Supporting information for

Electronic structure investigation and parameterization of biologically relevant iron-sulfur clusters

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Table S1. Bond stretching force constants and equilibrium distances.

Type of cluster	Bond	K_r	r_{eq}
$[Fe_2S_2]^{2+}$	F2-S2	88.2	2.21
	F2-S1	63.3	2.32
$[Fe_2S_2]^{+}$	F2-S2	52.6	2.29
	FR-S2	90.1	2.21
	F2-S1	39.3	2.34
	FR-S1	46.1	2.38
$[Fe_3S_4]^{+}$	FA-S2	80.7	2.22
	FA-S3	63.0	2.28
	FB-S2	104.5	2.19
	FB-S3	66.6	2.26
	FA-S1	82.0	2.25
	FB-S1	82.0	2.25
$[Fe_3S_4]^{0}$	FA-S2	68.5	2.27
	FA-S3	52.5	2.33
	FC-S2	79.0	2.24
	FC-S3	64.0	2.27
	FA-S1	56.2	2.35
	FC-S1	68.9	2.32
$[Fe_4S_4]^{2+}$	FU-SU	60.0	2.35
	FD-SD	60.0	2.35
	FU-S1	82.8	2.28
	FD-SU	75.3	2.22
	FU-SD	75.3	2.22
	FD-S1	82.8	2.28
$[Fe_4S_4]^{+}$	F4-S3	55.2	2.31
	FY-S3	55.2	2.31
	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 S2A. Comparison of the Bonds and angles for $[Fe_2S_2]^{2+}/[Fe_2S_2]^{+}$.

$[Fe_2S_2]^{2+}$	**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
			FR-S1	2.29±0.08	2.38	2.33	
F2-S2	2.2±0.06	2.21	F2-S2	2.18±0.06	2.21	2.24	2.06
			FR-S2	2.24±0.07	2.29	2.27	
S1-F2-S1	126.13±6.76	109.10	S1-F2-S1	100.96±8.19	108.2	103.2	100.0
			S1-FR-S1	106.76±7.59	105.6	109.4	
S1-F2-S2	100.76±10.46	110.50	S1-F2-S2	120.6±9.62	110.2	112.4	113.6
			S1-FR-S2	88.70±10.07	107.1	110.8	
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 S2B. Comparison of the Bonds and angles for $[Fe_4S_4]^{2+}$/ $[Fe_4S_4]^{+}$.

$[Fe_4S_4]^{2+}$	**MD**	**QM**	**$[Fe_4S_4]^{+}$**	**MD**	**QM**	**X-ray**
FD-S1 / FU-S1	2.28±0.06	2.28	F4-S1 / FY-S1	2.30±0.07	2.31	2.34±0.10
FD-SU / FU-SD	2.22±0.06	2.22	FY-SY	2.26±0.07	2.23	2.21±0.18
FU-SU / FD-SD	2.35±0.07	2.35	F4-S3 / FY-S3 / F4-SY	2.30±0.07	2.31	2.31±0.26
CT-S1-FU / CT-S1-FD	110.0±5.8	104.9	CT-S1-F4 / CT-S1-FY	106.7±6.7	105.6	107.9±19.4
FD-SD-FU / FU-SU-FD	73.4±4.4	73	F4/Y-S3-F4/Y	73.7±4.71	71.5	79.3±2.9
FD-SD-FD / FU-SU-FU	75.3±4.0	71.3				77.4±2.3
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-FD	-50.8±30.9		CT-CT-S1-FY	-50.4±26.01		-51.756
CT-CT-S1-FD	83.4±9.5		CT-CT-S1-FY	89.2±16.4		86.666

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

$[Fe_3S_4]^+$	**MD**	**QM**	**$[Fe_3S_4]^0$**	**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

Supporting information for

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Table S1. Bond stretching force constants and equilibrium distances.

Type of cluster	Bond	K_r	r_{eq}
$[Fe_2S_2]^{2+}$	F2-S2	88.2	2.21
	F2-S1	63.3	2.32
$[Fe_2S_2]^{+}$	F2-S2	52.6	2.29
	FR-S2	90.1	2.21
	F2-S1	39.3	2.34
	FR-S1	46.1	2.38
$[Fe_3S_4]^{+}$	FA-S2	80.7	2.22
	FA-S3	63.0	2.28
	FB-S2	104.5	2.19
	FB-S3	66.6	2.26
	FA-S1	82.0	2.25
	FB-S1	82.0	2.25
$[Fe_3S_4]^{0}$	FA-S2	68.5	2.27
	FA-S3	52.5	2.33
	FC-S2	79.0	2.24
	FC-S3	64.0	2.27
	FA-S1	56.2	2.35
	FC-S1	68.9	2.32
$[Fe_4S_4]^{2+}$	FU-SU	60.0	2.35
	FD-SD	60.0	2.35
	FU-S1	82.8	2.28
	FD-SU	75.3	2.22
	FU-SD	75.3	2.22
	FD-S1	82.8	2.28
$[Fe_4S_4]^{+}$	F4-S3	55.2	2.31
	FY-S3	55.2	2.31
	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 S2A. Comparison of the Bonds and angles for $[Fe_2S_2]^{2+}/[Fe_2S_2]^{+}$.

$[Fe_2S_2]^{2+}$	**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
			FR-S1	2.29±0.08	2.38	2.33	
F2-S2	2.2±0.06	2.21	F2-S2	2.18±0.06	2.21	2.24	2.06
			FR-S2	2.24±0.07	2.29	2.27	
S1-F2-S1	126.13±6.76	109.10	S1-F2-S1	100.96±8.19	108.2	103.2	100.0
			S1-FR-S1	106.76±7.59	105.6	109.4	
S1-F2-S2	100.76±10.46	110.50	S1-F2-S2	120.6±9.62	110.2	112.4	113.6
			S1-FR-S2	88.70±10.07	107.1	110.8	
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 S2B. Comparison of the Bonds and angles for $[Fe_4S_4]^{2+}$/ $[Fe_4S_4]^{+}$.

$[Fe_4S_4]^{2+}$	**MD**	**QM**	**$[Fe_4S_4]^{+}$**	**MD**	**QM**	**X-ray**
FD-S1 / FU-S1	2.28±0.06	2.28	F4-S1 / FY-S1	2.30±0.07	2.31	2.34±0.10
FD-SU / FU-SD	2.22±0.06	2.22	FY-SY	2.26±0.07	2.23	2.21±0.18
FU-SU / FD-SD	2.35±0.07	2.35	F4-S3 / FY-S3 / F4-SY	2.30±0.07	2.31	2.31±0.26
CT-S1-FU / CT-S1-FD	110.0±5.8	104.9	CT-S1-F4 / CT-S1-FY	106.7±6.7	105.6	107.9±19.4
FD-SD-FU / FU-SU-FD	73.4±4.4	73	F4/Y-S3-F4/Y	73.7±4.71	71.5	79.3±2.9
FD-SD-FD / FU-SU-FU	75.3±4.0	71.3				77.4±2.3
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-FD	-50.8±30.9		CT-CT-S1-FY	-50.4±26.01		-51.756
CT-CT-S1-FD	83.4±9.5		CT-CT-S1-FY	89.2±16.4		86.666

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

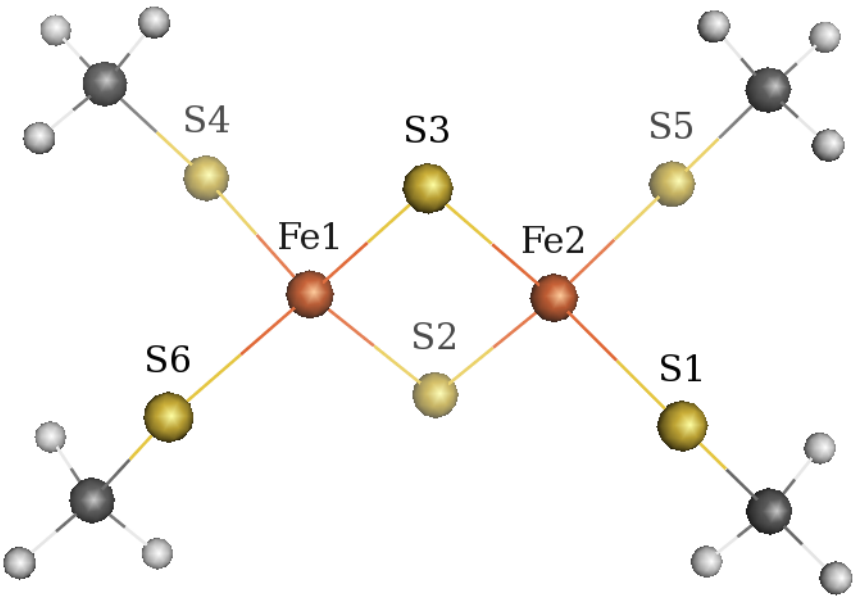
$[Fe_3S_4]^+$	**MD**	**QM**	**$[Fe_3S_4]^0$**	**MD**	**QM**	**X-ray**
FA-S1/FB-S1	2.25±0.06	2.25	FA-S1	2.34±0.07	2.35	2.33±0.13
			FC-S1	2.32±0.07	2.32	
FA-S2	2.21±0.06	2.22	FA-S2	2.25±0.07	2.27	2.07±0.13
FA-S3	2.27±0.07	2.28	FA-S3	2.31±0.07	2.33	2.03±0.03
FB-S2	2.19±0.05	2.19	FC-S2	2.23±0.06	2.24	2.12±0.31
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 S3 – Angle bending force constants and equilibrium values.

Type of cluster	Angle	K_θ	θ_{eq}
$[Fe_2S_4]^{2+}$	S2-F2-S2	20.2	75.20
	S2-F2-S1	14.6	110.50
	F2-S2-F2	20.3	104.80
	S1-F2-S1	10.1	109.05
$[Fe_2S_4]^{+}$	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
	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
	S1-F3-S1	8.3	105.60
$[Fe_3S_4]^{+}$	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
	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
$[Fe_3S_4]^{0}$	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
	FA-S2-FA	18.0	69.80
	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
	S1-FC-S3	17.6	114.20

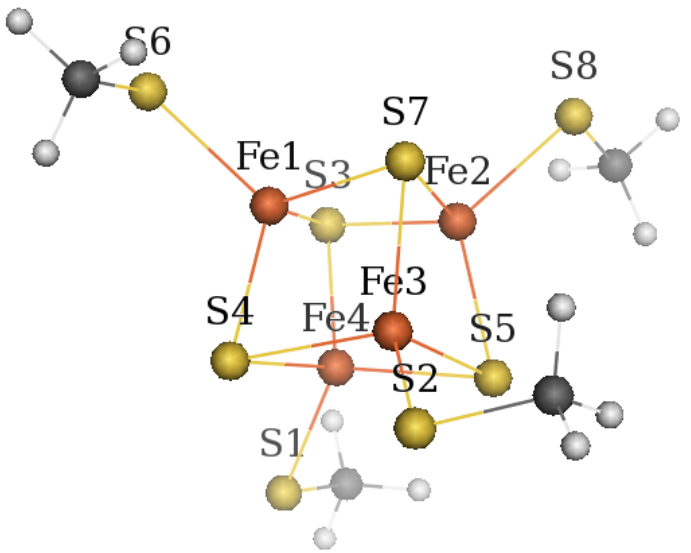
	S2-FA-S2	10.0	116.00
	S2-FA-S3	11.8	104.00
	S2-FC-S2	6.6	112.90
	S2-FC-S3	13.0	104.00
$[Fe_4S_4]^{2+}$	SU-FU-SU	7.0	107.00
	SD-FD-SD	7.0	107.00
	SD-FD-SU	13.0	104.50
	SU-FU-SD	13.0	104.50
	FD-SD-FU	10.5	73.00
	FU-SU-FD	10.5	73.00
	SU-FU-S1	12.1	110.00
	SD-FD-S1	12.1	110.00
	SD-FU-S1	12.8	120.00
	SU-FD-S1	12.8	120.00
	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
$[Fe_4S_4]^{+}$	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
	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-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

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



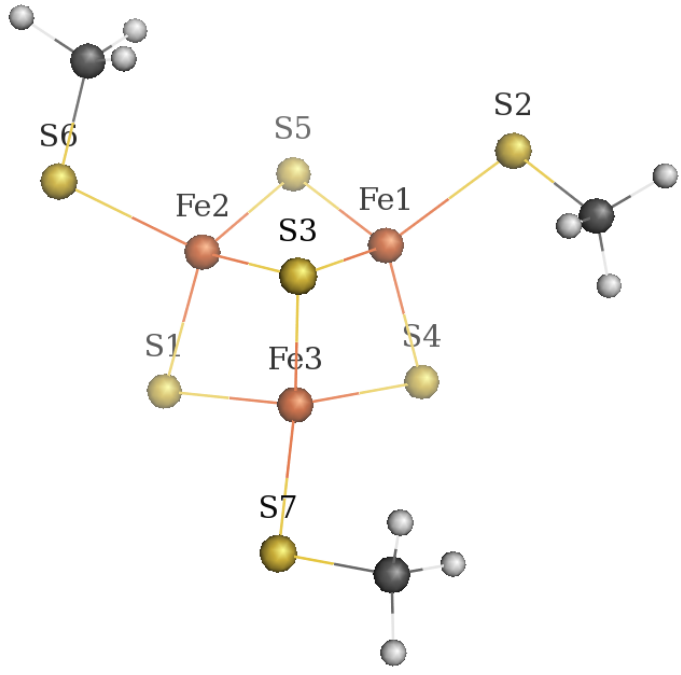
atom	$Fe_2S_2^{+2}$ S=0	$Fe_2S_2^{+1}$ S=9/2	$Fe_2S_2^{+1}$ S=1/2
Fe1	0.3527	0.4407	0.4011
Fe2	0.3533	0.4401	0.4162
S2	-0.5039	-0.8251	-0.7307
S3	-0.5015	-0.8254	-0.7315
S1	-0.6082	-0.7190	-0.7041
S4	-0.6053	-0.7180	-0.7895
S5	-0.6076	-0.7214	-0.7038
S6	-0.6086	-0.7207	-0.7908
$(CH_3)_4$	0.7291	0.6488	0.6331

Figure S2.
MDC-d charges
for $[Fe_4S_4]^{+2/+1}$ clusters



atom	$Fe_4S_4^{+2}$ S=0	$Fe_4S_4^{+1}$ S=1/2
Fe1	0.2200	0.2341
Fe2	0.2206	0.2416
Fe3	0.2184	0.2820
Fe4	0.2198	0.2749
S3	-0.3526	-0.4753
S4	-0.3538	-0.5267
S5	-0.3500	-0.5092
S7	-0.3508	-0.4753
S1	-0.5595	-0.6649
S2	-0.5619	-0.6700
S6	-0.5527	-0.6837
S8	-0.5617	-0.6925
$(CH_3)_4$	0.7642	0.6650

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



atom	$Fe_3S_4^{+1}$ S=3/2	$Fe_3S_4^{+1}$ S=5/2	$Fe_3S_4^{0}$ S=2
Fe1	0.2369	0.2200	0.2844
Fe2	0.2276	0.3055	0.3136
Fe3	0.1624	0.3056	0.3090
S1	-0.4429	-0.6189	-0.8045
S3	-0.2874	-0.3248	-0.4187
S4	-0.4474	-0.4574	-0.6213
S5	-0.4890	-0.4406	-0.6093
S2	-0.5397	-0.5232	-0.6209
S6	-0.5326	-0.5248	-0.6597
S7	-0.4662	-0.5276	-0.6633
$(CH_3)_3$	0.5783	0.5862	0.4907