Supplementary Information on

Lithiation Mechanism of Sulfur Surfaces During Discharge of Li-S Batteries from Quantum Chemical Calculations

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Table S1 shows the average reaction energies in the first lithiation reaction.

Table 1: Average reaction energies of the 1. lithiation step

Upper Layer [eV]	Lower Layer [eV]
-2.25	-2.73
-2.44	-2.36
-2.17	-2.65
-2.52	/
-2.22	/
-2.22	/
Average = -2.32	Average = -2.58

Figures S1 and S2 show all Li_2S_6/Li_2S_2 and Li_2S_7/Li_2S product structures found during the third lithiation are shown. Also included in the figures are the reaction enthalpies.

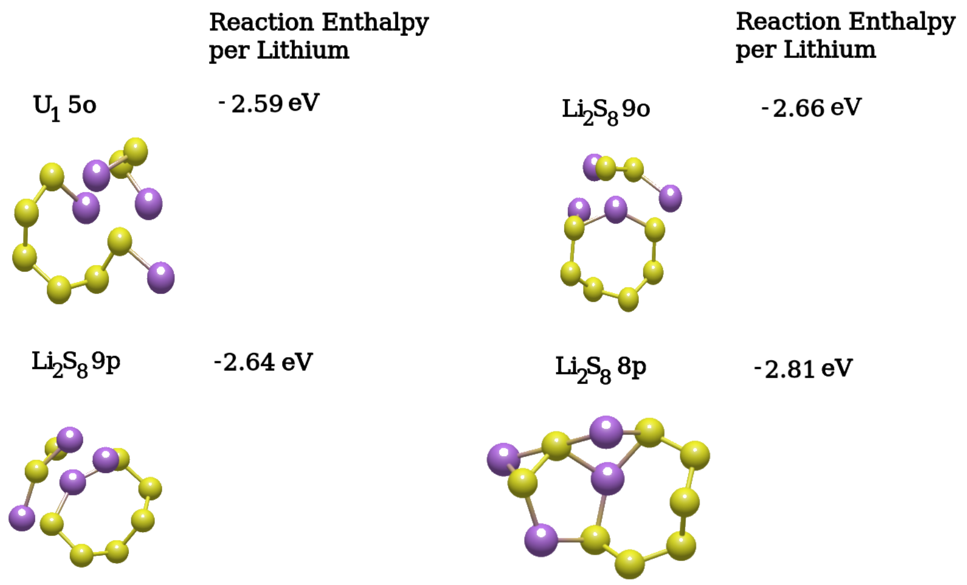

Figure 1: Reaction Enthalpies for Li_2S_6/Li_2S_2

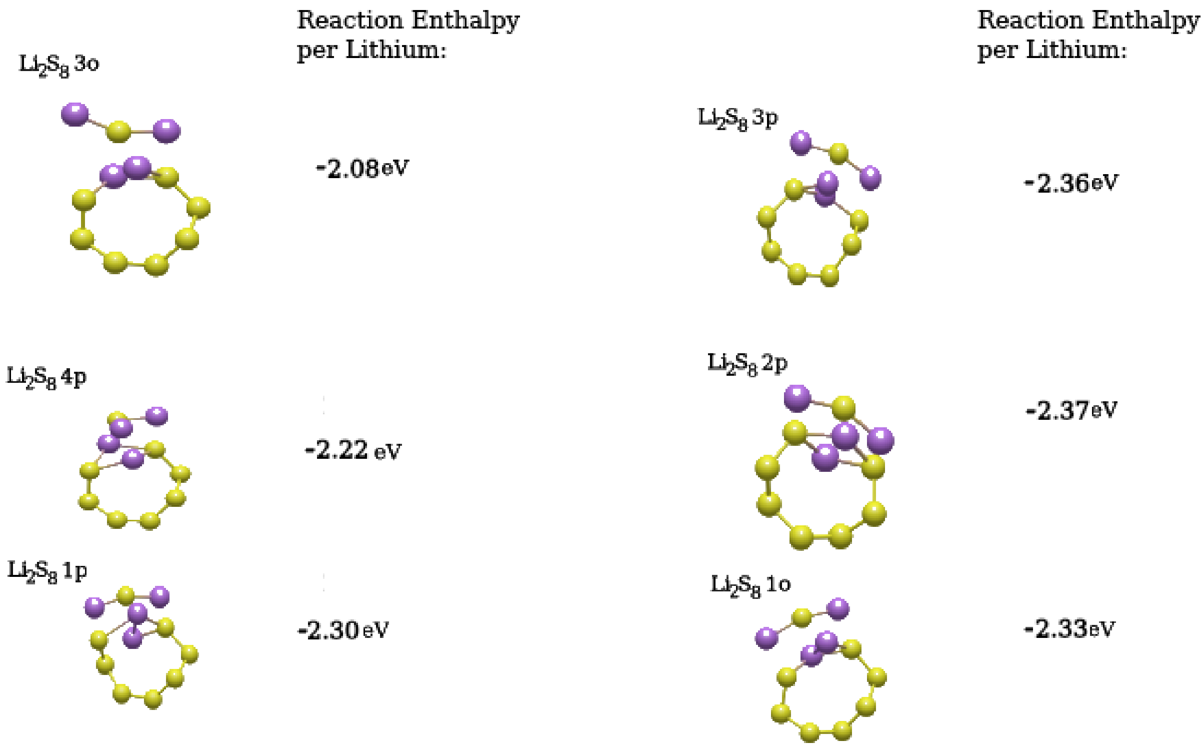

Figure 2: Reaction Enthalpies for Li_2S_7/Li_2S

Figures S3 and S4 show the Li_2S_x molecules found during consecutive lithiation reactions in the gas and liquid phase, respectively. The liquid-phase calculations were carried our using the self-consistent continuum solvation method [O. Andreussi, I. Dabo, N. Marzari, *J. Chem. Phys.* **136**, 064102 (2012)]. The dielectric constant for the solvent was set to 7.2, to represent a solvent consisting of a 1:1 v/v mixture of 1,3-dioxolane and 1,2-dimethoxyethane.

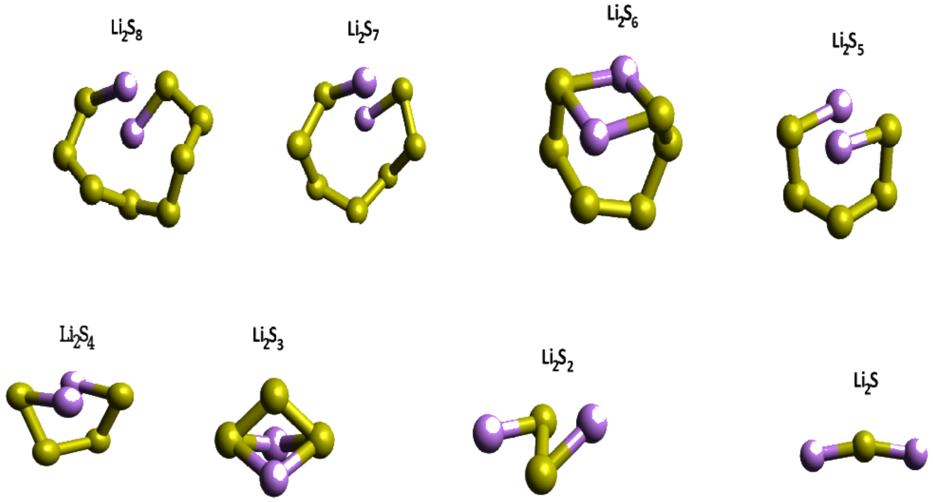

Figure 3: Li_2S_x molecules found in gas-phase lithiation reactions.

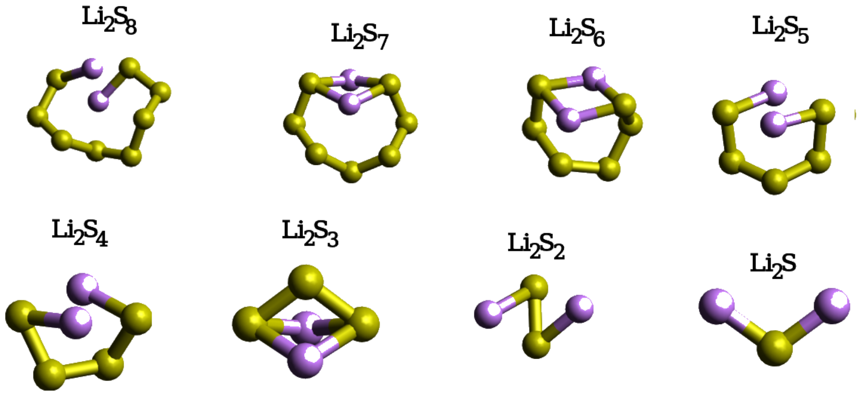

Figure 4: Li_2S_x molecules found in liquid-phase lithiation reactions.

Figure S5 presents a comparison between the structure of Li_2S_6 polysulfide found in the gas and liquid phase. The corresponding structural properties are given in Table S2. Li_2S_6 is selected for comparison in Table S2 as it represents a mid-order polysulfide species, balancing reactivity and stability while maintaining a distinct spectroscopic signature. Although static calculations do not capture the dynamic interconversion between ring-shaped and chain-like polysulfides, AIMD simulations could represent this transformation. In electrolyte solutions, chain-like structures may be favored due to reduced steric hindrance, increased surface area for solvent interactions, and greater conformational flexibility.

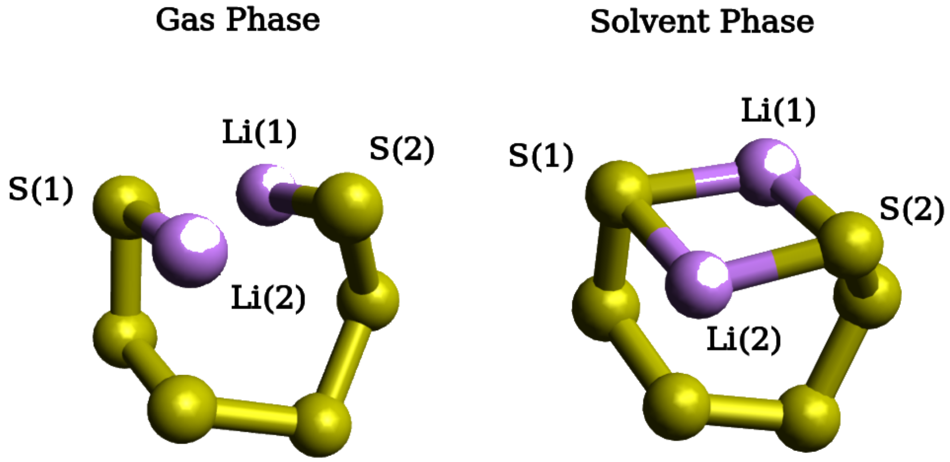

Figure 5: Li_2S_6 in vacuum and solvent.

Table 2: Comparison of Li_2S_6 bonds in vacuum and solvent

Bond	Vac. [Å]	Solv. [Å]
S(1)-Li(1)	2.36	2.35
S(1)-Li(2)	2.44	2.42
S(2)-Li(1)	2.40	2.40
S(2)-Li(2)	2.44	2.41

Table S3 lists the average reaction energies of all the reactions considered for each lithiation step. It should be noted that the products close to structures that have already undergone a lithiation are not included in these calculations. Although the average energies are significantly different for the S_8 molecules on the upper and lower structures, the trend of lower structures being more preferred for lithiation remains consistent.

Table 3: Average reaction energies of the first, second, and third litiation reactions in [eV].

Lithiation Step	Upper S_8	Lower S_8
1	-2.32	-2.58
2	-2.25	-2.31
3	-2.27	-2.45

Tables S4 and S5 present the lowest-energy structures for the first, second and third lithiation steps, classified according to the criteria of upper/lower and adjacent/isolated S_8 rings. A comparison of the energy values in these tables reveals that lithiation preferentially occurs on lower-adjacent S_8 rings, while upper-isolated rings are the least favorable for lithiation. The energetically intermediate products such as lower-isolated and upper-adjacent structures exhibit nearly equal probability for getting lithiated, as discussed further in the main text. Additionally, an interesting observation when examining the two tables separately is that the reaction energy difference between adjacent-upper and adjacent-lower lithiated S_8 rings is approximately 0.1 eV. In contrast, the reaction energy difference between isolated-upper and isolated-lower lithiated S_8 rings is higher, namely around 0.2 eV. This shows that the interaction between lithium and sulfur of two adjacent Li-polysulfide molecules has a greater influence (in terms of energy lowering) on the upper Li_2S_8 ring than a lower Li_2S_8 ring. If this was not be the case, both energy differences would have been approximately 0.2 eV. A possible explanation for this might be that Li atoms in the upper rings do have a weaker interaction with sulfur atoms from neighboring S_8 molecules and therefore interact more strongly with the adjacent Li-polysulfide.

Table 4: Lowest reaction energies, ΔE_R, in [eV] for the reactions involving lithiation of an adjacent S_8 ring in the second and third lithiation step.

Lithiation Step	Adjacent Product	ΔE_R
2	Li_2S_8 1p (upper)	-2.70
3	Li_2S_8 7p (lower)	-2.78
3	$L_4$2o, $L_4$3p,$L_4$3o (lower)	-2.81
3	$U_4$5o, $U_4$5p, $U_4$1p (upper)	-2.68

Table 5: Lowest reaction energies in [eV] for the reactions involving lithiation of an isolated S_8 ring.

Lithiation Step	Isolated Product	ΔE_R
1	Li_2S_8 3o (lower)	-2.73
1	Li_2S_8 2p (upper)	-2.51
2	$L_2$3o, $L_1$1p (lower)	-2.73
3	$L_2$3p, $L_3$1p, $L_3$3p (lower)	-2.68
3	$U_3$1p (upper)	-2.44

Table S6 and corresponding energy profile curve in Fig. S6 represent static DFT calculations, simulating the extraction of a Li_2S_8 ring from the (001) sulfur surface after the first lithiation step in an implicit DME/DOL solvent (1:1 v/v) environment. The relative energies, referenced to the fully bound configuration (0 Å), show a consistent increase as the Li_2S_8 molecule is pulled away from the surface. This is possibly due to the disruption of the stabilizing interactions (e.g., electrostatic and van der Waals forces) between Li_2S_8 and the sulfur surface. The monotonic trend of the curve reflects a barrier-like profile. Although these calculations neglect dynamic effects (no thermodynamic integration is performed) and the atomic structure of the solvent molecules, they nonetheless reveal a considerable energy barrier associated with Li_2S_8 dissociation.

Table 6: Dissociation energies, ΔE [eV] in [eV] of Li_2S_8 pulled out of the S_8-surface in implicit solvent for different surface distances.

Distance [Å]	Energy [H]	ΔE [eV]
0	-5897.9241	0.00
1	-5897.9225	0.04
2	-5897.9105	0.37
3	-5897.8942	0.81
4	-5897.8757	1.32
5	-5897.8727	1.48
6	-5897.8628	1.66

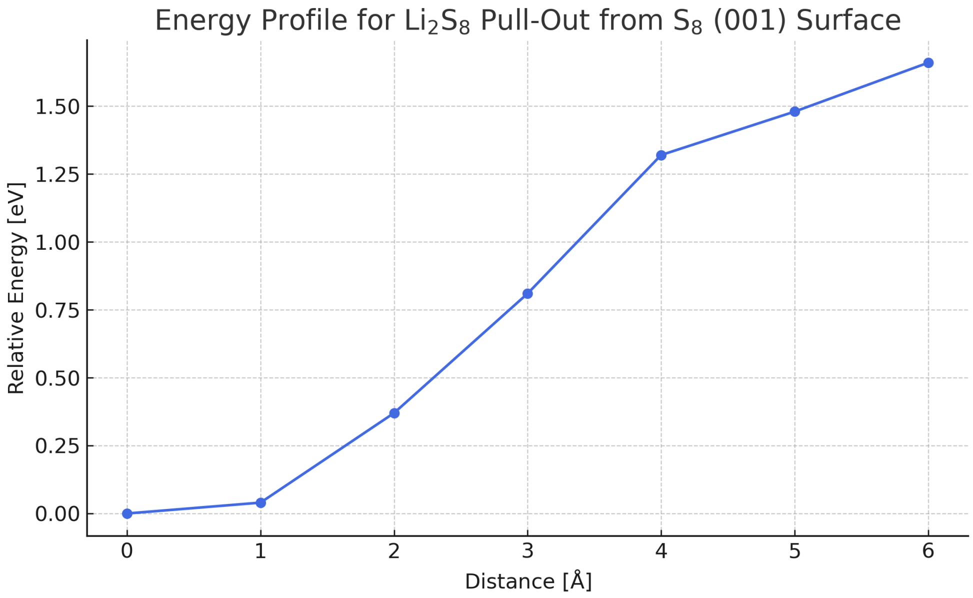

Figure 6: Dissociation curve of Li_2S_8.