J|A|C|S
COMMUNICATIONS

Bending a Bond within an Individual Adsorbed Molecule

Violeta Simic-Milosevic and Karina Morgenstern*

Institut für Festkörperphysik, Leibniz Universität Hannover, Appelstr. 2, D-30167 Hannover, Germany

Received August 31, 2008; E-mail: morgenstern@fkp.uni-hannover.de

Manipulation is one of the fascinating applications of scanning tunneling microscopy (STM). Mechanical manipulation of atoms and small molecules[1] was extended to large molecules including rotation of a bond.[2] Even more fascinating, STM may initiate surface chemistry on individual molecules by inelastic electron tunneling (IET). IET transfers energy into vibrational molecular modes leading to breakage or formation of individual bonds.[3,4]

We demonstrate the ability to distort a molecular bond for individual chloronitrobenzene molecules adsorbed on Cu(111), where the chlorine either keeps the gas phase bonding angle of 120° for the Cl−C−C bond and is adsorbed near an on-top site or gets distorted from this value to be adsorbed near a hollow site. Noise spectroscopy reveals that the excitation of a multitude of vibrational modes may initiate this bending of a molecular bond. Though IET was applied to surface diffusion[3,5] and a variety of elementary chemical reactions, e.g., dissociation[6] and isomerization,[7,8] bond angle manipulation within an individual molecule has not been achieved prior to this study. Manipulation of the internal bond angle of individual molecules on the submolecular scale may be used in molecular electronics to control the conductance by changing the bonding to a lead.

The experiments are performed with a custom-built STM housed in an ultrahigh vacuum chamber.[9] The Cu(111) surface is cleaned by repeated cycles of Ne^+ sputtering and annealing. The chloronitrobenzene (ClNB) molecules are deposited onto the sample held at 17 K. Measurements are performed at 5 K.

STM images acquired by low temperature STM of different ClNB isomers on Cu(111) were characterized before.[10] The phenyl ring is imaged as a shallow depression; the ellipsoidal protrusion corresponds to the nitro group; the circular protrusion of smaller apparent height corresponds to the chlorine atom. The relative position of the chlorine atom to the nitro group allows identification of the molecule shown in Figure 1a as the *meta*-isomer[10] (cf. Figure 1f). This submolecular resolution allows positioning the tip exactly above the position of the chlorine atom during IET manipulation at increased voltage and current. In the first manipulation (Figure 1b to d) the current drops after ~3 ms from 0.4 to 0.2 nA (Figure 1c) but raises again to the original value after 40 ms. The manipulation is ended at the lower current value. The angle between the long axis of the nitro group ellipse and the connecting line of its center to the chlorine atoms for the *ortho*- and *meta*-isomer, respectively, are ~5° and ~50°.[10] The image taken after the manipulation (Figure 1d) shows the chlorine in an intermediate position at ~27°. The next manipulation restores the starting *meta*-constitution (Figure 1e). Similar manipulation series are feasible also from the *ortho*-isomer (not shown).

We rationalize this finding as follows: ClNB molecules adsorb preferentially with the center of the phenyl ring in an on-top site.[10,11] In this adsorption geometry the chlorine resides close to an on-top site as long as the molecule keeps its gas phase bonding angles (Figure 1f, left molecule). However, single chlorine atoms prefer adsorption in hollow sites on Cu(111),[12] and thus the molecular bonding forces the chlorine into an energetically unfavorable on-top adsorption site. Changing the C−C−Cl bonding angle from 120° to 60° (Figure 1f, right molecule) moves the chlorine into an energetically more favorable adsorption site at the cost of changing its bonding angle to the carbon atom. The STM image with the chlorine related protrusion in an intermediate site corresponds to such a distorted molecule. Thus, the changes in the $I-t$ characteristics are due to a repeated change of the chlorine between its preferred bonding angle and its preferred adsorption site. Such an angle distortion manipulation is feasible, if its energy costs are compensated by the higher adsorption energy.

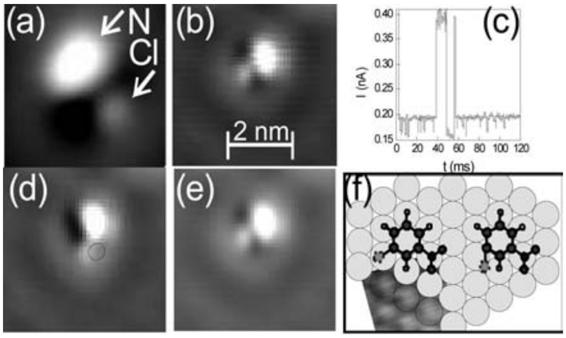

Figure 1. Manipulation series of ClNB on Cu(111): (a) *meta*-ClNB molecule with arrows pointing to the nitro group (N) and to the chlorine atom (Cl) (b to e) manipulation with 400 mV, 0.4 nA for 120 ms with the tip positioned above the chlorine atom; 100 mV, 44 pA: (b) before manipulation; (c) $I-t$ characteristics during manipulation; (d) after manipulation showing distorted molecule; circle indicates position of the chlorine in the *ortho* isomer[10] (e) after next manipulation showing *meta*-ClNB (f) schematics with regular bond angle (left molecule) and distorted bond (right molecule); STM image shows atomic resolution to scale with the schematics and in same orientation as the STM images. For a second example in color representation see abstract.

The alternative explanation of dissociation and reattachment of the chlorine atom has to be disregarded because of the low voltages involved (see below).

A related adsorption site change between hcp- and three neighboring fcc-sites was proposed from the four values within the $I-t$ characteristics for Co atoms on Cu(111). However, in this study the intermediate site was not stable without the tip and could thus not be imaged in the STM image.[13] Furthermore, in contrast to our measurement, no directional bonds were involved.

The two bonding angles of the chlorine constitute a two-state fluctuator. Such fluctuators are fundamental in the theory of 1/f noise in solids.[14] Figure 2a shows the fluctuation in the $I-t$ characteristics between two well-defined values for different manipulation parameters. The residence time in the configurations, i.e., the time until the current changes, is found to be much shorter for higher current and/or voltage.

We analyze the fluctuation quantitatively, and obtain separate histograms for the residence times in one of the two molecular configurations (Figure 2b and c). If there is no memory effect for

10.1021/ja805571b CCC: $40.75

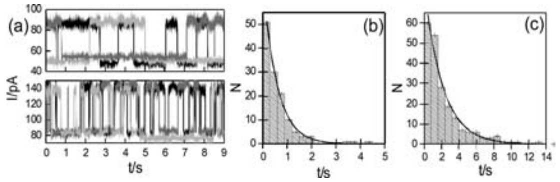

Figure 2. Analysis of two-state fluctuator: (a) Three independent manipulation curves each during manipulation with 100 mV and 90 pA (upper curves) and with 150 mV and 140 pA (lower curves); the values at 50 and 80 pA, respectively, are attributed to the distorted molecule. (b) Histogram of time spent in regular position before changing into distorted position for manipulation with 120 mV and 220 pA with exponential fit giving $\tau = (0.58 \pm 0.02)$ s. (c) Histogram of time spent in distorted position before changing into regular position for manipulation with 130 mV and 80 pA with exponential fit giving $\tau = (2.14 \pm 0.14)$ s.

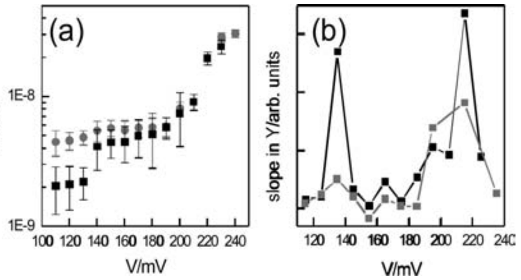

Figure 3. Reaction yield *Y* in dependence of voltage *V*: (a) for *meta*-isomer from regular position (black squares) and distorted position (gray circles); (b) slope of (a) giving maxima at 136 (134) ± 2, 199 (194) ± 4, and 218 (219) ± 3 meV for the regular (distorted) position.

the chlorine having been in one of the two configurations, an exponentially distributed resonance time probability is expected. As this exponential behavior is indeed observed, it is possible to determine the time constants τ from exponential fits. The histograms found hardly depend on the direction of the reaction but strongly on manipulation parameters. For similar voltage but much smaller current, τ thus is found to increase.

To determine the excitation mechanism we calculate the yields per electron from τ and display their dependence on the manipulation voltage (Figure 3). For the *meta*-isomer, statistically relevant data on bond distortion are gathered between 110 and 240 meV (Figure 3a) and reveal three thresholds for the forward direction in the derivative (Figure 3b). Also assuming these for the backward direction gives values of $U_{\mathrm{th1}} = (135 \pm 2)$ meV, $U_{\mathrm{th2}} = (196 \pm 5)$ meV, and $U_{\mathrm{th3}} = (218 \pm 3)$ meV.

All energy thresholds lie within the typical region of vibrational excitations, which we have calculated before for ClNB isomers.[7,15] Due to the multitude of vibrational modes and the experimental and theoretical uncertainty, there is not a single mode that can be assigned to any of the thresholds. For U_{th1} the C−H in-plane bent at 133 meV, the C−NO_2 stretch at 136 meV, and the C−Cl stretch at 137 meV lie within the threshold region. While the C−NO_2 stretch seems unlikely to be involved in a bending of the C−Cl bond, both the C−Cl stretch and the C−H in-plane bent give the right momentum for the adsorption site change.

For U_{th2} two of the C−C stretch modes at 196 and 199 meV and the NO_2 stretch at 192 meV are possible candidates for excitation. Again we exclude the NO_2 stretch vibration as not being a likely vibration resulting in a chlorine position change.

Most interesting is the case of U_{th3} with the largest change in yield, which lies not at any of the calculated modes. We suggest that the simultaneous excitation of the C−C stretch modes at either 196 or 199 meV (responsible for U_{th2}) and the excitation of the C−Cl out-of plane bent at 24 meV lead to this strong increase.

We point out that below the lowest threshold determined here the bonding angle manipulation yield is not zero. Thus, the excitation of other modes at lower energies also overcomes the energy barrier between the two adsorption states. The low yields below $2 \times 10^{-9}/e^-$ lead, however, to unreasonably long manipulation times and are thus experimentally inaccessible. We conclude that a quite low energy barrier below 100 meV lies between the molecule with two different bonding angles and that this barrier can be overcome by excitation of different vibrational modes.

Finally, the yield for bond angle distortion and recovery are mostly identical within the error bars. Only at voltages below 140 mV the regular bond angle is more stable by approximately a factor of 2. This gives an upper limit to a small energetic difference between the two minima in the potential energy curve.

In conclusion, we observe that the surface potential and the molecular bonding confine the chlorine into two possible sites, between which we can switch the molecule reversibly. The prerequisite for such a manipulation is an appropriate energy balance between the energy costs for distorting the molecule and the energy gain for a better adsorption site, so that the distorted molecule has a local minimum, which is stable without the tip. We suggest that this balance could be determined theoretically for choosing an appropriate adsorbate−substrate system and that organic chemistry could provide the appropriate molecule. Along this route this study opens fascinating possibilities for manipulating the internal structure of an individual molecule on a submolecular scale.

References

(1) (a) Eigler, D. M.; Schweizer, E. K. *Nature* **1990**, *344*, 524. (b) Zeppenfeld, P.; Lutz, C. P.; Eigler, D. M. *Ultramicroscopy* **1992**, *42−44*, 128. (c) Crommie, M. F.; Lutz, C. P.; Eigler, D. M. *Science* **1993**, *262*, 218.

(2) (a) Gross, L.; Rieder, K.-H.; Moresco, F.; Stojkovic, S. M.; Gourdon, A.; Joachim, Chr. *Nat. Mater.* **2005**, *4*, 892. (b) Chiaravalloti, F.; Gross, L.; Rieder, K.-H.; Stojkovic, S. M.; Gourdon, A.; Joachim, Chr.; Moresco, F. *Nat. Mater.* **2007**, *6*, 30. (c) Moresco, F.; Meyer, G.; Rieder, K. H.; Tang, H.; Gourdon, A.; Joachim, Ch. *Phys. Rev. Lett.* **2001**, *86*, 672.

(3) Ho, W. *J. Chem. Phys.* **2002**, *117*, 11033.

(4) Komeda, T. *Prog. Surf. Sci.* **2005**, *78*, 41.

(5) (a) Gawronski, H.; Morgenstern, K.; Rieder, K. H. *Eur. Phys. J. D* **2005**, *35*, 349. (b) Komeda, T.; Kim, Y.; Kawai, M.; Persson, B. N. J.; Ueba, H. *Science* **2002**, *295*, 2055. (c) Morgenstern, K.; Rieder, K. H. *J. Chem. Phys.* **2002**, *116*, 5746. (d) Pascual, J. I.; Lorente, N.; Song, Z.; Conrad, H.; Rust, H.-P. *Nature* **2003**, *423*, 525.

(6) (a) Stipe, B. C.; Rezaei, M. A.; Ho, W.; Gao, S.; Persson, M.; Lundqvist, B. I. *Phys. Rev. Lett.* **1997**, *78*, 4410. (b) Hla, S.-W.; Bartels, L.; Meyer, G.; Rieder, K. H. *Phys. Rev. Lett.* **2000**, *85*, 2777. (c) Morgenstern, K.; Rieder, K. H. *Chem. Phys. Lett.* **2002**, *358*, 250. (d) Kim, Y.; Komeda, T.; Kawai, M. *Phys. Rev. Lett.* **2002**, *89*, 126104.

(7) Simic-Milosevic, V.; Mehlhorn, M.; Rieder, K.-H.; Meyer, J.; Morgenstern, K. *Phys. Rev. Lett.* **2007**, *98*, 116102.

(8) (a) Henzl, J.; Mehlhorn, M.; Gawronski, H.; Rieder, K. H.; Morgenstern, K. *Angew. Chem., Int. Ed.* **2006**, *45*, 603. (b) Henzl, J.; Bredow, Th.; Morgenstern, K. *Chem. Phys. Lett.* **2007**, *435*, 278. (c) Henzl, J.; Mehlhorn, M.; Morgenstern, K. *Nanotechnology* **2007**, *18*, 495502. (d) Simic-Milosevic, V.; Meyer, J.; Morgenstern, K. *Phys. Chem. Chem. Phys.* **2008**, *10*, 1916.

(9) Mehlhorn, M.; Gawronski, H.; Nedelmann, L.; Grujic, A.; Morgenstern, K. *Rev. Sci. Instrum.* **2007**, *78*, 033905.

(10) Niemi, E.; Simic-Milosevic, V.; Morgenstern, K.; Korventausta, A.; Paavilainen, S.; Nieminen, J. *J. Chem. Phys.* **2006**, *125*, 184708.

(11) Nieminen, J.; Niemi, E.; Simic-Milosevic, V.; Morgenstern, K. *Phys. Rev. B* **2005**, *72*, 195421.

(12) Shard, A. G.; Ton-That, C.; Campbell, P. A.; Dhanak, V. R. *Phys. Rev. B* **2004**, *70*, 155409.

(13) Stroscio, J. A.; Celotta, R. J. *Science* **2004**, *306*, 242.

(14) Weissman, M. B. *Rev. Mod. Phys.* **1988**, *60*, 537.

(15) The complete results of the calculation can be found on http://www.fkp.unihannover.de/∼morgenstern/ClNB/index-ClNB.html.

JA805571B