

**Supporting Information for Article entitled
“Disulfide Passivation of the Ge(100)-2x1 Surface”**

Jessica S. Kachian, John Tannaci, Robert J. Wright, T. Don Tilley, and Stacey F. Bent

Table S1. Vibrational assignments for ethyl disulfide (eds) on Ge(100)-2x1. Multilayer assignments were made using References 46-48. The frequency assignments for the chemisorbed spectrum are based on the normal modes obtained from DFT calculations of the S-S dissociated adduct. ^av_{ar} = stretch associated with aromatic ring; v = stretch; δ = bend; δ_{sc} = scissoring; δ_{as} = asymmetric deformation; δ_s = symmetric deformation; ω = wag; τ = twist; ρ = rock; modes that appear to be listed multiple times do not constitute the same atomic motions.

	<u>Frequency, cm⁻¹</u>	
<u>Mode^a</u>	<u>Multilayer</u>	<u>Chemisorbed</u>
τ(CH ₂)	1256	1256
ω(CH ₂)	1283	----
δ _s (CH ₃)	1379	1379
δ _{sc} (CH ₂)	1441	1427
δ _{as} (CH ₃)	1462	1450
v(C-H)	2853, 2872, 2928, 2968	2874, 2921, 2972

Table S2. Vibrational assignments for 1,8-naphthylene disulfide (nds) on Ge(100)-2x1. Peaks in the multilayer spectra were assigned based on Reference 49 and on the normal modes obtained from DFT calculations of the nds molecule. The frequency assignments for the chemisorbed spectrum are based on the normal modes obtained from DFT calculations of the S-S dissociated adduct.

	<u>Frequency, cm⁻¹</u>	
<u>Mode^a</u>	<u>Multilayer</u>	<u>Chemisorbed</u>
δ(C-H)	1146	1150
δ(C-H)	1209	1196
δ(C-H) + some v _{ar} (C=C)	1312	1316
δ(C-H) + some v _{ar} (C=C)	1352	1350
δ(C-H)	1416	1422
δ(C-H) + some v _{ar} (C=C)	1489	1493
v _{ar} (C=C) + δ(C-H)	1549	1543
v _{ar} (C=C) + δ(C-H)	1605	1601
v _{ar} (C-H)	3051	3057

Figure S1. Energy diagrams calculated for intradimer (solid line) and interdimer (dashed line) S-S dissociation of eds (blue curve) and nds (red curve) on a two-dimer, intrarow $\text{Ge}_{15}\text{H}_{16}$ cluster. Energies are calculated with respect to the reactants (a). Only critical points are shown and correspond to (b) the S dative-bonded state, (c) the transition state to interdimer S-S dissociation, (d) the interdimer S-S dissociated state, (e) the transition state to intradimer S-S dissociation, and (f) the intradimer S-S dissociated state. We also performed calculations for an alternative pathway for interdimer S-S dissociation, which begins with formation of (b) and leads to the product (d) but has a transition state in which the dimers are of the same tilt and in which the unreacted S atom of the dative-bonded adduct is forming a bond with the “down” atom of the unoccupied dimer while the S-S bond is breaking. However, this pathway is not shown, as the corresponding transition state is 1.4 kcal/mol higher in energy than that in the interdimer pathway displayed in Figure S1 for eds, and for nds, searching for such a transition state simply led to convergence on (c), indicating that reaction of nds on Ge does not proceed via the alternate interdimer pathway.

