Adsorption and activation of SO_2 and SO_3 over [$Fe(CB_6)$]: A DFT study

Packirisamy Kuzhalmozhi Madarasi[*]

Department of Chemistry, National Institute of Technology Pondicherry, Karaikal – 609 609, India.

Supporting information

SO_2

S	-0.47520660	1.07438015	0.00000000
O	-1.03266405	2.64859144	0.00000000
O	1.19479340	1.07438015	0.00000000

SO_3

S	-0.53719007	-1.38429750	0.00000000
O	-1.15245242	-0.04969029	0.00000000
O	0.92624485	-1.51876828	0.00000000
O	-1.50102254	-2.74808890	0.00000000

$[Fe(CB)_6]$

C	-2.42327075	0.63915891	-0.01846063
B	-0.91235784	1.76600726	0.03591648
B	-2.56410113	-1.22470801	-0.02832883
B	-2.09490811	-0.49476678	-1.49489598
B	-1.33797821	1.04068914	-1.46165513
B	-1.40328622	1.01074647	1.49149240
B	-2.15494724	-0.51917522	1.46144170
Fe	-0.76263263	-0.24896551	0.01072644

$[Fe(CB)_6]$-SO_2

C	-0.33057850	0.06198347	0.00000000
B	-0.28575350	1.63556947	0.56392500
B	-0.37679350	-1.51455453	0.55424600
B	1.01030950	-0.76671353	0.55857200
B	1.05563450	0.80850747	0.56286400
B	-1.67265750	0.88734447	0.55928600
B	-1.71836850	-0.68786353	0.55538500
Fe	-0.33325850	0.05608847	1.95730100
S	-0.33626613	0.04956047	4.12728910

O	0.29027886	1.15457154	4.86628575
O	-0.96484800	-1.05987160	4.85788439

$[Fe(CB)_6]$-SO_2-2

C	2.00525100	0.43282200	0.35424100
B	1.63746300	1.01520200	-1.17058600
B	1.40622800	-0.52041700	1.56554700
B	0.78088000	0.91379800	1.40875200
B	0.94107300	1.71069400	0.04748000
B	2.39580000	-0.37903900	-0.97700500
B	2.22923800	-1.17026300	0.37171600
Fe	0.31327800	-0.40989600	-0.32184600
O	-0.72275196	-1.57833842	-1.25661026
O	-1.46748231	-0.71506349	-0.54131245
S	-2.38714177	-1.47153794	-1.17116893

$[Fe(CB)_6]$-SO_3

C	-0.36231884	0.19667051	-0.00257456
B	-0.73010684	0.77905051	-1.52740156
B	-0.96134184	-0.75656849	1.20873144
B	-1.58668984	0.67764651	1.05193644
B	-1.42649684	1.47454251	-0.30933556
B	0.02823016	-0.61519049	-1.33382056
B	-0.13833184	-1.40641449	0.01490044
Fe	-2.05429184	-0.64604749	-0.67866156
S	-4.11227284	-0.22737149	-0.46302356
O	-4.32423274	0.57687489	0.74858072
O	-4.85952313	-1.48786462	-0.35122807
O	-4.65018049	0.62227489	-1.79631137

$[Fe(CB)_6]$-SO_3-2

C	-0.73360488	-2.20188411	-0.12501136
B	-0.73289588	-3.57956311	-1.00544936
B	0.02135812	-0.81889111	0.36524864
B	0.48576512	-2.19706111	1.01482164
B	0.02593012	-3.57966711	0.37158364
B	-1.19383088	-2.20683011	-1.66649736
B	-0.73586988	-0.82898211	-1.01236636
Fe	1.00782412	-2.20040111	-1.14130636
S	3.02055412	-2.20167911	-0.66089736
O	4.11003612	-2.20322511	0.30361164
O	2.69875212	-0.96121811	-1.48946936
O	2.69900012	-3.43946611	-1.49326336

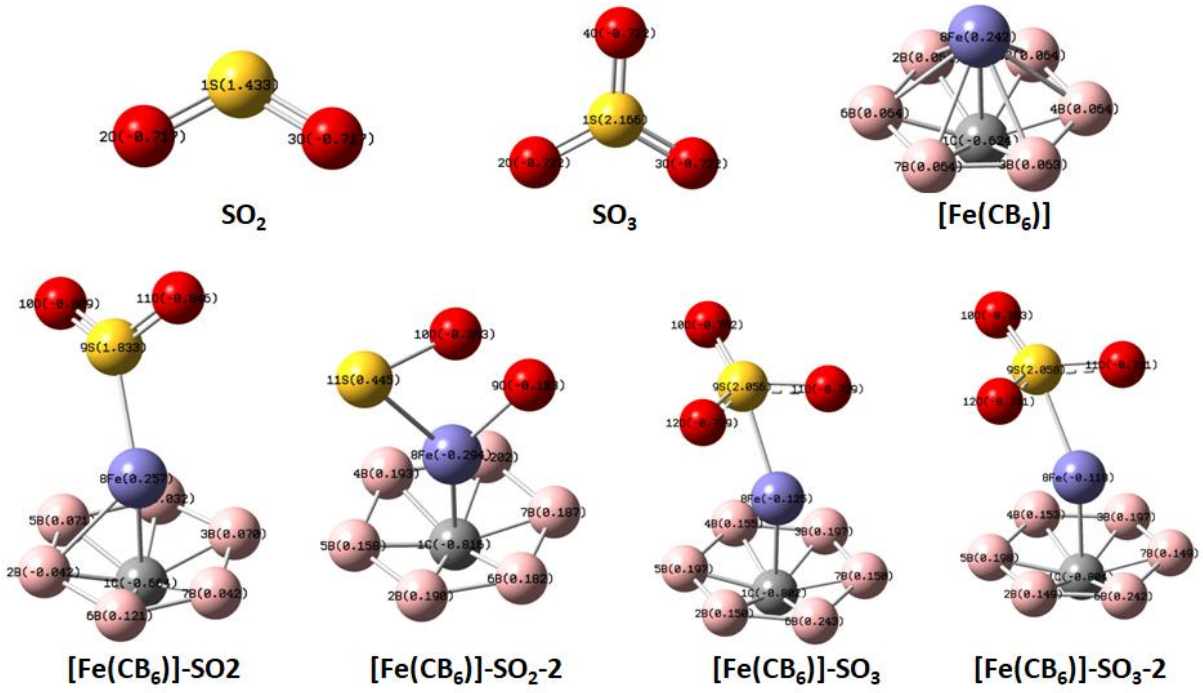

Figure S1: Optimized structures with NBO charges.

Table S1: Natural population analysis (NPA) of optimized structures.

System	Bond	Charge	Population	Contribution (%)	Hybrid
SO_2	S1-O2	S-0.5882	1.99366	S-34.60	$sp^{4.94}$
		O-0.8087		O-65.40	$sp^{4.38}$
	S1-O3	S-5820	1.99917	S-33.88	$sp^{1.00}$
		O-0.8132		O-66.12	$sp^{1.00}$
	S1-O3	S-0.5882	1.99366	S-34.60	$sp^{4.94}$
		O-0.8087		O-65.40	$sp^{4.38}$
SO_3	S1-O2	S-0.6356	1.9796	S-40.39	$sp^{2.00}$
		O-0.7721		O-59.61	$sp^{6.31}$
	S1-O3	S-0.6356	1.976	S-40.39	$sp^{2.00}$
		O-0.7721		O-59.61	$sp^{6.31}$
	S1-O3	S-0.5487	1.99865	S-30.11	$sp^{1.00}$
		O-0.836		O-69.89	$sp^{1.00}$
	S1-O4	S-0.6356	1.9796	S-40.38	$sp^{2.00}$
		O-0.7721		O-59.62	$sp^{6.30}$
[Fe(CB_6)]	C1-B3	C-0.8715	1.58508	C-75.96	$sp^{2.29}d^{0.01}$
		B-0.4903		B-24.04	$sp^{15.81}d^{0.05}$
	C1-B5	C-0.8716	1.58491	C-75.97	$sp^{2.29}d^{0.01}$
		B-0.4902		B-24.03	$sp^{15.83}d^{0.05}$
	C1-B6	C-0.8716	1.58501	C-75.96	$sp^{2.29}d^{0.01}$
		B-0.4903		B-24.04	$sp^{15.81}d^{0.05}$
	B2-B5	B-0.7071	1.9087	B-50.00	$sp^{1.16}$
		B-0.7071		B-50.00	$sp^{1.16}$
	B2-B6	B-0.7071	1.90869	B-50.00	$sp^{1.16}$
		B-0.7071		B-50.00	$sp^{1.16}$
	B3-B4	B-0.7071	1.90867	B-50.00	$sp^{1.16}$
		B-0.7071		B-50.00	$sp^{1.16}$
	B3-B7	B-0.7071	1.90865	B-50.00	$sp^{1.16}$
		B-0.7071		B-50.00	$sp^{1.16}$
	B4-B5	B-0.7071	1.90871	B-50.00	$sp^{1.16}$
		B-0.7071		B-50.00	$sp^{1.16}$
	B6-B7	B-0.7071	1.90867	B-50.00	$sp^{1.16}$
		B-0.7071		B-50.00	$sp^{1.16}$
[Fe(CB_6)]-SO_2	S9-O10	0.6112	1.98787	S-37.35	$sp^{3.69}$
		0.7915		O-62.65	$sp^{4.32}$
	S9-O11	0.6053	1.98767	S-36.63	$sp^{4.27}$
		0.796		O-63.37	$sp^{4.50}$
[Fe(CB_6)]-SO_2-2	Fe8-S11	0.6237	1.93656	Fe-38.90	$sp^{2.59}d^{9.77}$
		0.7817		S-61.10	$sp^{6.13}$

	O10-S11	0.8595	1.93198	O-73.87	$sp^{4.54}$
		0.5112		S-26.13	$sp^{23.64}$
[Fe(CB$_6$)]-SO$_3$	S9-O10	0.6411	1.97567	S-41.10	$sp^{1.82}$
		0.7675		O-58.90	$sp^{5.72}$
	S9-O11	0.6218	1.95846	S-38.67	$sp^{2.45}$
		0.7832		O-61.33	$sp^{6.23}$
	S9-O12	0.6218	1.95851	S-38.67	$sp^{2.45}$
		0.7832		O-61.33	$sp^{6.23}$
[Fe(CB$_6$)]-SO$_3$-2	S9-O10	0.6409	1.97565	S-41.08	$sp^{1.82}$
		0.7676		O-458.92	$sp^{5.71}$
	S9-O11	0.6219	1.95887	S-38.67	$sp^{2.45}$
		0.7831		O-61.33	$sp^{6.23}$
	S9-O12	0.6219	1.95889	S-38.68	$sp^{2.45}$
		0.7831		O-61.32	$sp^{6.23}$