

Supplementary Material

Structures and Bonding Properties of Lithium Polysulfide Clusters $\text{LiS}_n^{-/0}$ ($n = 3-5$) and $\text{Li}_2\text{S}_4^{-/0}$: Size-Selected Anion Photoelectron Spectroscopy and Theoretical Calculations

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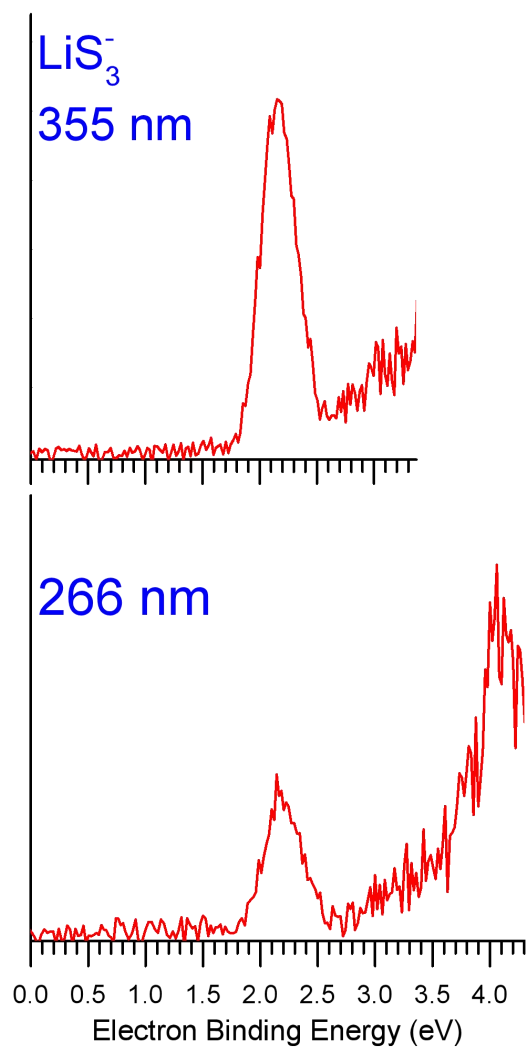


FIG. S1. Photoelectron spectra of LiS_3^- recorded at different wavelength.

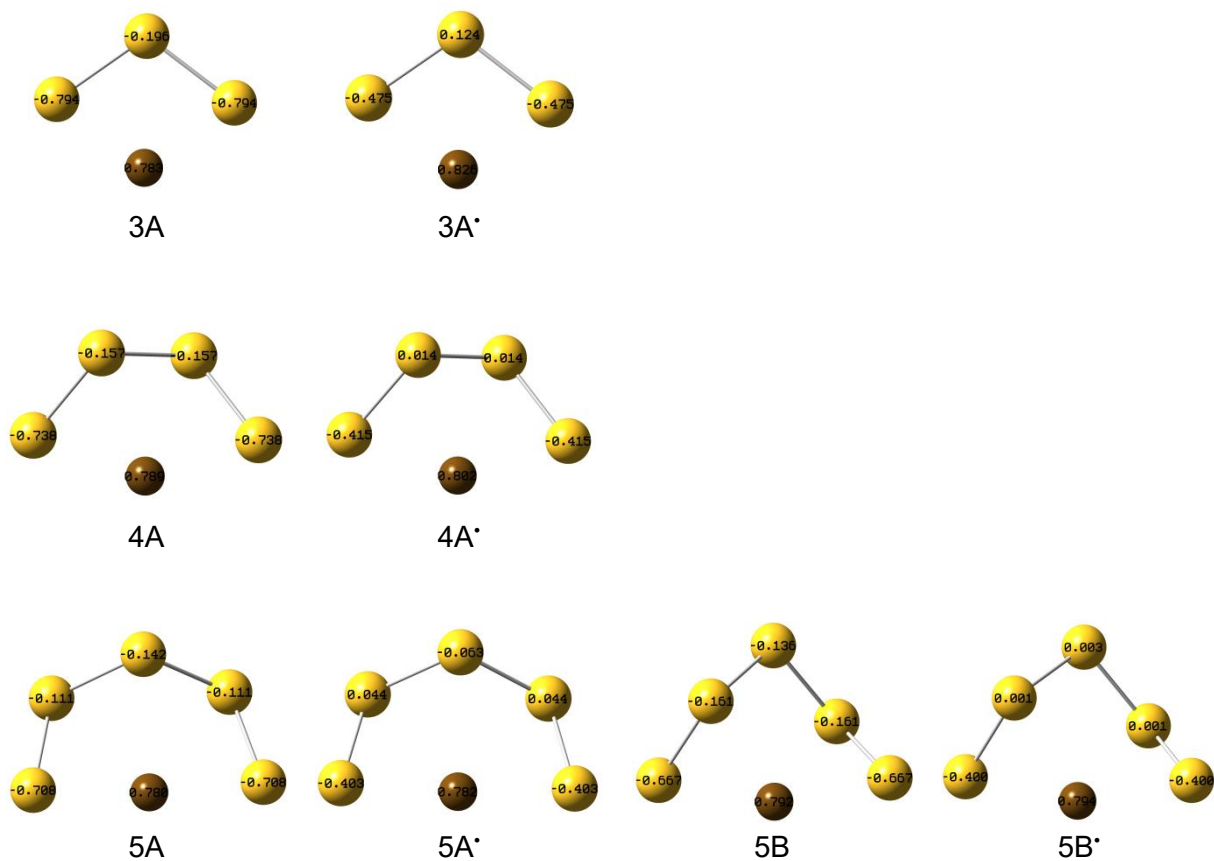


FIG. S2. The NPA charge distributions of the most stable structures of LiS_n^{n-} ($n = 3-5$) based on the fixed anions' geometries. The calculations are conducted at the B3LYP/6-311+G(d) level. The brown and yellow balls represent lithium and sulfur atoms, respectively.

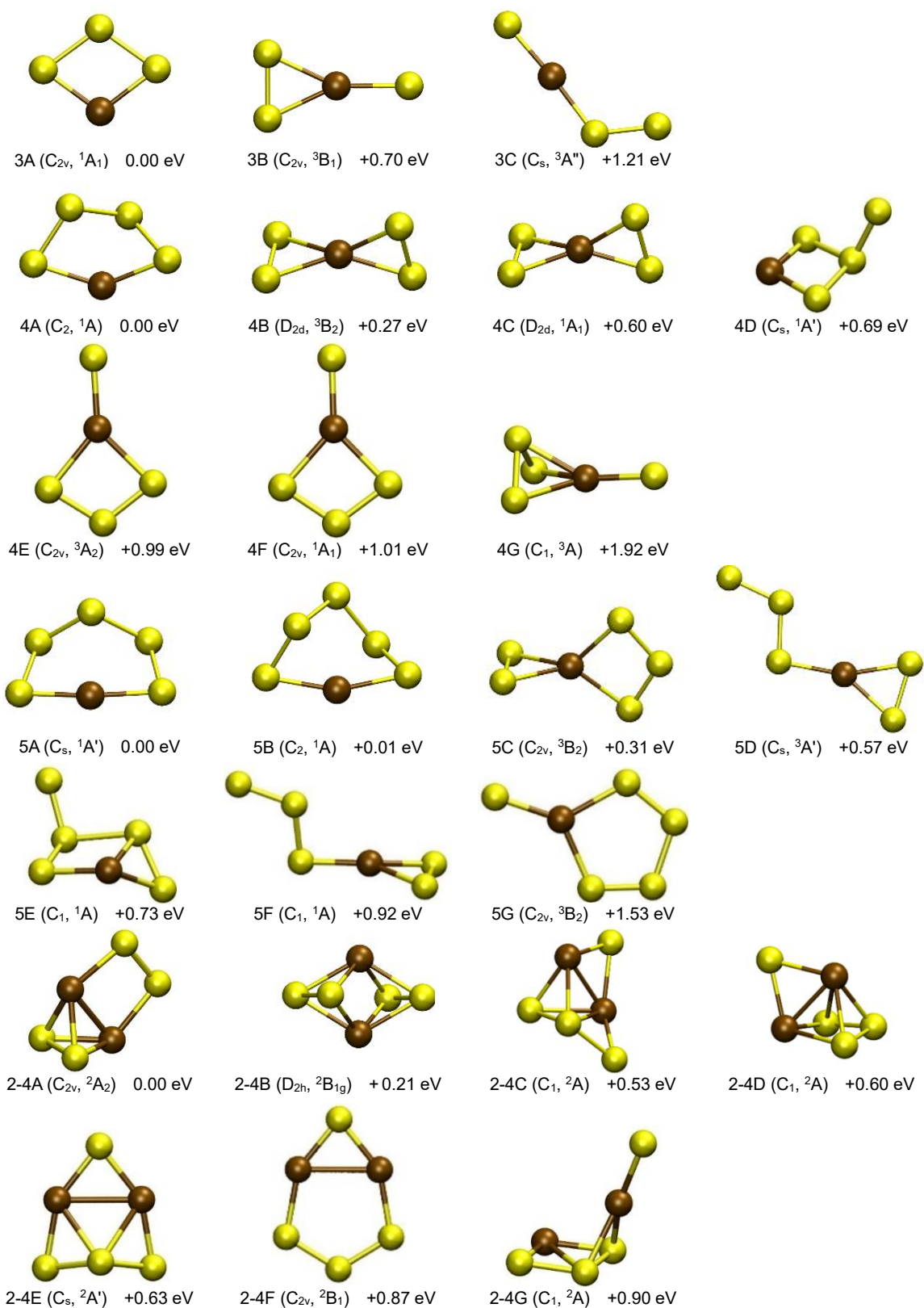


FIG. S3. Typical low-lying isomers of LiS_n^- ($n = 3-5$) and $Li_2S_4^-$. The relative energies were calculated at the CCSD(T)/aug-cc-pVTZ//B3LYP/6-311+G(d) level and by including the zero-point energies (ZPEs) calculated at the B3LYP/6-311+G(d) level. The brown and yellow balls represent lithium and sulfur atoms, respectively.

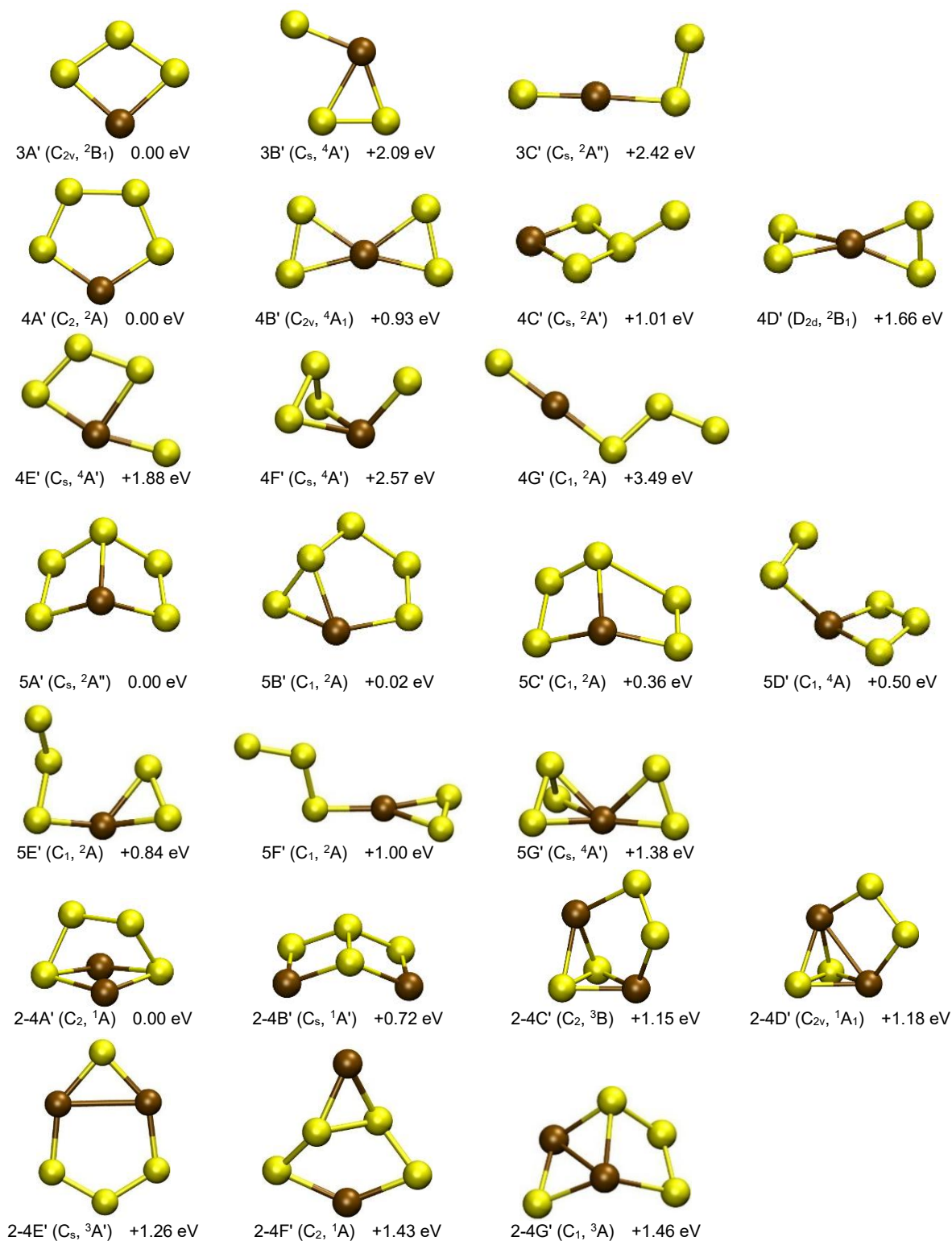


FIG. S4. Typical low-lying isomers of Li_3S_3 ($n = 3-5$) and Li_2S_4 . The relative energies were calculated at the CCSD(T)/aug-cc-pVTZ//B3LYP/6-311+G(d) level and by including the zero-point energies (ZPEs) calculated at the B3LYP/6-311+G(d) level. The brown and yellow balls represent lithium and sulfur atoms, respectively.

TABLE S1. The Cartesian coordinates for the low-lying isomers of $\text{LiS}_n^{-/0}$ ($n = 3-5$) and $\text{Li}_2\text{S}_4^{-/0}$ calculated at the B3LYP/6-311+G(d) level.

LiS_3^-							
3A			3B				
	X	Y	Z		X	Y	Z
S	0.00000000	0.00000000	0.95664700	S	0.00000000	1.02591000	-1.52316800
S	0.00000000	1.76161800	-0.32432800	S	0.00000000	0.00000000	2.92631800
S	0.00000000	-1.76161800	-0.32432800	S	0.00000000	-1.02591000	-1.52316800
Li	0.00000000	0.00000000	-1.64262300	Li	0.00000000	0.00000000	0.64009200
3C							
	X	Y	Z				
S	-0.98413300	0.91259800	0.00000000				
S	0.18627600	2.56684200	0.00000000				
S	0.79785700	-3.25493900	0.00000000				
Li	0.00000000	-1.19733600	0.00000000				
LiS_3							
3A'			3B'				
	X	Y	Z		X	Y	Z
S	0.00000000	0.00000000	0.89262600	S	0.000000	-1.170420	0.000000
S	0.00000000	1.69226700	-0.27615900	S	-1.860638	-0.433041	0.000000
S	0.00000000	-1.69226700	-0.27615900	S	1.925430	1.354552	0.000000
Li	0.00000000	0.00000000	-1.81497600	Li	-0.345558	1.327511	0.000000
3C'							
	X	Y	Z				
S	-0.00000100	0.89268400	-0.00000700				
S	1.69236000	-0.27620400	0.00000600				
S	-1.69235900	-0.27620400	0.00000600				
Li	0.00000100	-1.81480500	-0.00002900				
LiS_4^-							
4A			4B				
	X	Y	Z		X	Y	Z
S	0.00000000	2.16217600	0.73236700	S	-1.02614600	-0.00000600	2.17083900
S	0.62509400	0.87006000	-0.87055300	S	0.00000700	1.02614800	-2.17083800
S	-0.62509400	-0.87006000	-0.87055300	S	1.02614800	0.00000400	2.17083300
S	0.00000000	-2.16217600	0.73236700	S	-0.00000300	-1.02614900	-2.17083400
Li	0.00000000	0.00000000	1.47398200	Li	-0.00000500	0.00000400	0.00000000

4C			4D				
	X	Y	Z		X	Y	Z
S	-1.02679000	0.00000000	2.12635800	Li	-1.99617	-0.00001	-0.93223
S	0.00000000	1.02679000	-2.12635800	S	-0.94581	-1.73323	-0.06420
S	1.02679000	0.00000000	2.12635800	S	0.22300	-0.00000	0.59878
S	0.00000000	-1.02679000	-2.12635800	S	2.04291	0.00001	-0.29560
Li	0.00000000	0.00000000	0.00000000	S	-0.94582	1.73322	-0.06420

4E			4F				
	X	Y	Z		X	Y	Z
Li	1.06571000	0.00051000	0.00047000	Li	-1.04474000	-0.00002000	-0.00090000
S	-1.96406000	-0.00030000	-0.00015000	S	-3.28225000	-0.00001000	0.00058000
S	-0.79375000	1.67887000	-0.00009000	S	0.76586000	1.66671000	-0.00041000
S	-0.79291000	-1.67888000	-0.00008000	S	1.94638000	0.00002000	0.00041000
S	3.35090000	0.00021000	0.00023000	S	0.76590000	-1.66671000	-0.00041000

4G			
	X	Y	Z
Li	0.96454000	-0.00609000	-0.16139000
S	-1.08276000	-1.42920000	-0.53226000
S	3.25478000	-0.00086000	0.06056000
S	-1.27449000	0.00107000	1.03476000
S	-1.07838000	1.43013000	-0.53279000

LiS₄

4A'			4B'				
	X	Y	Z		X	Y	Z
S	-1.88852700	0.83027000	-0.05138600	S	-2.29429600	0.96132800	0.00022300
S	-1.07299900	-1.02846400	0.09031700	S	-1.92794100	-0.99830900	-0.00027500
S	1.07302000	-1.02843700	-0.09024200	S	1.92819500	-0.99832900	0.00027000
S	1.88852500	0.83028800	0.05120200	S	2.29393800	0.96158800	-0.00023500
Li	-0.00010000	2.11383000	0.00058300	Li	0.00055400	0.39318300	0.00008800

4C'			4D'				
	X	Y	Z		X	Y	Z
S	2.09433900	-0.00007200	-0.19288100	S	0.00000000	0.99487500	2.15165400
S	-0.92243600	1.69637200	-0.04787700	S	0.99487500	0.00000000	-2.15165400
S	-0.92263400	-1.69650900	-0.04789200	S	0.00000000	-0.99487500	2.15165400
Li	-2.38651200	0.00073100	-0.53318000	S	-0.99487500	0.00000000	-2.15165400
S	0.19820200	0.00007200	0.38862200	Li	0.00000000	0.00000000	0.00000000

4E'			4F'				
	X	Y	Z	X	Y	Z	
Li	-0.48767000	-1.28433000	0.00115000	Li	-0.54510000	0.00073000	-1.37000000
S	-2.70784000	-0.58845000	-0.00020000	S	-2.49099000	0.00010000	-0.08922000
S	1.84674000	-1.20801000	-0.00004000	S	0.37281000	-0.00030000	1.01236000
S	1.49623000	0.79790000	-0.00017000	S	1.11006000	-1.42951000	-0.33331000
S	-0.54369000	1.23937000	0.00020000	S	1.11033000	1.42957000	-0.33295000

4G'			
	X	Y	Z
Li	-2.01949000	0.38638000	0.00010000
S	1.20319000	-0.54173000	0.00014000
S	3.14913000	-0.34298000	-0.00011000
S	0.17808000	1.21264000	0.00001000
S	-4.15175000	-0.40037000	-0.00005000

LiS₅⁻

5A			5B				
	X	Y	Z	X	Y	Z	
S	0.95912100	-1.08683800	0.00000000	S	0.00000000	0.00000000	1.65446700
S	-0.23290100	-0.82564500	1.76126700	S	0.00000000	1.71367300	0.33481700
S	-0.23290100	-0.82564500	-1.76126700	S	0.00000000	-1.71367300	0.33481700
S	-0.23290100	1.23553400	-2.27912200	S	-1.60597300	-1.62240500	-1.02348400
S	-0.23290100	1.23553400	2.27912200	S	1.60597300	1.62240500	-1.02348400
Li	-0.14675800	1.42432000	0.00000000	Li	0.00000000	0.00000000	-1.47803600

5C			5D				
	X	Y	Z	X	Y	Z	
S	0.00000000	1.68064800	1.39015700	S	0.23387100	3.65974200	0.00000000
S	-1.02422000	0.00000000	-2.62657600	S	-0.78981200	-3.89814400	0.00000000
S	0.00000000	0.00000000	2.55970200	S	-1.42617600	-0.53747000	0.00000000
S	0.00000000	-1.68064800	1.39015700	Li	0.00000000	1.32222900	0.00000000
S	1.02422000	0.00000000	-2.62657600	S	0.00338600	-2.04892000	0.00000000
Li	0.00000000	0.00000000	-0.46326700	S	1.97873200	2.57687300	0.00000000

5E			5F				
	X	Y	Z		X	Y	Z
S	1.08025000	-1.10444000	-0.24863000	S	0.90770000	-0.09071000	1.26203000
S	-2.38138000	-1.07364000	-0.21951000	S	3.90735000	0.02644000	-0.36437000
S	-0.77401000	1.96151000	-0.16413000	S	-3.24463000	-1.01878000	-0.28285000
Li	1.17832000	1.07985000	-1.02127000	Li	-1.24333000	-0.02088000	0.28573000
S	-0.95203000	0.03288000	0.65647000	S	1.90628000	0.03772000	-0.53223000
S	2.80623000	-0.01879000	0.16728000	S	-3.24359000	1.04924000	-0.13615000

5G			
	X	Y	Z
S	0.00000000	1.80678000	-0.09463000
S	0.00000000	1.10175000	-1.98427000
S	-0.00000000	-1.10175000	-1.98427000
S	-0.00000000	-1.80678000	-0.09463000
Li	0.00000000	0.00000000	1.57487000
S	0.00000000	0.00000000	3.86252000

LiS₅

5A'			5B'				
	X	Y	Z		X	Y	Z
S	0.98646100	-1.15897800	0.00000000	S	0.07309000	1.65227000	-0.07270500
S	-0.28686500	-0.78684800	1.68670800	S	1.90742400	0.46790600	-0.44099400
S	-0.28686500	-0.78684800	-1.68670800	S	-1.38336100	0.41616600	0.78974200
S	-0.28686500	1.23837500	-2.01451800	S	-2.30031200	-0.80987200	-0.62585100
S	-0.28686500	1.23837500	2.01451800	S	1.80659600	-1.37938100	0.29356300
Li	0.85866700	1.36493100	0.00000000	Li	-0.55166400	-1.85114200	0.29996800

5C'			5D'				
	X	Y	Z		X	Y	Z
S	-0.47185200	-1.38924300	-0.64210500	S	0.93922400	1.61315800	-0.55082300
S	1.96116000	-0.67679800	0.66135200	S	1.68400000	-1.62863000	-0.01307700
S	-2.04762200	-0.55231400	0.31516000	S	-2.32159300	0.80149300	0.48908600
S	-1.99286600	1.47248600	0.09793000	Li	-0.08471700	-0.44405100	-0.97831700
S	2.52142300	0.97069400	-0.29241400	S	2.14122200	0.30112700	0.50042800
Li	0.15870100	0.93426700	-0.74625600	S	-2.42696800	-1.00388800	-0.24217900

5E'			5F'				
	X	Y	Z	X	Y	Z	
S	-1.77914000	-1.02069000	-0.55630000	S	-3.22681000	-0.69744000	-0.77640000
S	2.34137000	-1.24081000	0.59194000	S	3.90070000	0.15830000	-0.32129000
S	1.09900000	1.85004000	0.06605000	S	0.93410000	-0.79517000	0.90775000
Li	-1.05510000	1.26095000	-0.50410000	Li	-1.28083000	-0.19025000	0.41345000
S	1.36619000	-0.04747000	-0.61211000	S	1.96683000	0.45223000	-0.30667000
S	-2.82960000	0.22251000	0.60494000	S	-3.33467000	0.91775000	0.41908000

5G'			
	X	Y	Z
S	2.63704000	0.00103000	-0.88759000
S	2.11169000	-0.00112000	1.01621000
S	-1.67889000	-1.43767000	-0.50103000
S	-1.67905000	1.43860000	-0.49849000
Li	0.22909000	0.00085000	-0.75311000
S	-1.43374000	-0.00099000	1.01211000

Li₂S₄⁻

2-4A			2-4B				
	X	Y	Z	X	Y	Z	
S	1.10494200	0.00000000	-1.93666800	S	1.79147100	1.06532100	0.00000000
S	0.00000000	1.02732900	2.00833100	S	-1.79147100	1.06532100	0.00000000
S	-1.10494200	0.00000000	-1.93666800	S	1.79147100	-1.06532100	0.00000000
S	0.00000000	-1.02732900	2.00833100	S	-1.79147100	-1.06532100	0.00000000
Li	0.00000000	-1.28993400	-0.38220400	Li	0.00000000	0.00000000	1.23076300
Li	0.00000000	1.28993400	-0.38220400	Li	0.00000000	0.00000000	-1.23076300

2-4C			2-4D				
	X	Y	Z	X	Y	Z	
S	-1.65004200	1.41711800	0.29893000	S	-0.12930500	1.72794200	0.36193800
S	-1.21569500	-0.37826800	-0.75553400	S	-1.46307100	0.37779000	-0.60124100
S	-0.14790100	-1.68705900	0.55941000	S	2.54319000	-0.35722200	-0.17276300
S	2.68636500	0.64061900	-0.07208500	S	-1.18740200	-1.52619400	0.38550800
Li	0.53480800	0.79859200	0.88129300	Li	0.73657900	-0.27225000	1.26964300
Li	1.21064700	-0.75811400	-1.04513500	Li	0.52522400	-0.91343800	-1.12799900

2-4E			2-4F				
	X	Y	Z		X	Y	Z
S	-0.24923000	-1.19211000	1.76128000	Li	0.00000000	1.37308000	1.43134000
S	-0.24923000	-1.19211000	-1.76128000	Li	-0.00000000	-1.37308000	1.43134000
S	-0.27109000	2.83608000	0.00000000	S	0.00000000	1.77012000	-0.86292000
Li	-0.24923000	1.06017000	-1.38361000	S	0.00000000	0.00000000	3.14275000
S	0.86302000	-0.84943000	0.00000000	S	0.00000000	-0.00000000	-1.95366000
Li	-0.24923000	1.06017000	1.38361000	S	-0.00000000	-1.77012000	-0.86292000

2-4G			
	X	Y	Z
S	-3.51426000	-0.56124	-0.10188000
S	2.10349000	-1.29586	-0.34902000
S	0.37015000	1.73576	-0.22572000
Li	-1.35384000	0.13106	0.10167000
S	0.99981000	0.01368000	0.95828000
Li	1.57153000	0.44313000	-1.60389000

Li₂S₄

2-4A'			2-4B'				
	X	Y	Z		X	Y	Z
S	0.95592000	1.60754500	-0.81854000	S	-0.50317300	-0.93441400	1.71568600
S	-0.95592000	-1.60754500	-0.81854000	S	-0.50317300	-0.93441400	-1.71568600
S	0.95592000	0.51263900	1.01385500	S	0.62195500	1.79665900	0.00000000
S	-0.95592000	-0.51263900	1.01385500	Li	-0.50317300	1.29711100	-1.92024400
Li	-1.21820500	0.69827100	-1.04168100	S	0.57308100	-0.41424700	0.00000000
Li	1.21820500	-0.69827100	-1.04168100	Li	-0.50317300	1.29711100	1.92024400

2-4C'			2-4D'				
	X	Y	Z		X	Y	Z
S	0.51950600	0.90352000	-1.81621200	S	1.05067300	0.00000000	-1.91114400
S	-0.51950600	0.87225800	1.88142500	S	0.00000000	1.00234700	1.97373500
S	-0.51950600	-0.90352000	-1.81621200	S	-1.05067300	0.00000000	-1.91114400
S	0.51950600	-0.87225800	1.88142500	S	0.00000000	-1.00234700	1.97373500
Li	1.31522600	-0.77920500	-0.34779900	Li	0.00000000	-1.38238800	-0.33382200
Li	-1.31522600	0.77920500	-0.34779900	Li	0.00000000	1.38238800	-0.33382200

2-4E'			2-4F'				
	X	Y	Z		X	Y	Z
S	-0.0436400	-0.88296	1.7570500	S	0.0000000	1.1152300	0.6984400
S	-0.0436400	-0.88296	-1.7570500	S	0.0000000	-1.1152300	0.6984400
S	-0.0342900	3.14462	-0.0000000	S	-1.3460600	-1.7020900	-0.7894100
Li	-0.0436400	1.42527	-1.5130100	S	1.3460600	1.7020900	-0.7894100
S	0.1379300	-1.91318	0.0000000	Li	0.0000000	0.0000000	-1.7464900
Li	-0.0436400	1.42527	1.5130100	Li	0.0000000	0.0000000	2.7167900

2-4G'			
	X	Y	Z
S	-1.2374500	-1.5993200	-0.2017700
S	-1.5763800	0.2510900	0.5479800
S	2.7760500	-0.4456900	0.1184200
S	-0.3824900	1.6514900	-0.4417900
Li	0.7408100	-0.5049700	-1.0578200
Li	1.5006100	1.2645800	0.9360300