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Supplementary information: Adsorption and reaction of H_2S on Cu(110) studied with scanning tunneling microscopy

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Fig. S1: (a) and (b) STM images of β -SH on Cu(110) (V = 30 mV, I = 0.5 nA). The yellow arrows indicate the direction of the S-H axis. (a) 54 Å × 54 Å. (b) 76 Å × 76 Å. (c) Simulated STM topography of SH on the short bridge site at a charge density of $6.748 \times 10^{-8} \text{ e/Å}^3$ at V = 50 mV. A small (large) round indicates the location of the H (S) atom.

1 STM images of β -SH

Fig. S1a and b show typical STM images of SH groups adsorbed at the short-bridge site (β -SH) on Cu(110). Two equivalent configurations of β -SH can be discriminated by the location of faint depressions. The upward (downward) arrows in Fig. S1a and b represent the configuration with the depressions displaced in the [001] ([001]) direction. Fig. S1c shows a simulated STM image of β -SH, which were performed using the Tersoff-Hamann theory.¹ The topography shows an elliptic protrusion with side depressions, well reproducing the experimental image. Based on the simulation, we tentatively assign to the upward-arrow (downward-arrow) configuration to SH with the axis along to the [001] ([001]) direction.



Fig. S2: Potential energy surfaces for the flip motion of SH adsorbed at the (a) long-bridge site and (b) short-bridge site. The geometries along the reaction pathways are shown in the lower panels.

2 Flip barriers of α -SH and β -SH

We calculated potential energy surfaces for the flip motion of SH groups on Cu(110). Fig. S2a and b show the energy surfaces of SH adsorbed at the long-bridge site and short-bridge site, respectively. The reaction coordinate is the coordinate of hydrogen atom along the $[1\bar{1}0]$ ([001]) direction for SH at the long-bridge (short-bridge) site. The activation barrier of SH at the long-bridge (short-bridge) site is estimated to be 337 (647) meV.

3 Fitting function for the yield of H₂O–SH and H₂O

The reaction yield curves for the intermediate complex (H₂O–SH) and water monomer in Fig. 5e are analyzed by a recently proposed analytical modeling.^{2,3} When the reaction is induced via single-electron process, the yield Y(V) is defined by

$$Y(V) = \frac{R(V)}{I(V)/e},$$
(1)

where R(V) is the reaction rate and I(V) is the electrical current through the adsorbate level at an applied voltage V.

Now we use the extendend wide-band limit (EWBL) modeling, which has been applied to fitting yield curves of several reactions.^{4–10} In this modeling, the yield is described as

$$Y(V) = K_{\text{eff}} \frac{1}{|eV|} \int_0^{|eV|/\hbar} \rho_{\text{ph}}(\omega) \left(|eV| - \hbar\omega\right) d\omega,$$
(2)

where K_{eff} is an effective prefactor determined by the elementary process^{2,3} and where $\rho_{\text{ph}}(\omega)$ is the vibrational density of states (VDOS).

The VDOS, which is centered around a characteristic vibrational energy $\hbar\Omega$, can be represented by the Dirac delta function, Gaussian distribution, or Lorentzian distribution.^{3,11} Here we use a Gaussian distribution since this has successfully reproduced the experimental yield curves for water-related adsorbates on Cu(110).^{3,5–7} Then $\rho_{\rm ph}(\omega)$ is given by

$$\rho_{\rm ph}(\omega) = \frac{1}{\sigma_{\rm ph}\sqrt{2\pi}} \frac{1}{\operatorname{erf}\left(\frac{\Omega}{\sqrt{2}\sigma_{\rm ph}}\right)} \left\{ \exp\left[-\left(\frac{\omega-\Omega}{\sqrt{2}\sigma_{\rm ph}}\right)^2\right] - \exp\left[-\left(\frac{\omega+\Omega}{\sqrt{2}\sigma_{\rm ph}}\right)^2\right] \right\},\tag{3}$$

where $\operatorname{erf}(x)$ is the error function, *i.e.*,

$$\operatorname{erf}(x) = \frac{2}{\sqrt{\pi}} \int_0^x \exp(-t^2) \, \mathrm{d}t.$$
(4)

Equation 3 takes into account all broadening effects in a standard deviation $\sigma_{\rm ph}$.

Using Equation 3, the yield reads as

$$Y(V) = \frac{K_{\text{eff}}}{|eV| \operatorname{erf}\left(\frac{\Omega}{\sqrt{2}\sigma_{\text{ph}}}\right)} \left(|eV| \operatorname{erf}\left(\frac{\Omega}{\sqrt{2}\sigma_{\text{ph}}}\right) + \frac{\hbar\sigma_{\text{ph}}}{\sqrt{2\pi}} \left\{ \exp\left[-\left(\frac{|eV| - \hbar\Omega}{\sqrt{2}\hbar\sigma_{\text{ph}}}\right)^{2}\right] - \exp\left[-\left(\frac{|eV| + \hbar\Omega}{\sqrt{2}\hbar\sigma_{\text{ph}}}\right)^{2}\right] \right\} + \frac{|eV| - \hbar\Omega}{2} \operatorname{erf}\left(\frac{|eV| - \hbar\Omega}{\sqrt{2}\hbar\sigma_{\text{ph}}}\right) - \frac{|eV| + \hbar\Omega}{2} \operatorname{erf}\left(\frac{|eV| + \hbar\Omega}{\sqrt{2}\hbar\sigma_{\text{ph}}}\right) \right).$$
(5)

By using Equations 2 and 5, the experimental yield curves can be fitted, and thus the optimized parameters K_{eff} , $\hbar\Omega$, and $\hbar\sigma_{\text{ph}}$ can be obtained.

The hopping motion of an isolated H₂O monomer on Cu(110) was analyzed previously.¹² At lower bias (below ~40 mV), the rate is constant ($R_0 = 0.1 \text{ s}^{-1}$), indicating that this hopping motion is induced thermally and independent from vibrational modes. Above ~40 mV, on the other hand, the hopping rate is increased by vibrational excitation via single electron process. Thus the yield per electron $Y_{\text{H}_2\text{O}}(V)$ is described after removing R_0 contribution:

$$Y_{\rm H_2O}(V) = \frac{R_{\rm H_2O}(V) - R_0}{I_{\rm H_2O}(V)/e}.$$
(6)

By using Equation 6, the hopping yield of H_2O is obtained (blue dots in Fig. 5e). For the flip rate of the H_2O-SH complex, in contrast, the intrinsic motion can be ignored, *i.e.*,

$$Y_{\rm H_2O-SH}(V) = \frac{R_{\rm H_2O-SH}(V)}{I_{\rm H_2O-SH}(V)/e},$$
(7)

which leads to the flipping yield (black dots in Fig. 5e).

By using Equation 5, we calculate the fitting curves of $Y_{\rm H_2O-SH}(V)$ and $Y_{\rm H_2O}(V)$ as shown by a black and blue curve in Fig. 5e, respectively. Then the following optimized parameters are obtained: $K_{\rm eff} = (3.2 \pm 0.1) \times 10^{-7}$ [(4± 1) × 10⁻⁷], $\hbar\Omega = 70.3 \pm 0.5$ meV (60 ± 5 meV), and $\hbar\sigma_{\rm ph} = 11.6 \pm 0.2$ meV (11 ± 3 meV) for the complex (H₂O). Similarity of the parameters between the intermediate complex and water monomer suggests that both reactions are induced by the identical vibrational mode. This $\hbar\Omega$ is related to the stretch mode between H₂O and the Cu substrate.¹²

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