

Azobenzene on Cu(110): Adsorption Site-Dependent Diffusion

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The adsorption of molecules on surfaces plays an important role in bottom-up nanofabrication.^{1,2} Azobenzene and derivatives thereof are particularly interesting since these molecules are considered as model systems for molecular switches,^{3–6} based on light-induced reversible *trans*–*cis* isomerizations. Consequently, they play an important role for optically active materials and devices. Switching of azobenzene derivatives at the liquid–solid interface has been demonstrated,^{7–10} while investigations into the adsorption and switching behavior of azobenzene at surfaces under well-defined ultrahigh vacuum (UHV) conditions are only just emerging.^{11,12} In this Communication, we investigate the adsorption geometries of azobenzene on the Cu(110) surface at low coverage and saturation limits. We show that only the *trans*-isomer is observed, and we investigate its diffusion behavior in both preferred and energetically metastable adsorption states.

Scanning tunneling microscopy (STM) measurements were acquired with the variable-temperature Aarhus STM under UHV conditions.^{13,14} Azobenzene (Sigma-Aldrich, 99.5% purity) was held in a transparent glass vial at room temperature and admitted into the UHV system via a leak valve. The Cu(110) surface was cleaned by repeated cycles of 1.5 keV Ar⁺ ion bombardment followed by annealing to 820 K. All STM measurements were obtained in a temperature range of 120–170 K.

Upon deposition at room temperature, individual molecules appear as two bright protrusions, attributed to flat lying phenyl rings, separated by a darker line associated with the N=N bond (Figure 1a). This molecular signature is qualitatively as expected for the *trans*-isomer. The molecules adsorb with their axis at a slight angle to the close-packed [1 $\bar{1}$ 0] direction and with their N=N bond at a bridge site as determined from images showing the Cu lattice at atomic resolution (Figure 1c). Loss of symmetry upon adsorption results in two different surface enantiomers, distinguishable by the direction of the central dark line, as indicated by arrows in Figure 1a. A possible model of the molecular adsorption geometry is depicted in Figure 1b (the enantiomer with the N=N bond along the dark line is tentatively chosen to correspond to the shown direction of rotation).

As the coverage is increased, the molecules do not show a strong tendency to cluster together, even if annealed to 500 K. Near half of saturation coverage (Figure 1d), the molecules begin to order by stacking sideways into columns running along the substrate [001] direction. The molecular head-to-head interaction appears to be weak or even repulsive as no ordering is observed along this direction. At saturation coverage (Figure 1e), the molecules form columns along the [001] direction with a periodicity of 7.9 ± 0.8 Å (dimension a in Figure 1e), consistent with two lattice spacings of the Cu substrate. At this separation, intermolecular H–N

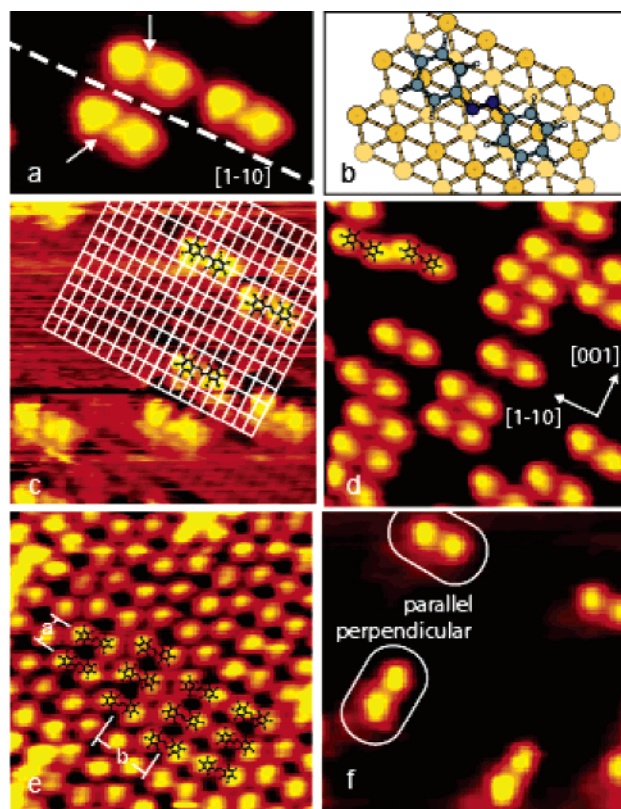


Figure 1. Azobenzene on Cu(110). STM images acquired at $V_t = -2.0$ V, $I_t \sim 0.350$ nA unless stated otherwise. For (a) through (e), azobenzene is deposited onto Cu(110) held at room temperature. (a) Single molecules in two enantiomeric forms (50×30 Å²). (b) Ball model of the adsorption geometry. (c) Determination of adsorption geometry from the underlying atomic lattice. Grid intersections correspond to the position of copper atoms ($V_t = -0.12$ V, $I_t = 0.850$ nA, 70×70 Å²). (d) Intermediate coverage (70×70 Å²). (e) Saturation coverage. The structure does not appear to involve chiral segregation (the choice of enantiomers for the superimposed molecular models is arbitrary) (80×80 Å²). (f) Perpendicular adsorption geometry observed upon deposition at a cold (~ 120 K) surface (60×60 Å²).

hydrogen bonding can occur with a reasonable bond length of less than 4 Å. The column–column distance along the [1 $\bar{1}$ 0] direction is 14.3 ± 1.4 Å (dimension b in Figure 1e). The structure has limited long-range order as entire columns are often shifted relative to each other by one lattice spacing along the [001] direction, leading to either head-to-head or interdigitating molecular arrangements (see Figure 1e). Since the N=N bonds appear dark in the STM images, phenyl rings of adjacent molecules can appear to comprise a single molecule. However, the assignment of the molecular features shown in Figure 1e is confirmed by inspecting molecules close to step edges or defect sites.

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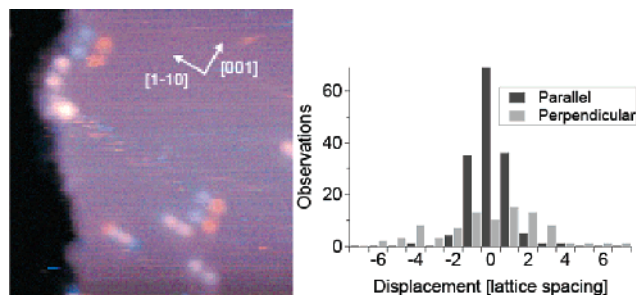


Figure 2. (a) Overlay of two time-separated STM images showing the diffusion of both the parallel and perpendicular configuration. Blue/orange colors correspond to initial/final positions, respectively. Stationary features appear gray ($140 \times 140 \text{ \AA}^2$). (b) A distribution of displacement for azobenzene at 168 K.

When azobenzene is deposited onto a Cu(110) surface held at low temperatures ($\sim 120 \text{ K}$), we observe a second adsorption geometry with the molecular axis perpendicular to the $[1 -1 0]$ direction (Figure 1f). Upon annealing the sample to $300\text{--}500 \text{ K}$, we no longer observe this perpendicular species. We therefore conclude that the parallel configuration is the most energetically favorable adsorption geometry, and that the perpendicular configuration is a metastable state that is trapped upon adsorption on a cold surface. The similar appearance of the parallel and perpendicular configuration indicates that both cases are the *trans*-isomer.

By acquiring sequences of time-lapsed STM images (STM movies¹⁵) at 168 K, we investigated the diffusion of azobenzene for these two adsorption states. The shift in position of the adsorbates is demonstrated in Figure 2a by superimposing two sequential STM images of the same portion of the surface. The images have been colored blue and orange, respectively, such that stationary molecules appear gray, and blue/orange indicates initial/final positions of the molecules that have moved. Both species diffuse along the closed-packed $[1 -1 0]$ direction. The molecular displacements, determined at lattice spacing resolution, are plotted in the two histograms of Figure 2b. The diffusion coefficients for the parallel and perpendicular configurations are 0.2×10^{-16} and $1.3 \times 10^{-16} \text{ cm}^2/\text{s}$, respectively, corresponding to a difference in activation energy of 0.03 eV. Using an attempt frequency^{15,16} of 10^{12} s^{-1} , we find activation energies of 0.44 eV (parallel) and 0.41 eV (perpendicular). This may be compared to recent results for adsorption of azobenzene on Au(111) showing a much higher mobility on this substrate.¹¹ The ~ 6 times greater diffusion coefficient for the perpendicular configuration compared to that of the parallel one demonstrates that different orientations of the same isomer influence the molecular diffusivity. A similar result was recently demonstrated by manipulating a large organic molecule into a metastable state using the STM tip.¹⁷ In the present system, however, the molecules spontaneously assume the metastable state of higher mobility by deposition onto a cold surface.

Although azobenzene may exist in either a *trans*- or a *cis*-conformation, we only appear to observe the former after deposition. (Since the *cis*-isomer has a nonplanar conformation in the gas phase, we expect it to adsorb with only one phenyl ring attached to the surface, appearing slightly larger than a single phenyl ring.) The ground state energy of the *trans*-isomer is $\sim 0.6 \text{ eV}$ lower than that

of the *cis*-isomer,⁵ and the fraction of *cis*-isomers in thermal equilibrium at room temperature should thus be negligible. However, in the photostationary state existing in the transparent glass vial holding the molecules (exposed to ordinary laboratory light), the fraction of *cis*-isomers is expected to be significantly higher, on the order of 10%.^{18,19} It is possible that *cis*-conformers dosed onto the surface relax to the *trans* form upon adsorption. Alternatively, a reduced molecule–surface interaction for the *cis*-isomer may lead to a more diffusive species. Occasionally, we observe highly mobile entities which we speculate could be *cis*-isomers, but the experimental setup does not allow for sufficiently low sample temperatures to stabilize them.

In summary, we have characterized adsorption states and thermal mobility of *trans*-azobenzene on the Cu(110) surface. To obtain conformational switching²⁰ in this model system with a comparatively¹¹ strong molecule–substrate interaction, it may prove helpful to provide thermal activation in conjunction with photoirradiation.

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