Supplementary information:
Adsorption and reaction of H$_2$S on Cu(110) studied with scanning tunneling microscopy

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Fig. S1: (a) and (b) STM images of $\beta$-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 $6.748 \times 10^{-8}$ e/A$^3$ at $V = 50$ mV. A small (large) round indicates the location of the H (S) atom.

1 STM images of $\beta$-SH

Fig. S1a and b show typical STM images of SH groups adsorbed at the short-bridge site ($\beta$-SH) on Cu(110). Two equivalent configurations of $\beta$-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] ([00 $\bar{1}$]) direction. Fig. S1c shows a simulated STM image of $\beta$-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 [00 $\bar{1}$] ([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 $\alpha$-SH and $\beta$-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\overline{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 H$_2$O–SH and H$_2$O

The reaction yield curves for the intermediate complex (H$_2$O–SH) and water monomer in Fig. 5e are analyzed by a recently proposed analytical modeling.\textsuperscript{2,3} When the reaction is induced via single-electron process, the yield $Y(V)$ is defined by

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

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.\textsuperscript{4–10} In this modeling, the yield is described as

$$Y(V) = K_{\text{eff}} \frac{1}{|eV|} \int_{0}^{\left|eV\right|/\hbar} \rho_{\text{ph}}(\omega) \left( |eV| - \hbar \omega \right) d\omega,$$

where $K_{\text{eff}}$ is an effective prefactor determined by the elementary process\textsuperscript{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.\textsuperscript{3,11} Here we use a Gaussian distribution since this has successfully reproduced the experimental yield curves for water-related adsorbates on Cu(110).\textsuperscript{3,5–7} Then $\rho_{\text{ph}}(\omega)$ is given by

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

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

$$\text{erf}(x) = \frac{2}{\sqrt{\pi}} \int_{0}^{x} \exp(-t^2) \ dt.$$

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

Using Equation 3, the yield reads as

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

$$+ \frac{|eV| - \hbar \Omega}{2} \text{erf}\left( \frac{|eV| - \hbar \Omega}{\sqrt{2\sigma_{\text{ph}}}} \right) - \frac{|eV| + \hbar \Omega}{2} \text{erf}\left( \frac{|eV| + \hbar \Omega}{\sqrt{2\sigma_{\text{ph}}}} \right).$$

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

The hopping motion of an isolated H$_2$O monomer on Cu(110) was analyzed previously. At lower bias (below $\sim$40 mV), the rate is constant ($R_0 = 0.1$ s$^{-1}$), indicating that this hopping motion is induced thermally and independent from vibrational modes. Above $\sim$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:

$$Y_{\text{H}_2\text{O}}(V) = \frac{R_{\text{H}_2\text{O}}(V) - R_0}{I_{\text{H}_2\text{O}}(V)/e}. \quad (6)$$

By using Equation 6, the hopping yield of H$_2$O is obtained (blue dots in Fig. 5e). For the flip rate of the H$_2$O–SH complex, in contrast, the intrinsic motion can be ignored, i.e.,

$$Y_{\text{H}_2\text{O}–\text{SH}}(V) = \frac{R_{\text{H}_2\text{O}–\text{SH}}(V)}{I_{\text{H}_2\text{O}–\text{SH}}(V)/e}, \quad (7)$$

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

By using Equation 5, we calculate the fitting curves of $Y_{\text{H}_2\text{O}–\text{SH}}(V)$ and $Y_{\text{H}_2\text{O}}(V)$ as shown by a black and blue curve in Fig. 5e, respectively. Then the following optimized parameters are obtained: $K_{\text{eff}} = (3.2 \pm 0.1) \times 10^{-7} \left[(4 \pm 1) \times 10^{-7}\right]$, $h\Omega = 70.3 \pm 0.5$ meV (60 $\pm$ 5 meV), and $h\sigma_{\text{ph}} = 11.6 \pm 0.2$ meV (11 $\pm$ 3 meV) for the complex (H$_2$O). Similarity of the parameters between the intermediate complex and water monomer suggests that both reactions are induced by the identical vibrational mode. This $h\Omega$ is related to the stretch mode between H$_2$O and the Cu substrate.\textsuperscript{12}

References


