.34871800
H	3.36601200	-1.28483000	2.18044800
H	3.36169100	0.29928100	0.00000000
H	0.02572600	-1.25912200	-2.18028800
H	0.00135000	-3.81492100	-1.35027500
H	0.00135000	-3.81492100	1.35027500
H	0.02572600	-1.25912200	2.18028800

C_1m Gas Phase

H	2.54128400	-2.73653500	1.36609800

C	1.95407500	-2.09543500	0.72443200
C	1.95199800	-2.09982300	-0.70166500
C	1.04684300	-1.08537000	1.15629500
C	1.04304900	-1.09179200	-1.13673200
H	2.53628200	-2.74548200	-1.34134200
C	0.41962100	-0.49565500	0.00945600
H	0.84301500	-0.82480500	2.18475600
H	0.83309800	-0.83979900	-2.16604300
C	-0.56585900	0.56222200	0.00689200
C	-1.16656900	1.16972900	-1.15575100
C	-1.17478200	1.17096200	1.16476100
C	-2.09572900	2.14461400	-0.71224800
H	-0.94961400	0.93107800	-2.18693700
C	-2.10091100	2.14535600	0.71340300
H	-0.96551200	0.93264100	2.19763100
H	-2.71703100	2.75852600	-1.34771900
H	-2.72690200	2.75970500	1.34385400
C	4.52279700	0.13072700	-0.83805500
C	3.65320600	1.23247700	-1.10514600
C	4.66087500	0.01821600	0.57731000
H	4.99975600	-0.49670100	-1.57704100
C	3.26534000	1.79699300	0.13976600
H	3.34310900	1.57627400	-2.08137300
C	3.87818500	1.04661700	1.17589300
H	5.24988100	-0.71854300	1.10428100
H	2.57881400	2.62083500	0.27575100
H	3.75346200	1.21195800	2.23669300
C	-4.56309600	-0.12203600	0.63683300
C	-4.49303400	-0.19647700	-0.78367900
C	-3.68454200	-1.10712400	1.17471100
H	-5.16351800	0.57239000	1.20654200
C	-3.56937500	-1.22581300	-1.12713500
H	-5.03114400	0.43186100	-1.47872000
C	-3.07332200	-1.78954200	0.08430500
H	-3.50809200	-1.29523800	2.22388100
H	-3.29349300	-1.52284200	-2.12860000
H	-2.34480300	-2.58432000	0.16234800
Fe	2.63728400	-0.27137600	-0.00037800
Fe	-2.61540800	0.24506500	-0.00023500

C_1m CH_2Cl_2

H	2.56707500	-2.72451100	1.37584900
C	1.96279200	-2.09478500	0.73270100
C	1.95581800	-2.10266300	-0.69492500
C	1.05029700	-1.08975000	1.16645700
C	1.03872600	-1.10195300	-1.13040000

H	2.55281700	-2.74003800	-1.33724800
C	0.43232300	-0.49850800	0.01827300
H	0.85729000	-0.81984700	2.19872300
H	0.83153800	-0.84615100	-2.16343000
C	-0.56196000	0.56095100	0.01548400
C	-1.15399300	1.16909500	-1.14703000
C	-1.16961800	1.16609800	1.17140700
C	-2.09293100	2.13967900	-0.70671900
H	-0.92841600	0.92655600	-2.17841200
C	-2.10274600	2.13765000	0.72060200
H	-0.95928700	0.91984200	2.20517000
H	-2.71891300	2.74926500	-1.34708200
H	-2.73798700	2.74548400	1.35350100
C	4.50883300	0.13048200	-0.83885100
C	3.63704400	1.22834500	-1.11807900
C	4.64338900	0.03096800	0.57964800
H	4.97722100	-0.51544300	-1.57262800
C	3.24400800	1.80283500	0.12199300
H	3.31567600	1.55355400	-2.10122300
C	3.85747000	1.06401900	1.16735600
H	5.22174100	-0.71230100	1.11671400
H	2.55032600	2.62677300	0.25015200
H	3.71692000	1.22963000	2.23000500
C	-4.55711100	-0.12975500	0.63484200
C	-4.48606300	-0.19519000	-0.78858900
C	-3.67283600	-1.11613200	1.16671900
H	-5.15397300	0.56657600	1.21159900
C	-3.55673000	-1.22045700	-1.13807000
H	-5.02005900	0.44319300	-1.48231300
C	-3.05631300	-1.78944300	0.07091200
H	-3.48343000	-1.30358200	2.21677400
H	-3.26616300	-1.50252600	-2.14285500
H	-2.31670900	-2.57754500	0.14464400
Fe	2.63255300	-0.26797100	-0.00031600
Fe	-2.61440100	0.24613000	0.00030300

C_1m CH_3CN

H	2.56756100	-2.72297300	1.37456600
C	1.96265700	-2.09395600	0.73110100
C	1.95716500	-2.10078300	-0.69658300
C	1.04861300	-1.09029400	1.16471300
C	1.03925000	-1.10085400	-1.13240300
H	2.55621500	-2.73647800	-1.33886600
C	0.43150600	-0.49881900	0.01626000
H	0.85418600	-0.82095400	2.19701000
H	0.83302200	-0.84419000	-2.16557400

C	-0.56315600	0.56054700	0.01348500
C	-1.15518600	1.16878400	-1.14886500
C	-1.16964900	1.16647000	1.16958800
C	-2.09314700	2.14031500	-0.70836400
H	-0.93053900	0.92576200	-2.18045800
C	-2.10225200	2.13875800	0.71900400
H	-0.95889100	0.92024600	2.20338700
H	-2.71910300	2.75042900	-1.34842800
H	-2.73668100	2.74739900	1.35212200
C	4.50338200	0.13296600	-0.84561800
C	3.63266200	1.23497900	-1.11209500
C	4.64632900	0.02335300	0.57131100
H	4.96502600	-0.50959200	-1.58676500
C	3.24867400	1.80179300	0.13452500
H	3.30613100	1.56810600	-2.09100800
C	3.86674600	1.05424300	1.17091800
H	5.22524000	-0.72577000	1.09982300
H	2.55819200	2.62688900	0.27306100
H	3.73261000	1.21230800	2.23567900
C	-4.55974100	-0.12922500	0.63047200
C	-4.48410100	-0.20272500	-0.79240900
C	-3.67473700	-1.11045400	1.17082300
H	-5.16014800	0.56927200	1.20108500
C	-3.55111500	-1.22773100	-1.13306700
H	-5.01732900	0.43050900	-1.49157700
C	-3.05309700	-1.78858100	0.08084400
H	-3.48793300	-1.29075900	2.22270000
H	-3.25637700	-1.51462000	-2.13537800
H	-2.31151600	-2.57426000	0.16154300
Fe	2.63101800	-0.26597600	-0.00004000
Fe	-2.61580600	0.24736000	-0.00014300

C_2ts Gas Phase

H	2.48313900	2.88722800	1.33508900
C	1.91776700	2.22089300	0.69985200
C	1.91033900	2.22471900	-0.72289100
C	1.02030600	1.21154700	1.14432700
C	1.00876500	1.21734700	-1.16337200
H	2.46935000	2.89431300	-1.36029500
C	0.48379000	0.53660800	-0.00868700
H	0.80121200	0.97511300	2.17527700
H	0.77848500	0.98696000	-2.19322300
C	-0.48379000	-0.53660800	-0.00868700
C	-1.00876500	-1.21734700	-1.16337200
C	-1.02030600	-1.21154700	1.14432700
C	-1.91033900	-2.22471900	-0.72289100

H	-0.77848500	-0.98696000	-2.19322300
C	-1.91776700	-2.22089300	0.69985200
H	-0.80121200	-0.97511300	2.17527700
H	-2.46935000	-2.89431300	-1.36029500
H	-2.48313900	-2.88722800	1.33508900
C	-0.56520900	4.48784000	-0.77790600
C	-1.55973200	3.51945500	-1.10836900
C	-0.48379000	4.56762500	0.64162400
H	0.02799400	5.05416500	-1.48113700
C	-2.09216100	3.00939200	0.10809100
H	-1.85465000	3.22549800	-2.10517500
C	-1.42775400	3.64919800	1.18868200
H	0.18392700	5.20276600	1.20538800
H	-2.84446400	2.23803200	0.19585800
H	-1.59893200	3.46494000	2.23939800
C	0.48379000	-4.56762500	0.64162400
C	0.56520900	-4.48784000	-0.77790600
C	1.42775400	-3.64919800	1.18868200
H	-0.18392700	-5.20276600	1.20538800
C	1.55973200	-3.51945500	-1.10836900
H	-0.02799400	-5.05416500	-1.48113700
C	2.09216100	-3.00939200	0.10809100
H	1.59893200	-3.46494000	2.23939800
H	1.85465000	-3.22549800	-2.10517500
H	2.84446400	-2.23803200	0.19585800
Fe	-0.00435100	2.62630500	-0.00074200
Fe	0.00435100	-2.62630500	-0.00074200

C_2ts CH_2Cl_2

H	2.48011500	2.89115700	1.32328100
C	1.91817000	2.21816700	0.68699600
C	1.90233100	2.22822700	-0.73695300
C	1.02702500	1.20344400	1.13319000
C	1.00219500	1.21905400	-1.17739700
H	2.45007000	2.91027300	-1.37594700
C	0.48586400	0.53428800	-0.02116700
H	0.80942800	0.96302000	2.16653400
H	0.76129800	0.99345200	-2.20887000
C	-0.48586400	-0.53428800	-0.02116700
C	-1.00219500	-1.21905400	-1.17739700
C	-1.02702500	-1.20344400	1.13319000
C	-1.90233100	-2.22822700	-0.73695300
H	-0.76129800	-0.99345200	-2.20887000
C	-1.91817000	-2.21816700	0.68699600
H	-0.80942800	-0.96302000	2.16653400
H	-2.45007000	-2.91027300	-1.37594700

H	-2.48011500	-2.89115700	1.32328100
C	-0.57631100	4.47803500	-0.76733500
C	-1.57144000	3.50779900	-1.09582400
C	-0.48586400	4.55210800	0.65312700
H	0.02068200	5.04181600	-1.47381000
C	-2.09525000	2.99116500	0.12285700
H	-1.86517400	3.20844900	-2.09448700
C	-1.42462500	3.62806100	1.20280900
H	0.19357500	5.17979000	1.21676200
H	-2.84510100	2.21412900	0.21252000
H	-1.58216300	3.43062000	2.25624800
C	0.48586400	-4.55210800	0.65312700
C	0.57631100	-4.47803500	-0.76733500
C	1.42462500	-3.62806100	1.20280900
H	-0.19357500	-5.17979000	1.21676200
C	1.57144000	-3.50779900	-1.09582400
H	-0.02068200	-5.04181600	-1.47381000
C	2.09525000	-2.99116500	0.12285700
H	1.58216300	-3.43062000	2.25624800
H	1.86517400	-3.20844900	-2.09448700
H	2.84510100	-2.21412900	0.21252000
Fe	-0.00715000	2.61744600	-0.00092500
Fe	0.00715000	-2.61744600	-0.00092500

C_2ts CH_3CN

H	2.47230800	2.89809100	1.33462200
C	1.91478300	2.22077100	0.69819600
C	1.90550700	2.22470300	-0.72623400
C	1.02230400	1.20726400	1.14482600
C	1.00770400	1.21320100	-1.16655500
H	2.45466900	2.90560400	-1.36607300
C	0.48635900	0.53377200	-0.00941000
H	0.79825800	0.97115300	2.17841100
H	0.76979800	0.98296800	-2.19832800
C	-0.48635900	-0.53377200	-0.00941000
C	-1.00770400	-1.21320100	-1.16655500
C	-1.02230400	-1.20726400	1.14482600
C	-1.90550700	-2.22470300	-0.72623400
H	-0.76979800	-0.98296800	-2.19832800
C	-1.91478300	-2.22077100	0.69819600
H	-0.79825800	-0.97115300	2.17841100
H	-2.45466900	-2.90560400	-1.36607300
H	-2.47230800	-2.89809100	1.33462200
C	-0.57007600	4.47327400	-0.77844300
C	-1.56481400	3.50226500	-1.10729400
C	-0.48635900	4.55381400	0.64241400

H	0.03289600	5.03147200	-1.48503500
C	-2.09493900	2.99157000	0.11153700
H	-1.85267500	3.19640000	-2.10625000
C	-1.42883100	3.63301200	1.19191300
H	0.19325600	5.18160500	1.20665800
H	-2.84491200	2.21377900	0.20182100
H	-1.58969700	3.43812400	2.24584100
C	0.48635900	-4.55381400	0.64241400
C	0.57007600	-4.47327400	-0.77844300
C	1.42883100	-3.63301200	1.19191300
H	-0.19325600	-5.18160500	1.20665800
C	1.56481400	-3.50226500	-1.10729400
H	-0.03289600	-5.03147200	-1.48503500
C	2.09493900	-2.99157000	0.11153700
H	1.58969700	-3.43812400	2.24584100
H	1.85267500	-3.19640000	-2.10625000
H	2.84491200	-2.21377900	0.20182100
Fe	-0.00670000	2.61610100	-0.00066800
Fe	0.00670000	-2.61610100	-0.00066800

C_{2h} 2D_5h Gas Phase

Fe	-1.74898000	1.95737600	0.00000000
C	-0.04957400	1.58192800	1.15389100
C	0.00455600	0.72271100	0.00000000
C	-0.04957400	2.93331400	0.71145200
C	-0.04957400	2.93331400	-0.71145200
H	-0.06281200	1.25764400	2.18405300
H	-0.07476100	3.80601400	1.34781900
H	-0.07476100	3.80601400	-1.34781900
C	-0.04957400	1.58192800	-1.15389100
H	-0.06281200	1.25764400	-2.18405300
C	-3.55762700	0.84235300	0.00000000
C	-3.49704600	1.67270000	1.15224000
C	-3.40706500	3.02674700	-0.71207300
C	-3.40706500	3.02674700	0.71207300
H	-3.59893000	-0.23783800	0.00000000
H	-3.50964600	1.33774900	2.17925800
H	-3.34123500	3.89782500	-1.34775800
H	-3.34123500	3.89782500	1.34775800
C	-3.49704600	1.67270000	-1.15224000
H	-3.50964600	1.33774900	-2.17925800
C	-0.00455600	-0.72271100	0.00000000
C	0.04957400	-1.58192800	1.15389100
C	0.04957400	-1.58192800	-1.15389100
C	0.04957400	-2.93331400	0.71145200
C	0.04957400	-2.93331400	-0.71145200

Fe	1.74898000	-1.95737600	0.00000000
C	3.49704600	-1.67270000	1.15224000
C	3.40706500	-3.02674700	0.71207300
C	3.40706500	-3.02674700	-0.71207300
C	3.49704600	-1.67270000	-1.15224000
C	3.55762700	-0.84235300	0.00000000
H	3.50964600	-1.33774900	-2.17925800
H	3.34123500	-3.89782500	-1.34775800
H	3.34123500	-3.89782500	1.34775800
H	3.50964600	-1.33774900	2.17925800
H	3.59893000	0.23783800	0.00000000
H	0.06281200	-1.25764400	-2.18405300
H	0.07476100	-3.80601400	-1.34781900
H	0.07476100	-3.80601400	1.34781900
H	0.06281200	-1.25764400	2.18405300

C_{2h} $2D_{5d}$ Gas Phase

Fe	-1.75797800	1.95092300	0.00000000
C	-0.05754700	1.58188300	1.15388800
C	-0.00020000	0.72241100	0.00000000
C	-0.05754700	2.93305000	0.71105400
C	-0.05754700	2.93305000	-0.71105400
H	-0.07320000	1.25817200	2.18431100
H	-0.08820200	3.80601300	1.34693800
H	-0.08820200	3.80601300	-1.34693800
C	-0.05754700	1.58188300	-1.15388800
H	-0.07320000	1.25817200	-2.18431100
C	-3.51513400	1.06064300	0.71384700
C	-3.47440700	2.41452200	1.15036300
C	-3.47440700	2.41452200	-1.15036300
C	-3.45293800	3.25110700	0.00000000
C	-3.51513400	1.06064300	-0.71384700
C	0.00020000	-0.72241100	0.00000000
C	0.05754700	-1.58188300	1.15388800
C	0.05754700	-1.58188300	-1.15388800
C	0.05754700	-2.93305000	0.71105400
C	0.05754700	-2.93305000	-0.71105400
Fe	1.75797800	-1.95092300	0.00000000
C	3.47440700	-2.41452200	1.15036300
C	3.45293800	-3.25110700	0.00000000
C	3.47440700	-2.41452200	-1.15036300
C	3.51513400	-1.06064300	-0.71384700
C	3.51513400	-1.06064300	0.71384700
H	0.07320000	-1.25817200	-2.18431100
H	0.08820200	-3.80601300	-1.34693800
H	0.08820200	-3.80601300	1.34693800

H	0.07320000	-1.25817200	2.18431100
H	3.39556100	-4.33003700	0.00000000
H	3.44220600	-2.74928100	-2.17743400
H	3.53718800	-0.18865600	-1.35150700
H	3.53718800	-0.18865600	1.35150700
H	3.44220600	-2.74928100	2.17743400
H	-3.44220600	2.74928100	2.17743400
H	-3.39556100	4.33003700	0.00000000
H	-3.44220600	2.74928100	-2.17743400
H	-3.53718800	0.18865600	-1.35150700
H	-3.53718800	0.18865600	1.35150700

C_i Gas Phase

H	-2.71282900	-2.28296400	1.93257200
C	-2.15470600	-1.76209800	1.16817500
C	-2.40898000	-1.80441900	-0.23112700
C	-1.01058600	-0.94633400	1.38536700
C	-1.42322700	-1.01443900	-0.88419200
H	-3.19517500	-2.36260700	-0.71840400
C	-0.57209600	-0.42585500	0.11674000
H	-0.56265400	-0.73502300	2.34524100
H	-1.34486100	-0.86287400	-1.95077500
C	0.57209600	0.42585500	-0.11674000
C	1.01058600	0.94633400	-1.38536700
C	1.42322700	1.01443900	0.88419200
C	2.15470600	1.76209800	-1.16817500
H	0.56265400	0.73502300	-2.34524100
C	2.40898000	1.80441900	0.23112700
H	1.34486100	0.86287400	1.95077500
H	2.71282900	2.28296400	-1.93257200
H	3.19517500	2.36260700	0.71840400
C	-0.46911800	-4.51939300	-0.59227500
C	0.62321500	-3.77634100	-1.13154300
C	-0.31798400	-4.55866100	0.82321400
H	-1.27407500	-4.96604100	-1.15775600
C	1.44697300	-3.36439300	-0.04724800
H	0.79346200	-3.56383900	-2.17691900
C	0.86736300	-3.84069200	1.15902100
H	-0.98907400	-5.03742600	1.52143400
H	2.33882500	-2.75844200	-0.12390900
H	1.24965600	-3.67676600	2.15616800
C	0.46911800	4.51939300	0.59227500
C	0.31798400	4.55866100	-0.82321400
C	-0.62321500	3.77634100	1.13154300
H	1.27407500	4.96604100	1.15775600
C	-0.86736300	3.84069200	-1.15902100

H	0.98907400	5.03742600	-1.52143400
C	-1.44697300	3.36439300	0.04724800
H	-0.79346200	3.56383900	2.17691900
H	-1.24965600	3.67676600	-2.15616800
H	-2.33882500	2.75844200	0.12390900
Fe	-0.51129400	-2.56943700	0.16946200
Fe	0.51129400	2.56943700	-0.16946200

C_1 $2D_{5d}$ Gas Phase

Fe	2.61575800	0.24308200	0.00001700
C	1.16343800	1.16041700	-1.15987700
C	0.56214900	0.54846400	-0.00001300
C	2.08283300	2.14216100	-0.71248700
C	2.08280600	2.14207800	0.71269200
H	0.95512200	0.91774900	-2.19194900
H	2.70481600	2.75833800	-1.34521900
H	2.70478800	2.75818000	1.34550000
C	1.16342200	1.16026600	1.15995100
H	0.95509800	0.91748700	2.19199500
C	3.24459200	-1.61268300	-0.71390200
C	4.14145600	-0.59966600	-1.15263200
C	4.14159400	-0.59930200	1.15269000
C	4.69211200	0.03096500	-0.00010800
C	3.24469200	-1.61246500	0.71437600
C	-0.42530200	-0.50625900	-0.00008200
C	-1.05302600	-1.09767000	-1.14672000
C	-1.05304100	-1.09780100	1.14647500
C	-1.96159600	-2.10569400	-0.71265800
C	-1.96160400	-2.10577400	0.71228600
Fe	-2.63781400	-0.26953200	-0.00009300
C	-4.24234100	0.56902100	-1.14918900
C	-4.80551900	-0.04609500	0.00015000
C	-4.24210100	0.56904300	1.14935700
C	-3.34017500	1.58408100	0.71320200
C	-3.34032100	1.58406900	-0.71323900
H	-0.84589700	-0.84197900	2.17545500
H	-2.55058400	-2.74627800	1.35304800
H	-2.55056000	-2.74613500	-1.35349800
H	-0.84585400	-0.84174200	-2.17566900
H	-5.50305600	-0.87180200	0.00023100
H	-4.45308200	0.30467200	2.17588100
H	-2.75981400	2.23568000	1.35032200
H	-2.76010400	2.23567100	-1.35048800
H	-4.45355400	0.30464600	-2.17566500
H	4.34884400	-0.33504400	-2.17957400
H	5.39054500	0.85524200	-0.00027500

H	4.34909900	-0.33437700	2.17953100
H	2.66170700	-2.26256500	1.35110100
H	2.66154100	-2.26297600	-1.35036800

C_1 $1D_{5d}$ $1D_{5h}$ Gas Phase

Fe	-2.61403600	0.24431200	0.00008900
C	-1.17416200	1.17802600	1.15953200
C	-0.56649900	0.57185500	-0.00036700
C	-2.10659500	2.14768600	0.71132900
C	-2.10669000	2.14657500	-0.71428800
H	-0.96035200	0.94090400	2.19174100
H	-2.73325200	2.75921000	1.34384900
H	-2.73333400	2.75720300	-1.34768500
C	-1.17441200	1.17615900	-1.16109000
H	-0.96035500	0.93769100	-2.19293200
C	-3.05970400	-1.79441900	0.00442800
C	-3.61980800	-1.16969700	1.15594600
C	-4.52535000	-0.16895700	-0.71394300
C	-4.52759500	-0.16549900	0.71023000
H	-2.32567900	-2.58796700	0.00754700
H	-3.39385800	-1.40945300	2.18490400
H	-5.09840900	0.48966000	-1.35051000
H	-5.10263000	0.49618600	1.34180900
C	-3.61610900	-1.17523700	-1.15191500
H	-3.38695500	-1.42000500	-2.17898000
C	0.41958900	-0.48460100	0.00000800
C	1.04415600	-1.07942700	1.14682400
C	1.03992000	-1.08503700	-1.14637900
C	1.94239900	-2.09577200	0.71462000
C	1.93720500	-2.10090000	-0.70950600
Fe	2.63563000	-0.26515900	-0.00582600
C	4.24022100	0.55352200	1.15322900
C	4.80544400	-0.06486100	0.00718000
C	4.25331700	0.55361600	-1.14534000
C	3.35724400	1.57757000	-0.71329900
C	3.34676600	1.57590500	0.71409500
H	0.83145300	-0.83279700	-2.17593100
H	2.51822300	-2.74971300	-1.34930300
H	2.52758300	-2.73942500	1.35566700
H	0.84111500	-0.81806900	2.17526800
H	5.49479600	-0.89749000	0.01133300
H	4.46836500	0.28792400	-2.17066600
H	2.78675200	2.23432700	-1.35405000
H	2.76742400	2.23060800	1.34890200
H	4.44163400	0.28419800	2.18045100

C_1ex Gas Phase

H	2.57896100	-2.76428100	1.34451500
C	1.98104400	-2.12732700	0.70882800
C	1.97978200	-2.12436600	-0.71787600
C	1.07515700	-1.11582100	1.14704000
C	1.07342800	-1.11131800	-1.15023100
H	2.57705000	-2.75820000	-1.35726200
C	0.46238500	-0.50180400	0.00015000
H	0.87981700	-0.85653200	2.17740300
H	0.87621300	-0.84820600	-2.17923600
C	-0.53367300	0.55085900	0.00045400
C	-1.13182300	1.16043200	-1.16030900
C	-1.13395100	1.16354600	1.15867000
C	-2.05898300	2.13837400	-0.71582600
H	-0.91965000	0.91890100	-2.19196000
C	-2.06029800	2.14045500	0.70941700
H	-0.92371400	0.92454400	2.19133800
H	-2.68040700	2.75264000	-1.35082700
H	-2.68288500	2.75655900	1.34150600
C	4.50750200	0.21774300	-0.80194800
C	3.55654200	1.24173700	-1.10659900
C	4.60075700	0.11347700	0.61560400
H	5.04409300	-0.38463700	-1.52060700
C	3.06510800	1.77359900	0.12122500
H	3.24656900	1.54370300	-2.09661700
C	3.70526200	1.07036100	1.18582000
H	5.21916800	-0.58300600	1.16294800
H	2.31210200	2.54084800	0.22668500
H	3.52780800	1.22045600	2.24107700
C	-4.53137100	-0.12072800	0.63831200
C	-4.46125800	-0.20161400	-0.78186400
C	-3.65240500	-1.10292500	1.18054300
H	-5.13207100	0.57593900	1.20499600
C	-3.53739300	-1.23231000	-1.12046600
H	-4.99987200	0.42297100	-1.47989100
C	-3.04042800	-1.79021000	0.09336600
H	-3.47595400	-1.28586500	2.23067300
H	-3.26157600	-1.53370200	-2.12068300
H	-2.31346600	-2.58603000	0.17505800
Fe	2.61912500	-0.27815600	-0.00053200
Fe	-2.58314400	0.24319100	-0.00042900

Potential energy surfaces and vibronic modes for MV BF^+.

Within the borders of PKS model the *overall* vibrational modes of interest couple vibrational modes that are centered on both metal centers. In particular, in the case of the MV $\mathbf{BF}^+$ cation, these new coordinates take the following form:[1]

$$Q_{\pm} = 2^{-1/2}(Q_{Fe^{II}} \pm Q_{Fe^{III}}) \quad (1)$$

where $Q_{Fe^{II}}$ and $Q_{Fe^{III}}$ are stretches localized on Fe^{II} and Fe^{III} centers, respectively. The symmetric combination gives the symmetric stretch and the antisymmetric combination gives the antisymmetric stretch. It was first suggested that, within the PKS model, the symmetric stretch did not significantly contribute to the electron transfer process and thus it can be disregarded in vibronic coupling analyses, while only the antisymmetric stretch, Q_-, should be retained. However, Hush[2] has shown that the symmetric stretch is indeed important and should be considered in the analysis of spectral properties of $\mathbf{BF}^+$. Again, analyses of MV systems in the context of DFT have focused largely on class III compounds such as the Creutz-Taube ion,[3] $[Fe_2(OH)_3(NH_3)_6]^{2+}$, and $[Mn_2(O)_2(NH_3)_8]^{3+}$.[4] These investigations include PES analyses of both the symmetric and antisymmetric stretches, and have successfully reproduced the quadratic, single-welled behavior of the class III complexes as well as the double-welled character of the class II complexes. The vibrations considered in the usual vibronic coupling analyses of the MV complexes are normal modes in which various bond lengths are lengthened or shortened and then frozen while the rest of the molecule optimizes (a so-called *relaxed* scan of the PES). *Rigid* scans can also be created where the identical bond length changes are made as in the *relaxed* scan, but the rest of the molecule does not undergo relaxation, or a partial optimization. In the creation of PESs for high symmetry complexes such as the Creutz-Taube ion, there is certainty that the true symmetric and antisymmetric stretches are being used. However, in the case of $\mathbf{BF}^+$ the

antisymmetric and symmetric stretches are difficult to define due to the fact that, in the C_1 point group, all molecular vibrations will couple to one another.

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