Dynamics of Molecular Adsorption and Rotation on Nonequilibrium Sites
Heather L. Tierney, April D. Jewell, Ashleigh E. Baber, Erin V. Iski, and E. Charles H. Sykes*

Department of Chemistry, Tufts University, Medford, Massachusetts 02155

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It is generally accepted that important events on surfaces such as diffusion and reactions can be adsorption site dependent. However, due to their short lifetime and low concentration in most systems, adsorbates on nonequilibrium adsorption sites remain largely understudied. Using low-temperature scanning tunneling microscopy, site-dependent adsorption is shown for the molecule butyl methyl sulfide, which is trapped in multiple metastable adsorption sites upon deposition onto a Au(111) surface at 5 K. As this molecule does not have enough energy to diffuse to its preferred adsorption site on the surface, it is possible to study the behavior of individual molecules in a variety of nonequilibrium sites. Here we present atomic-scale data of the same chemical species in three independent, metastable adsorption sites and equilibration to a single equilibrium site as a function of either electrical or thermal excitation. Butyl methyl sulfide exhibits distinctly different physical properties at all four adsorption sites, including rotational dynamics and appearance in scanning tunneling microscopy (STM) images. An energy profile is proposed for the adsorption and equilibration of these species, and a correlation is drawn between rotational barrier and adsorption energy.

Introduction

While it is known that reactions can be adsorption site dependent,1-5 it is most often assumed that molecules occupy equilibrium sites when adsorbed on surfaces. This is not always the case; for example, on crowded surfaces, molecules can be forced to adopt less energetically favorable sites.3 A few careful studies have shown reaction dependence on adsorption sites1,2 as well as site-dependent diffusion,2,4 adsorption,5 and lateral forces; however, in most cases, very little is known about mechanisms for diffusion between adsorption sites. It has also been demonstrated that molecules with multiple attachment sites to a surface can exhibit a mismatch with the surface lattice. This forced binding to nonequilibrium adsorption sites can lead to highly directional diffusion properties.13

Since intermediate or precursor states only exist on the surface in small quantities or for short periods of times, it is very difficult to study their physical properties.4,15 Using low-temperature scanning tunneling microscopy (STM), it is possible to monitor the properties of these nonequilibrium or precursor species on a molecule-by-molecule basis,16 and if imaging conditions are chosen carefully, metastable species can be imaged without being perturbed.17,18 Previous studies have used step edges and defects to trap molecules19,20 however, we have chosen molecules that are trapped in multiple metastable adsorption sites on terraces when deposited at low surface temperatures. The molecule under consideration in this paper is butyl methyl sulfide, which is a simple asymmetric thioether (RSH) molecule. This molecule and others like it have been studied as molecular rotors; however, only equilibrated molecules have been considered in previous studies.21-23 As precursor-adsorbed molecules do not have enough energy to make it to their preferred sites (which are most likely < 1 A away), we are able study the rotational and equilibration behavior of these metastable molecules and relate these properties to each molecule’s adsorption site. Herein we report data for the same chemical species in three metastable adsorption sites and their subsequent equilibration to a single site as a function of either applied bias voltage or temperature. Using STM, it is also possible to show the differences in physical properties of this molecule at all four adsorption sites, including rotational rates and appearance in STM images. From these measurements, a relative energy landscape is proposed for each adsorption site, and a correlation is drawn between rotational barrier and adsorption energy.
Materials and Methods

All STM experiments were performed in a low-temperature, ultrahigh vacuum (LT-UHV) microscope built by Omicron Nanotechnology. The Au(111) sample was purchased from MAtEcK and was prepared by cycles of Ar sputtering (1.0 keV/14 A) for 30 min followed by 2 min anneal periods up to 1000 K. Approximately 12 of these sputter/anneal cycles were performed upon receiving the crystal, followed by another two sputter/anneal cycles between each STM experiment. After the final anneal, the crystal was transferred in less than 5 min in vacuum (<5 × 10⁻¹⁰ mbar) into the precooled STM. In approximately 30 min, the sample cooled from room temperature to 5–7 K. All images were recorded with etched W or cut Pt/Ir tips, and voltages refer to the sample bias. Butyl methyl sulfide was obtained from the rare chemical library of Sigma Aldrich and was further purified by cycles of freeze/pump/thaw prior to introduction to the STM chamber via a leak valve. Purity was verified with mass spectrometry. Images were recorded with etched W or cut Pt/Ir tips, and voltages refer to the sample bias. Butyl methyl sulfide was obtained from the rare chemical library of Sigma Aldrich and was further purified by cycles of freeze/pump/thaw prior to introduction to the STM chamber via a leak valve. Purity was verified with mass spectrometry (see the Supporting Information). Butyl methyl sulfide was deposited onto the cold sample by using a collimated molecular doser while the tip was scanning. The STM stage was equipped with a sample heater capable of controllably heating the sample and tip up to 40 K above the base temperature.

Results and Discussion

When dosed at low coverage (<0.3 ML) and at 5 K on Au(111), thioether molecules (including butyl methyl sulfide) do not preferentially adsorb in any region of the Au herringbone reconstruction, or even on any preferred adsorption site. Figure 1 shows a large-scale STM image of an initial dose of butyl methyl sulfide (left) as well as the same area of the surface after all of the molecules have been equilibrated (right). While initially there appear to be four types of species on the surface, after supplying electrical energy to the molecules from the STM tip, it is clear that they are all of the same molecular identity. The insets in Figure 1 show zoomed-in images of the four as-dosed adsorbed species, which are assumed to image differently due to their different adsorption site on the underlying Au surface. These four sites are labeled as \( \alpha, \beta, \gamma, \) and \( \delta \), and butyl methyl sulfide molecules are seen to rotate about their central S–Au bond at perturbative tunneling conditions when adsorbed on any of these four sites. While thioethers have only two unbranched alkyl chains, these molecules appear hexagonal due to the superposition of their six equivalent orientations on the underlying hexagonal surface, as they rotate faster than the time scale of the STM images shown in Figure 1. At elevated tunneling currents and low bias voltages, the STM tip is brought extremely close to the sample, and will interact very strongly with the adsorbed species. In this case, the STM tip perturbs the molecules on the surface which causes molecular rotation at lower than normal temperatures for these molecules.

Molecules in all of the adsorption sites can be distinguished based on their distinctive contrasts and shapes upon STM imaging. Measured diameters of 2.3, 2.3, 3.0, and 2.3 nm and apparent heights of 0.10, 0.10, 0.23, and 0.15 nm were found for \( \alpha, \beta, \gamma, \) and \( \delta \) species, respectively. While \( \alpha \) and \( \beta \) species imaged with the same dimensions, close inspection of these species in Figure 1 shows that their hexagonal outlines are offset 30° from one another. It should be noted that these measured dimensions are partially STM tip dependent and do not represent the exact dimensions of the rotating molecules; however, comparisons of species for many hundreds of molecules imaged with many tip states support these general, relative characteristics (see the Supporting Information for the same equilibration experiment as Figure 1 in multiple areas of the surface with different STM tip states that show the appearance of the molecules before and after equilibration).

We have observed no accumulation at more favorable sites such as step edges, which supports our hypothesis that when deposited on the surface at 5 K these molecules cannot equilibrate to their preferred adsorption sites. Figure 2 shows a step edge after dosing butyl methyl sulfide at 5 K. While there are a couple of molecules that have adsorbed directly at the step, there are also molecules very close to the step that have not diffused to it. Step edges are very attractive sites for adsorption due to the undercoordination of the metal atoms, and it has previously been postulated that an accumulation of molecules at a step edge should occur if adsorbed species have low barriers to diffusion. We have previously shown that similar thioether molecules aggregate at step edges at temperatures as low as 80 K.

Figure 1. STM images of butyl methyl sulfide rotors on Au(111). The different adsorption site of each molecule leads to different rotational properties and different appearance in STM imaging. Left: As-dosed collection of molecules on Au(111) appear as if there are four types of molecules present. Insets in the middle show high-resolution images of each type of species. After supplying energy to the molecules via the tunneling current from the STM tip (right), it is seen that all molecules are indeed the same and have all converted to their global minimum energy state, which is labeled here as \( \alpha \). The slight differences in contrast observed on the right are due to the natural \( 22 \times \sqrt{3} \) reconstruction of the surface. (Tunneling conditions: Left and right: 300 pA, 100 mV, 7 K. Inset: \( (\alpha, \beta, \gamma, \delta) \) 700 pA, 50 mV, 5 K; \( (\gamma) \) 5 pA, 50 mV, 5 K). Scale bars in insets = 0.5 nm.


Interconversion between adsorbed species was studied as a function of temperature and bias voltage. These conversions, which are the equilibration of a given molecule to its preferred adsorption site, are represented in Figure 3. As can be seen in Figure 1, these molecules only need to move a very small distance to equilibrate (<1 surface lattice spacing), and this lateral displacement is almost indistinguishable in the before and after images such as those in Figure 1. It can be seen from Figure 3 that the \( R \) species were at the lowest energy sites, which is consistent with previous studies of the equilibrium adsorption site of this rotor molecule.\(^{21}\) \( \beta \) rotors were also very stable and exhibited high electrical and thermal barriers for equilibration to \( R \) rotors, while \( \gamma \) and \( \delta \) rotors were less stable and could be equilibrated at lower temperatures and voltages. By increasing the voltage while keeping the tunneling current constant, progressively higher energy electrons were supplied to the molecules under investigation. Molecules were imaged in this incremental manner until a change in adsorption site occurred. This type of scan “locally annealed” the surface by supplying energy only to the molecules within the area of the image. The same process was performed as a function of temperature, wherein the entire surface was annealed to investigate the thermal equilibration of the metastable species. Using the combination of these thermal and electrical treatments, it was possible to deduce both the true equilibrium site (\( R \)) and the relative stability of the metastable adsorption sites (\( \gamma < \delta < \beta \)).

To further understand the properties of butyl methyl sulfide in its unequilibrated states, the rotational properties of all the adsorbed species were studied. At nonperturbative tunneling conditions, most of the rotors did not spin at 5 K; only the \( \gamma \) rotors continued to spin at such a low temperature (see lower images in Figure 4 for static \( \alpha, \beta \) and \( \delta \) rotors). The temperature was then increased at nonperturbative imaging conditions until the rotors appeared to be spinning on the time scale of STM imaging (~1–10 s to image a molecule). Figure 4 shows the temperatures at which rotation began for all the adsorbed species. Within error, all but the \( \gamma \)-adsorbed rotors began to spin at the same temperature of ~8.5 K. This rotational onset temperature is a crude way to measure the thermal barrier to rotation;\(^{22}\) however, a more accurate measurement of this barrier utilizes Arrhenius plots, which are described in the following paragraphs.

With STM, it is possible to measure the rotational rates for the adsorbed molecular rotors.\(^{21–25}\) In these measurements, the feedback loop (which is normally used to modulate the STM tip height in order to maintain a constant tunneling current) is turned off and the tunneling current is monitored with respect to time (\( I \) vs \( t \)). As the molecule rotates beneath the STM tip, changes in the orientation of its alkyl tails lead to a modulation of the tunneling current between discrete values.\(^{21–23}\) By measuring the
rotational rate in this manner as the temperature is increased, it is possible to generate Arrhenius plots to further understand the rotational energetics and specifically the torsional barriers of the butyl methyl sulfide molecules at different adsorption sites (Figure 5). All rate measurements were calculated by counting the number of switching events in I vs t curves. It is also important to note that these molecules are assumed to have rotational properties which are independent from the reconstruction of the Au(111) surface. Our previous molecular rotor studies have shown that thioethers such as butyl methyl sulfide have very similar rotational energetics on hcp and fcc regions of the surface,21 so the hcp and fcc regions can be considered nearly identical and precautions were taken to ensure that molecules were not directly on top of the soliton walls that separate hcp and fcc regions.

While α, β and δ rotors had very similar thermal rotational onset temperatures, Figure 5 reveals that δ-rotors have distinctly different rotational energetics. α and β rotors still appear to have almost identical rotational properties (within error), but upon examination of their rotational rates it is clear that δ-adsorbed species have very different rotational rates at lower temperatures and have a lower activation energy. γ rotor species spin so quickly even at 5 K that it is not possible to measure their rotational rates due to the time resolution of the I vs t curves (1–3 kHz for our setup depending on tunneling current set-point).20 Figure 5 reveals the marked difference in rotational rates for the same molecules at the same measurement conditions and the same temperature, with the only difference between them being their adsorption sites.

The activation energies (Ea) and the attempt frequencies (A) calculated from the Arrhenius plots are displayed in Table 1. The attempt frequencies are noticeably low compared to expected molecular event frequencies; however, this low attempt frequency has been observed previously for single molecule rotors, including this group’s work of similar molecular rotors. It has been postulated that the low A values arise due to multiple configurations of the alkyl tails in the ground state that lead to entropic effects in the transition state or tunneling effects.21,23,31,32 Although it is not possible to plot Arrhenius data for the γ rotors, a barrier was estimated for comparison to other adsorbed rotor species. In this calculation, the minimum rate was used (estimated based on experimental limitations) and 10^8 Hz was used as an attempt frequency (based on all of the other adsorbed species). It is expected that this is an overestimation of the activation energy for the γ rotors; however, it emphasizes the differences in rotational properties between these rotor molecules based solely on their different adsorption sites.

It is well-known that there is an approximately linear relationship between adsorption energy and barrier to diffusion;28,33,34 therefore, we propose that there exists a similar correlation between adsorption energy and barrier to rotation. Molecular dynamics simulations have shown that there is a delicate interplay between S–Au bond length, alkyl tail length, and rotational dynamics of thioether molecules, which suggests that the S–Au bond strength is strongly coupled to the rotational properties of similar molecular species.25 Previous studies by Lavrich et al. used temperature programmed desorption (TPD) to find the desorption energies for a range of alkane thiol and thiocarbon.35 Lavrich and co-workers reported desorption energies for dibutyl sulfide and diethyl sulfide of 86 and 68 kJ/mol, respectively.35 We have previously studied the rotation of symmetric thioethers, including both dibutyl and diethyl sulfides22 and have found their barriers to rotation to be 1.2 ± 0.1 and 0.65 ± 0.06 kJ/mol, respectively (see the Supporting Information for Arrhenius data). Both of these molecules give a ratio of desorption energy to rotational barrier of ~0.01. This ratio, coupled with the knowledge that the equilibrated butyl methyl sulfide rotors have a rotational barrier of 0.9 kJ/mol, leads to an interpolated desorption energy for butyl methyl sulfide of 78 ± 8 kJ/mol. From this value for the most stable rotors (α) and the ratios of the rotational barriers to that of the α species, adsorption energies are calculated for the three metastable species (see Table 1). α and β were measured to have the same rotational rates within error, but from equilibration data like that shown in Figure 3 it is clear that the α molecules are in lower energy sites than the β species. The energetic difference between these species was then calculated using a Boltzmann distribution at 45 K, which yields a 2 kJ/mol difference between these two species.

Using the experimentally measured temperatures at which the metastable rotors equilibrated (Figure 3), it was possible to calculate the energetic barriers to transition between adsorption sites (i.e., diffusion barriers). For these calculations, an equilibration rate of 1 event every 1000 s was estimated from experimental data, and an attempt frequency of 10^{12} Hz was assumed (which is an average attempt frequency for diffusion of molecular species).28 Using all the calculated diffusion barriers and adsorption energies, it is possible to create an energetic landscape for all

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Table 1. Arrhenius Data for α, β, and δ Adsorption Sites

<table>
<thead>
<tr>
<th></th>
<th>Ea (kJ/mol)</th>
<th>A (Hz)</th>
<th>ΔEads (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>α</td>
<td>0.9 ± 0.1</td>
<td>9 × 10^{10.9}</td>
<td>–78 ± 8</td>
</tr>
<tr>
<td>β</td>
<td>0.9 ± 0.1</td>
<td>2 × 10^{8.1}</td>
<td>–76 ± 8</td>
</tr>
<tr>
<td>γ</td>
<td>≤0.12</td>
<td>1 × 10^{8.1}</td>
<td>17 ± 2</td>
</tr>
<tr>
<td>δ</td>
<td>0.6 ± 0.1</td>
<td>1 × 10^{8.1}</td>
<td>–52 ± 5</td>
</tr>
</tbody>
</table>

*All italicized numbers are estimated. All γ rotors spin too quickly to measure rotational rates experimentally even at 5 K; therefore, it was not possible to take rate measurements for this adsorption site. However, using the minimum rate based on experimental limitations, an upper limit for the barrier was estimated for comparison to other adsorbed rotor species. Adsorption energies are estimated based on an interpolated value for the equilibrated species and a common ratio between adsorption energy and rotational barrier. While α and β have the same rotational rate within error, an experimentally measured Boltzmann distribution at 45 K shows that there is a 2 kJ/mol difference between these species. Errors are reported to 1 standard deviation.*

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adsorbed species, which is shown in Figure 6 (see the Supporting Information for error analysis). It is interesting to note that the more stable adsorption sites have higher diffusion barriers for moving to the equilibration site, while less stable sites have lower barriers ($\gamma < \delta < \beta$). This makes sense based on transition state theory, which predicts that the more stable the initial state, the higher the barrier for transitioning to a stable final state.

Based on the rotational energetics data and the appearance upon STM imaging, we can propose adsorption sites for the three metastable species. Figure 7 shows 3D renderings of high-resolution STM images for molecules in each of the four adsorption sites using the same STM tip state, where it can be seen that the adsorption site difference leads to dramatically different appearances. Images such as those in Figure 7 help provide insight into the adsorption site of each molecule. Based on previous density functional theory (DFT) studies,21,26 we know that the most stable (a) species adsorbs nearly atop a Au atom and rotates off axis with the S atom precessing as the alkyl tails rotate. This leads to the chiral pinwheel appearance of the molecules.21 It is unlikely that atop and off atop sites (which are <0.05 nm apart) would have extremely different adsorption energies. By this argument, we postulate that $\beta$ rotors adsorb directly atop, with an adsorption energy very similar to that of the $\alpha$ adsorption sites. This hypothesis is supported by the appearance of $\beta$ rotors in STM images. $\beta$ rotors appear hexagonal and do not appear to possess chirality (as evidenced by the pinwheel appearance of the $\alpha$ rotors), as would be expected for a high symmetry site like atop adsorption. $\delta$ rotors are postulated to adsorb on a bridge site, which is supported by their two distinct sets of three lobes seen in STM imaging. Adsorption at a bridge site would be expected to lead to such a mirror plane being imposed on the six-fold symmetry of the rotating molecule. Finally, $\gamma$ rotors are proposed to be in the remaining sites, the three-fold hollows, with less favorable adsorption energies and lower barriers to diffusion and rotation. Again, three-fold hollow sites have high symmetry as supported by the hexagonal appearance of the $\gamma$ rotors.

Percentages of molecules in each of the sites were both calculated based on these assignments and quantified from experimental data for a population of >100 molecules (Table 1). The classical adsorption sites are atop, bridge, and three-fold hollows, which occur in a ratio of 1:3:2 (Figure 8). This ratio does not account for the off-atop sites which were found to be the energetic minimum for the equilibrated rotor species using DFT.21 The classical sites are typically the only ones considered, as it usually assumed that if a molecule is close to a classical adsorption site, it can relax into the lowest energy site. However, in our system, we are working with a surface at 5 K and a molecule that does not possess the energy needed to diffuse even a fraction of a nanometer, so this adsorption site area, or “footprint”, becomes important. By calculating an approximate area for the off-atop “ring” shown in Figure 8 (and knowing the approximate radius of this ring from previous DFT calculations21), it is found that the relative areas presented are $\sim$1:1 for bridge sites and the off atop ring based on their approximate sizes. Random, as-dosed populations

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were then estimated using these adsorption site surface area ratios (as shown in Table 2) which match well with the experimentally measured as-dosed populations of the sites. The estimated populations should be viewed with caution, as an incoming molecule does not encounter a ratio of possible sites but only senses the potential energy landscape at the point of its impact. With this in mind, there appears to be a relatively strong correlation with the experimental data, which suggests that this ratio of possible sites may be a simple descriptor for a very complex phenomenon. While in-depth DFT studies may provide further insight into the exact sites of adsorption for these species, these studies would not be trivial as local minima sites are found in abundance for any potential energy surface. While this study does not necessarily yield definitive evidence for the exact assignment of each of the three nonequilibrium adsorption sites of butyl methyl sulfide, absolute assignment of these sites is not needed to appreciate the distinct differences in physical properties exhibited by the same molecule in each of these four different adsorption sites.

### Conclusions

Low-temperature STM has been used to elucidate details of the adsorption of a simple thioether molecule (butyl methyl sulfide) on a Au(111) surface. Interestingly, when adsorbed at 5 K, these molecules did not have sufficient energy to reach their equilibrium adsorption sites and existed in four distinct adsorption sites on the surface. Molecular adsorption in these nonequilibrium sites was shown to lead to markedly different appearances of the molecules in STM imaging and very different rotational energetics. Equilibration of each of the nonequilibrium (or precursor) species was studied as a function of bias voltage and temperature, and it was observed that the vast majority of the molecules eventually diffused to their equilibrium site, the properties of which had been studied previously using STM and DFT. From experimental measurements, a relationship was proposed between the adsorption energy and the barrier to rotation, somewhat analogous to well-known corrugation ratios which relate adsorption energy to diffusion barrier. It was found that molecules in more stable adsorption sites had higher barriers to diffuse to their equilibrium adsorption sites, which would be expected from transition state theory. This work illustrates the distinctly different physical properties exhibited by molecules in different adsorption sites and emphasizes the need for an understanding of the atomic-scale details of adsorption sites and the behavior of nonequilibrium molecular species. While it is true that surface assemblies and reactions involve mainly equilibrated species, it is often the case that some proportion of the ensemble is adsorbed at nonequilibrium sites. Even if this number is small, the differences in adsorption site energy and barriers to motion which we report here may lead to reactivity of the minority that overwhelms the majority and dominates the ensemble properties.

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### Supporting Information Available

Purity analysis of butyl methyl sulfide; images showing butyl methyl sulfide on Au(111) before and after equilibration; Arrhenius plot of diethyl sulfide adsorbed on the hcp region of Au(111); discussion of error analysis. This material is available free of charge via the Internet at http://pubs.acs.org.

### Table 2. Comparison of the Simplest, Estimated Population Based on the Ratio of Possible Adsorption Sites and the Experimentally Measured Data for As-Deposited Molecules at 5 K

<table>
<thead>
<tr>
<th>proposed site</th>
<th>estimated population</th>
<th>actual population</th>
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<tbody>
<tr>
<td>α off atop</td>
<td>33%</td>
<td>38%</td>
</tr>
<tr>
<td>β atop</td>
<td>11%</td>
<td>12%</td>
</tr>
<tr>
<td>γ three-fold</td>
<td>22%</td>
<td>17%</td>
</tr>
<tr>
<td>δ bridge</td>
<td>33%</td>
<td>33%</td>
</tr>
</tbody>
</table>

*Off atop sites are estimated based on their available surface area for adsorption.*