Vibrationally induced flip motion of a hydroxyl dimer on Cu(110)

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Recent low-temperature scanning-tunneling microscopy experiments [T. Kumagai et al., Phys. Rev. B 79, 035423 (2009)] observed the vibrationally induced flip motion of a hydroxyl dimer (OD)$_2$ on Cu(110). We propose a model to describe two-level fluctuations and current-voltage characteristics of nanoscale systems which undergo vibrationally induced switching. The parameters of the model are based on comprehensive density-functional calculations of the system’s vibrational properties. For the dimer (OD)$_2$ the calculated population of the high and low conductance states, the $I - V$, $dI/dV$, and $d^2I/dV^2$ curves are in good agreement with the experimental results and underlines the different roles played by the free and shared OD stretch modes of the dimer.

Electron transport through single-molecule junctions has been receiving enthusiastic interest for a development of novel molecular devices. Nonlinear $I - V$ characteristics associated with the vibrationally mediated configurational change with different conductances have been observed in a series of systems such as pyrrolidine on a Cu(001)$_2$, H$_2$ on Cu$_2$, CO bridging a Pt contact$_{12}$, and H$_2$ in Au contacts$_{2-4}$. In these systems $dI/dV$ spectra show anomalous spikes—in contrast to steps usually observed in inelastic electron tunneling spectroscopy (IETS)$_5$—at the bias voltage related to the vibrational mode energies.

Recently Kumagai et al.$^{2,5}$ studied the dynamics of a single hydroxyl (OH, OD) molecule and the dimer (OD)$_2$ on Cu(110) using a scanning tunneling microscope (STM). The STM images observed for the monomer suggested the possible quantum tunneling of a hydroxyl atom bridging between two equivalent adsorption configurations on Cu(110), as supported by the density functional theory (DFT) calculations of the transition path and rate of the flipping of OH on Cu(110)$_2$. This spontaneous flip motion of hydrogen atoms in the monomer is quenched for the dimer at low temperatures, but can be induced by excitation of the OH/OD stretch mode by tunneling electrons. Time-averaged measurements of the current show a non-linear current ($I$) increase at the bias voltage ($V$) inducing the transition from the high and low conductance states. The appearance of the peak in $dI/dV$ and the peak and dip in $d^2I/dV^2$ from transitions between states with distinct conductances have also been reported previously$^{2,5,6}$.

In this paper we have performed calculations on a 6 atom thick Cu $4 \times 3$ slab using periodic boundary conditions. The tip was mod-
eled as one protruding Cu atom on the reverse side of the slab. All calculations were performed with the PBE GGA functional, DZP (SZP) basis set for dimer (bulk Cu), $3 \times 4$ $k$-point sampling, and a 300 Ry mesh cutoff. The elastic transport properties were calculated using the DFT+NEGF method where 6 additional layers of Cu were used to connect the central region to semi-infinite metallic leads. Fig. 1 shows the schematic side view of the dimer in the $H$ and $L$ conductance states. The calculated low-bias conductance ratio $G_H/G_L = 2.0$ closely matches the experimental ratio. However, the calculated absolute conductances are much larger than in the experiment since numerical considerations demand the calculations to be performed at a small tip-dimer distance. The relaxed hydrogen-bonded OD-O distance is 2.90 Å while the OD bond length and tilt angle to the surface normal are 1.00 (0.98) Å and 81° (51°), respectively. The two hydroxyl groups, bonded near adjacent bridge sites along (001) are oriented according to the optimal configuration for hydrogen bonding. The D atom pointing towards the adjacent OD molecule form the OD-O bond (with characteristic shared OD stretch mode) in contrast to the D atom pointing away from the adjacent OD molecule (with free OD stretch mode). These nonequivalent configurations of each OD molecule lift the degeneracies of the vibrational energies for the two OD molecules.

The vibrational modes and frequencies of the molecular adsorbates and the corresponding electron-phonon couplings are calculated from a finite difference scheme\textsuperscript{10,11}. These calculations were repeated with the tip scanned over the surface as indicated by the black dots in Fig. 2. Table I lists the calculated vibrational modes for the $H$ and $L$ configurations. Here $\nu$(OD) labels the free OD stretch mode, $\nu$(OD-O) the shared OD stretch mode involving the D atom between two oxygen atoms, and rot$_{xy}$ rotation modes in the surface plane (surface normal). Values for the low-energy modes mainly involving motion of the oxygen atoms have been omitted from the table.

In addition to the vibrational energies ($\hbar \omega$), the electron-hole pair damping rate $\gamma_{eh}$ and vibration generation rate $\gamma_{em}$ were calculated for each tip position within the lowest order expansion (LOE) scheme\textsuperscript{10,11}. In the low-temperature limit the emission rate is give by

$$\gamma_{em}(V) = \lambda_{em}(|eV| - \hbar \omega) \theta(|eV| - \hbar \omega)$$

(1)

where $V$ is the applied bias, $\theta$ the step function, and

$$\lambda_{em} = \frac{1}{2} \text{Tr}[\text{MA}_1 \text{MA}_2] = \frac{1}{2} \sum_{\alpha \beta} \left| \langle \psi_\beta | M | \psi_\alpha \rangle \right|^2$$

the emission rate constant written in terms of electron-phonon coupling matrix $M$ and partial spectral density $A_{1/2}$ at the Fermi energy, cf. Ref. \textsuperscript{10}. The spectral density can further be rewritten in terms of a sum over scattering states $|\psi_\alpha^{1/2}\rangle$ at the Fermi-energy incident from substrate / tip (1/2) showing the equivalence of the LOE scheme with the Fermi-golden rule, assuming a constant density of states around the Fermi-energy.\textsuperscript{10} Furthermore, for weak coupling between tip-adsorbate, the emission rate constants scale with the tip-adsorbate coupling ($\tau$) squared ($\lambda \propto \tau^2$). Since the current scales in the same way, the emission rate at a given voltage is proportional to the current. The electron-hole pair damping rate $\gamma_{eh}$ is insensitive to the position of the STM tip since the damping is dominated by the metal surface. The emission rate map for the two $\nu$(OD) and $\nu$(OD-O)
modes are shown in Fig. 2, where the emission rates were calculated by scanning the tip over the surface at a constant height of 5.6 Å above the oxygen atoms, i.e., the DFT calculations of e-ph coupling, transmission, emission rates, and damping were repeated for geometries with the tip displaced relative to the OD dimer. We note that the emission rate for the free OD stretch is more localized around the high conductance site than the shared OD-O stretch mode which is also evident from Table I. The green points in Fig. 2 correspond to the free OD stretch mode.

To describe vibrationally induced switching in nanoscale systems we propose a simple model which expresses the current in terms of the occupation \( n_{H,L} \) and conductance \( \sigma_{H,L} \) of the \( H \) and \( L \) conductance states,

\[
I = \sigma_{H} n_{H}(V) + \sigma_{L} n_{L}(V), \tag{2}
\]

where \( n_{H,L} \) is determined as a stationary solution of the rate equations,

\[
\frac{dn_{H}}{dt} = \Gamma_{L \rightarrow H}(V)n_{L} - \Gamma_{H \rightarrow L}(V)n_{H} \tag{3}
\]

\[
\frac{dn_{L}}{dt} = \Gamma_{H \rightarrow L}(V)n_{H} - \Gamma_{L \rightarrow H}(V)n_{L} \tag{4}
\]

with the condition \( n_{H} + n_{L} = 1 \). This gives

\[
n_{L}(V) = \frac{\Gamma_{H \rightarrow L}}{\Gamma_{H \rightarrow L} + \Gamma_{L \rightarrow H}}, \quad n_{H}(V) = \frac{\Gamma_{L \rightarrow H}}{\Gamma_{H \rightarrow L} + \Gamma_{L \rightarrow H}}, \tag{5}
\]

where \( \Gamma_{H \rightarrow L} \) is the transition rate from \( H \) to \( L \). The experiments show that the reaction rate at a constant voltage is proportional to the current, i.e., the reaction rate is proportional to the emission rate of the vibrations. The simplest way to model the transition rates is therefore to assume a linear dependence on the vibrational occupation \( \propto \gamma_{em}/\gamma_{ch} \), or equivalently the vibrational generation rates \( \gamma_{em,\beta} \), i.e.,

\[
\Gamma_{H \rightarrow L(L \rightarrow H)}(V) = \Gamma_{0}^{H(L)} + \sum_{i} C_{i} \Gamma_{em,i}^{H(L)}(V), \tag{6}
\]

where a constant rate \( \Gamma_{0}^{H(L)} \) is introduced to model the collective effect of many low-energy vibration modes and where \( \Gamma_{em,i}^{H(L)} \) represents the broadened vibrational generation rate \( \beta \) of a distinct mode \( i \) given by

\[
\Gamma_{em,i}^{H(L)} = \int_{0}^{\infty} W(\omega - \Omega_{i}^{H(L)}, \sigma_{ph}) \gamma_{em,i}(eV, \omega) \, d\omega. \tag{7}
\]

In the above equation we use a Gaussian distribution function \( W(\omega, \sigma_{ph}) \propto e^{-\omega^{2}/(2\sigma_{ph}^{2})} \) characterized by a standard deviation \( \sigma_{ph} \). The prefactors \( C_{i} \) describe the likelihood of the generated vibrational excitation to induce the flip motion, i.e., the probability of transferring the motion from the vibration to the reaction coordinate.

We obtain a good fit to the experimental OD dimer data from Ref. 8 considering only three different vibrational modes, see Fig. 3. The fitting parameters used \( (C_{i}, h\Omega_{i}^{H(L)}, \sigma_{ph}^{i}) \) are \((0.2 \times 10^{-4}, 327.2/326.6 \text{ meV}, 20 \text{ meV})\) for \( \nu(\text{OD}) \), \((1.0 \times 10^{-4}, 301.2/301.8 \text{ meV}, 8 \text{ meV})\) for \( \nu(\text{OD-O}) \), \((1.2 \times 10^{-7}, 76.8/76.5 \text{ meV}, 19 \text{ meV})\) for \( \text{rot}_{xy}(\text{OD-O}) \), and \( \Gamma_{0}^{H/L} = 0.7 \times 10^{2}/1 \times 10^{4} \text{ s}^{-1} \). We first note that we need to use large values for the broadening \( \sigma_{ph}^{i} \approx 10 - 20 \text{ meV} \) to fit the experimental data. We believe this to be caused by the statistical nature of the experimental data collection and do not reflect thermal or phonon DOS broadening. The fitting constants \( C_{i} \) and \( \Gamma_{0}^{H/L} \) are only determined up to a multiplicative factor.

| Mode          | \( h\nu \text{ [meV]} \) | \( \lambda_{em} \text{ [cm}^{-1}] \) | \( \gamma_{ch} \text{ [s}^{-1}] \) |
|---------------|--------------------------|--------------------------|--------------------------|
| \( \nu(\text{OD}) \ L \) | 327.2 | 0.17 | 47.3 |
| \( \nu(\text{OD}) \ H \) | 326.6 | 4.42 | 52.3 |
| \( \nu(\text{OD-O}) \ L \) | 301.2 | 0.49 | 248.0 |
| \( \nu(\text{OD-O}) \ H \) | 301.8 | 0.35 | 249.6 |
| \( \text{rot}_{xy}(\text{OD-O}) \ L \) | 76.8 | 1.19 | 250.7 |
| \( \text{rot}_{xy}(\text{OD-O}) \ H \) | 76.5 | 0.67 | 268.0 |
| \( \text{rot}_{xy}(\text{OD}) \ L \) | 77.0 | 0.24 | 103.7 |
| \( \text{rot}_{xy}(\text{OD}) \ H \) | 76.9 | 0.10 | 76.0 |

![Fig. 3](image-url)
factor since the occupations are determined by the ratios in Eq. 3. We choose the prefactor of the shared ν(OD-O) mode as the reference and set it to $10^{-3}$ based on an order of magnitude estimate from the experimental flip frequency. The values for $\Gamma_0^H/L$ only determine the low-bias occupation where $\Gamma_0^H \gg \Gamma_0^L$ because the system is experimentally only observed in the $L$ configuration. The reason for this preference of $L$ at low bias might be due to the larger current and thus larger vibrational generation rate of low-energy phonons in the $H$ configuration. However, in the intermediate bias range $200 \sim 300$ meV we see a slight change in the occupation as shown in Fig. 3(b). Although we cannot unambiguously assign a vibrational mode to this change in occupation from the available experimental data, we have chosen to model this by the rot$_z$(OD-O) mode. In contrast, there is much less latitude in the fitting parameters for the $\nu$(OD) and $\nu$(OD-O) modes. We note that the change in occupation at 300 meV do not fit with the free $\nu$(OD) vibrational energy ($\approx 330$ meV) and clearly indicate that the shared $\nu$(OD-O) mode is the main culprit in inducing the flip motion. This assignment is supported by the fact that the occupation quickly approaches 50/50 which implies because the system is

Using the calculated conductances ($\sigma_H = 145.62$ nA/V, $\sigma_L = 78.34$ nA/V) scaled by the constant factor $2.56 \times 10^{-2}$ to account for the small tip-sample distance used in the calculation and the bias dependent population [$n_H(V)$, $n_L(V)$] shown in Fig. 3(b), the $I-V$ characteristics were calculated from Eq. 3. As shown in Fig. 4, the calculated time averaged $I-V$ curve [Fig. 4(a)] and $d^2I/dV^2$ [Fig. 4(b)] show remarkable agreement with the experimental results. We note that the lineshape of the $d^2I/dV^2$ signal is clearly different from inelastic electron tunneling spectra which normally only shows a peak or dip. In addition, the size of the signal from the vibration is much larger than what one normally associates with IETS spectra.

In summary, we have shown that the flip motion between high and low conductance configuration of the OD dimer on Cu(110) is mainly induced by the excitation of the hydrogen-bonded shared OD stretch mode. Because of the unique asymmetric inclined orientation of each hydroxyl, the shared and free OD stretch modes have different vibrational frequencies and consequently affect the flip motion at different applied bias voltages. The relative occupations ($n_H$ and $n_L$) of the high and low conductance state as a function of the bias voltage were nicely reproduced by solving a simple rate equation for $n_H$ and $n_L$ in terms of the transition rate between the $H$ and $L$ configurations. The calculated high and low conductance ($\sigma_H$, $\sigma_L$) and their occupations [$n_H(V)$, $n_L(V)$] enabled us to obtain the nonlinear $I-V$ curve, $dI/dV$ and $d^2I/dV^2$ in excellent agreement with the experimental results. The presented theoretical analysis based on extensive DFT calculations (stable configurations, vibrational modes including their generation rates by tunneling electrons and damping rates) is not limited to the specific case of hydroxyl dimers on Cu(110), but can also be applied to other systems which exhibit nonlinear $I-V$ characteristics arising from the vibrationally mediated switching between high and low conductance states.

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