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Electron Stimulation of Internal Torsion of a Surface-Mounted Molecular Rotor

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Abstract

A molecular rotor which includes a central rotator group was investigated by scanning tunneling microscopy at 4.9 K as it was grafted on a Cu(111) surface via its two terminal stand groups. Sub-molecular resolution topographs revealed alternating molecular conformations which we attribute to distinct angular orientations of the rotator, and which are locally stable states according to density functional theory calculations. Time-resolved tunneling current spectra manifested that the rotator undergoes torsional motions around the molecular long axis as stimulated by tunneling electrons in one-electron processes and obtained an excitation energy threshold of 355 meV. Calculations identified an intrinsic axial vibration mode of the rotator group at 370 meV, which we propose to be the channel for effectively converting the tunneling electron energy into the mechanical energy of the intra-molecular torsion.
Molecular motions of artificial molecules are of great interest in the study of molecular machines and molecular electronics.\textsuperscript{1-5} In particular, surface-mounted molecules that move relative to the surface are regarded to have the best potential for applications. It has been demonstrated that scanning tunneling microscopy (STM) is a powerful tool to address molecular motions on surfaces owing to its ability to directly reveal such motions by imaging different motional states with sub-molecular resolution. In addition, STM can manipulate or induce single molecular motions by tip-molecule interaction or electron tunneling, which provides a unique approach to investigate the mechanism of molecular motions.\textsuperscript{6} To date, molecular motions in which molecules move as an entity, for example, molecular rotation, vibration or lateral motion has been documented in the literature.\textsuperscript{7-11} However, large-angle intra-molecular torsional motions (rotation or oscillation of part of a molecule around a fixed molecular axle) have rarely been addressed experimentally even though such motions are fundamental to future molecular machinery.\textsuperscript{1, 12-13}

Here we report on a study of intra-molecular torsional motions of an “altitudinal” rotor, defined as having its torsion axis parallel to the surface.\textsuperscript{16} The chemical structure of the rotor molecule \( (4',4''''-(\text{bicyclo}[2, 2, 2]\text{octane}-1, 4\text{-diyldi}-4,1\text{-phenylene})\text{-bis}-2,2':6',2''\text{-terpyridine}) \) (hereafter BTP-BCO) is shown in Figure 1(a). It consists of two terminal terpyridine (\textit{tpy}) groups acting as stands fixed to a substrate, a central bicyclo[2, 2, 2]octane (BCO) group acting as the rotator and two biphenylene groups acting as axle shafts that link the rotator to the stands. As illustrated schematically in
Figure 1(b), the molecule is mounted on a Cu(111) surface, and the central rotator undergoes torsional motions around the shaft axis under the stimulation of tunneling electrons. The motions were monitored by STM topographs and time-resolved tunneling current spectra ($I$-$t$ spectra), which revealed several molecular conformations that can be attributed to distinctive axial angular states of the BCO group. These conformations were confirmed to be stable or metastable states by density functional theory (DFT) calculations. On account of the $I$-$t$ spectra, the motions were found to be excited by one-electron processes and an excitation energy threshold of 355 meV was derived. This value is close to the calculated energy of an intrinsic torsional vibration mode (370 meV) of the BCO group. We propose that this vibration mode may effectively convert the tunneling electron energy into the mechanical energy of the intra-molecular torsion.

**Methods.** Our experiments were carried out in an ultra-high vacuum scanning tunneling microscope (Omicron) operated at 4.9 K. The molecules were deposited onto a clean Cu(111) substrate held at 180 K, and the sample was transferred into the low-temperature STM immediately after deposition. DFT calculations were performed within the projector-augmented wave (PAW) plane wave approach as implemented in the VASP code.\textsuperscript{15-17} The exchange-correlation functional was treated with the generalized gradient approximation in the Perdew-Burke-Ernzerhof (PBE) form.\textsuperscript{18} The simulated STM images were obtained in constant current mode within the Tersoff-Hamann approximation (i.e., computing an iso-density surface $z(x,y)$ above
the adsorbed molecule). For the comparison of the energies of the metastable states, the Van der Waals interactions were included through a Van der Waals density functional as implemented in the GPAW code. The simulation model contained the molecule on one copper layer. Only one copper layer was included due to the rather weak molecule-to-substrate interaction and due to the computational cost. Our test calculations confirmed that one layer is sufficient for these studies.

Results and Discussion. Figure 1(c) represents a STM topograph of a single BTP-BCO molecule acquired at a low sample bias voltage of 0.1 V, revealing the two tpy end groups and the central BCO group. A cross-sectional profile along the molecular long axis (Figure 1(d)) shows that the BCO group clearly protrudes above the tpy groups, by an apparent height difference of about 1 Å. This apparent value is much smaller than the actual height difference (in theory the height difference between nuclei is about 2.5 Å) due to the low density of states of the BCO at this imaging condition. At a higher sample bias, for example 1.2 V as for Figure 1(e), noisy spikes appeared in STM topographs, indicating that the tunneling current changes sharply. Figure 1(f), a noise image (obtained by low-pass filtering the noise of Figure 1(e)), indicates that the noise is mostly distributed at the BCO group, in particular near its edges, but not at the other parts of the molecule or at the clean Cu(111) surface. So we can exclude that the noise was caused by an unstable tip.

STM data have revealed that the single TPE-BCO topographs acquired at 0.1 V bias take three distinct shapes, as shown in Figure 2(a), (b) and (c), which we ascribe to
three distinct molecular conformations. Figure 2(a) shows a symmetric conformation in which the BCO group is centered (denoted as C-state) on the molecular long axis as indicated by the dashed line in Figure 2a. Figure 2(b) and 2(c) show two asymmetric conformations (mirroring each other) in which the BCO group is shifted either “southward” (denoted as S-state) or “northward” (denoted as N-state) relative to the molecular long axis (dashed lines in Figure 2(b) and (c)) in the topograph. The asymmetric molecular conformations are unambiguously displayed in the differential topographs as shown as the inset in Figure 2(b) and (c). In addition to these distinctive static molecular conformations, the dynamic processes for switching between the molecular conformations were probed by I-t spectra – positioning the tip over a specific site of the BCO group and applying a voltage pulse for a period of time with open feedback loop, while recording the tunneling current as a function of time. We found that the I-t spectra typically exhibit three levels – high (H), medium (M) and low (L) – indicating three conductance states, as shown in Figure 2(d), (e) and (f).

To correlate the three molecular conformational states with the I-t spectra, we have carried out the following measurements: First an initial molecular state was recorded by acquiring an STM topograph at a low sample bias voltage of 0.1 V, which did not induce the motion (cf. Figure 2(a)). Then an I-t spectrum (for example, Figure 2(d)) was recorded at a defined position (black dot in Figure 2(a)). Hereafter the same molecule was rescanned at 0.1 V to record its final state (cf. Figure 2(b)). This process was repeated many times on a single molecule under various conditions, e.g., bias voltage,
set tunneling current and tip location. We found that, whenever the final conductance level of an I-t spectrum was different from its initial level, the molecular topographs showed different initial and final conformational states. For example, Figure 2(d) shows an initial conductance level M and a final level H, whereas the initial state is C (Figure 2(a)) and the final state is S (Figure 2(b)). By contrast, whenever the final conductance level of an I-t spectrum was the same as its initial level, the initial and final conformation states were always identical.

Furthermore, we identified a correlation between the initial conformational state and the subsequently acquired I-t spectra: For a C-state molecule (as in Figure 2(a)), the I-t spectra acquired at either the north or south side of the BCO group always start with the M level (as in Figure 2(d)). For an S-state molecule (as in Figure 2(b)), the I-t spectra acquired at the north side of its BCO group (red dot) always start with the L level (as Figure 2(e)), while the I-t spectra acquired at the south side of its BCO group always start with the H level (not illustrated). For a N-state molecule (as in Figure 2(c)), the I-t spectra acquired at the north side of its BCO group always start with the H level (not illustrated), while the I-t spectra acquired at the south side of its BCO group (blue dot) always start with the L level (as Figure 2(f)). A similar correlation was also observed between the final conductance level and the final conformational state.

To understand the observed molecular conformations and the conductance behavior, we performed ab initio structure relaxations for the molecule adsorbed on a Cu(111) surface for various torsion angles of the BCO group, as illustrated in Figure 3(a) and
(b). First, the adsorbed molecule was fully relaxed in the “up” geometry shown in Figure 3(a) with the Cu(111) surface kept fixed. Next, the two \textit{tpy} groups as well as the Cu surface were kept rigid while the BCO group was rotated and then relaxed freely to find other potential local minima of the total energy (the \textit{tpy} height above the metal was also re-optimized). Finally, we applied a third, complete re-optimization of the whole molecule, including the central BCO and the \textit{tpy} groups, for each local minimum found for different BCO group rotations. Among all configurations, we found that three structures, named “up”, “side” and “down”, produce local minima of the total energy, as shown in Figure 3(a). The up structure is the most stable, while the side and down structures are metastable, 0.233 eV and 0.364 eV higher in energy, respectively (the side structure is degenerate between equivalent right-side and left-side structures). These energy differences are mainly caused by changes in three sets of interactions: between the lowest hydrogen atoms and the copper surface (physisorption); between the central BCO and the adjacent phenyl rings (intra-molecular torsion and bending); and between the phenyl rings and the end \textit{tpy} groups (intra-molecular bending). Table 1 summarizes the energy differences between the three configurations contributed by molecular conformation as well as by molecule-surface adsorption.

The calculated height differences between the topmost carbon atom and the Cu(111) surface (kept flat) are given in Figure 3(b), in which on-axis views of the BCO group are shown. In the up structure, a pair of carbon atoms of the BCO group points upward and is 5.49 Å above the Cu surface. In the side structure, the upper left pair of carbon
atoms of the BCO group is 5.54 Å above the Cu surface while the right pair of carbon atoms is 4.16 Å above the Cu surface. In the down structure, the two pairs of carbon atoms on either side of the BCO group are 5.30 Å above the Cu surface. Simulated STM topographs of the three configurations are shown in Figure 3(c). In comparison with Figure 2, the main features of the experimental STM topographs are nicely reproduced by the simulations as either the symmetrical up or down configurations is assigned to the C state, and the asymmetrical right-side or left-side configuration to the N or S states, respectively. On account of this assignment, the experimentally observed correlation between the I-t spectra and the conformational states can be rationalized as follows: When the tip was positioned over the left (right) side of the BCO group in the three structures of Figure 3b, the tip height over the nearest carbon atom was the smallest (largest) in the side structure and intermediate in the up or down structures. For a molecule in the up or down conformation (left or right panel), the I-t spectra started with an M level current when the tip was over either the left or right side of the BCO group; for a molecule in the side conformation (central panel), the I-t spectra started with an H (L) level current when the tip was over the left (right) side of the BCO group.

Based on the foregoing discussion, we attribute the switching from one conformation to another to an intra-molecular torsional rotation of the BCO group relative to the rest of the molecule which remains largely immobile. In this molecule, the central BCO group is linked to the phenyl groups through C-C σ bonds. It is known that the C-C σ bond may easily undergo axial rotations. This rotation abruptly changed the separation
between the tip apex atom and the nearest atoms of the BCO group, resulting in a jump of conductance in the \( I-t \) spectra.

Since the intra-molecular torsional motions of the BCO group were monitored by the \( I-t \) spectra, we can extract further information from the tunneling current trace in the \( I-t \) spectra. The statistics of the residence time in each conformation exhibit an exponential decay, from which a time constant may be derived. As this time constant directly reflects the molecule’s residence time in a specific conformation, the inverse of the time constant defines the jumping rate from a certain conformation at the chosen sample bias and tunneling current. As an example, Figure 4(a) shows a distribution of events with residence time in the M level longer than the time given on the horizontal axis. The exponential decay fits a jumping rate from the M level of 1.55±0.02 Hz. In Figure 4(b), we plot the jumping rate from the M level to the H or L level as a function of tunneling current for four sample biases. The power-law fits of the data, \( R \propto I^N \), obtain \( N=1.22\pm0.03, 1.01\pm0.23, 1.06\pm0.03 \) and \( 1.04\pm0.06 \) for sample bias of 0.25, 0.30, 0.35 and 0.40 V, respectively. These values are close to unit, so we conclude that in our experimental conditions (sample bias 0.25 to 0.40V and tunneling current 0.5 to 10 nA), the intra-molecular torsional motions were stimulated by tunneling electrons and the stimulation is a one-electron process.

To quantify the stimulating energy threshold, we acquired the \( I-t \) spectra in a wide range of bias voltage. In Figure 4(c), we plot the jumping rate from the M level as a function of sample bias\(^7b,9a\). It is clear that a drastic increase of jumping rate appears at
355 ± 5 mV. This indicates that the threshold energy to stimulate the torsional motion is about 355 meV. At negative bias, the jumping rate from the M level shows a threshold energy near 355 meV as well. So, the electrons emitted from or injected into the tip stimulate the torsional motions equally. Our calculations reveal that a vibration mode of the BCO group undergoes torsional motions around the molecular axis with an energy barrier of about 370 meV (from up to side conformation). Since this energy is very close to the experimental threshold energy of the stimulation, we conjecture that this vibration mode may effectively assist the excitation of the intra-molecular mechanical motion by the tunneling electrons. 7b

The noise image of Figure 1(f) highlights that the intra-molecular torsional motions are very sensitive to the tip position. This sensitivity allows us to determine the most effective stimulation points. To that end, we recorded I-t spectra while positioning the tip at various points along a line perpendicular to the molecular long axis. We found that, at a fixed sample bias and tunneling current set point, the jumping rates between states M and H (M-H) or between states M and L (M-L) exhibit a strong dependence on the tip position. Figure 4(d) shows the M-H and M-L jumping events per unit time as a function of tip position. The M-H jumping rate shows two maxima at the two edges of the BCO group and a local minimum in the center, while the M-L jumping rate shows a maximum in the center. At the two maxima, the M-H jumping rate is 10 times higher than the M-L jumping rate. Note that the molecular conformation that gives the H level current at one side gives the L level current at the other side, i.e., M-H jumping at one
side corresponds to the M-L jumping at the opposite side. Thus when the tip was positioned at one side of the BCO group, the observed M-L jumping was actually the M-H jumping for the other side and vice versa. Therefore we can express the same molecular conformation change by the solid bell-shaped curves in Figure 4(d). The curves imply that the molecular conformation changes have two stimulating centers located at either edge of the BCO group. When the tip was positioned at one stimulating center, it predominantly stimulates M-H jumping, but also M-L jumping with a much lower efficiency.

Finally, we point out that the calculated images reproduce symmetric-shaped STM topographs for both the up and down structures, but we cannot unambiguously determine which one is the experimentally observed C state. Nonetheless, since the down structure is 0.364 eV higher in energy, we assume that the up structure is the observed C state. It is worth noting that in our measurements we found a fourth conductance level in the \( I-t \) spectra when the bias voltage is higher than 0.35 V. As shown in Figure 5(a), another medium level, denoted as state \( M' \), was observed. We propose that this \( M' \) level probably corresponds to the down structure. Presumably because of its higher energy, this structure appears much less frequently than the two other structures. In Figure 5(b), we plot each individual state of Figure 5(a) according to its current level. The arrows highlight the torsional motions between adjacent states, in which each red (blue) arrow indicates a \( 30^\circ \) counterclockwise (clockwise) torsion.
Clearly the BCO group undergoes torsional motions in both rotational directions randomly.

In conclusion, we have studied a single-molecule altitudinal rotor fixed on a surface. Stimulated by tunneling electrons, the central BCO group is found to undergo intra-molecular torsional motions around the molecular long axis parallel to the surface. The motion was monitored by STM topographs, which revealed several molecular conformations corresponding to distinctive torsional rotation states that were reproduced by DFT calculations. On account of the I-t spectra, the motions were found to be excited by one-electron processes and an excitation energy threshold of about 355 meV was derived, which is likely assisted by an intrinsic vibration mode at 370 meV.

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References:


Table 1. Energy differences (in eV) between the three adsorption configurations contributed by molecule-substrate adsorption and molecular conformation. (energies in the “up” geometry as references (energy zero).)

<table>
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<th>configuration</th>
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<th>Side</th>
<th>Down</th>
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Figure 1 (a) Chemical structure of the BCO-BTP molecule. (b) Illustration of stimulating the intra-molecular torsional motion of the BTP-BCO molecule on the Cu(111) surface by tunneling electrons. (c) Representative STM topograph of a single BTP-BCO molecule acquired at low bias ($V=0.1\ \text{V}$ and $I=0.5\ \text{nA}$). (d) A cross-sectional profile along the red line in (c). (e) STM topograph of the same molecule acquired at high bias ($V=1.2\ \text{V}$ and $I=0.5\ \text{nA}$). (f) Corresponding noise image of (e). The scale bars in (c), (d) and (e) are $10\ \text{Å}$. 
Figure 2 (a-c) Three STM topographs of the same BTP-BCO molecule scanned sequentially at a low bias showing three conformations C, S and N, respectively (V=0.1 V and I=0.5 nA; the scale bar is 10 Å long). Insets in (b) and (c): Differential topographs of (b)-(a) and (c)-(a). (d-f) I-t spectra recorded at the defined positions illustrated by black, red or blue dots after acquiring the topographs of (a), (b) and (c), respectively. (Sample bias : 0.35 V)
Figure 3 (a) Three calculated molecular conformations with locally minimum total energy, named up, side and down structures from left to right, respectively. (b) Cross-sectional view of the BCO group in the above three structures (for clarity, H atoms are not shown), and the calculated distances from the topmost carbon atom to the Cu(111) surface are also given. (c) Simulated STM topographs (33 Å × 18 Å) of the three conformations in (a).
Figure 4 (a) Distribution of the events with residence time in the M level longer than the time given on the horizontal axis. The solid line is an exponential decay fit. The example given here is measured with a sample bias of 0.36 V and tunneling current set point of 4.0 nA. (b) Jumping rates from the M level as a function of tunneling current, for four sample biases. The solid lines are the power-law fits to the data, $R \propto I^N$, where $N=1.22\pm0.03, 1.01\pm0.23, 1.06\pm0.03$ and $1.04\pm0.06$ for sample biases of 0.25, 0.30, 0.35 and 0.40 V, resp. (c) Jumping rate from the M level as a function of sample bias voltage. It increases markedly at $355 \pm 5$ mV. (d) M-H and M-L jumping events per unit time as a function of tip lateral distance from the molecular center. The tip is
approximately positioned along the middle line perpendicular to the molecular central axis. The data were measured with a sample bias of 0.4 V. The solid lines illustrate the molecular motions corresponding to the same molecular conformation change. The stimulating centers are indicated by dashed lines. The set point of tunneling current is 4.0 nA for (a), (c) and (d). The measuring time per point is 200–800 s for (a) and (c), and 100 s for (d). The original $I$-$t$ spectra were measured at the side of the BCO group for (a)–(c).
Figure 5 (a) A representative $I$-$t$ spectrum that shows four conductance levels, where the two middle levels are denoted by M and M’. (Sample bias : 0.38 V) (b) The BCO group conformation of each individual state according to the conductance level in (a), where a red (blue) arrow indicates a $30^\circ$ counterclockwise (clockwise) torsion between the adjacent states. It is assumed that the M and M’ states correspond to the up and down BCO conformations, respectively. (Suppose the tip is positioned over the left side of the BCO group.)