

Supplemental Information

Chirality and Rotation of Asymmetric Surface-Bound Thioethers

Heather L. Tierney¹, Jeong Woo Han², April D. Jewell¹, Erin V. Iski¹, Ashleigh E. Baber¹, David S. Sholl² and E. Charles H. Sykes¹

¹ *Department of Chemistry, Tufts University, Medford MA 02155*

² *School of Chemical and Biomolecular Engineering, Georgia Institute of Technology, Atlanta GA 30332*

BuSMe Purity Verification with Mass Spectra

Mass spectra acquired w/ Extorr Residual Gas Analyzer XT200 quadrupole mass spectrometer. Mass sweep was taken from 40 to 110 amu (Figure S1). Peaks ≤ 40 amu occurred due to typical background gases in the UHV chamber (including the peak at 40 from Ar used to sputter clean the metal substrates). The full mass of butyl methyl sulfide is 104 amu.

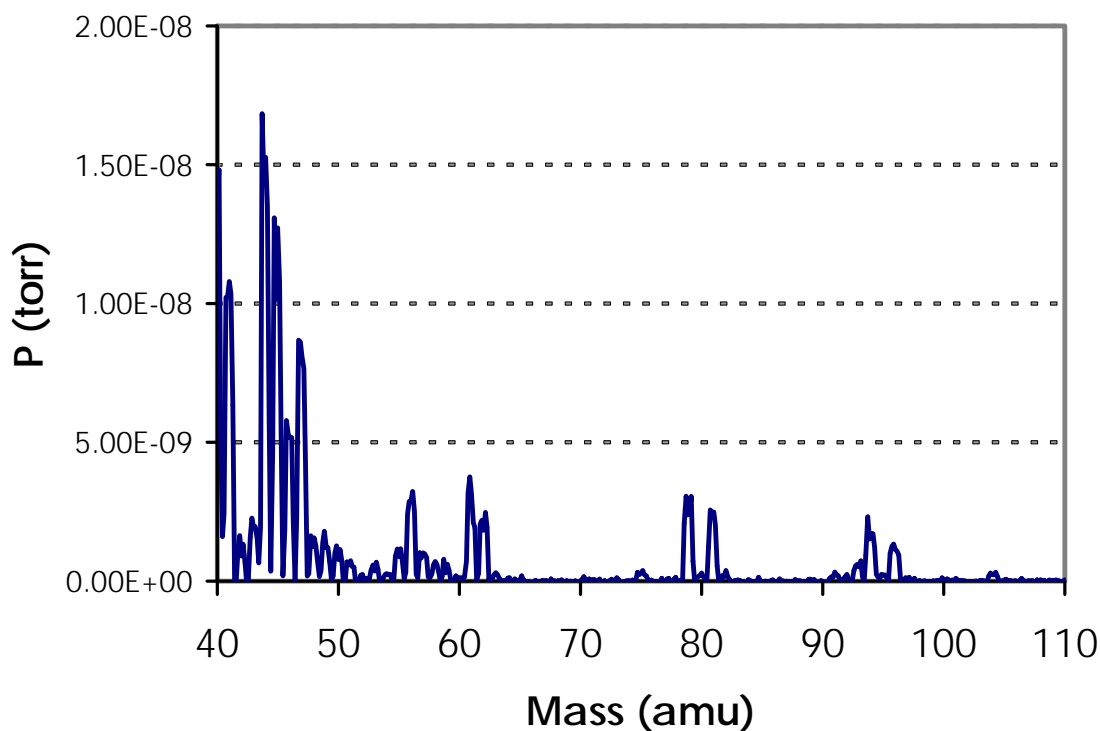


Figure S1: MS of butyl methyl sulfide for purity analysis.

STM Movie

An STM movie is included with the supplemental information, which is a compilation of many consecutive STM images (each of which takes ~ 2 min to acquire). This movie reveals that the chirality of individual surface-bound butyl methyl sulfide molecules does not change, even at moderately high biases at 78 K. Multiple pulsing of individual molecules at voltages ≥ 400 mV caused them to change chirality, but more often lead them to change adsorption site (78% changed adsorption site, while 22% inverted chirality). This result suggests that there are competing pathways between translation and chirality inversion, and the translational barrier is smaller than that for inversion. This movie shows that even at elevated biases, the short time the tip is in the proximity of the molecule during a normal scan is not long enough to invert the chirality of the butyl methyl sulfide molecules over a time period of many hours. (Imaging conditions: $I = 50$ pA, $V = -400$ mV)

This movie also illustrates an important point about chirality identification; Even if the STM is not sharp enough to easily image all 6 of the lobes of butyl methyl sulfide, it is still possible to identify the chirality of the molecules based on their orientation. Within their mirror symmetry these rotors have a slight tilt away from their central mirror plane, which allows for easy identification even without the clarity of the images in Figure S2.

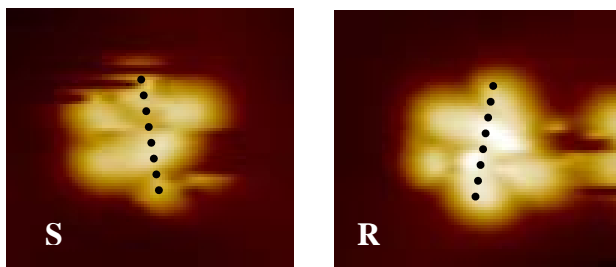


Figure S2: Rotors of both chirality are shown to have a slight tilt away from their central mirror plane, which allows their identification even with more blunt STM tips as hexagons rotated at two different angles. (Imaging conditions: 300 pA, 100 mV, 7K.)

Arrhenius Plot for hcp-adsorbed BMS

By measuring the rotational rate as the temperature is increased, it is possible to create an Arrhenius plot to further understand the rotational energetics and specifically the torsional barrier for rotation of the butyl methyl sulfide molecules (Figure S3).

Arrhenius data is shown for a single butyl methyl sulfide molecule in the hcp region of the Au(111) surface. The activation energy (E_a) and the attempt frequency (A) calculated from this plot are also displayed in Figure S3. All rate measurements are calculated by measuring the number of switching events during the course of current vs. time (I vs. t) curves.

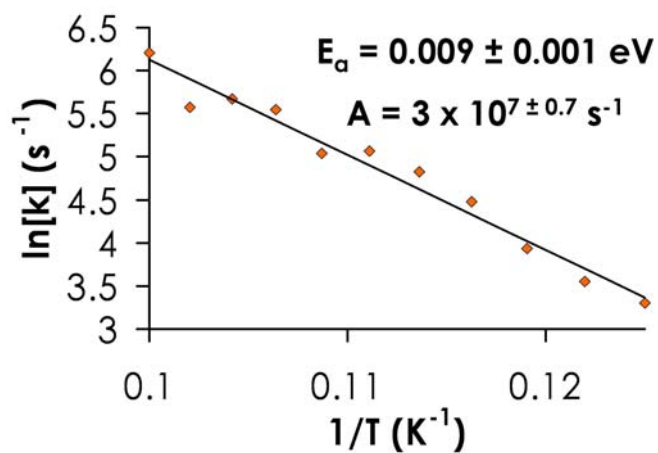


Figure S3: Arrhenius plot for butyl methyl adsorbed in an hcp area of the Au(111) surface. (Tunneling conditions: $I = 5 \text{ pA}$, $V = 100 \text{ mV}$).

DFT Rotation Pathway Investigations

Only symmetric pathways that reproduced the six-fold rotational symmetry observed in STM images were considered, however due to extremely high rotational barriers, all pathways other than rotation around an atop site have been ruled out. Figures S3 and S4 show the energetic pathway for the rotation of a butyl methyl sulfide molecule around a fcc 3-fold hollow and a hcp 3-fold hollow, respectively.

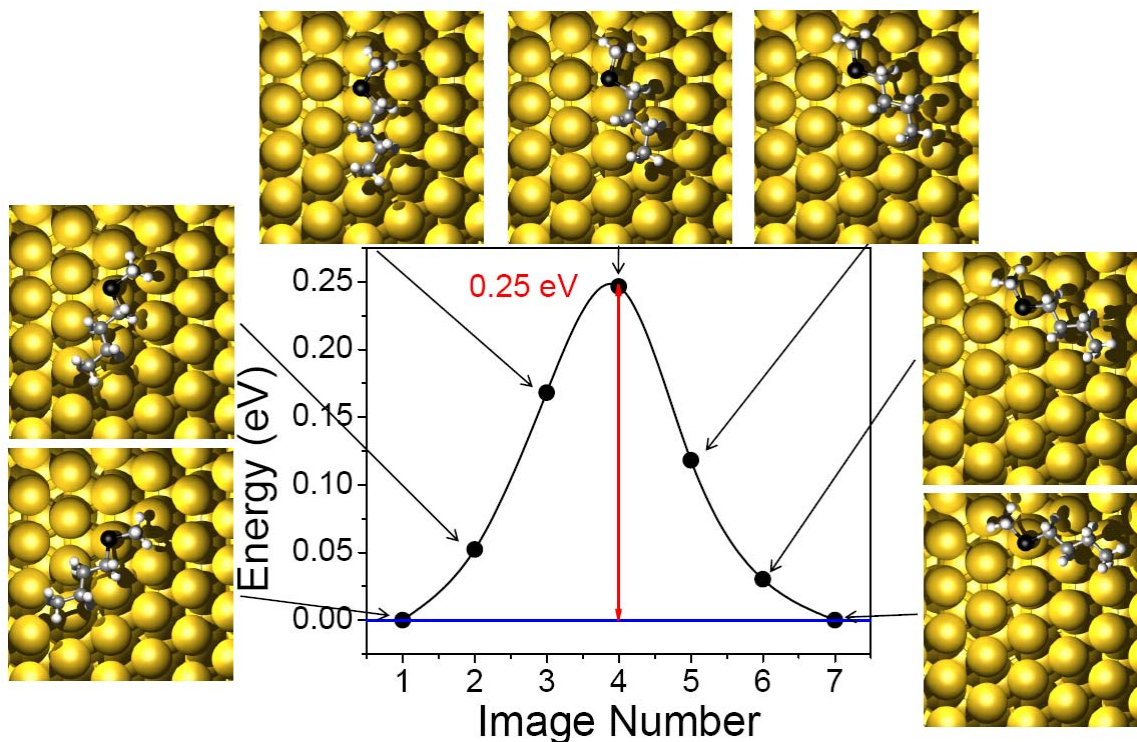


Figure S3: Nudged elastic band results for the rotational barrier of the S atom around a fcc 3-fold hollow. The rotation of this molecule by 120° is enough to cover the whole rotational angle; the initial state is equivalent to the state rotated by 120° which is the final state here. The rotational pathway for the adsorbed butyl methyl sulfide on Au(111) is exhibited along with each corresponding energy state. The barrier to this rotation is 0.25 eV.

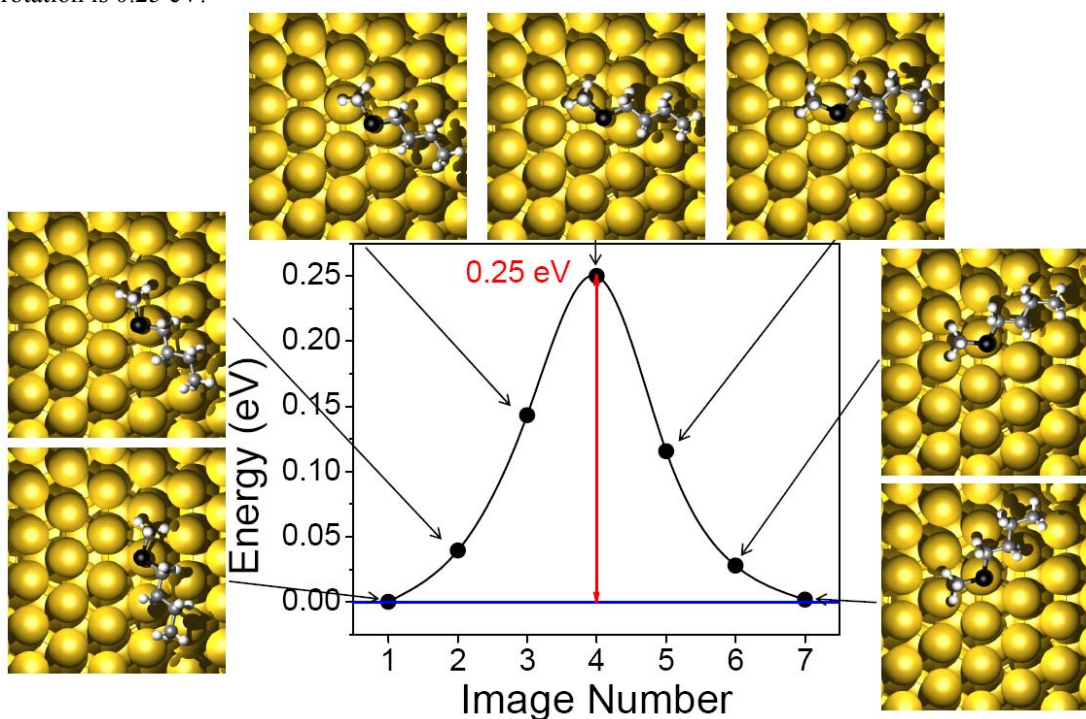


Figure S4: Same as Figure S3, but for the rotational barrier of the S atom around a hcp 3-fold hollow.