Supporting information for

Electronic structure investigation and parameterization of biologically relevant ironsulfur clusters

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08010 Barcelona, Spain

Type of cluster	Bond	K _r	r _{eq}
[Fe ₂ S ₂] ²⁺	F2-S2	88.2	2.21
	F2-S1	63.3	2.32
			·
	F2-S2	52.6	2.29
[Fe ₂ S ₂] ⁺	FR-S2	90.1	2.21
12~ 21	F2-S1	39.3	2.34
	FR-S1	46.1	2.38
	FA-S2	80.7	2.22
	FA-S3	63.0	2.28
[Fe ₂ S ₄] ⁺	FB-S2	104.5	2.19
15~41	FB-S3	66.6	2.26
	FA-S1	82.0	2.25
	FB-S1	82.0	2.25
	FA-S2	68.5	2.27
	FA-S3	52.5	2.33
[Fe ₂ S ₁] ⁰	FC-S2	79.0	2.24
	FC-S3	64.0	2.27
	FA-S1	56.2	2.35
	FC-S1	68.9	2.32
	·	·	·
	FU-SU	60.0	2.35
	FD-SD	60.0	2.35
[Fe.S.] ²⁺	FU-S1	82.8	2.28
[1 0404]	FD-SU	75.3	2.22
	FU-SD	75.3	2.22
	FD-S1	82.8	2.28
	·	·	·
	F4-S3	55.2	2.31
	FY-S3	55.2	2.31
[Fe.S.] ⁺	F4-S1	60.9	2.31
	S1-FY	60.9	2.31
	SY-FY	76.4	2.23
	F4-SY	55.2	2.31
	S1-CT	154.2	1.82

 Table S1. Bond stretching force constants and equilibrium distances.

$[Fe_2S_2]^{2+}$	MD	QM	$[Fe_2S_2]^+$	MD	QM1	QM2	X-ray
F2-S1	2 28+0 07	2 32	F2-S1	2.22±0.09	2.34	2.31	2 33
12.51	2.20.01	2.52	FR-S1	2.29±0.08	2.38	2.33	2.55
F2-S2	2 2+0 06	2.21	F2-S2	2.18±0.06	2.21	2.24	2.06
12 52	2.220.000	2.21	FR-S2	2.24±0.07	2.29	2.27	2.00
\$1-F2-\$1	126.13+6.76	109.10	S1-F2-S1	100.96±8.19	108.2	103.2	100.0
5112 51	12011020110	105.10	S1-FR-S1	106.76±7.59	105.6	109.4	10010
\$1-F2-\$2	100 76+10 46	110 50	S1-F2-S2	120.6±9.62	110.2	112.4	113.6
511252	100000210000	110.00	S1-FR-S2	88.70±10.07	107.1	110.8	11010
CT-CT-S1-F2	-57.72±12.29		C-C-S1-F2	-51.46±15.27		-58.6	-59.3
CT-CT-S1-Fe	-95.99±10.52		C-C-S1-F2	-65.75±15.83		-65.4	-61.2
CT-CT-S1-Fe	-120.96±9.91		C-C-S1-FR	107.16±7.57		109.8	103.1
CT-CT-S1-Fe	-138.94±8.55		C-C-S1-FR	-128.66±9.12		-128.0	-115.3

Table S2A. Comparison of the Bonds and angles for $[Fe_2S_2]^{2+}/[Fe_2S_2]^+$.

$[{\rm Fe}_4 {\rm S}_4]^{2+}$	MD	QM	[Fe₄S₄]⁺	MD	QM	X-ray
FD-S1 /	2.28±0.06	2.28	F4-S1 /	2.30±0.07	2.31	2.34±0.10
FU-S1			FY-S1			
FD-SU /	2.22±0.06	2.22	FY-SY	2.26±0.07	2.23	2.21±0.18
FU-SD						
FU-SU /			F4-S3 /			
FD-SD	2.35±0.07	2.35	FY-S3 /	2.30±0.07	2.31	2.31±0.26
			F4-SY			
CT-S1-FU /	110.0±5.8	104.9	CT-S1-F4 /	106.7±6.7	105.6	107.9±19.4
CT-S1-FD			CT-S1-FY			
FD-SD-FU /	73.4±4.4	73				79.3±2.9
FU-SU-FD			F4/Y-S3-F4/Y	73.7±4.71	71.5	
FD-SD-FD /	75.3±4.0	71.3				77.4±2.3
FU-SU-FU						
CT-CT-S1-FU	76.9±10.2		CT-CT-S1-F4	71.15±12.5		65.106
CT-CT-S1-FU	-104.1±7.5		CT-CT-S1-F4	-100.27±8.47		-111.012
CT CT S1 ED	50 8+30 0		CT CT S1 EV	50.4+26.01		51 756
	-50.0150.9		01-01-51-11	-50.4120.01		-51.750
CT-CT-S1-FD	83.4±9.5		CT-CT-S1-FY	89.2±16.4		86.666

Table S2B. Comparison of the Bonds and angles for $[Fe_4S_4]^{2+}/[Fe_4S_4]^+$.

[Fe ₃ S ₄] ⁺	MD	QM	[Fe ₃ S ₄] ⁰	MD	QM	X-ray
FA-S1/FB-S1	2.25±0.06	2.25	FA-S1	2.34±0.07	2.35	2.33±0.13
			FC-S1	2.32±0.07	2.32	
FA-S2	2.21±0.06	2.22	FA-S2	2.25±0.07	2.27	2.07±0.13
FA-S3	2.27±0.07	2.28	FA-S3	2.31±0.07	2.33	2.03±0.03
FB-S2	2.19±0.05	2.19	FC-S2	2.23±0.06	2.24	2.12±0.31
FB-S3	2.25±0.06	2.26	FC-S3	2.24±0.07	2.23	2.36
CT-S1-FA/C	104.4±6.6	106.8	CT-S1-FA/C	97.2±5.4	105.1	109.8±6.3
FA-S2-FB	72.9±3.9	71.5	FA-S2-FA	75.3±4.1	69.8	81.4±17.4
FA-S2-FA	75.2±5.3	74.1	FA-S2-FC	72.6±4.3	73.8	67.4
FA-S3-FB	70.6±3.8	69.3	FA-S3-FA	73.0±4.1	68.8	76.7±8.6
FA-S3-FA	72.4±5	71.7	FA-S3-FC	71.2±4.3	72	67.4
CT-CT-S1-FA	104.7±8.50		CT-CT-S1-FC	106.9±8.3		103.6
CT-CT-S1-FA	60.3±11.4		CT-CT-S1-FA	75.70±13.5		69.9
CT-CT-S1-FB	-118.08±7.89		CT-CT-S1-FA	-117.21±7.4		-106.3

Table S2C. Comparison of the Bonds and angles for $[Fe_3S_4]^+/ [Fe_3S_4]^0$.

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12~ 21	F2-S1	39.3	2.34
	FR-S1	46.1	2.38
	FA-S2	80.7	2.22
	FA-S3	63.0	2.28
[Fe ₂ S ₄] ⁺	FB-S2	104.5	2.19
15~41	FB-S3	66.6	2.26
	FA-S1	82.0	2.25
	FB-S1	82.0	2.25
	FA-S2	68.5	2.27
	FA-S3	52.5	2.33
[Fe ₂ S ₁] ⁰	FC-S2	79.0	2.24
	FC-S3	64.0	2.27
	FA-S1	56.2	2.35
	FC-S1	68.9	2.32
	·	·	·
	FU-SU	60.0	2.35
	FD-SD	60.0	2.35
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	FY-S3	55.2	2.31
[Fe.S.] ⁺	F4-S1	60.9	2.31
	S1-FY	60.9	2.31
	SY-FY	76.4	2.23
	F4-SY	55.2	2.31
	S1-CT	154.2	1.82

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F2-S1	2 28+0 07	2 32	F2-S1	2.22±0.09	2.34	2.31	2 33
12.51	2.20.01	2.52	FR-S1	2.29±0.08	2.38	2.33	2.55
F2-S2	2 2+0 06	2.21	F2-S2	2.18±0.06	2.21	2.24	2.06
12 52	2.220.000	2.21	FR-S2	2.24±0.07	2.29	2.27	2.00
\$1-F2-\$1	126.13+6.76	109.10	S1-F2-S1	100.96±8.19	108.2	103.2	100.0
5112 51	12011020110	105.10	S1-FR-S1	106.76±7.59	105.6	109.4	10010
\$1-F2-\$2	100 76+10 46	110 50	S1-F2-S2	120.6±9.62	110.2	112.4	113.6
511252	100000210000	110.00	S1-FR-S2	88.70±10.07	107.1	110.8	11010
CT-CT-S1-F2	-57.72±12.29		C-C-S1-F2	-51.46±15.27		-58.6	-59.3
CT-CT-S1-Fe	-95.99±10.52		C-C-S1-F2	-65.75±15.83		-65.4	-61.2
CT-CT-S1-Fe	-120.96±9.91		C-C-S1-FR	107.16±7.57		109.8	103.1
CT-CT-S1-Fe	-138.94±8.55		C-C-S1-FR	-128.66±9.12		-128.0	-115.3

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$[{\rm Fe}_4 {\rm S}_4]^{2+}$	MD	QM	[Fe₄S₄]⁺	MD	QM	X-ray
FD-S1 /	2.28±0.06	2.28	F4-S1 /	2.30±0.07	2.31	2.34±0.10
FU-S1			FY-S1			
FD-SU /	2.22±0.06	2.22	FY-SY	2.26±0.07	2.23	2.21±0.18
FU-SD						
FU-SU /			F4-S3 /			
FD-SD	2.35±0.07	2.35	FY-S3 /	2.30±0.07	2.31	2.31±0.26
			F4-SY			
CT-S1-FU /	110.0±5.8	104.9	CT-S1-F4 /	106.7±6.7	105.6	107.9±19.4
CT-S1-FD			CT-S1-FY			
FD-SD-FU /	73.4±4.4	73				79.3±2.9
FU-SU-FD			F4/Y-S3-F4/Y	73.7±4.71	71.5	
FD-SD-FD /	75.3±4.0	71.3				77.4±2.3
FU-SU-FU						
CT-CT-S1-FU	76.9±10.2		CT-CT-S1-F4	71.15±12.5		65.106
CT-CT-S1-FU	-104.1±7.5		CT-CT-S1-F4	-100.27±8.47		-111.012
CT CT S1 ED	50 8+30 0		CT CT S1 EV	50.4+26.01		51 756
	-50.0150.9		01-01-51-11	-50.4120.01		-51.750
CT-CT-S1-FD	83.4±9.5		CT-CT-S1-FY	89.2±16.4		86.666

Table S2B. Comparison of the Bonds and angles for $[Fe_4S_4]^{2+}/[Fe_4S_4]^+$.

[Fe ₃ S ₄] ⁺	MD	QM	[Fe ₃ S ₄] ⁰	MD	QM	X-ray
FA-S1/FB-S1	2.25±0.06	2.25	FA-S1	2.34±0.07	2.35	2.33±0.13
			FC-S1	2.32±0.07	2.32	
FA-S2	2.21±0.06	2.22	FA-S2	2.25±0.07	2.27	2.07±0.13
FA-S3	2.27±0.07	2.28	FA-S3	2.31±0.07	2.33	2.03±0.03
FB-S2	2.19±0.05	2.19	FC-S2	2.23±0.06	2.24	2.12±0.31
FB-S3	2.25±0.06	2.26	FC-S3	2.24±0.07	2.23	2.36
CT-S1-FA/C	104.4±6.6	106.8	CT-S1-FA/C	97.2±5.4	105.1	109.8±6.3
FA-S2-FB	72.9±3.9	71.5	FA-S2-FA	75.3±4.1	69.8	81.4±17.4
FA-S2-FA	75.2±5.3	74.1	FA-S2-FC	72.6±4.3	73.8	67.4
FA-S3-FB	70.6±3.8	69.3	FA-S3-FA	73.0±4.1	68.8	76.7±8.6
FA-S3-FA	72.4±5	71.7	FA-S3-FC	71.2±4.3	72	67.4
CT-CT-S1-FA	104.7±8.50		CT-CT-S1-FC	106.9±8.3		103.6
CT-CT-S1-FA	60.3±11.4		CT-CT-S1-FA	75.70±13.5		69.9
CT-CT-S1-FB	-118.08±7.89		CT-CT-S1-FA	-117.21±7.4		-106.3

Table S2C. Comparison of the Bonds and angles for $[Fe_3S_4]^+/ [Fe_3S_4]^0$.

 Table S3 – Angle bending force constants and equilibrium values.

Type of cluster	Angle	$K_{ heta}$	$ heta_{eq}$
	S2-F2-S2	20.2	75.20
$[Fe_2S_4]^{2+}$	S2-F2-S1	14.6	110.50
	F2-S2-F2	20.3	104.80
	S1-F2-S1	10.1	109.05
	F2-S2-F3	16.6	75.60
	S2-F3-S1	12.8	107.40
	S2-F2-S2	14.2	101.80
	S2-F3-S2	20.8	107.10
[Fe ₂ S ₄]+	S2-F2-S1	8.9	110.20
	F2-S1-CT	10.9	109.60
	F3-S1-CT	15.8	104.40
	S1-F2-S1	8.2	108.20
	\$1-F3-\$1	8.3	105.60
	CT-S1-FA	11.5	106.80
	CT-S1-FB	11.5	106.80
	FA-S2-FB	21.0	71.50
	FA-S3-FA	6.0	71.70
	FA-S2-FA	6.1	74.10
	FA-S3-FB	15.7	69.30
	S1-FA-S2	11.1	112.20
[Fe354]	S1-FA-S3	9.2	112.20
	S1-FB-S2	6.8	107.50
	S1-FB-S3	7.8	115.00
	S2-FA-S2	13.8	112.20
	S2-FA-S3	9.5	103.60
	S2-FB-S2	5.6	113.20
	S2-FB-S3	13.3	106.80
	CT-S1-FA	8.6	105.10
	CT-S1-FC	8.6	105.10
	FA-S2-FC	13.5	73.80
	FA-S3-FA	14.4	68.80
[FeeS.10	FA-S2-FA	18.0	69.80
[I [·] C354] [°]	FA-S3-FC	9.8	72.00
	S1-FA-S2	11.0	110.60
	S1-FA-S3	5.0	112.00
	S1-FC-S2	8.4	110.80
	\$1-FC-\$3	17.6	114.20

S2-FA-S2 10.0 116.00 S2-FA-S3 11.8 104.00 S2-FC-S2 6.6 112.90 S2-FC-S3 13.0 104.00 S2-FC-S3 13.0 104.00 S2-FC-S3 13.0 107.00 SU-FU-SU 7.0 107.00 SD-FD-SD 7.0 107.00 SD-FD-SU 13.0 104.50 SU-FU-SU 13.0 104.50 SU-FU-SU 13.0 104.50 SU-FU-SU 10.5 73.00 FU-SU-FD 10.5 73.00 SU-FU-S1 12.1 110.00 SU-FU-S1 12.8 120.00 SU-FU-S1 12.8 120.00 FU-SU-FU 8.5 71.30 FU-SU-FU 8.5 71.30 FU-SU-FU 18.2 104.90 CT-SI-FU 18.2 105.40 S3-F4-S1 11.0 113.20 F4-S1-FU 18.2 105.40 S3-F4-S1 11.0		1	1	1
S2-FA-S311.8104.00S2-FC-S26.6112.90S2-FC-S313.0104.00S2-FC-S313.0104.00SU-FU-S07.0107.00S0-FD-S07.0107.00S0-FD-S07.0104.50S0-FD-S013.0104.50S0-FD-S013.0104.50S0-FD-S113.0104.50FD-SD-FU10.573.00FU-SU-FD10.573.00S0-FD-S112.1110.00S0-FD-S112.1110.00S0-FD-S112.8120.00S0-FD-S112.8120.00FU-SU-FU8.571.30FU-SU-FU8.571.30FD-SD-FD8.571.30FD-SD-FD8.571.30CT-S1-FU18.2104.90CT-S1-FU18.2104.90CT-S1-FU18.2105.40S3-F4-S111.0113.20F4-S1-FD58.671.50S3-F4-S111.0113.20F4-S1-FS11.0113.20F4-S1-FS11.0113.20F4-S1-FS8.871.50S3-FY-S111.0113.20F4-S1-FS8.871.50S3-FY-S18.871.50S3-FY-S18.871.50S3-FY-S18.871.50S3-FY-S18.871.50S3-FY-S18.871.50S3-FY-S18.871.50S3-FY-S18.871.50S3-FY-S1 <td></td> <td>S2-FA-S2</td> <td>10.0</td> <td>116.00</td>		S2-FA-S2	10.0	116.00
S2-FC-S26.6112.90S2-FC-S313.0104.00SU-FU-S07.0107.00S0-FD-SD7.0107.00S0-FD-SU13.0104.50S0-FD-SU13.0104.50FD-SD-FU10.573.00FU-SU-FD10.573.00FU-SU-FD10.573.00S0-FD-S112.1110.00S0-FD-S112.1110.00S0-FD-S112.8120.00S0-FU-S112.8120.00S0-FU-S112.8120.00FU-SU-FU8.571.30FU-SU-FU8.571.30FD-SD-FD8.571.30FD-SD-FD8.571.30FD-SD-FD8.571.30FU-SU-FU18.2104.90CT-S1-FU18.2104.90CT-S1-FU18.2105.40S3-F4-S111.0113.20F4-S1-FD58.775.0S3-F4-S111.0113.20F4-S1-FS8.871.50S3-FY-S38.2105.40S3-FY-S111.0113.20F4-S1-FS11.0113.20F4-S1-FS8.871.50S3-FY-S18.871.50S3-FY-S18.871.50S3-FY-SY8.871.50S3-FY-SY8.871.50S3-FY-SY8.871.50S3-FY-SY8.871.50S3-FY-SY8.871.50S3-FY-SY8.871.50S3-FY-SY		S2-FA-S3	11.8	104.00
S2-FC-S313.0104.00SU-FU-SU7.0107.00SD-FD-SD7.0107.00SD-FD-SU13.0104.50SU-FU-SD13.0104.50SU-FU-SD13.0104.50SU-FU-SD10.573.00FU-SU-FD10.573.00FU-SU-FD10.573.00SU-FU-S112.1110.00SD-FD-S112.8120.00SU-FU-S112.8120.00FU-SU-FU8.571.30FU-SU-FU8.571.30FD-SD-FD8.571.30FD-SD-FD8.571.30CT-S1-FU18.2104.90CT-S1-FU18.2104.90CT-S1-FU18.2105.40S3-F4-S38.2105.40S3-F4-S111.0113.20F4-S1-CT15.6105.60F4-S3-F48.871.50S3-FY-S38.2105.40S3-FY-S111.0113.20FY-S1-CT15.6105.60FY-S3-FY8.871.50S1-F4-SY8.871.50S1-F4-SY8.871.50S1-F4-SY8.871.50S3-FY-SY8.2105.40F4-SY-FY8.871.50S1-F4-SY8.871.50S1-F4-SY8.871.50S1-F4-SY8.871.50S1-F4-SY8.871.50S1-F4-SY8.871.50S1-F4-SY8.871.50S1-F4-SY8.		S2-FC-S2	6.6	112.90
SU-FU-SU 7.0 107.00 SD-FD-SD 7.0 107.00 SD-FD-SU 13.0 104.50 SU-FU-SD 13.0 104.50 SU-FU-SD 13.0 104.50 FD-SD-FU 10.5 73.00 FU-SU-FD 10.5 73.00 FU-SU-FD 10.5 73.00 SU-FU-S1 12.1 110.00 SD-FD-S1 12.8 120.00 SU-FD-S1 12.8 120.00 FU-SU-FU 8.5 71.30 FD-SD-FD 8.5 71.30 FD-SD-FD 8.5 71.30 CT-S1-FU 18.2 104.90 CT-S1-FU 18.2 104.90 CT-S1-FU 18.2 105.40 S3-F4-S3 8.2 105.40 S3-F4-S3 8.2 105.40 S3-F4-S1 11.0 113.20 F4-S1-CT 15.6 105.60 F4-S3-F4 8.8 71.50 S3-F4-S1 11.0		\$2-FC-\$3	13.0	104.00
SU-FU-SU7.0107.00SD-FD-SD7.0107.00SD-FD-SU13.0104.50SD-FD-SU13.0104.50FD-SD-FU10.573.00FU-SU-FD10.573.00SU-FU-S112.1110.00SD-FD-S112.1110.00SD-FD-S112.8120.00SD-FD-S112.8120.00SU-FD-S112.8120.00FU-SU-FU8.571.30FD-SD-FD8.571.30FD-SD-FD8.571.30CT-S1-FU18.2104.90CT-S1-FU18.2104.90CT-S1-FU18.2104.90CT-S1-FU18.2105.40S3-F4-S38.2105.40S3-F4-S48.871.50S3-F4-S511.0113.20F4-S1-CT15.6105.60F4-S3-F48.871.50S1-F4-SY11.0113.20S1-F4-SY8.871.50S1-F4-SY8.871.50S1-F4-SY8.871.50S1-F4-SY8.871.50S1-F4-SY8.871.50F4-S1-FY8.871.50S1-F4-SY8.871.50S1-F4-SY8.871.50S1-F4-SY8.871.50S1-F4-SY8.871.50F4-S1-FY8.871.50F4-S1-FY8.871.50F4-S1-FY8.871.50F4-S1-FY8.871.50F4-S1-FY8.8<				1
SD-FD-SD7.0107.00SD-FD-SU13.0104.50SD-FD-SU13.0104.50FD-SD-FU10.573.00FU-SU-FD10.573.00SU-FU-S112.1110.00SD-FD-S112.1110.00SD-FD-S112.8120.00SD-FD-S112.8120.00SU-FD-S112.8120.00FU-SU-FU8.571.30FD-SD-FD8.571.30CT-S1-FU18.2104.90CT-S1-FU18.2104.90CT-S1-FU18.2104.90CT-S1-FU18.2105.40S3-F4-S38.2105.40S3-F4-S48.871.50F4-S1-CT15.6105.60F4-S3-F48.871.50S3-FY-S111.0113.20FY-S1-CT15.6105.60FY-S3-FY8.871.50S1-F4-SY11.0113.20S3-F4-SY8.871.50S1-F4-SY8.871.50S1-F4-SY8.871.50F4-S1-FY8.871.50S1-F4-SY8.871.50S1-F4-SY8.871.50F4-S1-FY8.871.50F4-S1-FY8.871.50S1-F4-SY8.871.50F4-S1-FY8.871.50F4-S1-FY8.871.50F4-S1-FY8.871.50F4-S1-FY8.871.50F4-S1-FY8.871.50F4-S1-FY8.8		SU-FU-SU	7.0	107.00
SD-FD-SU 13.0 104.50 SU-FU-SD 13.0 104.50 FD-SD-FU 10.5 73.00 FU-SU-FD 10.5 73.00 SU-FU-S1 12.1 110.00 SD-FD-S1 12.1 110.00 SD-FD-S1 12.8 120.00 SU-FD-S1 12.8 120.00 SU-FD-S1 12.8 120.00 FU-SU-FU 8.5 71.30 FD-SD-FD 8.5 71.30 CT-S1-FU 18.2 104.90 CT-S1-FD 18.2 104.90 CT-S1-FD 18.2 105.40 S3-F4-S3 8.2 105.40 S3-F4-S1 11.0 113.20 F4-S1-CT 15.6 105.60 F4-S3-F4 8.8 71.50 S3-FY-S3 8.2 105.40 S3-FY-S1 11.0 113.20 FY-S1-CT 15.6 105.60 FY-S1-FY 8.8 71.50 S1-F4-SY 11.0 <td></td> <td>SD-FD-SD</td> <td>7.0</td> <td>107.00</td>		SD-FD-SD	7.0	107.00
SU-FU-SD 13.0 104.50 FD-SD-FU 10.5 73.00 FU-SU-FD 10.5 73.00 SU-FU-S1 12.1 110.00 SD-FD-S1 12.1 110.00 SD-FU-S1 12.8 120.00 SU-FD-S1 12.8 120.00 SU-FD-S1 12.8 120.00 FU-SU-FU 8.5 71.30 FD-SD-FD 8.5 71.30 CT-S1-FU 18.2 104.90 CT-S1-FD 18.2 104.90 CT-S1-FD 18.2 104.90 CT-S1-FD 18.2 105.40 S3-F4-S3 8.2 105.40 S3-F4-S1 11.0 113.20 F4-S1-CT 15.6 105.60 F4-S3-F4 8.8 71.50 S3-FY-S3 8.2 105.40 S3-FY-S1 11.0 113.20 FV-S1-CT 15.6 105.60 FY-S3-FY 8.8 71.50 S1-F4-SY 11.0 <td></td> <td>SD-FD-SU</td> <td>13.0</td> <td>104.50</td>		SD-FD-SU	13.0	104.50
FD-SD-FU 10.5 73.00 FU-SU-FD 10.5 73.00 SU-FU-S1 12.1 110.00 SD-FD-S1 12.1 110.00 SD-FU-S1 12.8 120.00 SU-FD-S1 12.8 120.00 SU-FD-S1 12.8 120.00 FU-SU-FU 8.5 71.30 FD-SD-FD 8.5 71.30 CT-S1-FU 18.2 104.90 CT-S1-FD 18.2 104.90 CT-S1-FD 18.2 105.40 S3-F4-S3 8.2 105.40 S3-F4-S1 11.0 113.20 F4-S1-CT 15.6 105.60 F4-S1-F4 8.8 71.50 S3-FY-S3 8.2 105.40 S3-FY-S1 11.0 113.20 FY-S1-CT 15.6 105.60 FY-S1-FY 8.8 71.50 S3-FY-S1 11.0 113.20 S1-F4-SY 11.0 113.20 S3-F4-SY 8.2 <td></td> <td>SU-FU-SD</td> <td>13.0</td> <td>104.50</td>		SU-FU-SD	13.0	104.50
FU-SU-FD 10.5 73.00 SU-FU-S1 12.1 110.00 SD-FD-S1 12.1 110.00 SD-FU-S1 12.8 120.00 SU-FD-S1 12.8 120.00 FU-SU-FU 8.5 71.30 FD-SD-FD 8.5 71.30 CT-S1-FU 18.2 104.90 CT-S1-FD 18.2 104.90 CT-S1-FD 18.2 105.40 S3-F4-S3 8.2 105.40 S3-F4-S1 11.0 113.20 F4-S1-CT 15.6 105.60 F4-S1-F4 8.8 71.50 S3-F4-S3 8.2 105.40 S3-F4-S1 11.0 113.20 F4-S1-CT 15.6 105.60 F4-S3-F4 8.8 71.50 S3-F4-S3 8.2 105.40 S3-F4-S4 8.8 71.50 S3-F4-S4 8.8 71.50 S3-F4-S4 8.8 71.50 S3-F4-S4 8.8		FD-SD-FU	10.5	73.00
[Fe,S_] ²⁺ SU-FU-S1 12.1 110.00 SD-FD-S1 12.1 110.00 SD-FU-S1 12.8 120.00 SU-FD-S1 12.8 120.00 FU-SU-FU 8.5 71.30 FD-SD-FD 8.5 71.30 CT-S1-FU 18.2 104.90 CT-S1-FU 18.2 104.90 CT-S1-FD 18.2 105.40 S3-F4-S3 8.2 105.40 S3-F4-S1 11.0 113.20 F4-S1-CT 15.6 105.60 F4-S3-F4 8.8 71.50 S3-FY-S3 8.2 105.40 S3-FY-S3 8.2 105.40 S3-FY-S3 8.2 105.40 FY-S1-CT 15.6 105.60 FY-S3-FY 8.8 71.50 S1-F4-SY 11.0 113.20 S1-F4-SY 11.0 113.20 S3-FY-S4 8.2 105.40 S3-FY-S7 8.2 105.40 F4-S7-		FU-SU-FD	10.5	73.00
[Fe ₄ S ₄] ²⁺ SD-FD-S1 12.1 110.00 SD-FU-S1 12.8 120.00 SU-FD-S1 12.8 120.00 FU-SU-FU 8.5 71.30 FD-SD-FD 8.5 71.30 CT-S1-FU 18.2 104.90 CT-S1-FD 18.2 104.90 CT-S1-FD 18.2 104.90 S3-F4-S3 8.2 105.40 S3-F4-S1 11.0 113.20 F4-S1-CT 15.6 105.60 F4-S3-F4 8.8 71.50 S3-F4-S1 11.0 113.20 F4-S1-CT 15.6 105.60 F4-S3-F4 8.8 71.50 S3-F4-S1 11.0 113.20 F4-S1-CT 15.6 105.60 FY-S1-CT 15.6 105.60 FY-S1-CT 15.6 105.60 FY-S1-CT 15.6 105.40 S3-F4-SY 8.8 71.50 S1-F4-SY 10.0 113.20 <td< td=""><td></td><td>SU-FU-S1</td><td>12.1</td><td>110.00</td></td<>		SU-FU-S1	12.1	110.00
SD-FU-S1 12.8 120.00 SU-FD-S1 12.8 120.00 FU-SU-FU 8.5 71.30 FD-SD-FD 8.5 71.30 CT-S1-FU 18.2 104.90 CT-S1-FD 18.2 104.90 CT-S1-FD 18.2 105.40 S3-F4-S3 8.2 105.40 S3-F4-S1 11.0 113.20 F4-S1-CT 15.6 105.60 F4-S3-F4 8.8 71.50 S3-FY-S3 8.2 105.40 S3-FY-S3 8.2 105.40 S3-FY-S3 8.2 105.40 S3-FY-S1 11.0 113.20 FY-S1-CT 15.6 105.60 FY-S3-FY 8.8 71.50 S1-F4-SY 11.0 113.20 S3-F4-SY 8.8 71.50 S1-FY-SY 8.8 71.50 S3-FY-SY 8.2 105.40 S3-FY-SY 8.2 105.40 S3-FY-SY 8.2	[Fe ₄ S ₄] ²⁺	SD-FD-S1	12.1	110.00
SU-FD-S1 12.8 120.00 FU-SU-FU 8.5 71.30 FD-SD-FD 8.5 71.30 CT-S1-FU 18.2 104.90 CT-S1-FD 18.2 104.90 CT-S1-FD 18.2 105.40 S3-F4-S3 8.2 105.40 S3-F4-S1 11.0 113.20 F4-S1-CT 15.6 105.60 F4-S1-CT 15.6 105.60 F4-S3-F4 8.8 71.50 S3-FY-S3 8.2 105.40 S3-FY-S3 8.2 105.40 S3-FY-S3 8.2 105.40 S3-FY-S1 11.0 113.20 FY-S1-CT 15.6 105.60 FY-S3-FY 8.8 71.50 S1-F4-SY 11.0 113.20 S3-F4-SY 8.2 105.40 S3-F4-SY 8.2 105.40 S3-F4-SY 8.2 105.40 S3-F4-SY 8.2 105.40 S3-F4-SY 8.8		SD-FU-S1	12.8	120.00
FU-SU-FU 8.5 71.30 FD-SD-FD 8.5 71.30 CT-S1-FU 18.2 104.90 CT-S1-FD 18.2 104.90 CT-S1-FD 18.2 105.40 S3-F4-S3 8.2 105.40 S3-F4-S1 11.0 113.20 F4-S1-CT 15.6 105.60 F4-S1-F4 8.8 71.50 S3-FY-S3 8.2 105.40 S3-FY-S1 11.0 113.20 FY-S1-CT 15.6 105.60 FY-S3-FY 8.8 71.50 S1-F4-SY 11.0 113.20 S3-FY-SY 11.0 113.20 S3-FY-SY 8.2 105.40 S3-FY-SY 8.2 105.40 F4-SY-FY 8.8 71.50 SY-F4-SY 8.2		SU-FD-S1	12.8	120.00
FD-SD-FD 8.5 71.30 CT-S1-FU 18.2 104.90 CT-S1-FD 18.2 104.90 CT-S1-FD 18.2 105.40 S3-F4-S3 8.2 105.40 S3-F4-S1 11.0 113.20 F4-S1-CT 15.6 105.60 F4-S3-F4 8.8 71.50 S3-FY-S3 8.2 105.40 S3-FY-S1 11.0 113.20 FY-S1-CT 15.6 105.60 FY-S3-FY 8.8 71.50 S1-F4-SY 11.0 113.20 S3-FY-SY 8.2 105.40 S3-FY-SY 8.2 105.40 F4-SY-FY 8.8 71.50 F4-S3-FY 8.8 71.50 F4-S3-FY 8.8		FU-SU-FU	8.5	71.30
CT-S1-FU18.2104.90CT-S1-FD18.2104.90CT-S1-FD18.2104.90S3-F4-S38.2105.40S3-F4-S111.0113.20F4-S1-CT15.6105.60F4-S3-F48.871.50S3-FY-S38.2105.40S3-FY-S111.0113.20FY-S1-CT15.6105.60FY-S1-CT15.6105.60FY-S3-FY8.871.50S1-F4-SY11.0113.20S3-F4-SY8.2105.40S3-F4-SY8.2105.40S3-F4-SY8.2105.40F4-SY-FY8.871.50F4-S3-FY8.871.50F4-SY-FY8.871.50F4-SY-FY8.871.50F4-SY-FY8.871.50F4-SY-FY8.871.50F4-SY-FY8.871.50F4-SY-FY8.871.50F4-SY-FY8.871.50		FD-SD-FD	8.5	71.30
CT-S1-FD 18.2 104.90 S3-F4-S3 8.2 105.40 S3-F4-S1 11.0 113.20 F4-S1-CT 15.6 105.60 F4-S3-F4 8.8 71.50 S3-FY-S3 8.2 105.40 S3-FY-S1 11.0 113.20 F4-S1-CT 15.6 105.60 S3-FY-S3 8.2 105.40 S3-FY-S1 11.0 113.20 FY-S1-CT 15.6 105.60 FY-S3-FY 8.8 71.50 S1-F4-SY 11.0 113.20 FY-S3-FY 8.8 71.50 S1-F4-SY 11.0 113.20 S3-F4-SY 8.2 105.40 S3-F4-SY 8.2 105.40 S3-F4-SY 8.2 105.40 F4-SY-FY 8.8 71.50 F4-SY-FY 8.8 71.50 F4-SY-FY 8.8 71.50 F4-SY-FY 8.8 71.50 F4-SY-FY 8.8		CT-S1-FU	18.2	104.90
S3-F4-S3 8.2 105.40 S3-F4-S1 11.0 113.20 F4-S1-CT 15.6 105.60 F4-S3-F4 8.8 71.50 S3-FY-S3 8.2 105.40 S3-FY-S3 8.2 105.40 S3-FY-S3 8.2 105.40 S3-FY-S3 8.2 105.40 S3-FY-S1 11.0 113.20 FY-S1-CT 15.6 105.60 FY-S1-CT 15.6 105.60 FY-S3-FY 8.8 71.50 S1-F4-SY 11.0 113.20 S1-FY-SY 11.0 113.20 S3-FY-SY 8.8 71.50 S3-FY-SY 8.2 105.40 S3-FY-SY 8.2 105.40 F4-SY-FY 8.8 71.50 SY-F4-SY 8.2 105.40 F4-SY-FY 8.8 71.50 SY-F4-SY 8.2 105.40 F4-SY-F4 8.8 71.50 F4-SY-F4 8.8		CT-S1-FD	18.2	104.90
S3-F4-S3 8.2 105.40 S3-F4-S1 11.0 113.20 F4-S1-CT 15.6 105.60 F4-S3-F4 8.8 71.50 S3-FY-S3 8.2 105.40 S3-FY-S1 11.0 113.20 FY-S1-CT 15.6 105.60 FY-S1-CT 15.6 105.60 FY-S1-CT 15.6 105.60 FY-S3-FY 8.8 71.50 S1-F4-SY 11.0 113.20 FY-S3-FY 8.8 71.50 S1-F4-SY 11.0 113.20 S1-F4-SY 11.0 113.20 S3-FY-SY 8.8 71.50 S3-F4-SY 8.2 105.40 S3-F4-SY 8.2 105.40 F4-SY-FY 8.8 71.50 SY-F4-SY 8.8 71.50 SY-F4-SY 8.8 71.50 F4-SY-FY 8.8 71.50 F4-SY-FY 8.8 71.50 F4-SY-FY 8.8				1
S3-F4-S1 11.0 113.20 F4-S1-CT 15.6 105.60 F4-S3-F4 8.8 71.50 S3-FY-S3 8.2 105.40 S3-FY-S1 11.0 113.20 FY-S1-CT 15.6 105.60 FY-S1-CT 15.6 105.60 FY-S3-FY 8.8 71.50 S1-F4-SY 11.0 113.20 FY-S3-FY 8.8 71.50 S1-F4-SY 11.0 113.20 S1-F4-SY 11.0 113.20 S3-FY-S1 11.0 113.20 S3-FY-SY 8.2 105.40 S3-FY-SY 8.2 105.40 S3-FY-SY 8.2 105.40 F4-SY-FY 8.8 71.50 F4-SY-FY 8.8 71.50 SY-F4-SY 8.2 105.40 F4-SY-F4 8.8 71.50 F4-SY-F4 8.8 71.50 F4-SY-FY 8.8 71.50 F4-SY-FY 8.8		\$3-F4-\$3	8.2	105.40
F4-S1-CT 15.6 105.60 F4-S3-F4 8.8 71.50 S3-FY-S3 8.2 105.40 S3-FY-S1 11.0 113.20 FY-S1-CT 15.6 105.60 FY-S1-CT 15.6 105.60 FY-S1-CT 15.6 105.60 FY-S1-CT 15.6 105.60 FY-S3-FY 8.8 71.50 S1-F4-SY 11.0 113.20 S3-F4-SY 8.2 105.40 S3-F4-SY 8.2 105.40 S3-FY-SY 8.2 105.40 S3-FY-SY 8.2 105.40 F4-SY-FY 8.8 71.50 F4-SY-FY 8.8 71.50 F4-SY-FY 8.8 71.50 F4-SY-F4 8.8 71.50 F4-SY-FY 8.8 71.50 F4-SY-FY 8.8 71.50 F4-SY-FY 8.8 71.50 F4-SY-FY 8.8 71.50		\$3-F4-\$1	11.0	113.20
F4-S3-F4 8.8 71.50 S3-FY-S3 8.2 105.40 S3-FY-S1 11.0 113.20 FY-S1-CT 15.6 105.60 FY-S3-FY 8.8 71.50 S1-F4-SY 11.0 113.20 S1-F4-SY 11.0 113.20 S3-FY-S1 11.0 113.20 S1-F4-SY 11.0 113.20 S3-FY-SY 8.8 71.50 S3-FY-SY 8.2 105.40 S3-FY-SY 8.2 105.40 S3-FY-SY 8.2 105.40 S3-FY-SY 8.8 71.50 F4-SY-FY 8.8 71.50 SY-F4-SY 8.8 71.50 F4-SY-FY 8.8 71.50		F4-S1-CT	15.6	105.60
S3-FY-S3 8.2 105.40 S3-FY-S1 11.0 113.20 FY-S1-CT 15.6 105.60 FY-S3-FY 8.8 71.50 S1-F4-SY 11.0 113.20 S3-FY-S1 11.0 113.20 S1-F4-SY 11.0 113.20 S3-F4-SY 8.8 71.50 S3-F4-SY 8.2 105.40 S3-F4-SY 8.2 105.40 S3-FY-SY 8.2 105.40 F4-SY-FY 8.8 71.50		F4-S3-F4	8.8	71.50
S3-FY-S1 11.0 113.20 FY-S1-CT 15.6 105.60 FY-S3-FY 8.8 71.50 S1-F4-SY 11.0 113.20 S3-FY-S1 11.0 113.20 S1-F4-SY 11.0 113.20 S3-F4-SY 8.2 105.40 S3-FY-SY 8.2 105.40 F4-SY-FY 8.8 71.50		\$3-FY-\$3	8.2	105.40
FY-S1-CT 15.6 105.60 FY-S3-FY 8.8 71.50 S1-F4-SY 11.0 113.20 S1-FY-SY 11.0 113.20 S3-F4-SY 8.2 105.40 S3-FY-SY 8.2 105.40 F4-SY-FY 8.8 71.50		\$3-FY-\$1	11.0	113.20
FY-S3-FY 8.8 71.50 S1-F4-SY 11.0 113.20 S1-FY-SY 11.0 113.20 S3-F4-SY 8.2 105.40 S3-FY-SY 8.2 105.40 F4-SY-FY 8.8 71.50		FY-S1-CT	15.6	105.60
S1-F4-SY 11.0 113.20 [Fe ₄ S ₄]+ S1-FY-SY 11.0 113.20 S3-F4-SY 8.2 105.40 S3-FY-SY 8.2 105.40 F4-SY-FY 8.8 71.50 F4-S3-FY 8.2 105.40 F4-SY-FY 8.8 71.50 F4-SY-F4 8.8 71.50 F4-SY-F4 8.8 71.50 F4-SY-F4 8.8 71.50 F4-SY-FY 8.8 71.50 F4-SY-FY 8.8 71.50		FY-S3-FY	8.8	71.50
[Fe ₄ S ₄]+ S1-FY-SY 11.0 113.20 S3-F4-SY 8.2 105.40 S3-FY-SY 8.2 105.40 F4-SY-FY 8.8 71.50 F4-S3-FY 8.8 71.50 SY-F4-SY 8.2 105.40 F4-SY-FY 8.8 71.50 F4-SY-FY 8.8 71.50 F4-SY-F4 8.8 71.50 F4-SY-FY 8.8 71.50 F4-SY-FY 8.8 71.50 F4-SY-FY 8.8 71.50		S1-F4-SY	11.0	113.20
S3-F4-SY 8.2 105.40 S3-FY-SY 8.2 105.40 F4-SY-FY 8.8 71.50 F4-S3-FY 8.8 71.50 SY-F4-SY 8.2 105.40 F4-S3-FY 8.8 71.50 SY-F4-SY 8.2 105.40 F4-SY-F4 8.8 71.50 F4-SY-F4 8.8 71.50 F4-SY-FY 8.8 71.50 F4-SY-FY 8.8 71.50	[Fe ₄ S ₄]+	S1-FY-SY	11.0	113.20
S3-FY-SY 8.2 105.40 F4-SY-FY 8.8 71.50 F4-S3-FY 8.8 71.50 SY-F4-SY 8.2 105.40 F4-SY-F4 8.8 71.50 F4-SY-F4 8.8 71.50 F4-SY-F4 8.8 71.50 F4-SY-FY 8.8 71.50 F4-SY-FY 8.8 71.50		S3-F4-SY	8.2	105.40
F4-SY-FY 8.8 71.50 F4-S3-FY 8.8 71.50 SY-F4-SY 8.2 105.40 F4-SY-F4 8.8 71.50 F4-SY-F4 8.8 71.50 F4-SY-FY 8.8 71.50 F4-SY-FY 8.8 71.50		S3-FY-SY	8.2	105.40
F4-S3-FY 8.8 71.50 SY-F4-SY 8.2 105.40 F4-SY-F4 8.8 71.50 F4-SY-F4 8.8 71.50 F4-SY-FY 8.8 71.50 F4-SY-FY 8.8 71.50		F4-SY-FY	8.8	71.50
SY-F4-SY 8.2 105.40 F4-SY-F4 8.8 71.50 F4-SY-FY 8.8 71.50 F4-SY-FY 8.8 71.50		F4-S3-FY	8.8	71.50
F4-SY-F4 8.8 71.50 F4-SY-FY 8.8 71.50 F4-SY-FY 8.8 71.50		SY-F4-SY	8.2	105.40
F4-SY-FY 8.8 71.50 F4-SY-FY 8.8 71.50		F4-SY-F4	8.8	71.50
F4-SY-FY 8.8 71.50		F4-SY-FY	8.8	71.50
		F4-SY-FY	8.8	71.50
F4-S3-FY 8.8 71.50	ŀ	F4-S3-FY	8.8	71.50

Figure S1. MDC-d charges for $[Fe_2S_2]^{+2/+1}$ clusters



atom	$\operatorname{Fe}_2 \operatorname{S}_2^{+2}$	$\operatorname{Fe_2S_2^{+1}}$	$\operatorname{Fe_2S_2^{+1}}$
	S=0	S=9/2	S=1/2
Fe1	0.3527	0.4407	0.4011
Fe2	0.3533	0.4401	0.4162
S2	-0.5039	-0.8251	-0.7307
S 3	-0.5015	-0.8254	-0.7315
S 1	-0.6082	-0.7190	-0.7041
S4	-0.6053	-0.7180	-0.7895
S 5	-0.6076	-0.7214	-0.7038
S6	-0.6086	-0.7207	-0.7908
(CH ₃) ₄	0.7291	0.6488	0.6331
	l	l	l



atom	$\operatorname{Fe}_4S_4^{+2}$	$\operatorname{Fe}_4S_4^{+1}$
	S=0	S=1/2
Fe1	0.2200	0.2341
Fe2	0.2206	0.2416
Fe3	0.2184	0.2820
Fe4	0.2198	0.2749
S 3	-0.3526	-0.4753
S 4	-0.3538	-0.5267
S 5	-0.3500	-0.5092
S7	-0.3508	-0.4753
S1	-0.5595	-0.6649
S2	-0.5619	-0.6700
S 6	-0.5527	-0.6837
S 8	-0.5617	-0.6925
(CH ₃) ₄	0.7642	0.6650

Figure S3. MDC-d charges for $[Fe_3S_4]^{+/0}$ clusters



atom	$Fe_{3}S_{4}^{+1}$	$\operatorname{Fe_3S_4^{+1}}$	$\operatorname{Fe_3S_4^0}$
	S=3/2	S=5/2	S=2
Fe1	0.2369	0.2200	0.2844
Fe2	0.2276	0.3055	0.3136
Fe3	0.1624	0.3056	0.3090
S 1	-0.4429	-0.6189	-0.8045
S 3	-0.2874	-0.3248	-0.4187
S 4	-0.4474	-0.4574	-0.6213
S 5	-0.4890	-0.4406	-0.6093
S2	-0.5397	-0.5232	-0.6209
S 6	-0.5326	-0.5248	-0.6597
S7	-0.4662	-0.5276	-0.6633
(CH ₃) ₃	0.5783	0.5862	0.4907