Supporting Information:

Real-Space Observation of Quantum Tunneling by Carbon Atom: Flipping Reaction of Formaldehyde on Cu(110)

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1. Computational details

The density functional theory (DFT) calculations were based on version 5.3 of VASP. The plane-wave cut-off energy was set at 400 eV. The Brillouin zone was sampled with a 6×6×1 and a 3×3×1 k-point grid for the 2×3 and the 4×6 surface unit cells, respectively. Dipole corrections were applied perpendicular to the surfaces of each slab. The geometrical optimizations were done with the bottom two layers of the slabs being constrained at the calculated lattice constant of 3.579 Å[1] until the ionic forces were less than 0.01 eV/Å. The stability of equilibrium structures and the nature of the saddle points that were obtained from the nudged elastic band method were analyzed by calculating their vibrational spectra in the harmonic approximation. The larger unit cell was used in the simulations of topographical STM images in order to avoid overlapping images. These simulations were based on the Tersoff-Hamann approximation[2] at constant local density of states. Here the tails of the wave functions were extended analytically into the vacuum region[3] and with a Gaussian broadening of 0.1 eV around the Fermi level.

2. Estimate of tunneling rate

The tunneling rate R between the two mirror-reflected structures of the η^1- and η^3-configuration was obtained using the one-dimensional WKB approximation for tunneling as,

$$R = v\exp\left(-2\int_{\tilde{s}_1}^{\tilde{s}_2} \sqrt{2(V(\tilde{s}) - E)}\, d\tilde{s}\right),$$

Here v is the frequency of the vibrational mode at the equilibrium position along the MEP and $V(\tilde{s})$ is the potential energy curve along the MEPs parametrized by the isoinertial (mass-scaled coordinates) path length $\tilde{s}$ and the energy $E = \dfrac{hv}{2} + V_{\text{eq}}$. The isoinertial line element $d\tilde{s}$ is given in term of the line element ds as,

$$d\tilde{s} = \sqrt{\sum_i m_i \left(\frac{dx_i}{ds}\right)^2}\, ds$$

where x_i are cartesian coordinates for the atoms with the associated masses m_i. The effective barrier height, D_{eff}, is defined as $D_{\text{eff}} = E_{\text{a}} - \dfrac{hv}{2}$, where E_{a} is the activation energy.

3. Influence of the tip conditions on the flipping rate

The flipping rate is affected by the tip conditions. **Figure S1** shows the current dependence obtained under three different tip conditions which were changed by *in-situ* tip preparation methods such as an application of a strong voltage pulse and a controlled indentation of the tip into the surface. The difference may be explained by a slightly different long-range interaction between the tip apex and the molecule, which influence the potential energy landscape of the flipping reaction.
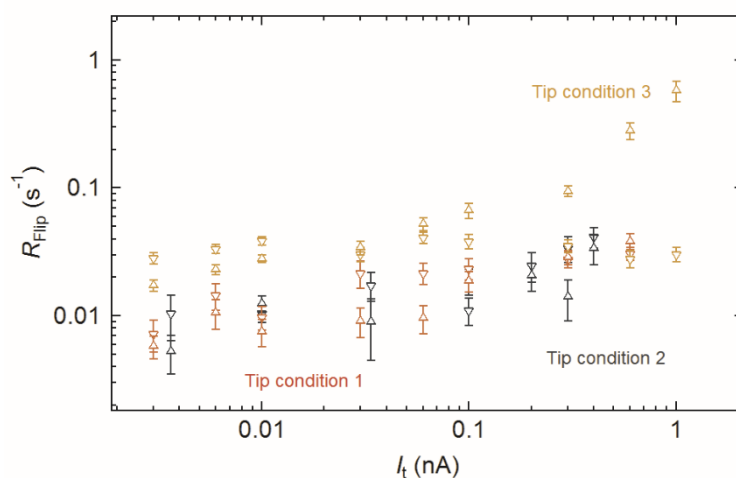
Figure S1. Tunneling-current and tip dependence of the rate for the "high" to "low" transition ($R_{H \to L}$, inverted triangle) and the reverse process ($R_{L \to H}$, triangle) for CH_2O acquired on the Cu(110) surface at 4.5 K. V_{bias} was fixed at 10 mV during the measurement and three different tip conditions were examined.

References

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