Spin-symmetrised structures and vibrational frequencies of iron-sulfur clusters

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An example of EBS mode decomposition is reported in Table 1 for $Fe_4S_4Cl_4$ cluster with OPBE functional (only BS modes that have a contribution bigger than 10% of the main one are shown). Percentages are calculated as normalized squares of dot product results. Exchange coupling constants evaluated at the different levels of theory and with different spin descriptions are reported in Table 2 and Table 3. Comparisons between EBS and BS vibrational frequencies are reported in Tables from Table 4 to Table 8 for, respectively, ${Fe_2S_2Cl_4}^{2-}$ and $Fe_4S_4Cl_4$ clusters. VMARD (Vibrational Mode Automatic Relevance Determination) analysis for ${Fe_2S_2Cl_4}^{2-}$ is reported in Table 9 and Table 10 for B3LYP, BP, M06 and OPBE levels of theory.

References

[1] M. C. Smith, Y. Xiao, H. Wang, S. J. George, D. Coucouvanis, M. Koutmos, W. Sturhahn, E. E. Alp, J. Zhao and S. P. Cramer, *Inorganic chemistry*, 2005, **44**, 5562–5570.

[2] G. B. Wong, M. Bobrik and R. Holm, *Inorganic Chemistry*, 1978, **17**, 578–584.

Table 1: Normal modes decomposition - $Fe_4S_4Cl_4$ OPBE

EBS mode	BS modes	EBS mode	BS modes
1	62% 1 + 15% 2 + 10% 3 + 10% 4	16	82% 15 + 16% 17
2	63% 4 + 18% 1 + 12% 5	17	91% 18
3	57% 2 + 17% 1 + 11% 3 + 8% 4	18	76% 19 + 18% 17
4	72% 3 + 15% 5 + 11% 2	19	50% 17 + 17% 20 + 16% 19 + 10% 15
5	54% 5 + 16% 4 + 12% 2 + 6% 6	20	95% 21
6	90% 6	21	76% 20 + 15% 17
7	69% 8 + 26% 7	22	99% 22
8	68% 7 + 22% 8	23	100% 23
9	96% 9	24	93% 25
10	60% 11 + 38% 10	25	93% 24
11	62% 10 + 37% 11	26	93% 26
12	95% 12	27	92% 27
13	98% 13	28	99% 28
14	95% 14	29	99% 29
15	97% 16	30	100% 30

Table 2: J coupling constants - ${Fe_2S_2Cl_4}^{2-}$

		J $[cm^{-1}]$
Exp[2]		-158
B3LYP	HS	-105.8
	BS	-159.8
	EBS	-174.1
BP	HS	-201.5
	BS	-356.0
	EBS	-377.3
M06	HS	-141.1
	BS	-193.5
	EBS	-205.8
OPBE	HS	-171.6
	BS	-297.8
	EBS	-328.1
MP2	HS	-47.5
	BS	-60.9
	EBS	-64.0
B2PLYP	HS	-91.2
	BS	-141.9
	EBS	-156.0

Table 3: J coupling constants - $Fe_4S_4Cl_4$

		J_1 $[cm^{-1}]$	J_2 $[cm^{-1}]$	J_3 $[cm^{-1}]$	J_4 $[cm^{-1}]$	J_5 $[cm^{-1}]$	J_6 $[cm^{-1}]$
B3LYP	HS	-74.4	-71.5	-73.5	-73.4	-74.0	-73.0
	BS	-117.8	-70.2	-115.5	-114.3	-73.7	-115.7
	EBS	-123.9	-70.4	-121.1	-120.1	-73.8	-121.7
BP	HS	-114.3	-114.3	-114.2	-114.4	-114.4	-113.7
	BS	-306.1	-306.4	-274.7	-274.8	-307.1	-306.7
	EBS	-323.9	-324.1	-298.7	-298.6	-324.2	-324.2
M06	HS	-86.9	-82.6	-85.7	-84.7	-87.8	-84.9
	BS	-128.0	-77.5	-126.4	-123.5	-82.2	-125.2
	EBS	-133.0	-77.4	-131.2	-128.3	-82.1	-130.4
OPBE	HS	-126.4	-126.1	-125.7	-126.0	-126.2	-125.8
	BS	-252.0	-152.7	-252.0	-252.2	-152.6	-251.9
	EBS	-268.3	-177.7	-267.9	-268.0	-177.6	-268.2

Table 4: Comparison between Extended Broken Symmetry and Broken Symmetry frequencies calculated on ${Fe_2S_2Cl_4}^{2-}$ - B3LYP and BP

B3LYP					BP				
EBS		BS		Shift	EBS		BS		Shift
mode	ν	mode	ν		mode	ν	mode	ν	
1	37	1	27	10	1	57	1	46	11
2	72	2	63	9	2	64	2	65	-1
3	88	3	84	4	3	88	3	87	1
4	99	4	96	3	4	94	4	91	3
5	108	5	118	-10	5	99	5	100	-1
6	120	7*	101	19	6	106	6	105	1
7	124	6	105	19	7	151	8	137	14
8	143	8	135	8	8	152	7	112	40
9	166	10*	164	2	9	173	10	172	1
10	173	9	149	24	10	183	9	152	31
11	263	11	263	0	11	240	11	237	3
12	286	12, 13	-	-	12	254	12	254	0
13	289	12, 13	-	-	13	277	13	271	6
14	301	14	297	4	14	291	14	290	1
15	306	15	305	1	15	320	15, 16	-	-
16	336	16	331	5	16	322	15, 16	-	-
17	378	17	383	-5	17	368	17	376	-8
18	401	18	401	0	18	402	18	406	-4

Frequencies and their differencies are $[cm^{-1}]$. Shifts are defined as $\nu_{EBS} - \nu_{BS}$. When * is present, correspondence is dubious. When more than one normal mode is present, EBS mode is a linear combination of BS modes and the shift has consequently not been calculated.

Table 5: Comparison between Extended Broken Symmetry and Broken Symmetry frequencies calculated on $Fe_2S_2Cl_4{}^{2-}$ - M06 and OPBE

M06					OPBE				
EBS		BS		Shift	EBS		BS		Shift
mode	ν	mode	ν		mode	ν	mode	ν	
1	25	1, 2		-	1	41	1	37	4
2	40	1, 2		-	2	62	2	61	1
3	79	3	71	8	3	90	3	89	1
4	97	4	94	3	4	94	4	91	3
5	115	5	111	4	5	96	5	96	0
6	126	7	123	3	6	108	6	107	1
7	129	6	121	8	7	116	7	112	4
8	145	8	140	5	8	142	8	138	4
9	178	9	175	3	9	158	9	153	5
10	180	10	171	9	10	174	10	175	-1
11	280	11	280	0	11	248	11	250	-2
12	298	12	285	13	12	276	12	276	0
13	311	13	307	4	13	293	13	291	2
14	324	14	319	5	14	305	14	304	1
15	330	15	326	4	15	322	15	321	1
16	341	16	339	2	16	328	16	332	-4
17	395	17	400	-5	17	379	17	389	-10
18	424	18	423	1	18	415	18	421	-6

Frequencies and their differencies are $[cm^{-1}]$. Shifts are defined as $\nu_{EBS} - \nu_{BS}$. When * is present, correspondence is dubious. When more than one normal mode is present, EBS mode is a linear combination of BS modes and the shift has consequently not been calculated.

Table 6: Comparison between Extended Broken Symmetry and Broken Symmetry frequencies calculated on $Fe_2S_2Cl_4{}^{2-}$ - B2PLYP and SCS-MP2

B2PLYP					SCS-MP2				
EBS		BS		Shift	EBS		BS		Shift
mode	ν	mode	ν		mode	ν	mode	ν	
1	42	1	39	3	1	29	1	28	1
2	66	2	65	1	2	60	2	60	0
3	91	3	91	0	3	93	3	94	-1
4	97	4	89	8	4	100	4	100	0
5	101	5	100	1	5	101	5	100	1
6	114	6	114	0	6	108	6	107	1
7	119	7	114	5	7	120	7	120	0
8	144	8	140	4	8	138	8	138	0
9	156	9	151	5	9	156	9	154	2
10	169	10	170	-1	10	174	10	176	-2
11	268	11	269	-1	11	276	11	277	-1
12	276	12	272	4	12	287	12	287	0
13	299	13	299	0	13	315	13	316	-1
14	312	14	311	1	14	326	14	325	1
15	312	15	312	0	15	328	15	328	0
16	340	16	342	-2	16	365	16	365	0
17	384	17	391	-7	17	401	17	406	-5
18	409	18	413	-4	18	422	18	425	-3

Frequencies and their differencies are $[cm^{-1}]$. Shifts are defined as $\nu_{EBS} - \nu_{BS}$. When * is present, correspondence is dubious. When more than one normal mode is present, EBS mode is a linear combination of BS modes and the shift has consequently not been calculated.

Table 7: Comparison between Extended Broken Symmetry and Broken Symmetry frequencies calculated on $Fe_4S_4Cl_4$ - B3LYP and BP

B3LYP					BP				
EBS		BS		Shift	EBS		BS		Shift
mode	ν	mode	ν		mode	ν	mode	ν	
1	82	2, 3*	-	-	1	56	1	49	7
2	89	4*	90	-1	2	61	3, 4, 5*	-	-
3	89	1, 2, 4*	-	-	3	64	3	60	+4
4	103	5*	96	+7	4	71	2	56	+15
5	112	1, 2*	-	-	5	81	4*	68	+13
6	122	7*	107	+15	6	102	6, 8	-	-
7	126	6*	104	+22	7	114	7	106	+8
8	130	8*	117	+13	8	119	8	110	+9
9	137	9, 10	-	-	9	129	9	125	+4
10	139	9, 10	-	-	10	150	11	134	+16
11	145	11	137	+8	11	151	10	133	+18
12	152	12*	142	+10	12	166	13	156	+10
13	158	13*	147	+11	13	168	14	157	+11
14	164	14*	154	+10	14	172	12	155	+17
15	247	15	227	+20	15	235	15, 16	-	-
16	250	16*	236	+14	16	249	15*	217	+32
17	259	17*	239	+20	17	256	19	256	0
18	263	16, 18*	-	-	18	265	17	239	+26
19	280	19*	263	+17	19	270	18	239	+31
20	283	20*	275	+8	20	277	20, 21	-	-
21	290	21	277	+13	21	285	20, 21	-	-
22	295	22	279	+16	22	303	22	292	+11
23	353	23	348	+5	23	364	23	352	+12
24	367	24	359	+8	24	385	25	375	+10
25	372	25	367	+5	25	391	24	374	+17
26	388	26	383	+5	26	415	26	403	+12
27	424	27	422	+2	27	426	27	421	+5
28	426	28	424	+2	28	430	29	425	+5
29	427	29	425	+2	29	430	28	425	+5
30	443	30	442	+1	30	447	30	443	+4

Frequencies and their differencies are $[cm^{-1}]$. Shifts are defined as $\nu_{EBS} - \nu_{BS}$. When * is present, correspondence is dubious. When more than one normal mode is present, EBS mode is a linear combination of BS modes.

Table 8: Comparison between Extended Broken Symmetry and Broken Symmetry frequencies calculated on $Fe_4S_4Cl_4$ - M06 and OPBE

M06					OPBE				
EBS		BS		Shift	EBS		BS		Shift
mode	ν	mode	ν		mode	ν	mode	ν	
1	45	1, 3*			1	54	1*	51	+3
2	76	3	98	-22	2	60	4*	64	-4
3	86	2*	86	0	3	62	2*	58	+4
4	98	4, 5*	-	-	4	67	3*	61	+6
5	103	4, 5, 6*	-	-	5	75	5*	78	-3
6	112	6*	120	-8	6	95	6	94	+1
7	118	8*	130	-12	7	109	8*	114	-5
8	128	7*	-	-	8	110	7*	105	+5
9	143	9	145	-2	9	130	9	128	+2
10	148	10*	147	-1	10	151	10, 11	-	-
11	151	11*	150	+1	11	154	10, 11	-	-
12	156	12*	157	-1	12	162	12	158	+4
13	165	13	165	0	13	165	13	160	+5
14	169	14	168	+1	14	170	14	164	+6
15	256	16*	267	-11	15	240	16	242	-2
16	261	17, 18	-	-	16	243	15	235	+8
17	270	17*	274	-4	17	257	18	262	-5
18	274	20*	292	-18	18	260	19	268	-8
19	289	19*	290	-1	19	265	17*	253	+12
20	293	15, 19, 21*	-	-	20	283	21	280	+3
21	298	22	336	-38	21	284	20	277	+7
22	300	21*	304	-4	22	309	22	300	+9
23	368	23	371	-3	23	362	23	358	+4
24	394	25	395	-1	24	393	25	388	+5
25	397	24	395	+2	25	394	24	387	+7
26	416	26	415	+1	26	421	26	415	+6
27	444	27	443	+1	27	428	27	425	+3
28	448	28, 29	-	-	28	433	28	430	+3
29	449	28, 29	-	-	29	434	29	431	+3
30	468	30	468	0	30	450	30	447	+3

Frequencies and their differencies are $[cm^{-1}]$. Shifts are defined as $\nu_{EBS} - \nu_{BS}$. When * is present, correspondence is dubious. When more than one normal mode is present, EBS mode is a linear combination of BS modes.

Table 9: Extended Broken Symmetry Vibrational Mode Automatic Relevance Determination on $Fe_2S_2{Cl_4}^{2-}$ - B3LYP and BP

B3LYP

mode	ν	VMARD
1	37	37% $\rho_{ClFeFeCl}$ + 21% β_{FeFeCl}
2	72	59% β_{FeFeCl}
3	88	25% β_{ClFeS} + 24% β_{FeSFe} + 33% β_{SFeCl}
4	99	20% ν_{FeFe} + 18% $\rho_{FeSFeCl}$ + 21% β_{ClFeCl}
5	108	43% β_{FeFeCl} + 41% ν_{FeCl}
6	120	31% β_{ClFeCl} + 13% β_{SFeCl} + 18% ν_{FeCl}
7	124	23% $\rho_{ClFeFeS}$ + 22% β_{FeFeCl} + 22% $\rho_{SFeFeCl}$
8	143	59% β_{SFeCl} + 14% β_{ClFeS}
9	166	18% ν_{FeFe} + 47% ν_{FeCl} + 15% β_{ClFeCl} + 12% β_{FeSFe}
10	173	37% ν_{FeCl} + 19% β_{SFeCl} + 17% β_{ClFeS}
11	263	72% ν_{FeCl} + 22% β_{SFeS}
12	286	56% ν_{FeCl} + 36% β_{FeFeS}
13	289	50% β_{FeFeS} + 38% ν_{FeCl}
14	301	76% ν_{FeCl}
15	306	67% ν_{FeCl} + 12% β_{FeSFe} + 15% ν_{FeS}
16	336	51% β_{SFeS} + 28% ν_{FeCl}
17	378	76% ν_{FeS}
18	401	82% β_{FeSFe}

BP

mode	ν	VMARD
1	57	59% β_{FeFeCl} + 12% β_{ClFeCl}
2	64	67% $\rho_{ClFeFeCl}$ + 16% β_{SFeCl}
3	88	27% ν_{FeFe} + 45% β_{ClFeCl}
4	94	45% β_{FeFeCl} + 11% β_{ClFeCl} + 41% ν_{FeCl}
5	99	26% β_{FeSFe} + 44% β_{SFeCl} + 22% β_{ClFeS}
6	106	44% β_{ClFeCl} + 22% ν_{FeCl} + 20% β_{SFeCl}
7	1^{51}	63% β_{SFeCl} + 21% β_{ClFeS}
8	152	31% $\rho_{SFeFeCl}$ + 31% $\rho_{ClFeFeS}$ + 25% β_{SFeCl}
9	173	23% ν_{FeFe} + 54% ν_{FeCl} + 10% β_{FeSFe}
10	183	42% ν_{FeCl} + 30% β_{SFeCl} + 10% β_{ClFeS}
11	240	74% ν_{FeCl} + 23% β_{SFeS}
12	254	99% ν_{FeCl}
13	277	69% ν_{FeCl}
14	291	64% ν_{FeCl} + 27% β_{FeSFe}
15	320	63% β_{FeFeS} + 21% ν_{FeCl}
16	322	78% β_{FeFeS}
17	368	82% ν_{FeS}
18	402	81% β_{FeSFe}

Frequencies are [cm^{-1}]. ν indicates bond stretching motions, β indicates angle bending motions and ρ indicated dihedral angles torsions. Contributions smaller than 10% have been ignored.

Table 10: Extended Broken Symmetry Vibrational Mode Automatic Relevance Determination on $Fe_2S_2{Cl_4}^{2-}$ - OPBE and SCS-MP2

OPBE

mode	ν	VMARD
1	41	69% β_{FeFeCl}
2	62	100% $\rho_{ClFeFeCl}$
3	90	35% ν_{FeFe} + 54% β_{ClFeCl}
4	94	52% β_{FeFeCl} + 47% ν_{FeCl}
5	96	32% β_{FeSFe} + 51% β_{SFeCl} + 17% β_{ClFeS}
6	108	56% β_{ClFeCl} + 17% β_{SFeS} + 24% ν_{FeCl}
7	116	49% $\rho_{ClFeFeS}$ + 47% $\rho_{SFeFeCl}$
8	142	63% β_{SFeCl} + 21% β_{ClFeS}
9	158	37% ν_{FeCl} + 41% β_{SFeCl} + 14% β_{ClFeS}
10	174	24% ν_{FeFe} + 55% ν_{FeCl} + 12% β_{FeSFe} + 9% β_{ClFeCl}
11	248	72% ν_{FeCl} + 28% β_{SFeS}
12	276	96% ν_{FeCl}
13	293	79% ν_{FeCl}
14	305	66% ν_{FeCl} + 21% β_{FeSFe} + 13% ν_{FeS}
15	322	98% β_{FeFeS}
16	328	59% β_{SFeS} + 37% ν_{FeCl}
17	379	77% ν_{FeS} + 13% ν_{FeCl}
18	415	83% β_{FeSFe}

SCS-MP2

mode	ν	VMARD
1	29	66% β_{FeFeCl} + 10% ρ_{SFeFeS}
2	60	100% $\rho_{ClFeFeCl}$
3	93	34% ν_{FeFe} + 49% β_{ClFeCl}
4	100	32% β_{FeSFe} + 68% β_{SFeCl}
5	101	51% β_{FeFeCl} + 47% ν_{FeCl}
6	108	93% $\rho_{ClFeFeS}$
7	120	59% β_{ClFeCl} + 18% β_{SFeS} + 24% ν_{FeCl}
8	138	90% β_{SFeCl}
9	156	35% ν_{FeCl} + 61% β_{SFeCl}
10	174	18% ν_{FeFe} + 50% ν_{FeCl} + 17% β_{FeSFe} + 15% β_{ClFeCl}
11	276	84% β_{FeFeS}
12	287	75% ν_{FeCl} + 25% β_{SFeS}
13	315	88% ν_{FeCl}
14	326	84% ν_{FeCl}
15	328	60% ν_{FeCl} + 16% β_{FeSFe} + 20% ν_{FeS}
16	365	71% β_{SFeS} + 25% ν_{FeCl}
17	401	75% ν_{FeS} + 21% ν_{FeCl}
18	422	83% β_{FeSFe}

Frequencies are $[cm^{-1}]$. ν indicates bond stretching motions, β indicates angle bending motions and ρ indicated dihedral angles torsions. Contributions smaller than 10% have been ignored.