Dynamics of Single-Molecule Rotations on Surfaces that Depend on Symmetry, Interactions, and Molecular Sizes

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Rotating surface-mounted molecules have attracted the attention of many research groups as a way to develop new nanoscale devices and materials. However, mechanisms of motion of these rotors at the single-molecule level are still not well-understood. Theoretical and experimental studies on thioether molecular rotors on gold surfaces suggest that the size of the molecules, their flexibility, and steric repulsions with the surface are important for dynamics of the system. A complex combination of these factors leads to the observation that the rotation speeds have not been hindered by increasing the length of the alkyl chains. However, experiments on diferrocene derivatives indicated a significant increase in the rotational barriers for longer molecules. We present here a comprehensive theoretical study that combines molecular dynamics simulations and simple models to investigate what factors influence single-molecule rotations on the surfaces. Our results suggest that rotational dynamics is determined by the size and by the symmetry of the molecules and surfaces and by interactions with surfaces. Our theoretical predictions are in excellent agreement with current experimental observations.

1. Introduction

Functioning of all biological systems depends critically on the activity of molecular motors that convert chemical, thermal, or light energy into useful mechanical work.[1-6] Observations of high efficiency, flexibility, and robustness of these biological machines have stimulated multiple efforts to develop analogous manmade nanoscale devices with controlled properties.[7-15] Although significant advances in synthesizing artificial molecular motors have been achieved,[11,15-29] a direct application of these nanoscale machines is still limited due to the fact that the fundamental issue of energy transformation at the single-molecule level is not well-understood.[3,4]

One of the most promising classes of artificial devices for application in nanotechnology is surface-mounted molecular rotors.[15,29-37] There are many advantages in using molecules attached to the surfaces, such as the ability to easily control and manipulate these rotors, the possibility of coupling to other nanoscale devices, and many other potential future nanotechnology applications. In addition, biological motors typically function most efficiently in close association with some surfaces.[29,31] Rotational dynamics of surface-mounted molecules has been studied by several experimental methods that include scanning tunneling microscopy (STM),[29-32,38,39] inelastic electron tunneling (IET),[40-44] and single-molecule fluorescence imaging.[45] Current theoretical investigations of artificial molecular rotors mostly rely on molecular dynamics (MD)[31,46,47] and molecular mechanics (MM)[48,49] computer simulations, quantum chemical density functional studies,[33,50] and fundamental thermodynamic approaches.[51,52] Although theoretical studies allowed explanation of several features of molecular rotors, the mechanism of rotations at the single-molecule level is still an open problem.

The detailed studies of molecular rotations have been performed for the system of thioethers bound to Au surfaces.[29-31] Thioethers, also known as dialkylsulfides, are linear molecules with the sulfur atom in the middle connected to two symmetric alkyl chains. The sulfur atom is strongly bound to the gold surface, and alkyl branches can rotate around it. Using STM techniques, it was found that activation rotational barriers do not depend much on the size of alkyl chains in thioethers, in contrast to naïve expectations.[31] We developed a theoretical model based on molecular dynamics calculations that argued that rotational dynamics of thioethers can be explained by a combination of molecular interactions with the surface, flexibility, and steric repulsions.[31] This model argued that for longer alkyl chains, the increased interactions with the surface are compensated for by increased steric repulsion and flexibility of the molecule, leading to the effective size independence in the rotational properties. However, different rotational dynamics have been observed recently for diferrocene derivatives.[32] These molecules can be viewed as single alkyl chains that contain a monocyclopentadienyl iron complex (FeCp) at one end and the ferrocene (Fc) group at the other end. The FeCp group is strongly bound to the metallic surface, while interactions of the Fc group with the surface are much weaker. This leads to rotation of the whole molecule around the FeCp complex. Again, using STM methods, it was shown[32] that the increase in the length of the alkyl chain connectors increases rotational barriers and threshold temperatures for rotation. This dynamic behavior was very different from the rotational dynamics of thioethers. Thus, a better microscopic description of molecular rotations on the surfaces is needed. In this paper, we present a theoretical study of mechanisms of single-molecule rotations that combines extensive MD computer simulations with simple models to determine the most important factors influencing the dynamic behavior.

2. Theoretical Calculations

To develop a microscopic picture of surface rotations, we performed extensive MD computer simulations for different molecular systems. Our computational approach is based on

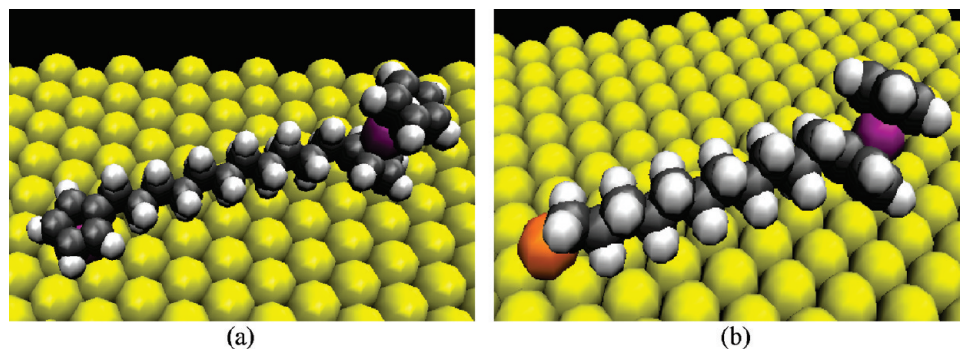* To whom correspondence should be addressed. E-mail: tolya@rice.edu.

Figure 1. Typical representatives of two structural classes of single-molecule rotors studied in this work, (a) $Fc-(CH_2)_{11}-FeCp$ and (b) $Fc-(CH_2)_{11}-S$.
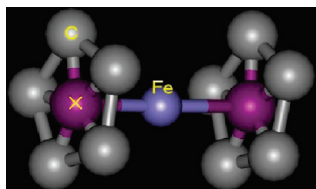

Figure 2. A schematic presentation of the ferrocene segment used in our MD computer simulations. Hydrogen atoms are omitted for clarity.

recent MD simulations method that was created for analysis of the motion of nanocars[53] and molecular rotors.[31] It utilizes a rigid-body approximation that considers molecules as consisting of coupled rigid segments, and it neglects some less important degrees of freedom, thus significantly accelerating calculations and providing a better description of dynamic properties of the system. A detailed description of the rigid-body MD computational method has been already presented.[31,53,54] It should be noted that, although predictions from this coarse-grained approach might differ from the full-atomic simulations in quantitative aspects, it is still capable to produce qualitatively and even semiquantitatively correct results.[54] In this work, we studied three different classes of molecular rotors on gold surfaces, (1) $CH_3(CH_2)_{m-1}-S-(CH_2)_{n-1}CH_3$ (with n and m ranging from 1 to 6), (2) $X-(CH_2)_n-FeCp$ (with $X = Fc$ or CH_3), and (3) $Fc-(CH_2)_n$-S (with n ranging from 11 to 20). The shortest molecules representing the last two structural classes are shown in Figure 1.

2.1. Computational Method. To describe intramolecular interactions, a UFF force field has been utilized in our MD simulations.[55] However, to simplify computations and to preserve geometry and internal dynamics in some species, we have also made several modifications. For example, the ferrocene molecule is a sandwich-type structure with possible internal rotations of the rings with respect to each other. To preserve the possibility of such rotations, we have added two artificial atoms (called X) in the centers of cyclopentadienyl rings, covalently connecting them to ring atoms and to the center iron atom (Figure 2). They have zero mass, zero charge, and a zero van der Waals interaction parameter, thus not affecting potential surfaces in the system at all. They are used just for the purposes of connecting the cyclopentadienyl rings and the iron atoms in order to preserve possibly important internal degrees of freedom. In our calculations, each molecule is viewed as collection of rigid fragments. We specify as rigid bodies the iron atom and the C_5H_5 ring in the ferrocene segment, CH_2 in the alkyl chains, FeC_5H_5 in the anchor of the cyclopentadienyl iron rotors, and the sulfur atom in the anchor of the thioether-based rotors.

Structural parameters and the charges on the ferrocene segment have been obtained from the B3LYP/6-31G(d) calcula-

TABLE 1: Force Field Parameters for Topological Fragments Including X Atoms[a]

bond	force constant, kcal/($Å^2 \cdot$mol)	equilibrium distance, Å
X−Fe	350.0	1.656
X−C	350.0	1.2164

angle	force constant, kcal/mol	equilibrium angle, degree
X−Fe−X	220.0	180.0
Fe−X−C	200.0	90.0
X−C−C	200.0	54.0
X−C−H	200.0	180.0
C−X−C	200.0	108.0

[a] Equilibrium distances and angles were calculated on the basis of B3LYP/6-31G(d) optimization and simple geometrical considerations, correspondingly. Utilized force constants are arbitrary (but are more or less similar to force constants of other bonded interactions).

TABLE 2: Average Mulliken Charges on Atoms of the Ferrocene Molecule

atom	charge, au
Fe	0.55630
C	−0.20486
H	0.14923

tions made with Gaussian 03 program package.[56] Structural parameters for the artificial atom X have been calculated on the basis of similar quantum mechanical calculations and some geometrical considerations. All interaction parameters utilized in MD simulations are presented in Table 1. The Mulliken charges on atoms of the optimized ferrocene structure are given in Table 2. Charges on atoms of CH_2 fragments were −0.1 (C) and 0.05 (H). Charges on all atoms of FeCp segments were taken to be equal to 0.

Finally, in order to simulate rotations of surface-mounted molecules, it is important to determine parameters that describe interactions of the iron atom in the FeCp segment and the gold surface. We have used a Morse potential to describe the potential of interactions of the anchor group with the whole surface. There are no specific S−Au or Fe−Au bonds, and there are no angular terms. The interactions are of nonbonded type, with a deep well so that the rotor is mounted on the surface even at quite high temperatures. Parameters have been determined as follows. The equilibrium distance was calculated using UFF parameters for bonded interactions of gold and iron, the shape parameter α was calculated utilizing a DREIDING force field,[57] and finally, the interaction strength was determined through the fitting to the adsorption energy of FeCp molecules on the Cu(110) surface.[32] Parameters for sulfur−gold interactions were taken from ref 58. All parameters are collected in Table 3:

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TABLE 3: Parameters for the Potential of Interactions of Fe (in the FeCp group) and S Atoms with the Gold Surface

parameter	values for Fe	values for S
D_e	23.763 kcal/mol	8.763 kcal/mol
A	$\sqrt{5} = 2.236$ Å^{-1}	1.470 Å^{-1}
R_0	2.532 Å	2.650 Å

The surface was represented as a slab of 1067 gold atoms organized in three layers (surface plane 111) and their 2D replicas, thus effectively leading to a quasi-infinite representation of the surface, similar to what was utilized in earlier studies.[31] Two different surfaces, Au(111) and Au(100), have been used in our calculations. Prior to all MD simulations, the molecular structures were equilibrated at simulation temperatures in a way that the total potential energy of the system did not decrease significantly over long time intervals (tens of ps). For each molecule considered, we calculated 8−10 trajectories of 3.5−5 ns long with the integration time step of 1 fs. Such calculations have been performed for five different temperatures (25−100 K in the case of thioethers and 50−350 K for other molecules) using the rigid-body MD integrator of Dullweber−McLachlan[59] combined with the Nose−Poincare thermostat.[60,61]

Molecular dynamics trajectories were analyzed by following the behavior of two dynamic quantities, the rotational diffusion coefficients and the average carbon height profiles. The rotation rates have been found by following the temporal evolution of a cumulative orientation angle Φ defined as follows

$$d\varphi_i = \varphi_i - \varphi_{i-1}$$
$$d\Phi_i = \begin{cases} d\varphi_i, & |d\varphi_i| < \pi \\ -\text{sign}(d\varphi_i)||d\varphi_i| - 2\pi|, & |d\varphi_i| > \pi \end{cases} \quad (1)$$
$$\Phi_i = \Phi_{i-1} + d\Phi_i$$

This definition keeps track of the direction of the molecule's rotation. The rotational diffusion coefficients were then calculated using the expression $D = \Phi^2 t$, where Φ^2 is a squared cumulative rotation angle. From the temperature dependence of the rotational diffusion coefficient, we have extracted the activation barriers of rotation for all molecules considered. In addition, the average distance from the carbon atoms in the connector chains to the surface have been calculated. These heights profiles provide important information about the flexibility of chains and about the strength of interactions with the surface.

3. Results and Discussion

3.1. Surface Symmetry. First, we investigated the role of surface symmetry in the rotational dynamics of single molecules. Extensive MD computer simulations have been performed for symmetric thioethers on Au(111) and Au(100) surfaces. The activation energies for rotations are shown in Figure 3. Surprisingly, it is much harder for thioethers to rotate on the Au(100) surface where activation barriers are larger by almost an order of magnitude. In addition, while on the (100) surface, the activation energies are almost independent of the chain size; the situation is different on the (111) surface, where the moderate growth as a function of the chain size is observed.

To understand a different behavior of single-molecule rotors on Au(111) and Au(100) surfaces, let us consider the simplest thioether molecule, namely, dimethylsulfide, as shown in Figure 4.

One can see that on the Au(100) surface, both CH_3 groups typically have similar local surface geometry, that is,, they both
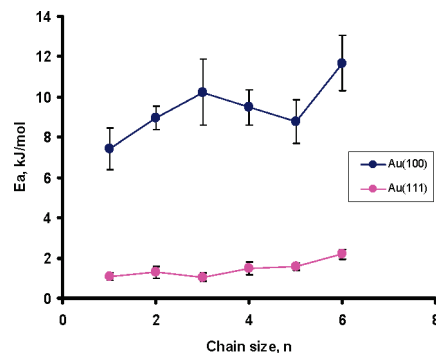

Figure 3. Activation energies for rotation of symmetric thioethers on Au(100) and Au(111) surfaces.

can be found on bridges connecting surface atoms, or both groups are simultaneously on top of the surface atoms; see Figure 4b. However, it is different for the Au(111) surface (Figure 4a), where CH_3 groups are always in different local environments. When one group is on the three-fold hollow site, another one is found sitting on the top site. During the rotation, the molecule explores the potential energy of interaction with the surface. Activation barriers correspond to a difference between saddle points and minima on this free-energy profile. The strongest repulsion between the CH_3 group and the surface is observed when the group is on top of the surface atoms. If both CH_3 groups do this at the same time (as in the case of the Au(100) surface), the activation barriers for each group will sum up, thus resulting in the bigger total activation energy (of order 7−10 kJ/mol). However, if one CH_3 is passing the atop site while another one is above the hollow site, the resulting activation barrier will be significantly smaller. Stronger interaction with the top-site surface atom is compensated for by much weaker interaction with the hollow site, leading to activation energies of 1−2 kJ/mol. These arguments can be easily extended for larger chains; although, because the molecules are quite flexible, the discussed trend will be followed less strictly. Thus, we can predict that the activation energies on Au(100) will grow faster because at transition states, more CH_3 groups will be on the top sites. For the Au(111) surface, the growth in activation energies should be much smaller because of approximate compensation. It agrees with the results obtained from our MD simulations (Figure 3).

It is important to note that according to our theoretical picture, the effect of the symmetry of the underlying surface is observed because the size of the groups in the rotating chains is similar to the interatomic distances on the surface. It suggests that the role of surface symmetry could diminish if chain groups are much larger or much smaller than the lattice cell dimensions or if there are too many surface defects to wash out the lattice periodicity. It will be interesting to test these ideas in future experimental and theoretical investigations.

3.2. Molecular Symmetry. The simple theoretical picture developed above assumes that combination of local configurations of surface atoms below the chain groups influences the overall rotational dynamics of single molecules. For the motion on the Au(111) surface, repulsive interactions with atop sites are compensated for by attractive interactions with hollow sites. However, only symmetric rotor molecules have been analyzed so far, and it raises a question of how the rotational dynamics will change for asymmetric thioethers. For example, let us consider a molecule with one chain containing six carbon atoms (five CH_2 groups and one CH_3 group at the end) and the other chain having only four carbon atoms (three CH_2 groups and
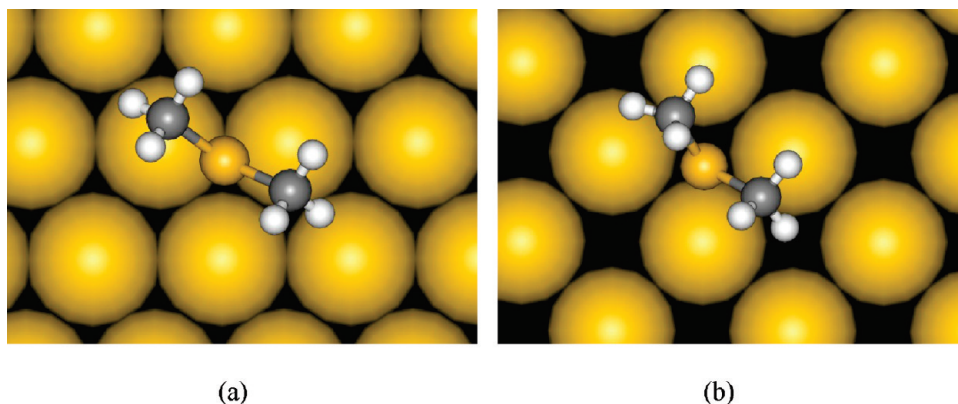
(a)   (b)

Figure 4. Dimethylsulfide molecule above (a) the three-fold hollow site of the Au(111) surface and above (b) the four-fold hollow site of the Au(100) surface (only the upper layer is shown for clarity).

TABLE 4: Activation Energies for Rotation of Asymmetric and Symmetric Thioethers on Au(111) Surface (in kJ/mol)

E_a	1	2	3	4	5	6
1	1.08	1.93	2.18	2.32	1.75	1.69
2		1.29	1.41	1.65	1.63	1.94
3			1.05	1.57	1.38	1.59
4				1.49	1.31	1.68
5					1.57	1.28
6						2.18

TABLE 5: Standard Errors for Determination of Activation Energies (in kJ/mol)

error	1	2	3	4	5	6
1	0.17	0.13	0.27	0.54	0.26	0.57
2		0.29	0.29	0.17	0.21	0.34
3			0.21	0.18	0.21	0.14
4				0.33	0.16	0.39
5					0.18	0.20
6						0.24

Figure 5. Activation energies for rotation of asymmetric and symmetric thioethers on the Au(111) surface. For each series, the activation energy is larger for those rotors that have a bigger value of $|m - n|$.

one CH_3 group at the end) rotating on the Au(111) surface. The first four groups on both chains will probably be compensated for by interactions with the surface for each other, as was done for symmetric dialkylsulphides. However, the remaining two groups on the longer chain will have to spend some extra energy to overcome barriers in order for the whole molecule to rotate. Thus, our simple theory argues that the activation energy for such a system should be higher than that for the equivalent system with chains of equal length, that is, the thioether with five groups in each chain. Then, it leads us to conclude that the fastest rotations are expected for most symmetric thioethers.

In order to test this hypothesis, we performed a series of MD simulations on different classes of molecular rotors. One of such classes was asymmetric thioethers of general formula $CH_3(CH_2)_{m-1}-S-(CH_2)_{n-1}CH_3$ for values of m and n ranging from 1 to 6. Symmetric thioethers correspond to the special case of $m = n$. The calculated activation energies are summarized in Tables 4 and 5.

Analysis of these calculations suggests that, indeed, for the same value of $m + n$, the activation barriers will be smaller for rotors with the smallest $|m - n|$, which specifies a degree of asymmetry in the two-chain molecules. There is an alternative way of viewing these results by considering 11 series of dialkylsulphides with a fixed value of $m + n$, as shown in Figure 5. Points on this figure are ordered with respect to the degree of asymmetry; more symmetric molecules lie closer to the center of the graph. The tendency of more symmetric molecules to rotate faster is clearly seen, although there are significant
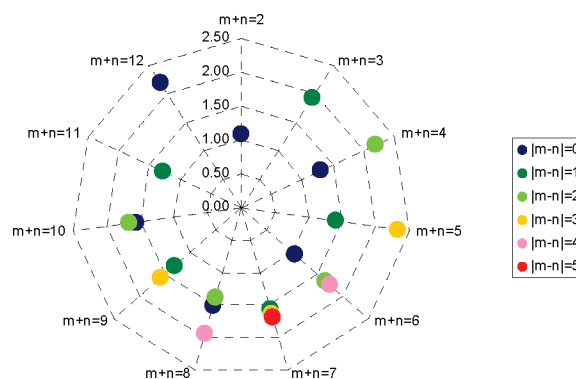
fluctuations in several cases due to probably insufficient collected statistics. One could also see that the effect of the symmetry becomes weaker for larger molecules.

Our theoretical predictions that more symmetric thioethers rotate faster can be supported by analyzing a simple phenomenological model of single-molecule rotations on the surface. Consider a molecule with only one chain of n groups rotating around the anchor. If this chain were a rigid segment, then one could estimate the activation barrier for the rotation

$$E_a \approx An \quad (2)$$

where A is some unknown coefficient of proportionality. However, alkyl chains in existing molecular rotors are not rigid but rather are very flexible; therefore, not all chain groups interact with the surface, and this must decrease the activation barrier

$$E_a \approx An^\nu \qquad \nu < 1 \quad (3)$$

For the molecule that has two chains with m and n groups, correspondingly, one can write the activation energy as follows

$$E_a \cong An^\nu + Am^\nu \quad (4)$$

Then, it can be easily shown that for the fixed value of $m + n$, the smallest barriers are found in the case of $m = n$, that is, for the most symmetric rotors.
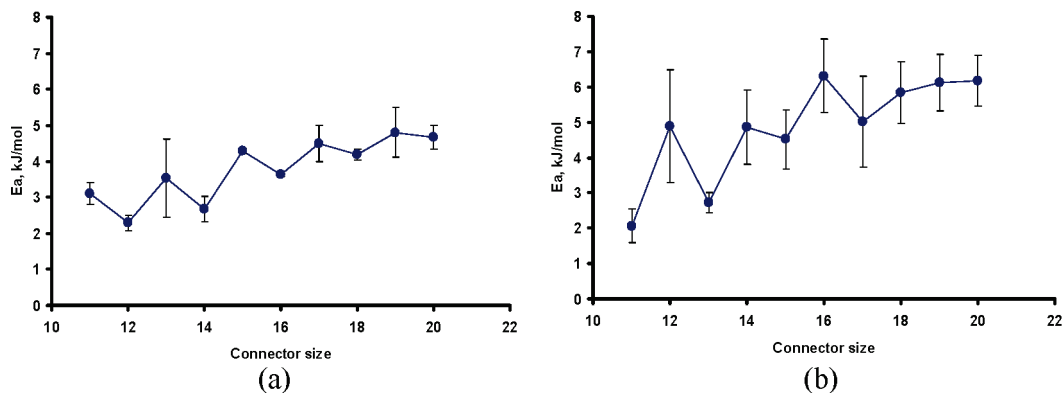
Figure 6. Activation energies for rotation as a function of the connector chain size for (a) $FeCp-(CH_2)_n-Fc$ and (b) $S-(CH_2)_n-Fc$.

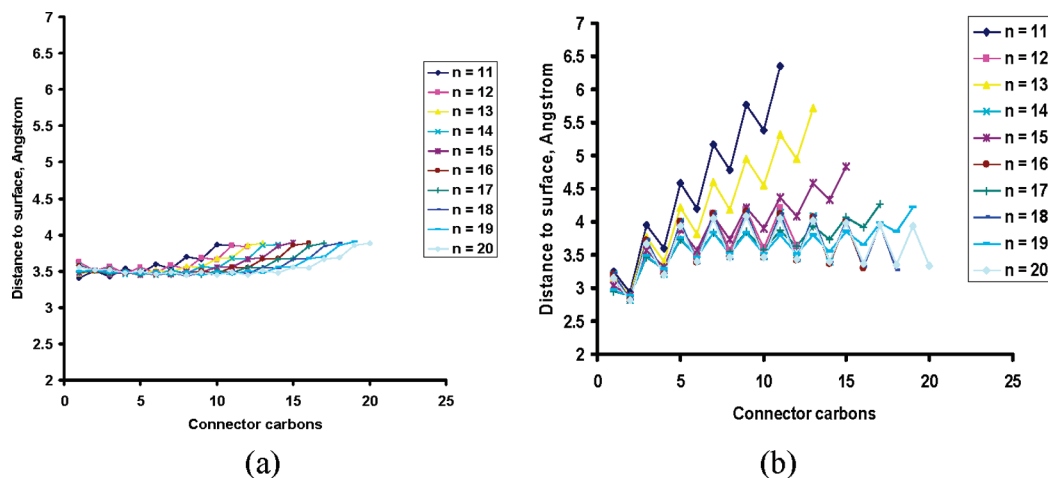**Figure 7.** Average distances between the carbon atoms and the surface for (a) $FeCp-(CH_2)_n-Fc$ and (b) $S-(CH_2)_n-Fc$ molecules at 150 K.

There is an important difference in rotational dynamics of two-chain and single-chain molecules on the surface of Au(111). For the molecular rotors with two branches, some compensation might take place, as discussed above, and the dependence of activation energies on the size of chains is relatively weak. Our theory predicts that for the molecules with one chain, the increase in the length of the branch makes rotations much harder. This observation is in agreement with recent experiments[32] on diferrocene derivatives $X-(CH_2)_n-Fc$ on Au(111) (where X = FeCp, or S), in which it was shown that the activation energy for rotation is larger for longer sizes of alkyl chains connecting X and Fc groups.

We have performed extensive MD simulations for diferrocene molecular rotors, and results are shown in Figure 6. For both types of anchor, the activation energies increases for larger connector sizes, as predicted by our simple theory. However, this growth is not monotonic, and we found odd−even alternations. Namely, for $FeCp-(CH_2)_n-Fc$ rotors, the activation energies for odd connector sizes are typically larger, while for $S-(CH_2)_n-Fc$ rotors, the opposite trend is observed. Our calculations also show that this alternating effect effectively disappears for larger sizes of connector chains. In addition, it can be seen that the rotational activation barriers for $FeCp-(CH_2)_n-Fc$ grow not as fast as those for $S-(CH_2)_n-Fc$ molecules.

3.3. Molecular Structure near the Surface. In order to understand the alternating effect for rotational barriers of diferrocene derivaties, one has to analyze molecular structures near the surface. In Figure 7, results for average distances from each carbon atom on the connector chain to the surface are computed by averaging many trajectories at the same temper-

ature. Here, we find that these height profiles are very different depending on the nature of the anchor group. In the case of the FeCp anchor, most carbon atoms reside at almost the same distance from the surface. This suggests that the connector chain is found in zigzag configurations parallel to the surface (see Figure 8a). However, when the thiol group plays the role of the anchor, the connector chain also has a zigzag shape but in the plane perpendicular to the surface (Figure 8b). In both cases, the molecular orientation near the surface is determined by geometry and details of chemical binding to the surface by the anchoring group. These molecular structures of rotors lead to different types of odd−even periodicity in the activation energies, as found in our computer simulations. The deviations from alternating behavior for larger connector chains is due to the fact the alkyl groups are not rigid, and this flexibility diminishes the role of zigzag configurations in the overall dynamics.

Our MD simulations indicate that in $FeCp-(CH_2)_n-Fc$ molecules, odd carbon atoms sit mostly at hollow sites or bridge positions, while the even carbon atoms are typically above the surface atoms (top sites). Then, adding a new odd carbon group will most probably lower the overall activation energy, while the addition of even carbon groups definitely increases the rotational barrier. This explains the behavior observed in Figure 6a.

For thiol-based rotors, the situation is different. Because of the nature of chemical interactions of the sulfur with the surface and due to the zigzag shape in the plane perpendicular to the surface, odd carbon atoms will always be further from the surface than neighboring even carbon atoms. As a result, the activation energy for rotation of the molecule with an odd
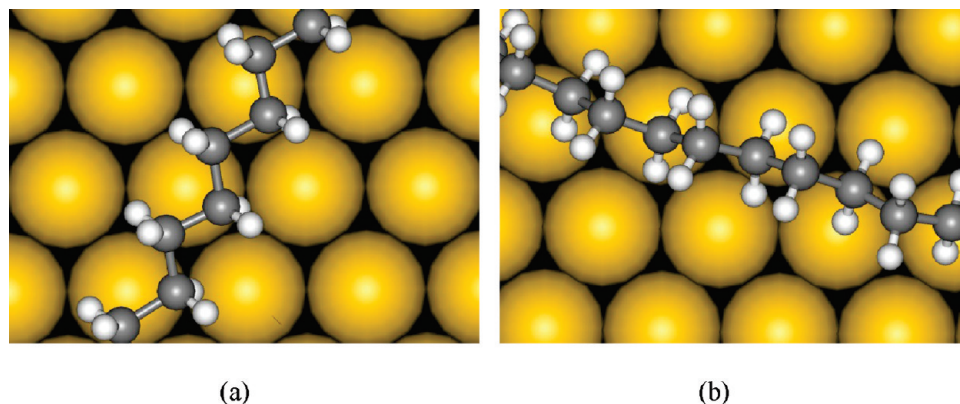
(a)   (b)

Figure 8. Different zigzag chain orientations for (a) $FeCp-(CH_2)_n-Fc$ parallel to the surface and (b) $S-(CH_2)_n-Fc$ perpendicular to the surface.

number of carbons in the connector chain will be smaller than that for rotors which have one carbon more in their connector chain (Figure 6b).

MD computer simulations indicate that activation barriers for $FeCp-(CH_2)_n-Fc$ rotors for almost all connector chain lengths are smaller than the corresponding values for $S-(CH_2)_n-Fc$ rotors (see Figure 6). This observation can be understood if we compare sizes of anchor groups. The sulfur atom is much smaller than the size of the FeCp group. This forces the first and the second carbon atoms in the thiol-based rotors to be very close to the surface at the distance closer to 3 Å (Figure 7b), creating strong interactions that hinder the rotation. The FeCp anchor is larger; therefore, the carbon atoms in the connector chain are found at distances of order 3.6 Å from the surface, maintaining lower rotational barriers. Thus, the size, structure, and chemical bonding of the anchor group might critically affect the rotational dynamics of surface-mounted single molecules.

Finally, it is also interesting to discuss the effect of the ending group in rotations of molecules. In experiments on diferrocene derivatives,[32] the ferrocene played the role of the ending group. Analysis of connector chain height profiles and MD trajectories suggests that the end group is very mobile, but mostly, it can be found in one of three configurations, (1) both rings of the ferrocene are parallel to the surface, and the ring attached to the connector chain is in contact with the surface, (2) both rings are parallel to the surface, and the ring attached to the connector chain is not in contact with the surface, and (3) both rings are perpendicular to the surface. These motions of the end group also increase the distance to the surface for neighboring carbon groups from the connector chain (Figure 7a). The effect is apparently stronger for shorter chains, as expected.

3.4. Critical Evaluation. Our theoretical method involves a combination of rigid-body MD computer simulations and simple phenomenological arguments. It is important to note that several approximations have been utilized in this theoretical picture. In the phenomenological model, we have assumed that chains are relatively rigid; therefore, positions of the carbon atoms with respect to the surface atoms are more or less known. However, alkyl chains in thioether and diferrocene rotors are quite flexible. As a result, the predictions of the simple model deviate stronger for larger chains.

Another important limitation is the nature of interactions. In the computer simulations, chemisorptions and charge-transfer effects have not been taken into account, except for the anchor groups. Our phenomenological model also implicitly assumes only van der Waals interactions for all chain groups. This is probably a very reasonable approximation for alkyl chains, but it might fail in future molecular rotors with more complex chemical structures.

In addition, the surface atoms have been taken to be frozen in all MD simulations and phenomenological arguments, neglecting the possibility of surface reconstruction. One could argue that this effect might be stronger for larger molecules. However, currently, it is hard to evaluate the effect of surface reconstruction on rotational dynamics. It will be important to investigate fully this question. Furthermore, our approach is a classical MD computer simulations method that mostly neglects quantum effects. This approximation is justified because most of the involved atoms are not known to exhibit quantum phenomena at these conditions. However, this question also requires a comprehensive theoretical study in the future.

Another possible weak point in our approach is a neglect of charges in the FeCp unit. One could argue that taking them into account would only modify the strength of interactions of the anchor group with the surface without changing the mechanisms of rotations. In addition, empirical Fe-Au parameters of interactions are already fitted to describe binding of FeCp to the golden surface reasonably well, suggesting that the neglect of the charges is not a critical issue. However, it will be also important to test the validity of this approximation carefully.

4. Conclusions

We have developed a comprehensive theoretical approach to investigate mechanisms of rotation of single molecules attached to metal surfaces. Our method couples extensive rigid-body MD computer simulations with simple phenomenological arguments. It allowed us to analyze several factors that specify rotational dynamics of known molecular rotors. It was found that the symmetry and the structure of the surface are important for controlling the speed of rotations. Thioether molecules rotate faster on the Au(111) surface than on the Au(100) surface because of different symmetry-dependent interactions between the chain groups and the surface. It was also argued that the structure and symmetry of the molecular rotor itself might influence the overall dynamics in the system. For two-chain rotors, we showed that more symmetric molecules rotate faster due to the compensation of interactions with the surface. In addition, the important role in single-molecule rotations is played by molecular configurations near the surface and the nature of anchor groups. The effect of odd-even alternation as a function of the chain length has been found and analyzed.

The presented theoretical approach explains successfully available experiments in thioether rotors and diferrocene derivatives rotors. We have shown that independence of the rotational properties as a function of molecular sizes in symmetric two-chain thioethers is due to a combination of the compensation,

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steric repulsion, and flexibility effects. For single-chain difer-rocene derivatives, the compensation effect and steric repulsion are much weaker, leading to size-dependent rotational dynamics.

The advantage of our theoretical method is that it connects extensive computer simulations and simple models with structural and chemical details of the system, and it allows understanding of dynamics with microscopic details. So far, we have studied the mechanisms of rotation of individual molecules, but it will be very important to analyze collective dynamics of many rotors. It is reasonable to suggest that a combination of this approach with experimental studies provides a powerful tool for creating and investigating advanced nanoscale devices and new materials.

Supporting Information Available: Animated movies of typical trajectories for single-molecule rotations on gold surfaces. This material is available free of charge via the Internet at http://pubs.acs.org.

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