

Diffusion of a Butanethiolate Molecule on a Au{111} Surface

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The diffusion of a butanethiolate molecule on a Au{111} surface has been modeled by molecular dynamics simulations. We find that internal chain motion enhances diffusion over that of a heavy atom of the same mass.

I. Introduction

The characteristics of diffusion of molecules on surfaces exhibit complexities beyond those observed for atomic diffusion. For example, Pai and Doren have shown that there is a correlation between the hindered rotational mode of a rigid triatomic molecule on a surface and the translational mode of the molecule along the diffusion path.¹ When the bending frequency of the molecule to the surface was increased, the diffusion rate also increased and was higher than the predicted transition-state-theory hopping rate. They attribute this dependence of diffusion rate on the hindered rotational mode to coupling of this motion with translational motion.

The diffusion of larger molecules such as alkanes has been examined by several groups. Cohen and Zeiri modeled the diffusion of *n*-alkanes (*n* = 3, 6, 10, 20) on a W{100} surface.² They found Arrhenius behavior and that the activation energy of diffusion increases with chain length. They also varied the stiffness of the chain (or the effective torsional barrier) and predicted that a stiff chain diffuses faster than a floppy chain.³ Their calculations indicate that floppy chains get trapped in bent configurations (*gauche* defects) for longer times than stiff chains (*all-trans*) and that the bent configurations diffuse at a slower rate. Zeiri went on to examine the effect of shape in the diffusion of isomers of hexane and decane and found that rotational motion of the molecules influenced the diffusion process.⁴

Silverberg also investigated the diffusion of *n*-pentane on a fcc{111} surface and found that the diffusion properties depend on the torsional configuration of the molecule.⁵ Cohen and Zeiri³ also found a dependence on torsional motion in their studies. Another series of investigations by Fichthorn and co-workers of diffusion of *n*-alkanes on a fcc{111} surface indicate, however, that the diffusive motion is a combination of translational and rotational motion of a rigid rod.^{6–9}

Obviously, diffusion of molecules can be more complex than for an atom due to the increased number of degrees of freedom. Recently there has been considerable interest in the motion of alkanethiolates on a metal surface.¹⁰ Although the ultimate interest is in the diffusion at high-adsorption coverages, the single-molecule diffusion process is the first step. We have investigated the tracer diffusion of a butanethiolate molecule on a Au{111} surface. This system differs from the alkane systems in that one end of the chain is preferentially attached to the substrate and the other end is relatively free to move around. It also differs from the rigid triatomic molecule in that there are internal angular degrees of freedom. We find that the rotational motion of the chain enhances the diffusion over what is calculated for an united atom (⁹⁰S) of the same mass.

In particular, the chain increases the average lateral force on the molecule, thus increasing the diffusion rate.

In section II, a description of the method of our calculation is given. In section III, the results are presented.

II. Description of the Calculation

The diffusion of a butanethiolate molecule on a Au{111} surface is modeled by molecular dynamics (MD) simulations in a manner similar to that used in the diffusion studies mentioned above and also alkanethiolate overlayers.¹¹ The Au substrate consists of 8 layers of 270 atoms each with periodic boundary conditions employed in the horizontal *x* and *y* directions. Each CH_{*x*} (*x* = 2, 3) unit in the butanethiolate chain is assumed to be a structureless sphere (i.e., the united atom limit). At least 50 trajectories of 50–100 ps each were calculated for the butanethiolate diffusion at temperatures of 200, 250, 300, 400, and 600 K. More trajectories (of longer durations) were required for lower temperatures. The first 15 ps was disregarded to allow for equilibration. The diffusion constant, *D*, is calculated from

$$D = \lim_{t \rightarrow \infty} \frac{\langle \Delta r \rangle^2}{4t} = \lim_{t \rightarrow \infty} \frac{\langle \Delta x^2 + \Delta y^2 \rangle}{4t} \quad (1)$$

where the position of the molecule vs time is extracted from the MD simulations.

The interaction potential employed for the Au interaction is the molecular dynamics/Monte Carlo-corrected effective medium (MD/MC-CEM) potential of DePristo and co-workers.^{12–14} This potential has been fit to bulk properties of Au as well as to the low coordination configuration of Au₂. Most importantly, it reasonably reproduces the experimental surface energies of Au.¹⁵ The temperature of the system is maintained through the Au substrate. Specifically, the Au atoms in the bottom layer are held rigid. The next five layers are subjected to stochastic forces via the generalized Langevin equation¹⁶ in addition to the MD/MC-CEM interactions. The top two layers only experience forces from the MD/MC-CEM interaction and the butanethiolate chain.

The butanethiolate chain is modeled within the united atom limit. The intra-chain angular interactions consist of bond-bend and torsional terms and have the same functional form and parameters as those used by Hauptman and Klein.¹¹ The bond-bend term is given by

$$V_b(\theta) = \frac{1}{2}k_\theta(\theta - \theta_0)^2 \quad (2)$$

where θ is the C–C–C or S–C–C angle. The torsional

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TABLE 1: Lennard-Jones 12-6 Parameters

interaction	ϵ , meV	σ , Å	ref
CH ₃ -CH ₃	7.59	3.905	11, 19
CH ₂ -CH ₂	5.12	3.905	11, 19
S-S	10.86	3.55	11, 20
Au-CH ₃	6.20	3.632	this work, 21
Au-CH ₂	4.48	3.632	this work, 21

interaction is given by

$$V_l(\varphi) = a_0 + a_1 \cos(\varphi) + a_2 \cos^2(\varphi) + a_3 \cos^3(\varphi) + a_4 \cos^4(\varphi) + a_5 \cos^5(\varphi) \quad (3)$$

where φ is the dihedral angle made by four atoms. In this case, there are two dihedral angles, one of which involves all four C units/pseudoatoms and the other of which involves the S atom plus three C units/pseudoatoms. The torsional parameters¹⁷ yield that the trans (T) configuration is lowest in energy. The gauche (G) conformer is 2.95 meV higher in energy, and the barrier for the T-to-G transition is 127 meV. Overall, there are four conformers of the butanethiolate molecule (TT, TG, GT, and GG). There is also a possibility of a bond-stretch interaction. Following previous work, the CH_x-CH_x and S-CH_x bond lengths are held constant at 1.53 and 1.82 Å,¹¹ respectively, via the RATTLE algorithm.¹⁸

In addition to the bending and torsional interactions, there are van der Waals interactions (Lennard-Jones 12-6 functions) between atoms in the chain that have at least three atoms between them.¹¹ The only van der Waals interaction in our simulation is the CH₃ unit with the S atom. These same potentials would have been used for interactions between chains if there were more than one chain. The parameters for the Lennard-Jones potentials are given in Table 1. Parameters for mixed interactions are obtained by using a geometric mean of parameter values.

The Au-CH_x interactions must be consistent with having explicit surface Au atoms. This is in contrast to ref 11 where the surface was assumed to be rigid. We chose to use the same functional form, i.e., a 12-6 Lennard-Jones potential, as has been used for chain-chain interactions. The parameters are fit to the interactions used by Tupper and Brenner²¹ for Au-CH_x interactions with a different functional form and are given in Table 1.

The bonding Au-S interaction is assumed to be a pairwise additive Morse potential of the form

$$V_M(r) = D_e \exp(-\alpha(r - r_e))(\exp(-\alpha(r - r_e)) - 2) \quad (4)$$

where r is the distance between the S atom and a Au atom and α , D_e , and r_e are parameters to be fit. The data used for fitting include the experimental TPD value for the bond strength of a methanethiolate group to a gold surface of 1.91 eV^{22,23} the calculated predictions²⁴ that the most stable site is a hollow site, that the bond length is 1.905 Å, and that the vibrational force constant is 0.695 mdyn/Å. The range of the pairwise sum of Morse potentials is $2.5r_e$. Fitting to a rigid Au surface yields values of $D_e = 0.38$ eV, $r_e = 2.65$ Å, and $\alpha = 1.47$ Å⁻¹. Given that the thiolate chain can change Au coordination during diffusion, it is not feasible to include a bond-bend term to maintain the surface-S-CH₂ angle at 180° as predicted by Sellers et al.²⁴ In practice, the symmetry of the 3-fold hollow site does not let this angle deviate too far from 180°.

This parameterization of the Au-S interaction predicts that the two distinct 3-fold hollow sites are essentially degenerate for bonding of the S atom. For the rigid surface, the barrier to diffusion is ~300 meV. The gold surface, however, is relatively

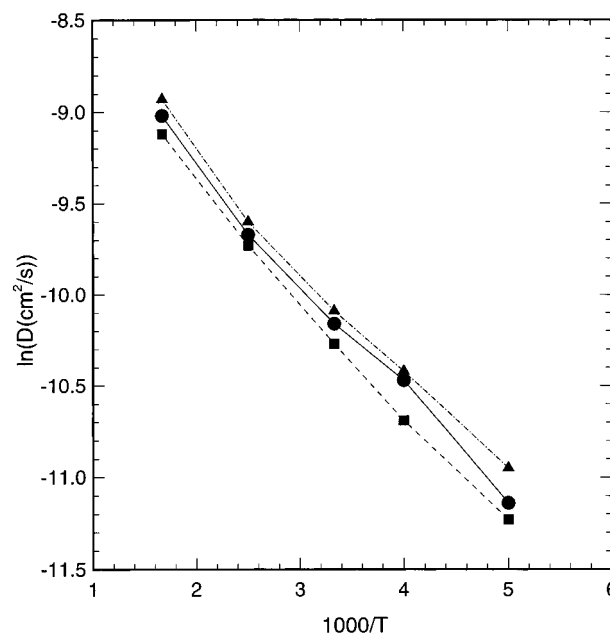


Figure 1. Calculated diffusion rates, D , vs $1000/T$. The diffusion constant is in units of cm^2/s . The statistical error bars are less than the point sizes. For example, the diffusion constant for butanethiolate at 300 K is calculated to be $(3.89 \pm 0.02) \times 10^{-5} \text{ cm}^2/\text{s}$ with a 2 standard deviation error bar. This deviation is less than 0.01 ln unit. (■) ⁹⁰S; (●) butanethiolate; (Δ) floppy butanethiolate.

soft, and there is significant motion and relaxation due to the S atom motion. The diffusion barrier with substrate relaxation is only 38 meV.²⁵ Unfortunately, the surface relaxation also changes the binding energy to 2.0 eV. This was not discovered, however, until after these simulations were run. We have reparameterized the potential²⁶ to include surface relaxation but the diffusion barrier does not change, thus we have used the original potential values given above in this study.

In order to examine the effect of internal chain motion on the diffusion process, we also modeled the diffusion of a S atom with the same mass (90 amu). The ⁹⁰S system should have approximately the same dominant interactions and, thus, energetics with the surface as the butanethiolate chain. Any differences in diffusive motion can therefore be primarily attributed to chain motion.

The diffusion constants for the chain are determined by the S atom position and are the same as using the center of mass of the chain. Since the “footprint” of the chain extension can be longer than the nearest-neighbor hollow site distance (1.67 Å), the definition of the residing site of the chain is sometimes ambiguous.

III. Results and Discussion

The results of our diffusion calculations are shown in Figure 1 as $\ln(D)$ vs $1/T$. Of note is that the thiolate chain diffuses faster than the ⁹⁰S atom.

We attempted to find a simple mechanistic reason for why the chain is diffusing faster than the ⁹⁰S atom. It is clear that the chain is undergoing significant motion during the diffusion events. There are conformational transitions among the TT, GT, TG, and GG configurations. At the lowest temperatures, however, there may be only 1–2 conformational transitions in a 100-ps simulation. There is clearly overall rotational motion in approximately the surface plane. It is not clear, however, if the rotation is occurring about the center of mass of the chain or about the S atom. Unlike in the simulations of the alkane chains, one of the ends (the S atom) in this case is bonded

considerably more strongly to the surface than the CH_x groups. The S atom can, thus, be the pivot point for the rotational motion. We also observe collisions of the free end of the chain with the surface that tend to abruptly change the direction of motion. This is not unusual, as there can be instances where the free end moves faster than the S atom (when the S atom is unable to make a needed hop), and as a result, the free end falls flat. Whenever this happens, there is an impulsive collision of the chain with the surface, resulting in a sudden change in direction of motion. It appears that all of these chain motions contribute to the diffusional motion.

The diffusion rates for a chain with the torsional parameters (and consequently torsional energies) reduced by a factor of 10 were calculated in order to verify that the internal chain motion is enhancing the diffusion. As shown in Figure 1, the diffusion rates at all five temperatures for this floppy chain are greater than those for the normal chain. Thus, with enhanced motion within the chain, the diffusion rate increases. Examination of the average parallel and upward force components on the S atom at various temperatures provides further confirmation of this point. The chain is exerting a greater force parallel to the surface on the S atom than that exerted by only the substrate Au atoms on the ⁹⁰S atom. There is also a slightly larger average upward force with the chain attached. An increase in force in either of these directions can only help the S atom end of the butanethiolate molecule overcome the barrier and, thus, lead to an enhanced diffusivity. Although this explanation helps us understand why a chain diffuses faster than a ⁹⁰S atom, it does not provide the whole story when comparing the two kinds of chains, as the forces on the ⁹⁰S atom due to the floppy and normal chains are very similar. Rather, the more likely scenario is that since a floppy chain is undergoing torsional changes more often, it increases the *likelihood* of the ⁹⁰S atom motion being affected (increased forces parallel and perpendicular to the surface) as a consequence of these changes and, hence, the increased diffusivity. The fact that increasing the frequency of changes in torsional modes enhances diffusivity again corroborates the fact that these changes play a role in making a chain move faster than the ⁹⁰S atom.

The curves in Figure 1 appear almost Arrhenius, even though it is clear after watching movies of the diffusive motion that a random hopping model does not provide a complete explanation for the diffusion process in this case even at the low temperatures. Other factors such as internal motion of the chain and the interactions between the substrate and the CH_x units cannot only alter the direction of diffusion but also alter the rate at which it diffuses in a given direction.

IV. Discussion

The MD simulations of a butanethiolate molecule on a Au{111} surface clearly show that intra-chain motion influences, and in this case enhances, the diffusion rate. This conclusion was not obvious a priori. Calculations of butanethiolate adsorption²⁷ onto the Au{111} surface show, for example, that

the adsorption process is 10–100 times slower than simple atom adsorption.²⁸ That is, the chains are providing a drag that slows down the adsorption process. In contrast to previous studies on diffusion of molecules with fewer degrees of freedom, it is clear that several factors are contributing to the enhanced motion.

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