

Molecular Switch on a Metal Surface

Bidisa Das and Shuji Abe*

Nanotechnology Research Institute and Synthetic Nano-Function Materials Project, National Institute of Advanced Industrial Science and Technology (AIST), Umezono 1-1-1, Tsukuba, Ibaraki 305-8568, Japan

Received: November 4, 2005; In Final Form: December 26, 2005

We report a theoretical study for the conformational switching of molecules on Au(111) surface in the presence of an applied electric field. Ab initio calculations for *N*-(2-mercaptoethyl)benzamide indicate that this molecule, when adsorbed, can exist as two stable conformers of nearly equal energies, but the dipoles point in reverse directions with respect to the surface. An electric field can be used to “switch” one conformer to the other, and during this process, there is an abrupt change in the height of the molecule from the surface. This change is expected to cause a conductance switching in the system. Further calculations for *N*-(2-mercaptoethyl)-4-phenylazobenzamide suggest that the experimentally observed phase switching of this molecule is associated with a conformational change accompanied by dipole reversal.

1. Introduction

Molecular switches are one of the basic components of molecular electronics, in which individual molecules are expected to perform electronic functions. There can be many types of interesting switching phenomena in molecules: namely, photoresponsive switching,^{1–3} switching devices based on interlocked molecules,^{4–6} molecular switches that are redox responsive,^{8–10} and conductance switching in molecules^{11–17} to name a few. To be useful as a device, the switching has to be reversible and triggered by an external stimuli. One basis for such a device is an adsorbed molecule that can be electrically switched between high- and low-conductance states. Here, the objective is to have a molecule that, at a specific voltage, switches from one stable conformer to another with a different conductance; the molecule stays in the other state until another voltage pulse is applied or thermal fluctuations cause it to decay into the former state. The two states of the molecule correspond to the ON and OFF states of the switch, and the stabilities of both the states lead to a hysteretic current/voltage response that forms the basis of the switch. A similar mechanism has already been used to make molecular switches in the case of [2]-rotaxanes^{5,6} anchored to a gold surface. A recent report discusses conductance switching of peptide helix bundles on a gold substrate by scanning tunneling microscopy (STM).⁷ Helical molecules that can exhibit two lengths in response to an applied electric field were chosen for the study.

In the present paper, we discuss a theoretical model of a simple molecular system that can behave as a molecular switch in the presence of an external electric field. The molecule is adsorbed on a gold surface, and the switching may be measured by a change in conductance of the system as a response to the electric field. There have been previous studies on adsorbed molecules on surfaces, where the application of an external bias voltage caused the molecular dipole to flip.^{16,18,19} There has also been a theoretical analysis,²⁰ which suggested that “off resonance rectification” can be achieved by exploiting the conformational changes in molecules sandwiched between metal electrodes, driven by an external electric field. Molecules with polar groups

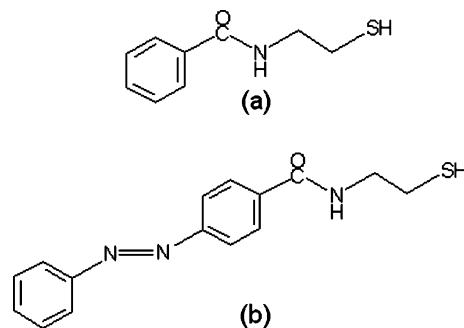


Figure 1. (a) *N*-(2-Mercaptoethyl)benzamide and (b) *N*-(2-mercaptoethyl)-4-phenylazobenzamide.

were suggested as possible candidates that rearrange in space by rotation around σ bonds.

The model molecule we study in the present paper is *N*-(2-mercaptoethyl)benzamide (see Figure 1a) on a Au(111) cluster. The dipole moment of the molecule arising from the amide unit plays the key role in switching. *N*-(2-Mercaptoethyl)benzamide can be chemisorbed onto the gold surface by means of Au–S bonds. Expectedly, the orientation of the amide unit in the adsorbed molecule is responsible for its dipole moment, which reverses its direction when the amide group rotates in space. Thus, when the C=O group points downward (toward the surface), the dipole of the molecule points upward, and with the C=O group pointing upward (away from the surface), the dipole points downward. This phenomenon is accompanied by a change in the height of the molecule from the metal surface. This can actually change the conductance of the system drastically, as it is already known that the conductance of a metal–molecule junction decreases exponentially with increasing the distance of the molecule from the metallic probe in case of STM experiments.^{14,15,18} The flipping or switching of the C=O unit can be brought about by means of externally applied voltage. We apply an external electric field perpendicular to the surface, and the molecule switches between high and low states in terms of the molecular height.

This simple model molecule can provide an essential mechanism of the phase switching of *N*-(2-mercaptoethyl)-4-phenylazobenzamide (see Figure 1b) on the Au(111) surface in the

* Author to whom correspondence should be addressed. E-mail: s.abe@aist.go.jp.

presence of an electric field, as studied by Yasuda et al.¹⁶ using STM. The model molecule *N*-(2-mercaptoethyl)benzamide is just a part of *N*-(2-mercaptoethyl)-4-phenylazobenzamide. Our study indicates that an adsorbate molecule in this case can have four conformations even for the *trans*-azo *trans*-amide structure. These conformers are similar in energies but have different dipole moments, and their responses to an electric field are different. Of course, in the experiment, the situation is more complicated with many influencing factors. Above all, there can be interactions from the neighboring molecules present in the self-assembled monolayer, which further complicate the situation. The experimental report¹⁶ qualitatively suggested a voltage-induced *cis*–*trans* isomerization of the azobenzene unit as a possible explanation for the phase switching behavior, but many aspects remain to be explained. They did not consider any other possible mechanism like the rotation of the amide unit or the conversion of a *trans*-amide conformer to a *cis*-amide conformer. They observed the conductance switching at room temperature with the application of a low bias voltage, indicating that the barrier height for the process is not very high. We propose a mechanism of the phase switching based on the rotation of the C=O bond near or away from the surface accompanied by a change in the height of the molecule as well as its dipole moment. This can, in turn, change the conductance of the molecule, as observed in the experiment.¹⁶

2. Theoretical Methods

All studies reported here are done using the density functional theory (DFT) with the hybrid functional B3LYP formulated by Lee, Yang, and Parr.^{21–23} For all the atoms except Au, the 6-31G** basis set was used, whereas for Au, we used the Lanl2DZ basis set and effective core potential.²⁴ Gaussian 03 software²⁵ was used for the calculations of the free and adsorbed molecules in the absence and presence of an external electric field. In the calculations for adsorbed *N*-(2-mercaptoethyl)benzamide, we modeled the Au(111) surface by a cluster of 21 Au atoms. There are 20 atoms in one layer with only one atom added in the second layer below the adsorption site to mimic the hcp and fcc adsorption sites. The Au atoms are placed according to the (111) arrangement with a Au–Au distance of 2.884 Å. Reconstruction of Au(111) when thiols are adsorbed is a delicate problem. We have not considered any reconstructions of the Au(111) surface for simplicity, but a few recent reports indicate that the reconstruction is lifted due to the adsorption of thiol molecules.^{26,33} Many previous theoretical studies^{33,35–37} have assumed unreconstructed Au(111).

The adsorbate geometry is fully optimized without any symmetry constraints. The Au unit-cell size was taken to be the bulk one, and the Au atoms were not allowed to relax during optimization. This had to be done as we are performing calculations on rather small metal clusters. But it is not unreasonable, because one does not expect the surface to be drastically modified by adsorption of a single molecule. Such kind of fixed bulk structures have been used before.^{27,28} The size of the cluster is limited by the huge computational time required for the studies. The 21-atom Au cluster we use has a length of 15 Å and a maximum width of 8.65 Å. With the maximum length and width of the molecule being 10 and 4.3 Å, respectively, the size of the cluster is adequate even if the molecule tends to lie flat on the surface. We also performed a check with the molecule adsorbed to smaller clusters of Au atoms and found the cluster edges to interact strongly with the adsorbate molecule; hence, they were discarded. For the study

TABLE 1: Optimized Bond Distances in Å for *N*-(2-Mercaptoethyl)benzamide

1–H	1–2	2–3	3–4	4–5	5–6	aromatic C–C
1.35	1.84	1.53	1.46	1.37	1.50	1.39

of *N*-(2-mercaptoethyl)-4-phenylazobenzamide, we used a slightly better basis set and a smaller Au cluster, which are described in section 4.

In the present paper, we are mainly interested in the conformations of the molecules, which are probably not strongly affected by the gold substrate. Therefore, the approximate treatment of the substrate in terms of small gold clusters is not unreasonable for the present purpose. However, cautions are necessary in interpreting the calculated results. First, the present method does not describe well the weak interactions between the molecule and the surface. Second, any possible deformation of the gold surface is not taken into account here. Also, we note that the redox states of the molecule under a strong electric field cannot be properly treated with a small metal cluster. We have checked that the molecule is always almost neutral with very small charge transfer from/to the metal even for the strongest electric field applied in the present study.

3. Model Molecule: *N*-(2-Mercaptoethyl)benzamide

3.1. Free Molecule Conformations. The optimized structure of the *N*-(2-mercaptoethyl)benzamide is presented in Table 1. In this structure the C=O bond is *trans* to the N–H bond. The studies of the free molecules reveal that the *cis*-amide form of *N*-(2-mercaptoethyl)benzamide is 6.38 kcal/mol less stable than the *trans*-amide form. The amide bond rotation barely occurs at room temperature as the barrier height is about 15 kcal/mol. But, there exists another bond rotation that becomes important only when the molecule is adsorbed onto a surface. A rotation about the C–N bond adjacent to the CONH unit of the molecule leaves the free molecule nearly unchanged but reverses the orientation of the molecular dipole with respect to the surface, as we will see below. We find that the barrier height for the rotation of this C–N bond is low (5.29 kcal/mol, see Figure 2 for the potential-energy curve), and the rate of reaction at 298 K is estimated to be $1.13 \times 10^8 \text{ sec}^{-1}$ using the transition state theory.^{28,29} This essentially means that the rotation occurs at room temperature due to thermal fluctuations.

3.2. Adsorbed Molecule Conformations. There are many studies^{27,30–34,37} on the bonding of thiol molecules on the Au(111) surface. There can be on-top, fcc-hollow, hcp-hollow, bridge, fcc-bridge, and hcp-bridge sites for the sulfur atom in the thiol molecule to bond to the surface. Most calculations indicate that upon adsorption of alkane thiols on Au(111), the S atom is bonded to two Au atoms on the surface (the bridge bond) with slight tilting toward the fcc site (called the fcc-bridge site).^{27,30,32,37} The studies also suggest that the hcp-bridge and fcc-bridge sites have virtually the same energy.^{27,30,32,37} Because we are using a limited cluster of Au atoms and it is kept fixed during optimization, we do not stress too much on the energetics of adsorption.

We have optimized *N*-(2-mercaptoethyl)benzamide on the 21 Au atom cluster, where the sole Au atom in the second layer has been placed to mimic the hcp or fcc adsorption sites (see Figure 3). It is found that the adsorbate prefers the hcp-bridge structure with a very slight displacement toward the hcp site. The S–C bond extends toward the fcc site. The Au–S distances are 2.75 Å, and the C–S distance is 1.85 Å. The molecule is largely tilted from the surface normal (*z* axis) with a tilting angle (of the S–C bond) nearly 60 degrees in all cases. A recent

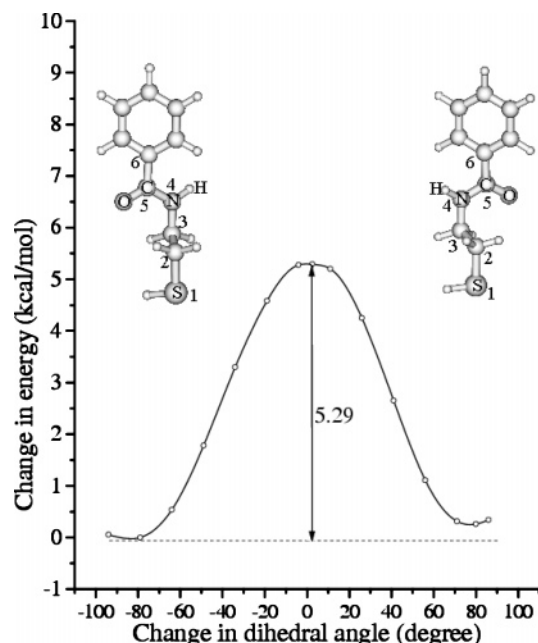


Figure 2. Potential energy change due to rotation about C3–N4 bond in *N*-(2-mercaptoethyl)benzamide. The energy is plotted against the (2–3–4–5) dihedral angle. The optimized structures corresponding to the left and right minima are shown.

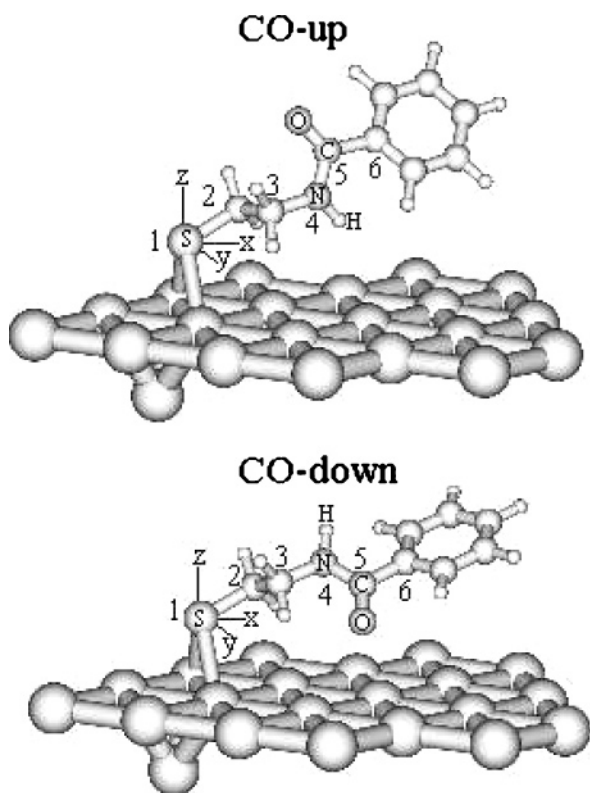


Figure 3. Optimized CO-up and CO-down structures of *N*-(2-mercaptoethyl)benzamide on Au(111). The dipole moment of the CO-down structure is 4.49 D (x : -0.84 , y : 2.45 , z : 3.68 , with z axis as surface normal) and that of the CO-up structure is 3.80 D (x : 0.23 , y : 2.84 , z : -2.51 with z axis as surface normal).

quantum chemical study³⁷ of ethanethiol on the Au(111) surface predicts the binding energy of the hcp-bridge site to be slightly (about 0.2 kcal/mol) more than the fcc-bridge site, with bond distances and a tilt angle similar to our results. The optimized, adsorbed structures are shown in Figure 3. Here we show only the trans conformation of the amide bond of *N*-(2-mercapto-

TABLE 2: Optimized Bond Distances in Å for the CO-down Conformer of *N*-(2-Mercaptoethyl)benzamide

1–Au	1–2	2–3	3–4	4–5	5–6	aromatic C–C	angle of S–C with surface normal
2.76	1.85	1.53	1.46	1.37	1.50	1.39	59.3

TABLE 3: Optimized Bond Distances in Å for the CO-up Conformer of *N*-(2-Mercaptoethyl)benzamide

1–Au	1–2	2–3	3–4	4–5	5–6	aromatic C–C	angle of S–C with surface normal
2.75	1.85	1.54	1.45	1.37	1.50	1.39	62.2

ethyl)benzamide, as we find that the cis conformation is less stable by 6.38 kcal/mol. It is evident from the figure that the molecule is not a perfect zigzag structure like alkane thiols, as reported before.^{30,34} The distortion from the usual structure occurs because the CONH unit in *N*-(2-mercaptoethyl)benzamide tends to remain coplanar.

We report two conformations for *N*-(2-mercaptoethyl)benzamide molecule on the Au(111) surface, and we call them “CO-up” and “CO-down” structures (for details see Figure 3, Table 2, and Table 3). A rotation about the C3–N4 bond (for numbering, see Figure 3) adjacent to the CONH unit of adsorbed molecule converts the CO-up conformer to the CO-down. It is not computationally feasible to calculate the barrier height for the C3–N4 bond rotation in the 21 atom cluster due to time requirements, but we checked that there is almost no change in the barrier height when the hydrogen atom bonded to sulfur in the free molecule is replaced by one gold atom (5.33 kcal/mol). The energies of CO-up and CO-down structures are nearly the same, with the CO-down structure more stable by merely 1.05 kcal/mol. The directions of dipole for the two conformations are reverse. The perpendicular height of the adsorbed molecule from the Au(111) surface is calculated for the optimized structures. It is found that the CO-down structure is nearer to the surface by 0.16 nm in comparison to the CO-up structure. This is associated with the difference in the orientation of the benzene ring with respect to the surface in CO-up and CO-down structures. The benzene ring in the CO-down structure tends to be more parallel to the surface due to stronger surface–molecule interaction.

3.3. Conformation Change Under an Electric Field. The height of a molecule is an important parameter in the case of STM experiments, where an exponential decrease in the tunneling current is observed due to an increase in the tip–sample distance. Therefore, a small increase in the height of the molecule on the surface can result in a large increase in the tunneling current, although other factors such as a change in the electronic structure also contributes to the current. Previous STM studies of phenylene ethynylene oligomers embedded in a matrix of an alkanethiolate monolayer done by Donhauser et al.^{14,15} indicated that molecules exhibited stochastic switching of conductance but remained anchored in the same spot on the surface. The observed switching was interpreted as a tilting of the inserted molecules or a change in the orientation of the molecule with respect to the STM tip. This type of motion can cause a change in the physical height of the molecule above the host matrix, which would result in a change in the apparent height of the molecule as observed with STM.

In this study, therefore, the height of the molecule from the surface is used as a relevant variable controlling the conductance switching. The molecular height is obtained from the coordinates of optimized structures. With the origin fixed on the sulfur atom

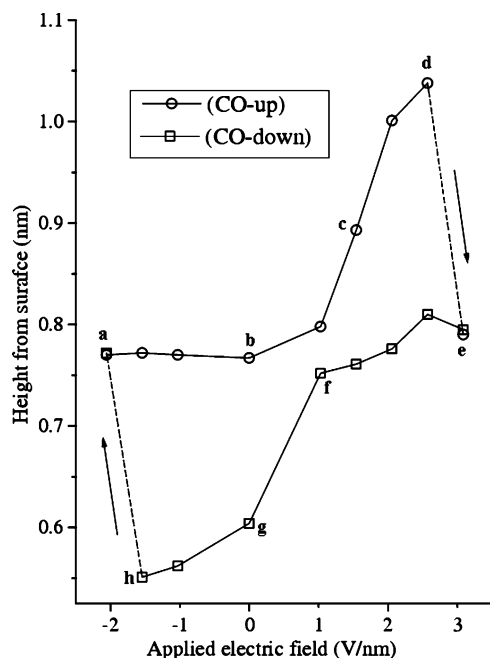


Figure 4. Effect of the applied electric field on the heights of CO-up and CO-down conformers of *N*-(2-mercaptoethyl)benzamide adsorbed on Au.

and *z* axis normal to the surface, the atom having a maximum *z*-coordinate value in the molecule is chosen. Assuming that to be the highest point of the molecule from the surface, the height of the molecule is then defined by this *z*-coordinate value added to the perpendicular distance of sulfur and the Au surface. An external electric field is applied along the *z* axis in all cases. We have looked into the atomic charges of the system before and after application of the electric field. The atomic charges indicate a negligible charge transfer between the surface and the molecule in external fields that we apply.

The change in the height of the two conformers under the electric field is shown in Figure 4. For the CO-up structure, there is a rapid increase in height at positive fields above 1.03 V/nm, and it rises to 1.04 nm from the surface at 2.57 V/nm, and then it sharply falls to 0.79 nm at an electric field of 3.08 V/nm. This fall in height results from the fact that the CO-up conformer is converted to CO-down with a rotation about the C–N bond. The increase in the height of the molecule would mean an increase in tunneling current in STM experiments, which would sharply fall when the height decreases. The CO-up structure remains of nearly the same height at negative fields till –2.06 V/nm. The optimized structures for the points **a**, **b**, **c**, and **d** marked in Figure 4 are shown separately in Figure 5. This figure shows how the angle between the molecule and the surface increases in positive field. This is responsible for the increase in height of the molecule. In the case of the CO-down conformer, however, the effect of the electric field is just the reverse. In this case, the height increases up to the electric field of 1.03 V/nm (see **f** in Figure 6) but remains almost unchanged above this field. At negative fields, the height gradually decreases with a minimum (0.55 nm) at –1.54 V/nm (see **h** in Figure 6). Then the molecule flips to the CO-up structure with a sudden jump in height to 0.77 nm (see **a** in Figure 5). Hence, at –2.06 V/nm, there exists only the CO-up structure, and at 3.08 V/nm, there exists only the CO-down structure. In any fields between these two extremes, both the structures exist. Thus, it is similar to a hysteresis effect, where bistable double well minima of the CO-up and CO-down conformations are converted to a single minimum of either CO-down (at 3.08

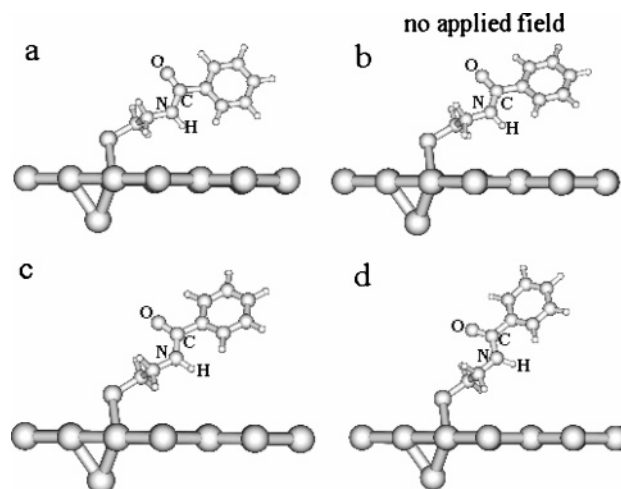


Figure 5. Selected optimized structures of adsorbed *N*-(2-mercaptoethyl)benzamide in applied electric field. The CO-up structures of points **a**, **b**, **c**, and **d** marked in Figure 4 are shown. Side view is shown for clarity.

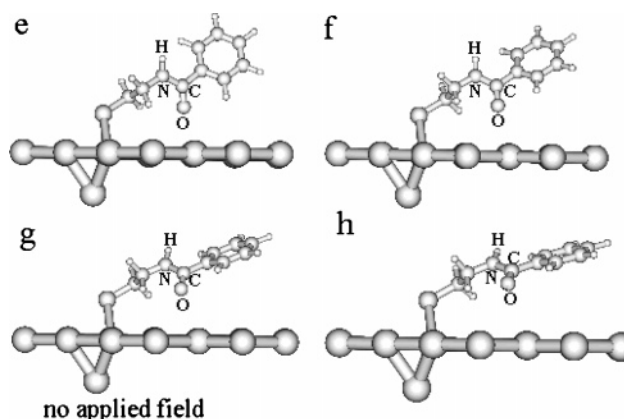


Figure 6. Selected optimized structures of adsorbed *N*-(2-mercaptoethyl)benzamide in applied electric field. The CO-down structures of points **e**, **f**, **g**, and **h** marked in Figure 4 are shown. Side view is shown for clarity.

V/nm) or CO-up (at –2.06 V/nm) under the effect of applied electric fields.

It is meaningful to study the change in the *z* component of the dipole moment of the molecule under an electric field applied along the *z* direction. We find that at no field the total dipole moment (and its components) of the CO-down structure is 4.49 D (*x*: –0.84, *y*: 2.45, *z*: 3.68) and that of the CO-up structure is 3.80 D (*x*: 0.23, *y*: 2.84, *z*: –2.51). The *z* components of the dipole moments of the two conformers vary with the electric field, as shown in Figure 7. The dipole component of the CO-up structure becomes more negative at negative fields, whereas it becomes positive at positive fields and becomes as high as 14.71 D at a field strength of 3.08 V/nm. The behavior is linear from –2.06 to 1 V/nm and, after that, there is a more rapid increase, approaching the dipole component of the CO-down conformation. The CO-down structure, which has a positive dipole component at zero field, maintains a linearity from –1.54 to 3.08 V/nm. Between –1.54 and –2.06 V/nm, there is a sharp drop corresponding to the flipping of the molecule to the CO-up structure.

When no electric field is applied, the CO-up and the CO-down structures are similar in energy, with the CO-down structure more stable by only 1.05 kcal/mol. The dependence of the energy on the electric field is different for the two structures, as shown in Figure 8. The CO-up conformation has

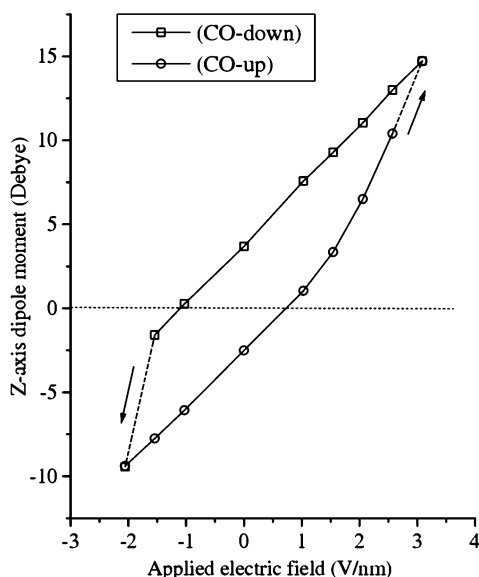


Figure 7. Effect of the applied electric field on the z -axis dipole moments of CO-up and CO-down conformers of adsorbed N -(2-mercaptoethyl)benzamide.

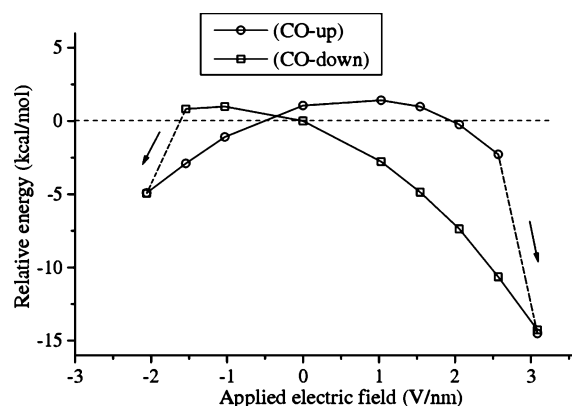


Figure 8. Effect of the applied electric field on the energies of CO-up and CO-down conformers of adsorbed N -(2-mercaptoethyl)benzamide. All the energies are relative to the energy of the CO-down conformer at no field.

a dipole pointing down toward the surface and stabilized more by an electric field in the negative z direction. In the case of a positive electric field, the energy of the CO-up structure first increases slightly, but soon it starts decreasing, with a sharp fall around 2.06 V/nm. This drastic change in energy is caused by the flipping of the molecule to the CO-down orientation. In the case of the CO-down conformation, the z component of the dipole moment is positive, so that there is stabilization at positive fields. But the energy increases for fields in the negative z direction. At -1.54 V/nm, there is a sudden decrease in energy because the molecule changes its conformation to CO-up. Only the CO-up structure exists at -2.06 V/nm, and only the CO-down structure exists at 3.08 V/nm. This is essentially a hysteresis phenomenon, where a bistability in the potential energy profile is reduced to a single minimum by the application of a threshold field. The single minimum outside the hysteresis region corresponds to the CO-down structure for positive fields and to the CO-up structure for negative fields.

3.4. Switching and Rectification. The CO-up and CO-down conformers of N -(2-mercaptoethyl)benzamide on Au(111) have different molecular heights and different dipole moments. Hence, the two conformations can act as high-conducting “ON” or low-conducting “OFF” states, which can be switched by means of

an external electric field. The studies of the free molecules reveal that the ON and OFF conformers are almost isoenergetic. The barrier height for the conversion of the CO-up and CO-down conformers is not very large (nearly 6 kcal/mol), and there is not much control about the choice of the starting geometry due to thermal equilibrium at room temperature. Despite the equilibrium between the two, there can still be rectification. If we study Figure 4, we find that there is an overall increase in the height of the molecule at positive applied fields, which corresponds to the ON state of the molecule. The molecule remains to be OFF at negative applied fields. This corresponds to the rectification of the current discussed by Troisi and Ratner.²⁰ Furthermore, the ON state is switched off by the application of external fields higher than 2.57 V/nm, corresponding to the negative differential conductance.

It should be noted that at low temperatures, the ON and OFF states, i.e., the CO-up and CO-down states, can be brought into separate observable states without thermal equilibrium. In this case, the full hysteresis curve of Figure 4 can be followed. Alternatively, if the molecule is embedded in a matrix of self-assembled monolayer on the surface, the interactions with surrounding molecules may cause a substantial increase in the barrier height for the conversion. We can also expect a cooperative switching in the case of an ordered monolayer of the switching molecules on the surface.

4. Switching in

N -(2-Mercaptoethyl)-4-phenylazobenzamide

Our study of switching in N -(2-mercaptoethyl)benzamide in the previous section forms a basis for understanding the phase switching behavior of the photoactive, isomeric N -(2-mercaptoethyl)-4-phenylazobenzamide molecule (Figure 1b) on Au(111), reported by Yasuda et al.¹⁶

4.1. Free Molecule Conformations. We investigated the free N -(2-mercaptoethyl)-4-phenylazobenzamide molecule in detail theoretically. There can be three possible isomerization processes in this molecule:

1. cis–trans isomerization of the azobenzene moiety
2. cis–trans isomerization of the amide bond
3. rotation around the C–N bond adjacent to the amide bond.

We have discussed processes 2 and 3 for N -(2-mercaptoethyl)benzamide. The rotation in process 3 gives rise to a very similar conformation in the free case but becomes important only on adsorption. For the free molecule, we have studied the barrier heights for all of these processes.

The cis–trans isomerization barrier of process 1 was found to be the highest. The cis and the trans structures of free N -(2-mercaptoethyl)-4-phenylazobenzamide are optimized (B3LYP/6-31++G**), and the trans form is found to be more stable by 15.44 kcal/mol than the cis form. The transition state for the cis–trans isomerization is located with a barrier height of 37.5 kcal/mol from the trans isomer. In the transition state, the two benzene rings of azobenzene are perpendicular to each other, with N=N making an angle of 180° with the C atom of one benzene ring to which it is bonded. The cis–trans isomerization barrier height that we find in this case is very similar to the barrier heights found for the cis–trans isomerization of the free azobenzene molecule in earlier studies.^{38–43} This shows that the introduction of a long amide-substituted alkyl group in the azobenzene molecule does not influence its cis–trans isomerization energetics significantly.

As normally expected, a conformation with the cis amide unit and the trans azobenzene unit is less stable than the trans amide and trans azobenzene conformation by 4.58 kcal/mol. The barrier

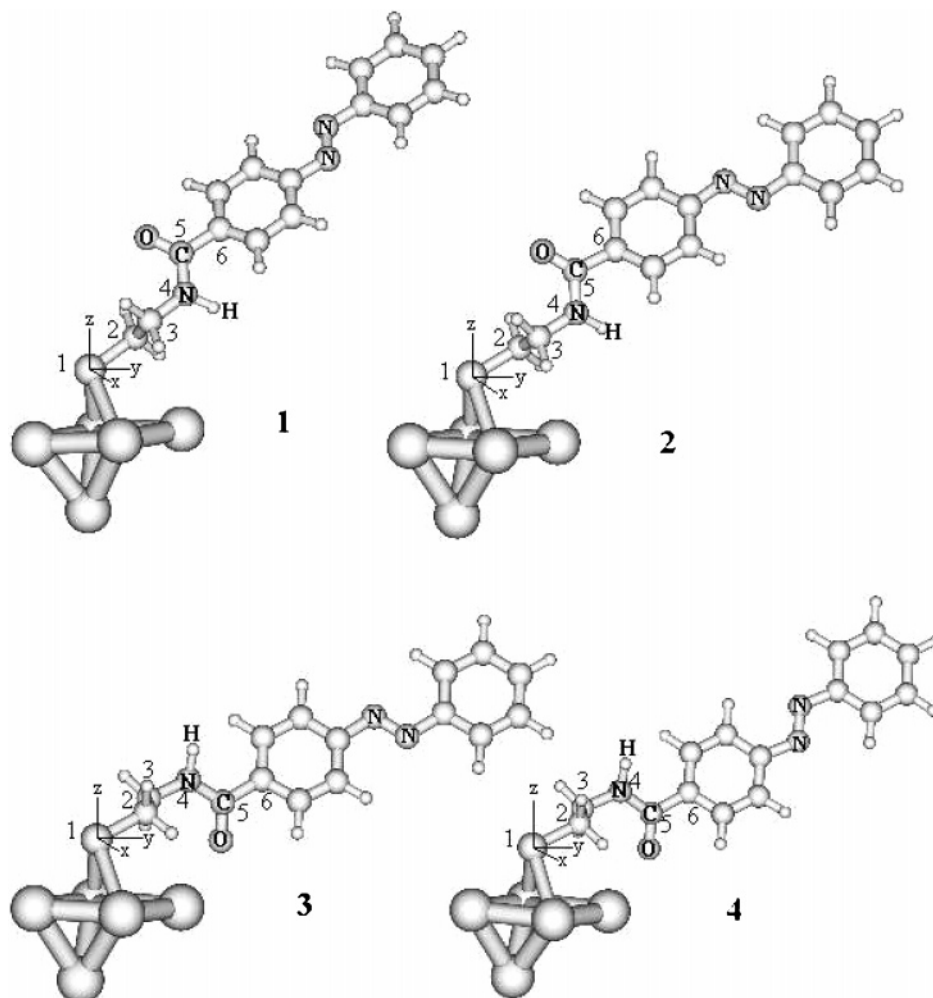


Figure 9. Optimized structures of *N*-(2-mercaptoethyl)-4-phenylazobenzamide on a five-atom Au cluster. The dipole moments of **1–4** are 2.98 D (x : 0.87, y : 2.17, z : -1.84), 3.12 D (x : 0.68, y : 2.28, z : -2.02), 4.87 D (x : -0.24, y : 2.37, z : 4.24), and 5.04 D (x : -0.42, y : 2.28, z : 4.47), respectively.

height for the amide bond to convert from *trans* to *cis* is calculated to be 14.51 kcal/mol. This rules out interconversions at ordinary temperatures.

In contrast to these two processes, the barrier height for the rotation about the C–N bond adjacent to the CONH unit (rotation about C3–N4 in Figure 9) is 5.68 kcal/mol, which is similar to the case of *N*-(2-mercaptoethyl)benzamide. The result of this rotation is a nearly identical conformation with a change in the orientation of the C=O bond. These two conformations would, however, be different when the molecule is adsorbed on a surface with a different orientation of the molecular dipole and a difference in molecular height from the surface.

4.2. Adsorbed Molecule Conformations. To test whether a flipping of the molecule takes place in the case of adsorbed *N*-(2-mercaptoethyl)-4-phenylazobenzamide, we optimized (B3LYP/6-31++G** for all atoms, Lanl2DZ basis set and effective core potential for Au) the *trans* structures on a five-atom Au cluster modeled as a surface. Optimization of all isomers on larger gold clusters were not feasible due to the huge computational time required. Though a five-atom cluster is too small to reflect the actual situation of the adsorbed molecule, it can still give us an idea about the conformational switching of the molecule under an electric field.

The *trans* azobenzene with the *trans* amide is the most stable structure for the free molecule and also on the five-atom Au cluster. The *cis* azobenzene form with a *trans* amide is less stable by 15.6 kcal/mol from the former and is not studied here due

to its higher energy. A *trans*-azobenzene structure with *cis*-amide is found to be less stable than the *trans*-amide case by 4.6 kcal/mol on the five-atom Au cluster. The *cis*–*trans* barrier height remains almost unaffected (37.6 kcal/mol) when the hydrogen atom bonded to the sulfur atom is replaced by one gold atom. Because the isomerisable azobenzene part is away from the surface, the barrier height for the isomerization process should not be greatly modified by adsorption.

The *trans*–*trans* (i.e., *trans*-azobenzene *trans*-amide) isomer of the molecule can exist as four different conformations when adsorbed: C=O and N=N, both pointing toward the surface (downward); C=O and N=N, both pointing away from the surface (upward); C=O pointing downward but N=N pointing upward and vice versa. These conformations are shown in Figure 9. All the conformers of *N*-(2-mercaptoethyl)-4-phenylazobenzamide form S–Au bridge bonds with bond lengths of 2.70 to 2.71 Å, and there is a very small tilting toward the hcp site. Conformers **1** and **2** both have a CO-up structure with the N=N bond pointing up and down, respectively. They are similar in energy with dipole moments of 2.98 D (x : 0.87, y : 2.17, z : -1.84) for **1** and 3.12 D (x : 0.68, y : 2.28, z : -2.02) for **2**. The height from the surface is 1.27 nm for **1** and 1.18 nm for **2**. Conformer **3** and **4** both have CO-down structures with N=N bond pointing down and up, respectively. They are similar in energies with dipole moments of 4.87 D (x : -0.24, y : 2.37, z : 4.24) for **3** and 5.04 D (x : -0.42, y : 2.28, z : 4.47) for **4**. The heights from the surface are 0.91 nm for **3** and 1.07 nm

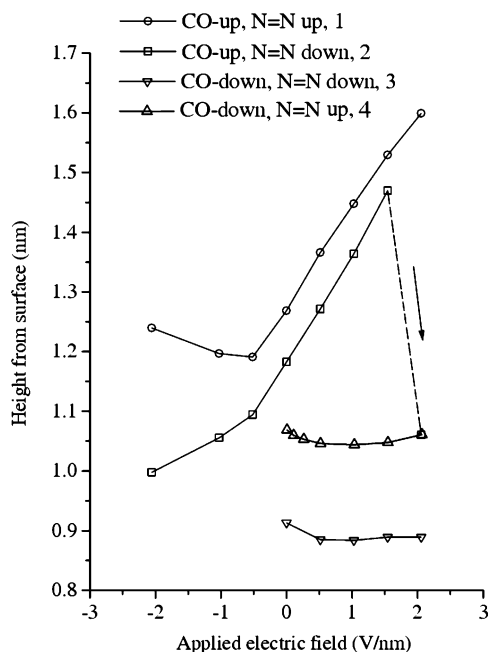


Figure 10. Effect of the applied electric field on the height of adsorbed *N*-(2-mercaptoethyl)-4-phenylazobenzamide.

for **4**. The CO-down conformers (**3** and **4**) are slightly higher in energy (by 0.5 kcal/mol) than the CO-up conformers (**1** and **2**). Structure **3** has the smallest value of the height from the surface among all four conformers. Because all four structures have similar energies, they can exist with almost equal probabilities on Au(111) at room temperature, if other interactions from the surroundings are not taken into account. Although we have not calculated the barrier heights for interconversions among the four conformations, we expect that the barrier height for the rotation about C3–N4 for an isolated adsorbed molecule is not much different from the case of the free molecule (5.68 kcal/mol). This rotation gives rise to interconversions between **1** and **3** or between **2** and **4**.

4.3. Conformation Change Under an Applied Electric Field. We have optimized all four trans–trans conformers in the presence of an external electric field along the *z* axis (B3LYP/6-31++G** for all atoms, Lanl2DZ basis set and effective core potential for Au). The cis forms of structures are not studied in electric fields as they are not expected to exist under ordinary conditions due to their higher energies. We find no trans to cis conversions (for azobenzene portion or the amide portion) in the range of the external field that we apply.

The dependence of the molecular height from the surface upon the electric field is shown in Figure 10. The heights of the CO-up structures (**1** and **2**) increase rapidly with the field applied in the positive *z* direction. This is a result of a decrease in the tilt angle of the molecule. When the field is applied in the negative *z* direction, the molecular height varies very slowly, and the molecule tends to lie down on the surface. The CO-down structures (**3** and **4**) exhibit little change in height due to their dipole alignment for positive fields.

The situation for this molecule is only partially similar to the case of *N*-(2-mercaptoethyl)benzamide, because now the dipole moment of the molecule is not only due to the CONH unit but also affected by the azobenzene unit. Therefore, the two CO-up structures **1** and **2** behave quite differently under an external field. In the case of **2**, the CO-up, and N=N down conformer, the molecule at first rises in height and then flips to **4** (CO-down, N=N up) after application of a field of 1.54 V/nm.

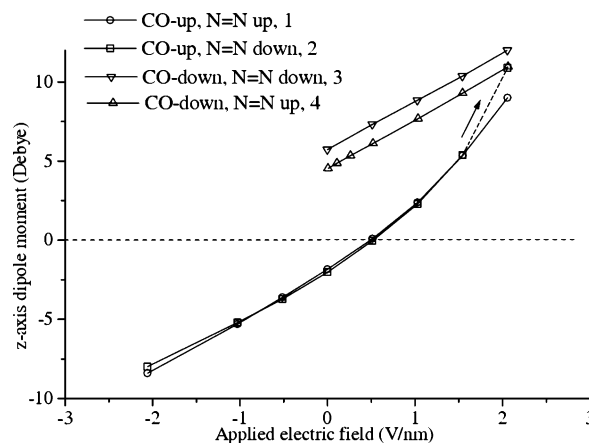


Figure 11. Effect of the applied electric field on the dipole moment of adsorbed *N*-(2-mercaptoethyl)-4-phenylazobenzamide. The change in the *z* component of the dipole moment is plotted.

But in the case of **1**, the CO-up, and N=N up conformer, the molecular height continues rising steadily even above 2 V/nm, and the molecule becomes more and more vertical to the surface. We further checked the structure of **1** at external fields as strong as 4 V/nm and found that it does not flip and the structure becomes almost perpendicular to the surface. When conformer **2** (CO-up, N=N down) flips to **4** (CO-down, N=N up), there is a sudden fall in the height of the molecule from 1.47 to 1.07 nm. This can result in a huge change in conductance for STM experiments. The flipping is also accompanied by a sudden change in the dipole moment from 6.96 D (*x*: 2.31, *y*: 3.78, *z*: 5.37) to 12.36 D (*x*: 0.85, *y*: 5.80, *z*: 10.88).

The dipole moments of the four conformations are shown as functions of the electric field in Figure 11. In analogy with the case of *N*-(2-mercaptoethyl)benzamide shown in Figure 4, the application of an electric field in the direction of negative *z* direction should always tend to lower the molecular height for all the conformations **1**–**4**. Such effects were found for **2**. In case of **1**, the molecular height increases slightly in negative fields. In our calculations for the CO-down structures **3** and **4**, the oxygen atom in the CONH unit interacts very strongly with Au atoms in the gold cluster, forming a Au–O bond; hence, we could not study the CO-down structures under negative fields. This obviously is an artificial effect arising from the unsatisfied valencies of Au atoms in the small gold cluster. This would not occur if we could use a larger Au cluster, as our study of *N*-(2-mercaptoethyl)benzamide on the 21-atom cluster proves. In any case, the conformers **3** and **4** are likely to always be low in height and, hence, of low conducting type.

A close inspection of the energy changes (see Figure 12) for all four conformations reveals that the CO-down structures **3** and **4** behave in a similar fashion. The CO-up structures **1** and **2** also behave in a similar manner. At first, the energy increases slightly with application of a positive field but soon starts decreasing rapidly. Between 1.54 and 2.06 V/nm, the energy of **2** suddenly falls sharply in contrast to **1**, and it is converted to **4**. Thus, in the positive field regime above 1.54 V/nm, there can be only three conformers present: **1**, **3**, and **4**. Among these three structures, **1** has a much greater height from surface than the other two structures (see Figure 10). Hence, **1** is likely to be much more conducting than **3** and **4**.

4.4. Discussion. The existence of the high and low conformations at positive fields shown in this theoretical study is consistent with the stochastic switching between high and low conducting states observed in the STM image of *N*-(2-mercaptoethyl)-4-phenylazobenzamide molecules on Au(111) under

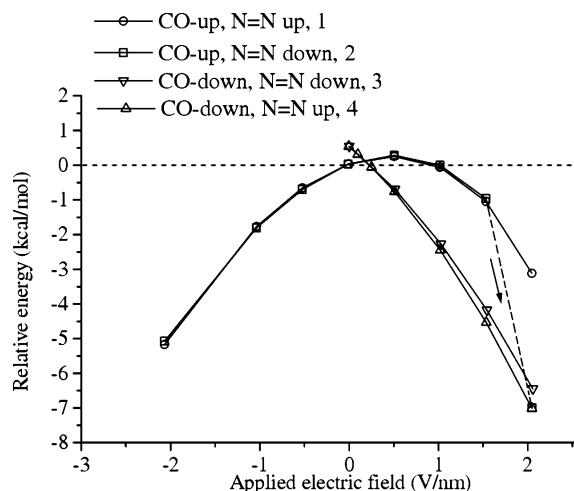


Figure 12. Effect of applied electric field on the energy of adsorbed *N*-(2-mercaptoethyl)-4-phenylazobenzamide. All the energies are relative to the most stable conformer, **1**, at no field.

positive sample bias voltages.¹⁶ Therefore, we propose the rotation about the bond between the amide unit and the alkyl chain to be the dominant mechanism of the observed conductance switching. The original claim of *cis*–*trans* isomerization in the azobenzene unit, which was certainly responsible for the observed photoinduced switching, would occur at much higher voltages, because the barrier height for this process is nearly seven times the barrier height for the amide rotation.

However, our results are for an isolated molecule on a metal cluster, and we have difficulties in reproducing the energetics of the switching states observed in actual molecules embedded in a self-assembled monolayer (SAM) of alkanethiol molecules.¹⁶ The theoretical barrier height of about 6 kcal/mol for the rotation of C–N bond would imply that the CO-up and CO-down conformations coexist at room temperature as mentioned before, and the conductance would be an average of thermally fluctuating high and low conducting states. However, the observed lifetime of switching was rather long, on the order of 1 ms. This suggests that the barrier height is strongly enhanced by the effect of surrounding molecules. The importance of this effect is evident also from the fact that the switching phenomenon was observed only for molecules located in domain boundaries but not inside the domains of the SAM. The relative energies of the various conformations shown in Figure 12 would be also affected by the intermolecular interaction.

5. Conclusion

We have presented a theoretical study for the switching of a *N*-(2-mercaptoethyl)benzamide molecule on a Au(111) surface. We find electric-field-dependent conformation switching in the adsorbed molecule. The conformational change involves the rotation of the amide unit in the molecule (more precisely, the rotation around the C–N bond adjacent to the amide unit) and, hence, reverses the direction of the dipole and changes the height of the molecule. The conductance of the system would be affected by this switching. Despite the small barrier height for interconversion between the conformers, it shows a kind of switching behavior as there is a net increase in conductance at positive applied electric fields, which abruptly falls after a threshold field. It is also to be noted that the barrier height reported here is for the isolated molecule and it would possibly increase due to adsorbate–adsorbate interactions when the molecules are self-assembled into a monolayer on a surface. Then the conformation change is likely to follow a hysteresis

curve. Therefore, we can think of a memory device consisting of a SAM of the switching molecules sandwiched between electrodes, where conformation switching can be induced by applying a sufficient voltage.

We have also qualitatively explained the voltage-induced phase switching of the photoactive, isomeric *N*-(2-mercaptoethyl)-4-phenylazobenzamide molecule on Au(111) reported by Yasuda et al.¹⁶ in terms of the rotation of the amide unit in the adsorbate molecule that may occur at room temperature. However, with our results being for isolated molecules on metal clusters, we cannot discuss the kinetics of switching that is likely to be strongly influenced by surrounding molecules in SAM. Theoretical methods designed to take into account intermolecular interactions on surfaces are likely to give results which can be compared with the experimental results quantitatively.

Acknowledgment. We thank Dr. Tohru Nakamura and Dr. Satoshi Yasuda for many useful discussions. This work was supported by NEDO under the Nanotechnology Program.

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