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STM-induced switching of the hydrogen molecule in naphthalocyanine

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Abstract

The switching induced by the scanning tunneling microscope (STM) current of an adsorbed hydrogen molecule in the cavity of a naphthalocyanine molecule between two perpendicular orientations is studied. We regard such a system as a good candidate for a molecular size electronic logic gate since it causes a well observed change in the STM tunneling current. To investigate the switching phenomenon theoretically, a dynamical model is proposed in this study. Our suggested model is a three-level system, with the switching as a rotation induced by tunneling electrons considered as a second-order time dependent perturbation, where the electrons tunnel from the STM-tip to the naphthalocyanine molecule then to the metal substrate. The tunneled electrons will excite the hydrogen molecule rotational modes to jump over a potential barrier and then the switching will occur. To verify the model, the probability of the switching is calculated and plotted against the bias voltage at different temperatures using first-principles calculated parameters to fit fairly with experimental observations. In the light of our model and the DFT results, we explain the energy level (highest occupied molecular orbital (HOMO), lowest unoccupied molecular orbital (LUMO), and LUMO + 1 orbitals) deviations with different substrates (NaCl and RbI) and the charge density distributions of these orbitals in different cases.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Currently, the field of molecular electronics is rapidly developing theoretically as well as experimentally, because of new experimental tools such as the scanning tunneling microscope (STM), which made it possible to observe and manipulate surfaces in the atomic range. Some of the experimental systems show potential phenomena to be a single molecule device, for instance, the switching in the naphthalocyanine molecule.

The study and understanding of such kinds of systems can lead to more powerful applications to electronics and computing in terms of speed, size, precision, and the like. Therefore, the electronic transport mechanism beyond these phenomena in the molecular dimension needs to be investigated to enable control and design for practical use [1–3].

Naphthalocyanine is an organic molecule where the adsorbate is a hydrogen molecule. In this case, the LUMO of this molecule can have two orientations resulting from its two-dimensional symmetry. These two orientations are directly related to the adsorbate hydrogen molecule orientation in the cavity, as shown in figure 1 [4–8].

It has been found that switching of the hydrogen molecule can be induced by STM current between two definite levels with a well defined change in the tunneling current. The measured current change is about 1.5 pA for a single molecule at a bias of 1.7 V [4]. With that change, the corresponding orbital images of the LUMO, and LUMO + 1 rotate 90°.

Hence, this system can represent a good candidate for an electronic logic gate because switching is well defined, highly localized, reversible, intrinsic to the molecule, and

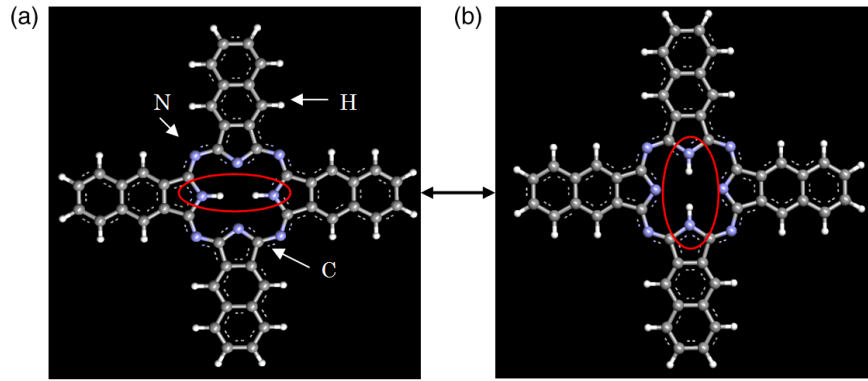


Figure 1. (a) Naphthalocyanine molecule with a hydrogen molecule adsorbed in its cavity. (b) Hydrogen molecule orientation changed by 90°.

does not involve changes in the molecule (tautomerization reaction) [4, 9]. Experimentally, the system is set as follows (figure 2): the naphthalocyanine is adsorbed on a thin insulating film, either a bilayer of NaCl or a bilayer of RbI, then on a metal substrate of Cu(111) surface. The STM-tip is positioned away from the center of the molecule to observe the change in the current when switching occurs. This change in the current cannot be observed at the center because of the two-dimensional symmetry of the molecule [4, 6].

Many theoretical investigations normally assume a sequence of a two-step mechanism for the tautomerization [7, 10]. Also, the molecular rotational and vibrational excitations and the dissociation processes can be induced by an STM current [1, 11].

Moreover, the highest rate of switching is achieved when the tip is positioned at a height of more than 10 Å from the molecule, in which the tip can be treated as a point-like probe and the surface or the molecule will simply be seen as a local density of states [12]. At this distance short-range interactions between the tip and the sample causing change in the tip apex configuration or the adsorbed molecule can be avoided [13, 14].

Under these circumstances, there is no significant distortion or molecular reorientation resulting from the non-uniformity of the electric field between the tip and the metal substrate [15–17], otherwise, the topographic image of the molecules' local density of states will not be true (i.e. similar to the calculated/expected one [4]).

In section 2, our suggested model Hamiltonian, the perturbation solution to the second-order probability and the DFT calculation method are introduced. In the first part of section 3, a discussion of the consequences of our model using parameters calculated based on density functional theory (DFT) is provided. The second part of section 3 is a comparison of our calculation results with experimental data and observations.

2. Models and methods

2.1. Model Hamiltonian

We consider the system to be stable and the switching (rotation) [1] of the hydrogen molecule is induced by tunneling

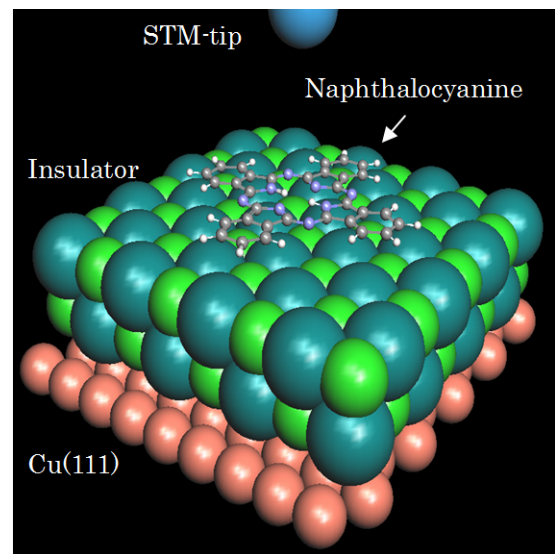


Figure 2. Experimental setup for the hydrogen switching by the STM-tip. The light green atoms and the dark green atoms are Cl and Na, respectively.

electrons as a time dependent perturbation. The complete Hamiltonian for the system is:

$$H = H_o + H' \quad (1)$$

with H_o the unperturbed Hamiltonian, and H' the perturbation Hamiltonian term.

We define the unperturbed Hamiltonian using the coordinates in figure 3 as:

$$H_o = -\frac{\hbar^2}{2\mu} \frac{\partial^2}{\partial R^2} + \frac{1}{2} \mu \omega_{vi}^2 (R - R_o)^2 - \frac{\hbar^2}{2I} \frac{\partial^2}{\partial \theta^2} + \frac{1}{2} I \omega_{ro}^2 (\theta - \theta_q)^2 + \sum_{\eta} \varepsilon_{\eta} a_{\eta}^{\dagger} a_{\eta} + \sum_{\tau} \varepsilon_{\tau} a_{\tau}^{\dagger} a_{\tau} + \sum_s \varepsilon_s a_s^{\dagger} a_s \quad (2)$$

where $\theta_q = q\pi/2$, and $q = 0, 1, 2 \dots$

R is the distance of the hydrogen atom from the center of the molecule (the origin) and θ is the angle of the hydrogen

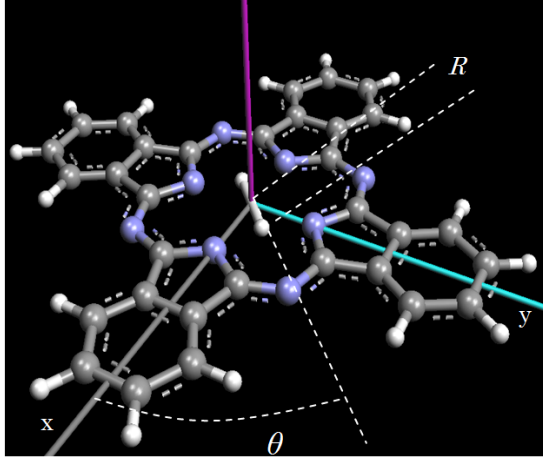


Figure 3. Coordinate definitions. R is the distance from the origin to the H atom, and θ is the angle of the H_2 bond axis and the original orientation at the initial state (x -axis).

molecule bond axis (see figure 3). $\mu = m_H/2$ is the reduced mass of the adsorbed hydrogen molecule, $I = \mu(2R_o)^2$ its moment of inertia, $2R_o$ the average distance between the two hydrogen atoms in the cavity (calculated to be 2.058 Å), and ω_{vi} , ω_{ro} the vibrational, rotational frequencies respectively ($\hbar\omega_{ro}$ calculated to be 0.1512 eV, $\hbar\omega_{vi}$ estimated to be of the order of meV),

$\varepsilon_\tau a_\tau^\dagger a_\tau$, $\varepsilon_\eta a_\eta^\dagger a_\eta$, $\varepsilon_s a_s^\dagger a_s$ are the corresponding energy and the creation and annihilation operators for an electron in the STM-tip (τ), naphthalocyanine molecule (η), and the metal substrate (s), respectively.

The Hamiltonian (equation (2)) describes a harmonic oscillator with R and θ , and the electronic structure of the whole system.

The perturbation Hamiltonian term can be expressed in two terms as:

$$H' = \sum_{\tau\eta,\sigma} \xi^{\tau \rightarrow \eta} a_{\eta\sigma}^\dagger a_{\tau\sigma} + \sum_{\eta s,\sigma} \xi^{\eta \rightarrow s} a_{s\sigma}^\dagger a_{\eta\sigma} + \text{h.c.} \quad (3)$$

Here $\xi^{\tau \rightarrow \eta}$, $\xi^{\eta \rightarrow s}$ are the hopping integrals for an electron with spin σ tunneling from the tip to the naphthalocyanine then from the naphthalocyanine to the metal substrate respectively.

When the tunneling electron occupies the LUMO of the molecule, it will make the electronic charge density larger and more diffuse. This change is usually compensated by molecular excitation. At the same time, electronic transition happens much faster than nuclei movement. Thus, it is possible to assume that the simultaneous excitation of rotation and vibration with electronic transition is reduced [18, 19].

Accordingly, for simplicity in our solution, the vibration effect is neglected since we can assume it to be very small in terms of its energy change with distance R compared to the rotational spectrum.

Fixing the distance of the hydrogen atoms from the center of the molecule at R_o and assuming no vibrational modes, the hopping integrals can then be approximated for only a change with θ as:

$$\xi^{\tau \rightarrow \eta} \approx \xi_o^{\tau \rightarrow \eta} e^{-y_H^\tau(\theta - \theta_q)^2} \quad (4)$$

$$\xi^{\eta \rightarrow s} \approx \xi_o^{\eta \rightarrow s} e^{-y_s^H(\theta - \theta_q)^2}, \quad (5)$$

where $\xi_o^{\tau \rightarrow \eta}$, $\xi_o^{\eta \rightarrow s}$ are constants to determine the distance dependence of the hopping from the tip to the molecule and from the molecule to the substrate respectively. y_H^τ , y_s^H are the constants that determine the θ dependence of the hopping between the tip and the molecule then between the molecule and the substrate, respectively.

If R is approximated to be equal to R_o , and neglecting the vibration effect, then:

$$\left(-\frac{\hbar^2}{2I} \frac{\partial^2}{\partial \theta^2} + \frac{1}{2} I \omega_{ro}^2 (\theta - \theta_q)^2 \right) \varphi_q^g(\theta) = E_{ro}^g \varphi_q^g(\theta). \quad (6)$$

The normalized solution for equation (7) is:

$$\begin{aligned} \varphi_q^g(\theta) &= \left(\frac{2IE_{ro}^g}{\pi \hbar^2} \right)^{1/4} \\ &\times \frac{1}{\sqrt{2^g g!}} H_g \left(\sqrt{\frac{2IE_{ro}^g}{\hbar^2}} (\theta - \theta_q) \right) e^{-\frac{IE_{ro}^g}{\hbar^2} (\theta - \theta_q)^2} \end{aligned} \quad (7)$$

where

$$E_{ro}^g = (g + \frac{1}{2}) \hbar \omega_{ro}, \quad g = 1, 2, 3, 4, \dots \quad (8)$$

is the rotational energy level of order g . $H_g(\sqrt{\frac{2IE_{ro}^g}{\hbar^2}} (\theta - \theta_q))$ is a g th degree Hermite polynomial and function of $\sqrt{\frac{2IE_{ro}^g}{\hbar^2}} (\theta - \theta_q)$.

Equation (8) is a simple harmonic oscillator dispersion relation with the equilibrium position θ_q . The shape of the potential curve, in equation (6) can be obtained by fitting with the DFT calculated rotational spectra.

2.2. Perturbation calculation

We assume the solution to be a linear combination of a three-level system due to transition between two levels through an intermediate state where an electron is created in the LUMO of the naphthalocyanine which results in second-order perturbation.

Let $|\varphi_{\text{ele}}\rangle = \prod_k^{|k| < k_F} a_{s k \sigma}^\dagger \prod_i^{|i| < i_F} a_{\eta i \sigma}^\dagger \prod_j^{|j| < j_F} a_{\tau j \sigma}^\dagger |0\rangle$ be the electronic ground state wavefunction of the whole system. We can then start a coherent process with applied bias voltage by assuming electron creation in the tip with the hydrogen molecule in the ground state rotational energy (state α), then annihilating it from the tip and creating it in the naphthalocyanine where it excites a rotational mode in the hydrogen molecule as an intermediate state (state β). Finally it is annihilated from the naphthalocyanine and created in the substrate, at the same time, the hydrogen molecule is either rotated by $\pi/2$ or excited without rotation as a final excited state (γ), prescribed below and in figure 4:

$$\psi_\alpha = a_{\tau\sigma}^\dagger |\varphi_{\text{ele}}\rangle |\varphi_0^0(\theta)\rangle = |\varphi_{\text{ele}}^\alpha\rangle |\varphi_0^0(\theta)\rangle, \quad (9)$$

$$\psi_\beta = a_{\eta\sigma}^\dagger a_{\tau\sigma} |\varphi_{\text{ele}}^\alpha\rangle |\varphi_0^{g\beta}(\theta)\rangle, \quad (10)$$

$$\text{and } \psi_\gamma = a_{s\sigma}^\dagger a_{\tau\sigma} |\varphi_{\text{ele}}^\alpha\rangle \left| \varphi_1^{g\gamma} \left(\theta - \frac{\pi}{2} \right) \right\rangle \quad (11)$$

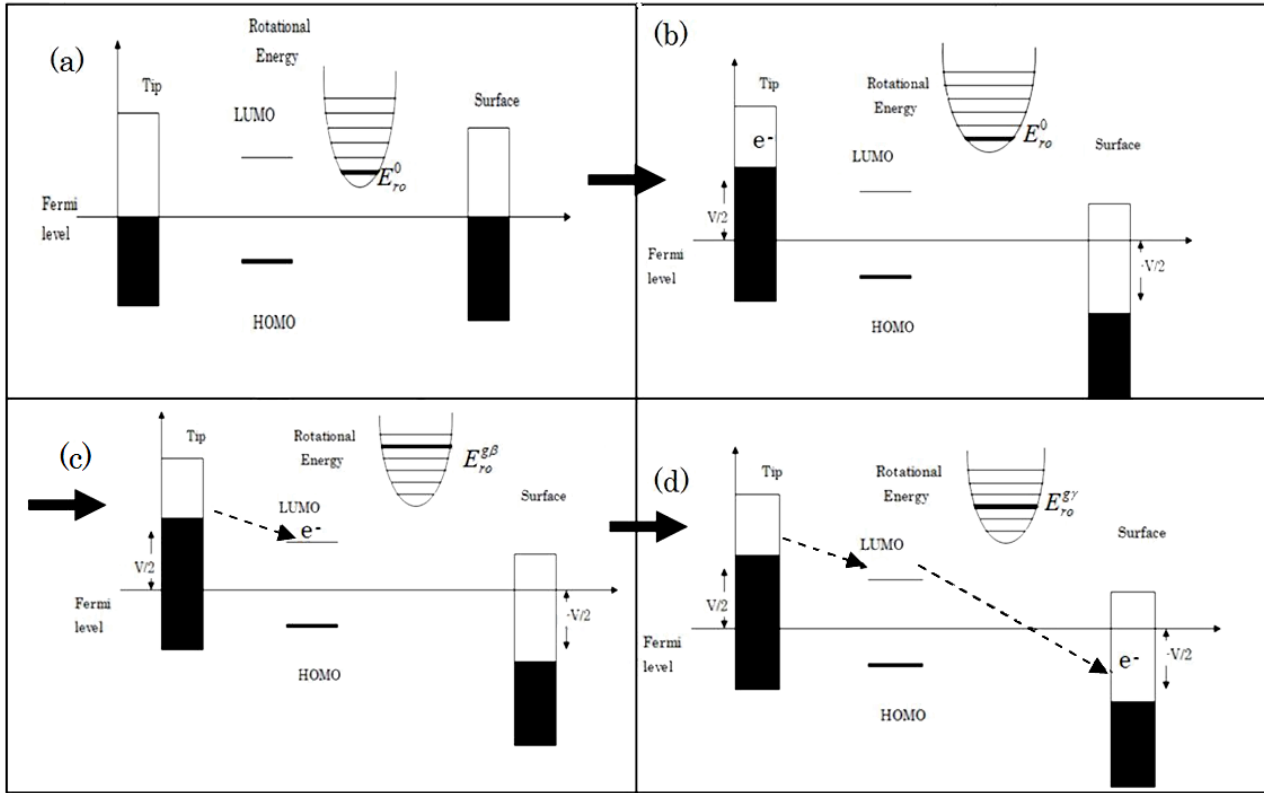


Figure 4. Schematic diagram of the electronic system in the experimental setup as a function of energy with respect to the Fermi level. Thick arrows describe transfer to another state. Dashed arrows describe electron transport. (a) The system is at equilibrium. (b) When a bias voltage V is applied, an electron creation is assumed in the STM-tip (state α). (c) The electron then occupies the LUMO of the naphthalocyanine (state β) with rotational excitation $E_{ro}^{g\beta}$ of the hydrogen molecule. (d) The electron tunnels to the Cu(111) substrate (state γ) with rotational excitation $E_{ro}^{g\gamma}$.

$$\text{or } \psi_\gamma = a_{s\alpha}^\dagger a_{\tau\sigma} |\varphi_{\text{ele}}^\alpha\rangle |\varphi_0^{g\gamma}(\theta)\rangle. \quad (12)$$

The second-order perturbation solution implies a transition from the initial state to the final state only via an intermediate state. Thus, the second-order Fermi golden rule for the probability per unit time of a transition from state α to state γ ($r_{\alpha \rightarrow \gamma}$) is:

$$r_{\alpha \rightarrow \gamma} = \frac{2\pi}{\hbar} \left| \frac{H'_{\beta\alpha} H'_{\gamma\beta}}{(E_\alpha - E_\beta)} \right|^2 \delta(E_\alpha - E_\gamma) \quad (13)$$

where $H'_{kq} = \langle \psi_k | H' | \psi_q \rangle$.

The thermal average is to be taken as $\langle a^\dagger a \rangle = \langle \hat{n} \rangle = f(E)$, where $f(E)$ is the Fermi–Dirac distribution function.

When the electron occupies the LUMO orbital in the naphthalocyanine, the density of the intermediate states can be approximated as:

$$\rho_\beta(E) = \delta(E_\beta - E_\beta^{\text{LUMO}}). \quad (14)$$

Also when the electron is in the substrate, the density of states of the surface as a final state is approximated as [20, 21].

$$\rho_\gamma = \rho_s = \text{constant} \quad (15)$$

Consequently:

$$\begin{aligned} r_{\alpha \rightarrow \gamma} &= \frac{2\pi}{\hbar} \left| \xi_o^{\tau \rightarrow \eta} \xi_o^{\eta \rightarrow s} \sqrt{\frac{E_{ro}^{g\beta}}{\pi \hbar^2 2^{g_\gamma} g_\gamma!}} \frac{2I (E_{ro}^0 E_{ro}^{g_\gamma})^{1/4}}{2^{g_\beta} (\frac{g_\beta}{2})!} \right. \\ &\times \frac{\left(\frac{2IE_{ro}^{g\beta}}{y_H^\tau \hbar^2 + I(E_{ro}^0 + E_{ro}^{g\beta})} - 1 \right)^{g_\beta/2}}{\sqrt{y_H^\tau \hbar^2 + I(E_{ro}^0 + E_{ro}^{g\beta})}} \\ &\times \int_{-\infty}^{\infty} H_{g_\beta} \left(\sqrt{\frac{2IE_{ro}^{g\beta}}{\hbar^2}} \theta \right) H_{g_\gamma} \left(\sqrt{\frac{2IE_{ro}^{g_\gamma}}{\hbar^2}} \left(\theta - \frac{\pi}{2} \right) \right) \\ &\times e^{-\left[\frac{IE_{ro}^{g_\gamma}}{\hbar^2} \left(\theta - \frac{\pi}{2} \right)^2 + \left(y_s^H + \frac{IE_{ro}^{g\beta}}{\hbar^2} \right) \theta^2 \right]} d\theta \\ &\times \frac{\left[1 - f \left(\frac{V}{2} + E_{ro}^{g\beta} - E_\beta^{\text{LUMO}} - E_{ro}^0 \right) \right]^2}{\frac{V}{2} + E_\beta^{\text{LUMO}} + E_{ro}^{g\beta} - E_{ro}^0} \rho_s \\ &\times \int_{E_\alpha}^{E_\gamma} \left[1 - f \left(V + E_{ro}^{g_\gamma} - E_\gamma - E_{ro}^{g\beta} \right) \right] dE_\gamma \left. \right|^2 \\ &\times \delta(E_\alpha - E_\gamma). \quad (16) \end{aligned}$$

Furthermore, $r_{\alpha \rightarrow \gamma}^{\text{no}}$ is the transfer probability per unit time without rotation if the excitation in the rotational states $E_{ro}^{g\beta}$,

$E_{\text{ro}}^{g_\gamma}$ is less than the energy barrier:

$$\begin{aligned}
 r_{\alpha \rightarrow \gamma}^{\text{no}} &= \frac{2\pi}{\hbar} \left| \xi_o^{\tau \rightarrow \eta} \xi_o^{\eta \rightarrow s} \sqrt{\frac{E_{\text{ro}}^{g_\beta}}{\pi \hbar^2 2^{g_\gamma} g_\gamma!}} \right. \\
 &\times \frac{2I (E_{\text{ro}}^0 E_{\text{ro}}^{g_\gamma})^{1/4}}{2^{g_\beta} \left(\frac{g_\beta}{2}\right)!} \frac{\left(\frac{2IE_{\text{ro}}^{g_\beta}}{y_s^{\tau} \hbar^2 + I(E_{\text{ro}}^0 + E_{\text{ro}}^{g_\beta})} - 1\right)^{g_\beta/2}}{\sqrt{y_s^{\tau} \hbar^2 + I(E_{\text{ro}}^0 + E_{\text{ro}}^{g_\beta})}} \\
 &\times g_\beta! g_\gamma! \sum_{m=0}^{g_\beta/2} \sum_{k=0}^{g_\gamma/2} \\
 &\times \left(\frac{(-1)^{m+k} \left(2\sqrt{\frac{2IE_{\text{ro}}^{g_\beta}}{\hbar^2}}\right)^{g_\beta-2m} \left(2\sqrt{\frac{2IE_{\text{ro}}^{g_\gamma}}{\hbar^2}}\right)^{g_\gamma-2k}}{m!k!(g_\beta-2m)!(g_\gamma-2k)!} \right. \\
 &\times \frac{(-1)^{g_\beta-2m+g_\gamma-2k} + 1}{\left[y_s^{\text{H}} + \frac{I(E_{\text{ro}}^{g_\gamma} + E_{\text{ro}}^{g_\beta})}{\hbar^2}\right]^{\frac{g_\beta-2m+g_\gamma-2k+1}{2}}} \\
 &\times \Gamma\left(\frac{g_\beta-2m+g_\gamma-2k+1}{2}\right) \\
 &\times \frac{\left[1 - f\left(\frac{V}{2} + E_{\text{ro}}^{g_\beta} - E_{\beta}^{\text{LUMO}} - E_{\text{ro}}^0\right)\right]^2}{\frac{V}{2} + E_{\beta}^{\text{LUMO}} + E_{\text{ro}}^{g_\beta} - E_{\text{ro}}^0} \rho_s \\
 &\times \int_{E_\alpha^\gamma}^{E_\beta^\gamma} [1 - f(V + E_{\text{ro}}^{g_\gamma} - E_\gamma - E_{\text{ro}}^{g_\beta})] dE_\gamma \Big| \\
 &\times \delta(E_\alpha - E_\gamma), \tag{17}
 \end{aligned}$$

where V is the bias voltage.

Defining the rate equations for a probability $P_j(t)$ of state j , assuming $r_{\gamma \rightarrow \alpha} = 0$, (i.e. no electron transfer back to the tip), and initially $P_\alpha(0) = 1$, then:

$$\frac{dP_\alpha(t)}{dt} = -(r_{\alpha \rightarrow \gamma} + r_{\alpha \rightarrow \gamma}^{\text{no}}) P_\alpha(t), \tag{18}$$

$$\frac{dP_\gamma^{\text{ro}}(t)}{dt} = r_{\alpha \rightarrow \gamma} P_\alpha(t). \tag{19}$$

After a sufficiently long time ($t \rightarrow \infty$) the probability of rotation can be obtained by summing all the possibilities of excitation in the rotational states, where $E_{\text{ro}}^{g_\beta}$ is the maximum rotational energy less than the height of the energy barrier. $E_{\text{ro}}^{g_\beta} > E_{\text{ro}}^{g_\beta}$ in the case of switching, while $E_{\text{ro}}^{g_\beta}$ and $E_{\text{ro}}^{g_\gamma} \leq E_{\text{ro}}^{g_\beta}$ in the case of ‘no switching’:

$$P_\gamma^{\text{ro}} = \frac{\sum_{E_{\text{ro}}^{g_\gamma}=E_{\text{ro}}^0}^{\infty} \sum_{E_{\text{ro}}^{g_\beta}=E_{\text{ro}}^{g_\beta+1}}^{\infty} r_{\alpha \rightarrow \gamma}}{\sum_{E_{\text{ro}}^{g_\gamma}=E_{\text{ro}}^0}^{\infty} \sum_{E_{\text{ro}}^{g_\beta}=E_{\text{ro}}^{g_\beta+1}}^{\infty} r_{\alpha \rightarrow \gamma} + \sum_{E_{\text{ro}}^{g_\gamma}=E_{\text{ro}}^0}^{\infty} \sum_{E_{\text{ro}}^{g_\beta}=E_{\text{ro}}^0}^{\infty} r_{\alpha \rightarrow \gamma}^{\text{no}}} \tag{20}$$

2.3. DFT method

The DFT-based calculations were performed using plane waves bases with cut-off energy of 400 eV and pseudopotentials with generalized gradient approximation for the exchange

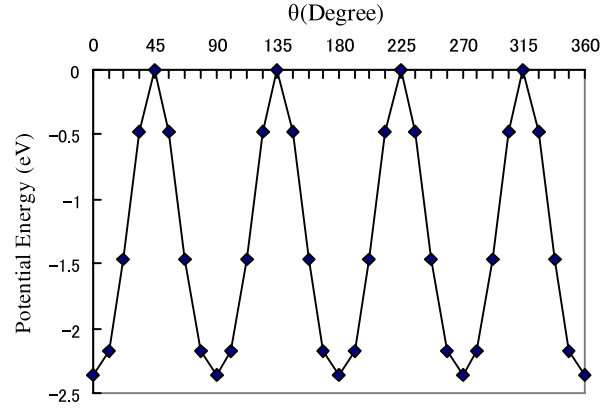


Figure 5. Potential energy change obtained from DFT calculation.

correlation energy. The super-cell is composed of the naphthalocyanine molecule on top of a bilayer of insulator (NaCl or RbI) with a vacuum distance of 15 Å. The number of atoms in the super-cell is 186 in the case of NaCl and 130 in the case of RbI bilayers. The Brillouin zone is sampled by $4 \times 4 \times 4$ k -points. The total energy minimization is set until the residual forces become less than $0.005 \text{ eV \AA}^{-3}$ [22, 23]. All of these calculations were done using the VASP (Vienna *Ab initio* Simulation Package).

3. Numerical results and discussion

3.1. DFT results

From the first-principles calculations, the potential energy change of the naphthalocyanine molecule as a function of θ is found to be a periodic sinusoidal potential barrier of height 2.362 eV as shown in figure 5. Hence, for the rotation to occur, the rotational excitation energy should be greater than E_{ro}^{16} (2.495 eV calculated by fitting with rotation spectra in figure 5). Whereas $2R_o = 2.058 \text{ \AA}$ obtained by relaxation calculation indicates a very weak binding between the two hydrogen atoms in the cavity to act normally like a molecule when it is in vibration.

If the excitation energy is lower than the energy barrier, the rotation will be hindered. The molecule will switch if the excitation energy is greater than the energy barrier, forming a hydrogen molecule momentarily, which rotates at 90° , then re-attaches to the N atoms of the naphthalocyanine molecule again.

In addition, the DFT calculated orbital energies with respect to the Fermi energy of the naphthalocyanine molecule shown in table 1 show very good agreement with experimental measurements. For a free molecule, the hydrogen atoms are placed inside the cavity ring in the plane of the molecule. Here, the difference between LUMO and LUMO + 1 is very small, almost negligible. In the case when the molecule is placed on an RbI bilayer, the hydrogen atoms bend out of the ring because of the surface charge density, which gives an energy difference of 0.07 eV between those orbitals. For most alkali and alkali-earth elements the semi-core s and p states should be treated as valence states. However, for lighter elements (Na), it

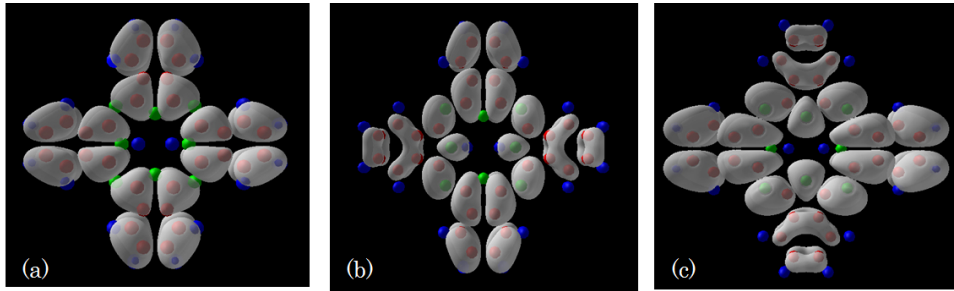


Figure 6. (a) HOMO, (b) LUMO and (c) LUMO + 1 charge density distributions from DFT calculations for free naphthalocyanine molecules. (Blue atoms are H, green atoms are N, and red atoms are C.)

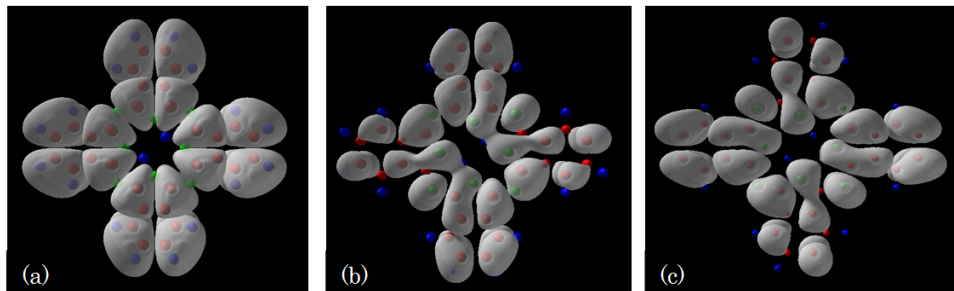


Figure 7. (a) HOMO, (b) LUMO, and (c) LUMO + 1 orbital maps from DFT calculations with the hydrogen molecule rotated 45° for the free naphthalocyanine molecule.

Table 1. Orbital energy for free naphthalocyanine.

System	Energy (eV)			
	Orbitals			
	HOMO	μ_F	LUMO	LUMO + 1
Symmetrical plane free molecule	-0.6629	0	0.6707	0.7034
Naphthalocyanine + 1e	-1.3547	0	0.0163	0.0327
On NaCl bilayer positioned on Na atom	-0.5397	0	0.5530	0.5784
On NaCl bilayer positioned on Cl atom	-0.6226	0	0.6262	0.6872
Between Na and Cl atoms	-0.5663	0	0.5743	0.6161
On RbI bilayer positioned on Rb atom	-0.5719	0	0.5653	0.6353
On RbI positioned on I atom	-0.6522	0	0.6342	0.6790
Between Rb and I atoms	-0.5781	0	0.5898	0.6118
Experimental, on NaCl [3, 10]	-1.5	0	~0.65	~0.65
Experimental, on RbI [3, 10]	Not available	0	~0.4	~0.63

is usually sufficient to treat the 2p and 3p states, respectively, as valence states, whereas for Rb we use the 4s, 4p and 5s, 5p states. Hence, that difference of energy (between LUMO and LUMO + 1) is very small when the molecule is on the NaCl bilayer (i.e. closely degenerate). This explains why it is impossible to resolve the LUMO and LUMO + 1 by STM in the dI/dV spectra when the molecule is adsorbed on the

NaCl thin film [4]. Adding the Cu metal substrate effect, since it is stronger in the case of lighter atoms of NaCl, will cause broadening to the LUMO and LUMO + 1 (i.e. FWHM of the resonances on NaCl is greater as compared to RbI) [24].

When adding one electron to the naphthalocyanine molecule, it will occupy either the LUMO with a large probability or the LUMO + 1 according to our DFT calculations, directly affecting the two hydrogen atoms in the cavity and lowering the energies of the orbitals.

The calculated charge density distributions (figure 6) of these states are consistent with experimental observations and DFT calculations of previous studies [4, 6]. The possible symmetrical perpendicular orientations of the LUMO and LUMO + 1 are clear in the partial charge density distributions, as shown in figure 6.

Figure 7 shows the orbital maps of the HOMO, LUMO, and LUMO + 1, when the hydrogen rotates about 45° as proposed in our model. The change of the molecule's LUMO and LUMO + 1 symmetry accompanying the change of the hydrogen position is clearly observed, while the HOMO charge density remains unchanged. This observation proves again that the change in the LUMO or LUMO + 1 orientation indicates the hydrogen molecule switching.

3.2. Switching probability calculation

The surface density of states of Cu(111) is taken to be constant and limited in a 5 eV work function with respect to the Fermi energy [20, 21]. In the simplest case when the tip is positioned directly above one of the hydrogen atoms of the adsorbate hydrogen molecule, we set the θ dependence constants of the

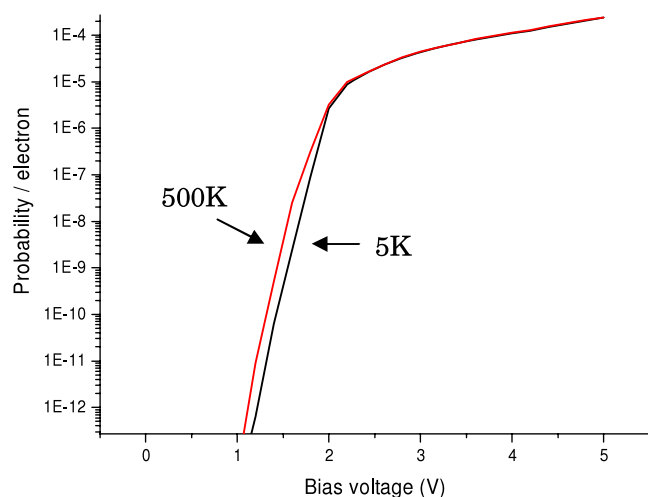


Figure 8. Probability of switching versus the bias voltage calculated theoretically from the model using DFT parameters.

hopping integrals to be $y_H^\tau \approx y_s^H \approx 0.1$. Then the calculated probability of switching versus the bias voltage at temperatures of 5 and 500 K is plotted in figure 8.

In figure 8, the one electron probability for the process of switching is shown to be independent of temperature only for very small change and is fairly consistent with the experimentally accessible range until 2 eV.

The probability of switching for an electron passing through the LUMO of the naphthalocyanine starts growing exponentially (from 10^{-9} at 1.4 V to almost 10^{-6} at 2 V in the experimental range [4]) when the energy is enough to overcome the LUMO barrier that makes it possible for the electron transport to occur then deviated and slowly increasing at higher voltages when the electron has enough energy to excite the hydrogen molecule, although this claim cannot be substantiated experimentally.

4. Conclusion

From our model, the mechanism of the switching was proven to be the induction of some molecular excitation modes by tunneling electrons jumping over the energy barrier. The probabilities of the rotation (switching) of a hydrogen molecule in the cavity of a naphthalocyanine molecule were calculated and found to be consistent with experimental observations. Here, one electron transport from the STM-tip to the LUMO of the molecule and exciting rotational modes then to the metal substrate was assumed. Also, we showed and discussed DFT calculated molecular energy levels and charge densities

of these levels for further understanding of the experimental results. Regarding the temperature dependence, the system shows high stability with temperature change according to our model. To have a finer model, the vibration effect can be included. Adding width to the LUMO of the molecule would also give more accurate probabilities as compared with experimental results. Instead of our approximation to the density of states of the molecule being the Dirac delta function, for simplicity, the Lorentzian function form can be used which, realistically, describes the finite width influenced by the charge density of the surface [25]. Finally, it can be suggested that we replace the hydrogen molecule with one of the hydrogen isotopes ^2H or ^3H , taking the problem of stability into consideration.

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