

Chapter 2

Principles and Methods

2.1 Principles and Equipment

2.1.1 Principles of STM

Figure 2.1a shows a schematic of STM. The scanning motion of the probe tip is controlled by a tube scanner located at the base of the tip. Three piezoelectric elements are attached to the scanner, allowing finely controlled motion of the tip in the x -, y -, and z -directions, as shown in Fig. 2.1b. A bias voltage (the sample bias) is applied to the sample, whereas the tip is grounded. When the tip approaches the sample with a gap distance less than ~ 10 Å, electrons can pass through the vacuum gap between the tip and sample owing to the tunneling effect, leading to the tunneling current I (typically 0.01–10 nA). The feedback loop controls the tip–sample distance by applying an appropriate voltage to the z -axial piezoelectric element of the tube scanner, so that the detected tunneling current becomes constant. Under these conditions, real-space topographic images (Fig. 2.1c) can be acquired by recording the feedback voltages during applying scanning voltages to the x - and y -axial piezoelectric elements (Fig. 2.1b).

Figure 2.1b shows a schematic illustration of the tip–sample junction. In this situation, the tunneling current flows from the tip apex (ideally, from only one atom at the apex) to an atom of the sample surface just beneath the tip apex (red sphere in Fig. 2.1b). Because the tunneling current increases exponentially as the tip–sample distance decreases, the spatial resolution of STM rises to the single-atom level. Notably, the STM images do not directly reflect the topography of the surface but correspond to the trajectory of the z -displacement of the tip; some adatoms/admolecules on surfaces can be imaged as depressions with STM (blue sphere in Fig. 2.1b and the corresponding depression in Fig. 2.1c). The apparent contradiction of the image height and the actual atomic height results from the fact that the tunneling current strictly depends on the local density of states (LDOS) of the tip and surface. If the tunneling current flows more readily at the bare surface than above an adatom, the

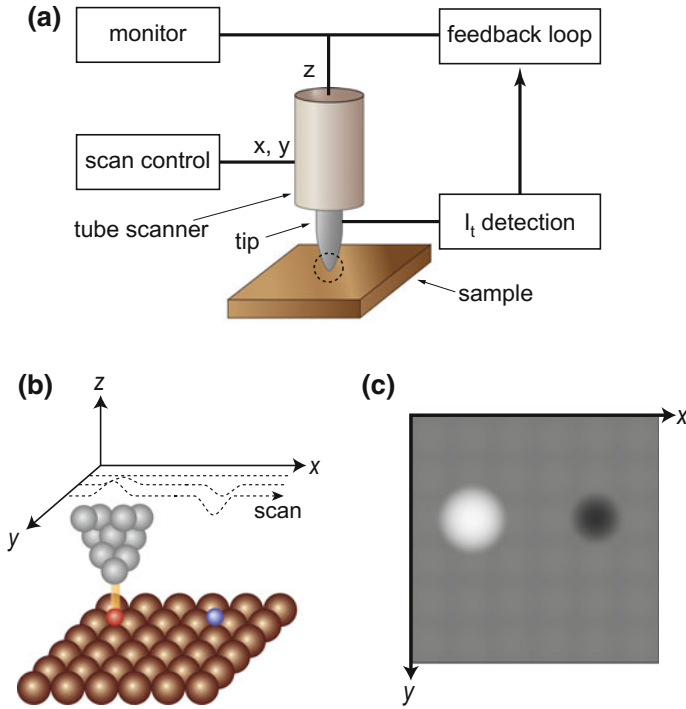


Fig. 2.1 **a** Schematic of an STM. **b** Schematic of the tunneling junction, corresponding to the illustration magnified in the *dotted circle* in **a**. **c** Schematic STM image, where the adatoms represented as the *red and blue spheres* in **b** are imaged as a protrusion and depression, respectively

tip height z is reduced over the adatoms because of the feedback loop; consequently, the adatom is observed as a depression in the STM image (Fig. 2.1b, c).

Here, I will briefly describe the relation between the tunneling current I and the tip-sample distance d . The sample bias V misaligns the Fermi levels of the tip and the sample, giving rise to the tunneling current. In a model using Wentzel-Kramers-Brillouin (WKB) approximation, I can be calculated using the following equation [1–3]:

$$I \propto \int_0^{eV} \rho_s(E) \rho_t(E - eV) T(d, eV, E) dE, \quad (2.1)$$

where

$$T(d, eV, E) \simeq \exp \left(-\frac{2d\sqrt{2m}}{\hbar} \sqrt{\frac{\phi_s + \phi_t}{2} + \frac{eV}{2} - E} \right). \quad (2.2)$$

For the tunneling probability T , the vacuum barrier in a trapezoidal shape is approximated by a square barrier. In Eqs. (2.1) and (2.2), $\rho_{t(s)}$ denotes the DOS of the tip (sample), $\phi_{t(s)}$ represents the work function of the tip (sample), and m is the mass of a free electron. These equations indicate that the tunneling current depends on the tunneling junction distance in an exponential manner.

2.1.1.1 Principles of STS

Scanning tunneling spectroscopy (STS) can be used to obtain the energy distribution of the LDOS of the sample just beneath the probe tip by measuring the tunneling conductance, i.e., dI/dV [4, 5]. If the tip state ρ_t has a constant distribution (i.e., $d\rho_t/dV = 0$), according to Eq. (2.1), the tunneling conductance is expressed in the following equation:

$$\frac{dI}{dV} \propto e\rho_s(eV)\rho_t(0)T(d, eV, eV) + \int_0^{eV} \rho_s(E)\rho_t(E - eV) \frac{\partial T(d, eV, E)}{\partial V} dE. \quad (2.3)$$

The second term of the right-hand side of Eq. (2.3) can be ignored when V is sufficiently small, which gives

$$\frac{dI}{dV} \propto \rho_s(eV). \quad (2.4)$$

Equation (2.4) indicates that dI/dV spectra reflect the energy distribution of the surface state ρ_s .

2.1.1.2 Principles of IETS

Thus far, I have mentioned elastic electron tunneling, i.e., electron tunneling without energy loss. In that case, the tunneling current I smoothly increases with increasing bias voltage V ; consequently, the second derivative of the current d^2I/dV^2 is almost zero.

The vibrational features of molecules at the tunneling junction can appear in d^2I/dV^2 spectra when the tunneling electrons excite vibrational modes. Characteristic peaks in the d^2I/dV^2 spectra recorded at tunneling junctions were first identified in 1966 [6]; these peak energies are ascribed to the vibrational excitation of molecules that are present at the tunneling junctions of metal–insulator–metal interfaces. This vibrational spectroscopic method is called inelastic electron tunneling spectroscopy (IETS) [7]. In 1998, Stipe et al. [8–10] first reported IETS of individual molecules adsorbed on metal surfaces by using STM (STM-IETS) and demonstrated chemical identification of single molecules. Later, in addition to the vibrational modes of adsorbates on surfaces [11–14], other excitation has been

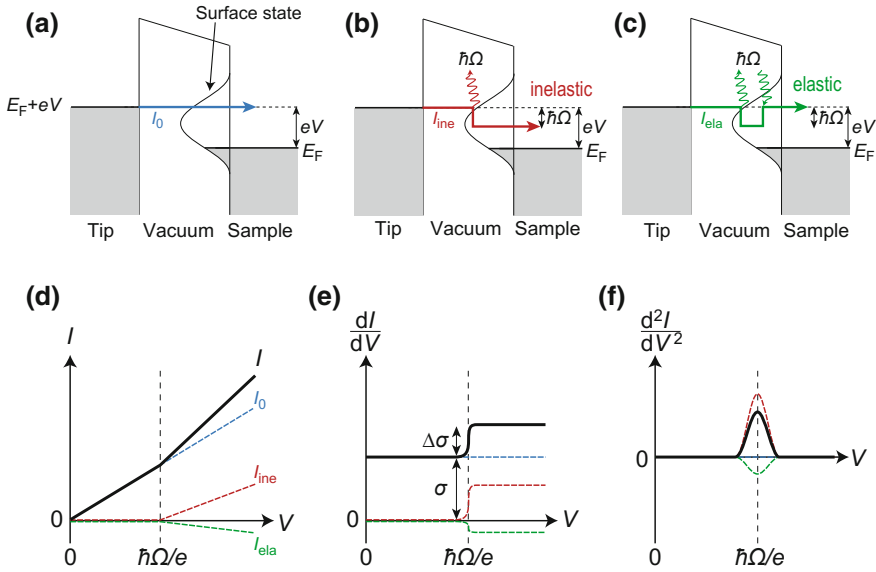


Fig. 2.2 **a–c** Schematic energy diagrams of tunneling current at an STM junction with a positive sample bias $V > 0$. I_0 , I_{ine} , and I_{ela} represent **a** the elastic tunneling current without vibrational excitation, **b** inelastic tunneling current with vibrational excitation, and **c** elastic tunneling current with both vibrational excitation and de-excitation, respectively. **d** The I – V , **e** dI/dV , and **f** d^2I/dV^2 spectra of the total current $I = I_0 + I_{ine} + I_{ela}$ together with each component

detected by STM-IETS, including molecular rotational modes [15, 16], spin flips of magnetic atoms/molecules [17, 18], and surface phonon modes [19–21]. Furthermore, IETS mapping can be used to resolve the constituent atoms of a molecule on surfaces; IETS maps measured over cobalt phthalocyanine adsorbed on metal surfaces using a CO-functionalized tip reflect the chemical bonding structures of the adsorbates [22, 23]. Thus, IETS is a powerful tool to directly observe elementary excitation on surfaces at the single-atom/molecule level. To explain the mechanism of inelastic electron tunneling process, the following three models have been proposed: resonance scattering [24], dipole scattering [25, 26], and impact scattering [27] models. Here, I describe the principle of IETS using the most widely recognized model: the resonance scattering model.

Figure 2.2a–c show schematic STM-IETS energy diagrams. At a tunneling junction, most electrons go through the tunneling barrier elastically (elastic tunneling current I_0 ; Fig. 2.2a). However, an additional tunneling channel is opened when the sample bias $|V|$ is greater than the vibrational eigenvalue $\hbar\Omega/e$ of any molecule located at the junction. In this channel, the energy of the electrons is used to vibrationally excite the molecule (inelastic tunneling current I_{ine} ; Fig. 2.2b). Because the total current I is the sum of the elastic and inelastic tunneling currents, the I – V curve has inflection points at $V = \pm\hbar\Omega/e$ (Fig. 2.2c), and thus, the d^2I/dV^2 curve has a peak at $V = +\hbar\Omega/e$ (Fig. 2.2e) and a dip at $V = -\hbar\Omega/e$. Notably, another elastic

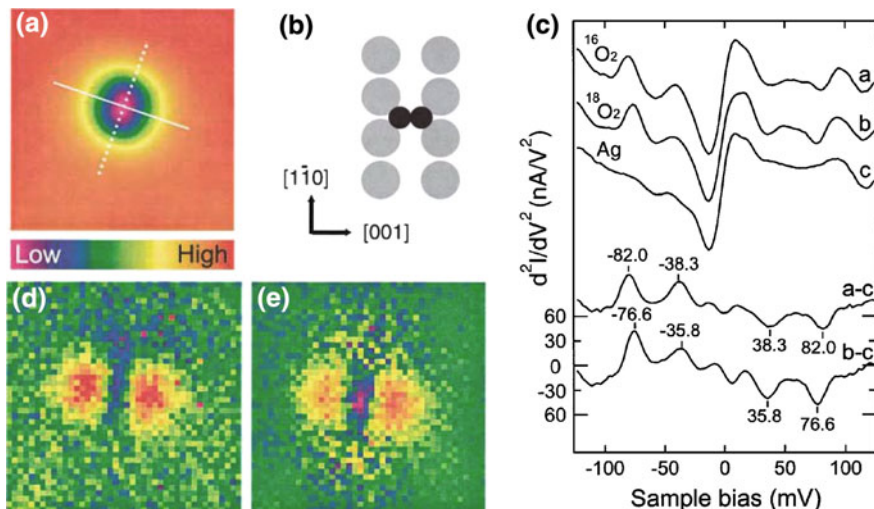


Fig. 2.3 STM-IETS measurements of $\text{O}_2/\text{Ag}(110)$. **a** STM image of a single O_2 molecule on $\text{Ag}(110)$ (size: $25 \text{ \AA} \times 25 \text{ \AA}$). **b** Schematic of the adsorption structure. The O_2 molecule is oriented in the $[001]$ direction. **c** IETS recorded over a point by $1.6 \text{ \AA}$ far from the molecular center along the $[001]$. **a**, **b**, and **c** represent the spectra of $^{16}\text{O}_2$, $^{18}\text{O}_2$, and the bare Ag surface, respectively. IETS spatial maps recorded at $V = \text{d} - 76.6$ and $\text{e} - 35.8$ mV (size: $12 \text{ \AA} \times 12 \text{ \AA}$). The former and latter are assigned to the O–O stretching mode and the asymmetric O_2 – Ag stretching mode, respectively. Reprinted with permission from Ref. [31]. Copyright 2000 by American Physical Society

tunneling process can exist, as shown in Fig. 2.2c; in this process, electrons give energies of $\hbar\Omega$ to adsorbates (vibrational excitation), and the equivalent energy is returned (de-excitation). The tunneling current in this process I_{ela} would make a negative contribution to the total current, as shown by the green curves in Fig. 2.2d–f. The actual measured current (black curves in Fig. 2.2d–f) is the sum of these processes, i.e., $I(V) = I_0(V) + I_{\text{ine}}(V) + I_{\text{ela}}(V)$, which determines the structure of the d^2I/dV^2 spectrum [27–30].

Paulsson et al. [29, 33] developed a theoretical method to propose that the intensity ratio of the inelastic and elastic tunneling components depends on the energy levels of MOs of the adsorbates. When the orbitals are located far from the Fermi level (i.e., off-resonance), the inelastic tunneling component dominates, increasing the tunneling conductance, leading to a peak (dip) in the IET spectrum at a positive (negative) sample bias. In contrast, the MO located at the Fermi level enhances the elastic component (on-resonance), which attenuates the total tunneling conductance and causes a dip (peak) in the IET spectrum at a positive (negative) sample bias.

The latter case has previously been reported in IETS of the $\text{O}_2/\text{Ag}(110)$ system (Figs. 2.3 and 2.4). As shown in Fig. 2.3c, the d^2I/dV^2 spectra recorded over the single molecule has two dips (two peaks) at positive (negative) sample biases [31]. In this system, the spin-polarized resonance state of the $\text{O}_2 \pi$ orbital ($\pi_g^\perp$) is located at the Fermi level (Fig. 2.4b). DFT calculations have successfully reproduced the

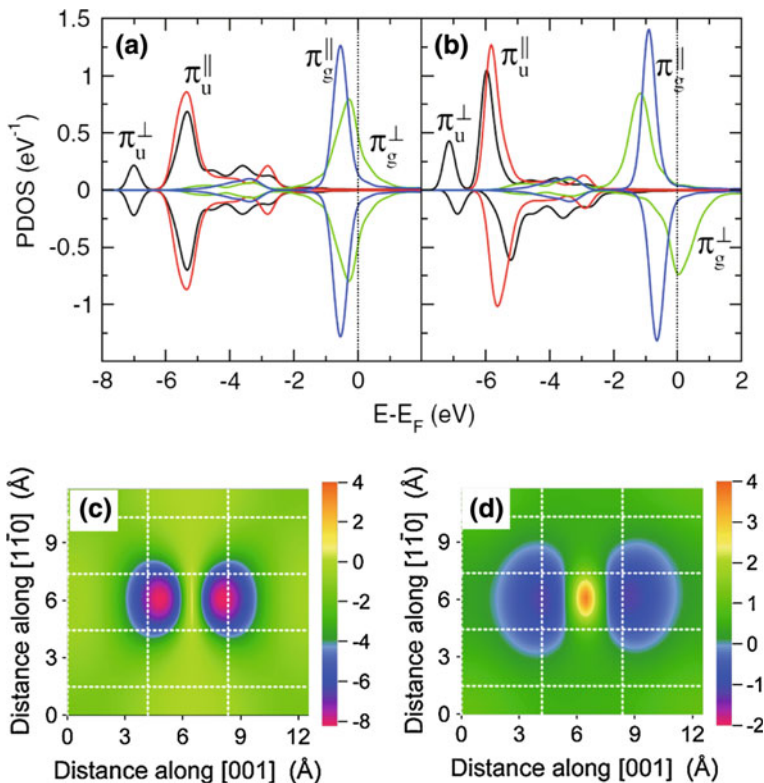


Fig. 2.4 Theoretical calculations of an O₂ molecule oriented in the [001] direction on Ag(110). **a** Projected DOS calculated by DFT-GGA. **b** Spin-resolved projected DOS calculated by DFT+*U* (*U* = 3 eV). Calculated spatial distributions of the conductance change $\frac{\Delta\sigma}{\sigma}$ for **c** the O–O stretching mode and **d** the asymmetric O₂–Ag stretching mode. Reprinted with permission from Ref. [32]. Copyright 2010 by American Physical Society

experimental spatial distribution of the peak intensities (Figs. 2.3c, d and 2.4c, d) [32, 34]. Very recently, characteristic on-resonant features were also observed in IETS of H₂O bonded to an ultrathin NaCl film on Au(111) [35]; the IETS intensities were enhanced by bringing the STM tip closer to the adsorbate, and the lineshapes changed from symmetric dips to asymmetric features in the d^2I/dV^2 spectra. Based on theoretical modeling, the authors argued that the modifications to the IETS result from the energy shift of the highest occupied MO states toward the Fermi level [35]. However, in another case, the d^2I/dV^2 spectrum of fullerene C₆₀ adsorbed onto Cu(111) had no characteristic structure, although a resonance state was observed near the Fermi level [36]. Because only a few IETS studies have been carried out in combination with STS [36, 37], the experimental understanding of the correlation between the vibrational modes and the electronic states of the adsorbates remains insufficient.

2.1.1.3 IETS Propensity Rules

In contrast to the intuitive selection rules of infrared and Raman spectroscopy, definitive selection rules to predict IETS-active/inactive vibration modes have not been established. Nonetheless, recent theoretical studies have demonstrated valid models for elastic and inelastic tunneling processes and have successfully reproduced experimental STM-IET spectra [29, 38–42]. As described above, the vibrational modes that can be detected in IETS are correlated with the electronic state of the adsorbates, which determines the IETS intensities and distributions.

Here I describe “propensity rules” of IETS proposed by Lorente and coworkers [27, 32, 34, 38], who developed the methodology based on the many-body extension of the Tersoff–Hamann theory for the STM [24]. The inelastic $\Delta\sigma_{\text{ine}}$ and elastic $\Delta\sigma_{\text{ela}}$ components of the differential conductance $\Delta\sigma$ are represented by

$$\Delta\sigma_{\text{ine}}(\mathbf{r}_0) = \sum_{\mu} \left| \sum_{\lambda} \frac{\langle \psi_{\mu} | v | \psi_{\lambda} \rangle \psi_{\lambda}(\mathbf{r}_0)}{\varepsilon_{\mu} - \varepsilon_{\lambda} + i0^+} \right|^2 \times [1 - f(\varepsilon_{\mu})] \delta(E_F + eV - \hbar\Omega - \varepsilon_{\mu}), \quad (2.5)$$

and

$$\Delta\sigma_{\text{ela}}(\mathbf{r}_0) = -2\pi^2 \sum_{\mu} \left| \sum_{\lambda} \langle \psi_{\mu} | v | \psi_{\lambda} \rangle \psi_{\lambda}(\mathbf{r}_0) [1 - f(\varepsilon_{\lambda})] \delta(\varepsilon_{\lambda} - \hbar\Omega - \varepsilon_{\mu}) \right|^2 \times [1 - f(\varepsilon_{\mu})] \delta(E_F + eV - \hbar\Omega - \varepsilon_{\mu}), \quad (2.6)$$

respectively, where $\mathbf{r}_0$ denotes the position of the tip apex, v is the local electron-vibration potential for a vibrational mode with energy $\hbar\Omega$, $|\psi\rangle$ is the electronic state with the eigenenergy ε , $f(\varepsilon)$ represents the Fermi–Dirac distribution, and $\delta(x)$ is the Dirac delta function. An IET signal corresponds to the sum of these components, i.e.,

$$\Delta\sigma(\mathbf{r}_0) = \Delta\sigma_{\text{inel}}(\mathbf{r}_0) + \Delta\sigma_{\text{el}}(\mathbf{r}_0). \quad (2.7)$$

As shown in Eqs. (2.5) and (2.6), an IET signal requires $\langle \psi_{\mu} | v | \psi_{\lambda} \rangle$ to be nonzero. Therefore, an IETS feature is “allowed” if the following equation holds:

$$\Gamma_{\text{IETS}} \otimes \Gamma_{\text{vib}} \otimes \Gamma_{\text{STM}} = \Gamma_{\text{sym}}, \quad (2.8)$$

where $\Gamma_{\text{STM(IETS)}}$ denotes the symmetry representation of the $\psi_{\lambda(\mu)}$ states involved in the electron-vibration coupling induced during the tunneling process, which are projected on a topography of the STM image (IETS map), where Γ_{vib} denotes the symmetry representation of the corresponding vibrational mode, and where Γ_{sym} denotes the totally symmetry representation (e.g., A_1 for the C_{nv} point groups). Hitherto “propensity rules” have successfully explained the spatial distributions of

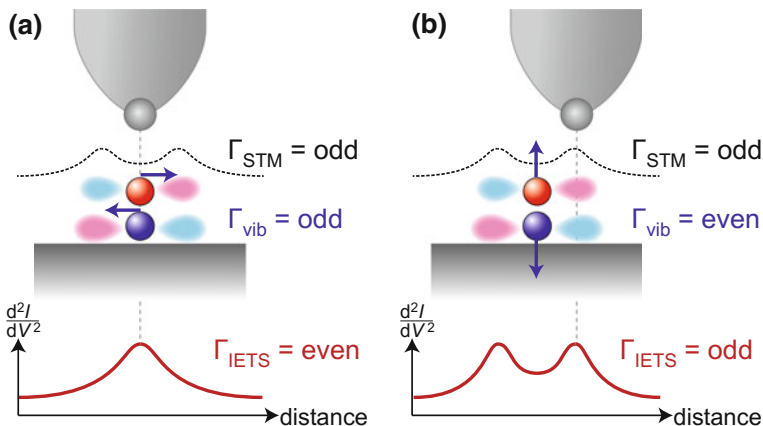


Fig. 2.5 Schematics of the correlation between the inelastic tunneling components and the electronic state of an adsorbate based on “propensity rules.” The resonance state contributing to the STM image is assumed to be the π^* orbital of a diatomic molecule bonded perpendicularly onto the surface. Then Γ_{STM} can be written as “odd” because the state has a node at the molecular center. The graphs at the *bottom* show the spatial distributions of inelastic components at the positive biases for **a** the frustrated rotational mode and **b** the intramolecular stretching mode of the molecule

IET signals for several systems, such as $\text{C}_2\text{H}_2/\text{Cu}(001)$ [27, 38], $\text{CO}/\text{Cu}(100)$ [38], $\text{O}_2/\text{Ag}(110)$ [32, 34], and $\text{HCOO}/\text{Cu}(111)$ [43].

Figure 2.5 shows typical examples of the use of Eq. (2.8). The sample is a diatomic molecule adsorbed upright on a metal surface. We assume that the antibonding π orbital contributes dominantly to the tunneling process, and that the tip apex is a metal atom with an s orbital. Providing the frustrated mode can be detected in IET spectrum recorded over the molecule, the maximum IET signal should appear over on top of the molecule (Fig. 2.5a). For the intramolecular stretching mode, on the other hand, the spatial distribution of the corresponding IET signals is expected to the similar shape to the π orbital. The intensity distribution has a node at the molecular center (Fig. 2.5b).

Although “propensity rules” given by Eq. (2.8) allow us to understand the shape of the spatial distribution of IETS, they do not give quantitative information about the intensity of the IETS signal. Indeed, previous studies have reported that the IET intensities strictly depend on the functional groups of the adsorbates [44, 46, 47], and some peaks that disagree with the “propensity rules” were detected in the experimental spectra [48]. Thus, to develop the “propensity rules” into a definitive selection rule for IETS, further theoretical and experimental studies are required.

In addition, the STM-IETS peak intensities can also be affected by the structure of the tip [49–52]. For example, for a single O_2 molecule of the $\text{Ag}(110)$ surface in a configuration oriented along the $[1\bar{1}0]$ direction, the IET spectrum recorded with a typical metal tip has no characteristic structure, whereas vibrational peaks were observed by using a tip functionalized with a CO molecule [50]. Garcia-Lekue

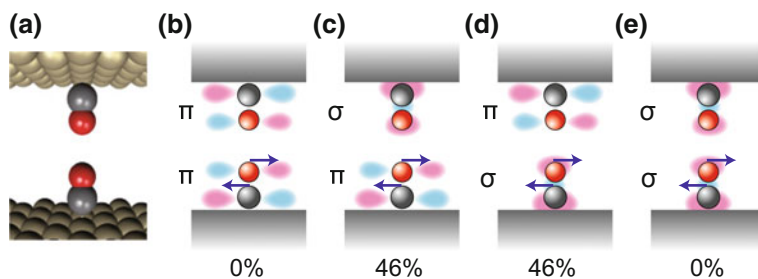


Fig. 2.6 Schematics of the correlation between the inelastic tunneling components and the MOs of the tip and sample. **a** Atomic structure of the system. Both the tip and the sample correspond to CO adsorbed on the Cu(111) surface, assuming that CO at the tip apex is located over on top of CO on the Cu(111) substrate. **b–e** Possible couples of the frontier MOs. The figure at the *bottom* of each panel indicates the ratio of the couple to the inelastic tunneling component for the frustrated rotational mode (35 meV) of CO of the sample calculated by Garcia-Lekue et al. [45]. **a** Reprinted with permission from Ref. [45]. Copyright 2011 by American Physical Society

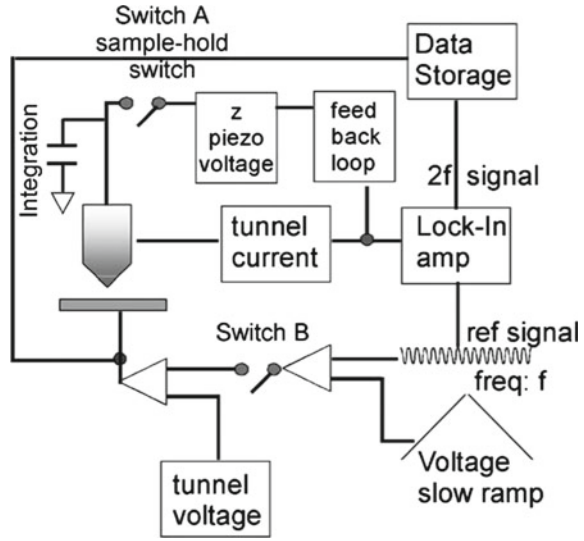
et al. [45] calculated the peak intensities using DFT and the IETS distributions with a metal tip and a molecule-functionalized tip. Figure 2.6a shows the calculated model of CO/Cu(111) with a CO-functionalized tip. The tip is fixed over on top of the CO molecule on the surface. Figure 2.6b–e show the possible couples between the frontier MOs of the tip and sample. The contribution of each couple to the inelastic tunneling component was calculated for the frustrated rotation mode of the sample-CO.¹ This result indicates that the IETS peaks of this frustrated rotational mode can be mainly ascribed to the inelastic components of the σ -to- π tunneling (Fig. 2.6b) and π -to- σ tunneling (Fig. 2.6c). On the other hand, the inelastic processes of the π -to- π tunneling (Fig. 2.6b) and the σ -to- σ tunneling (Fig. 2.6e) are unfavorable for this mode.

2.1.1.4 Lock-In Detection

In general, the relative changes in conductance ($\Delta\sigma/\sigma$; see Fig. 2.2d) are a few percent [11]; thus, such weak signals are probably not detectable by numerical differentiation of the I - V curves. Consequently, lock-in detection is usually employed to record STM-IETS signals [9]. Figure 2.7 shows a schematic diagram of the experimental setup [12]. A lock-in amplifier detects the first/second derivative tunneling current signals during the slow ramping of the sample bias. Then the primary sample bias V_0 is superimposed by a modulation bias $\Delta V \sin \omega t$, i.e., $V = V_0 + \Delta V \sin \omega t$. Under the modulation, the tunneling current $I(V)$ is described by the following equation using a Taylor series expansion:

¹The sum of the contribution ratios shown in Fig. 2.6b–e is not equal to 100% because there are contributions from other poorly conductive orbitals.

Fig. 2.7 Schematic diagram of an experimental setup for STM-IETS measurements Ref. [12]. Switch A controls the current feedback circuit. Switch B enables slow ramping and modulation of the sample bias voltage. To perform IETS, Switch A is opened, followed by the closing of Switch B. Reprinted from Ref. [12], Copyright 2005, with permission from Elsevier



$$\begin{aligned}
 I(V) &= I(V_0 + \Delta V \sin \omega t) \\
 &= I(V_0) + \frac{dI}{dV} \Delta V \sin \omega t + \frac{1}{2} \frac{d^2 I}{dV^2} (\Delta V \sin \omega t)^2 + \dots \\
 &= I(V_0) + \frac{dI}{dV} \Delta V \sin \omega t + \frac{(\Delta V)^2}{4} \frac{d^2 I}{dV^2} \left[1 + \sin \left(2\omega t - \frac{\pi}{2} \right) \right] + \dots
 \end{aligned} \tag{2.9}$$

According to this equation, a dI/dV ($d^2 I/dV^2$) signal is obtained at the modulation frequency ω (the harmonic of the modulation frequency 2ω) and the phase difference between the signal and reference of 0° (-90°).

The modulation of the sample bias causes uncertainty of the tunneling electron energies [53]. Therefore, using a large modulation bias worsens the energy resolution while improving the signal-to-noise ratio. Peak width (W) in a $d^2 I/dV^2$ spectrum is expressed by the following equation [13, 54, 55];

$$W \approx \sqrt{W_1^2 + (1.7V_{\text{mod}})^2 + (5.4k_B T)^2}, \tag{2.10}$$

where W_1 denotes the intrinsic width of the vibration, $V_{\text{mod}} = \frac{\Delta V}{\sqrt{2}}$ is the effective value of the modulation voltage, k_B is the Boltzmann constant, and T is the temperature. As described by Eq. (2.10), the energy resolution of IETS depends on temperature, and thus samples should typically be kept at a temperature below 10 K.

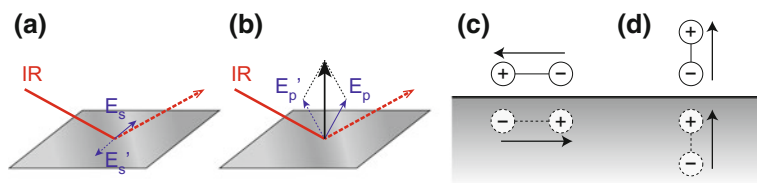


Fig. 2.8 Schematic illustrations of **a** s-polarized and **b** p-polarized lights irradiating a metal surface. The interference between the injected and reflected lights occurs at the surface. Schematic illustrations of dynamic dipole moments, which are oriented **c** perpendicular and **d** parallel to a metal surface, of adsorbate molecules. The correlation between the dynamic dipole and its mirror dipole is represented

2.1.1.5 STM Manipulation

With STM, under certain conditions, we can move individual atoms and molecules on a surface to arbitrary positions [56, 57]. This technique, STM manipulation, enables the bottom-up fabrication of complexes from isolated atoms or molecules. STM manipulation is classified roughly into two kinds: “lateral manipulation,” where target atoms/molecules are moved along the surface to other sites [56], and “vertical manipulation,” where atoms or molecules are transferred between the tip apex and the surface [58]. In both cases, the tip–sample distance is set shorter than that used in typical scanning conditions. The availability of STM manipulation (whether a target molecule can be manipulated) is determined by the competition between the substrate–molecule and tip–molecule interactions.

2.1.2 Principles of RAIRS

Reflection adsorption infrared spectroscopy (RAIRS)² is one of the most powerful methods of chemical analysis for surfaces [59–61]. Infrared light irradiating a sample surface can be absorbed into molecules on the surface if the energy of the light is equal to the eigenenergy of the vibrational modes of the molecules, resulting in the excitation of molecular vibration. The vibrational spectra can be obtained by measuring the intensity of the light reflected from the sample.

If an s-polarized light, which has the oscillating electric field normal to the incidence plane, is injected into a metal surface, the reflection light has the antiphase oscillating field (Fig. 2.8a). Therefore, the interference between the injected and reflected lights compensates their amplitudes; consequently, the electronic field of the standing wave near the surface becomes almost zero. In contrast, irradiating with p-polarized light—which has the oscillating field parallel to the incidence plane—at a grazing angle generates a strong electronic field due to the standing waves near

²Also known as infrared reflection absorption spectroscopy (IRAS).

the surface (Fig. 2.8b). For these reasons, only vibrational modes that have nonzero surface-normal components of the dynamic dipole moment can interact with a p-polarized injection wave, giving rise to the RAIRS “surface selection rules.”

This selection rule can also be explained from the viewpoint of the dynamic dipoles of molecules adsorbed onto a metal surface. In case that the dynamic dipole of a vibrational mode of an adsorbate is oriented parallel to the surface, a mirror dipole with the opposite charge appears on the metal surface (Fig. 2.8c). Because the mirror dipole counterbalances the molecular dynamic dipole, this vibrational mode is RAIRS-inactive. On the other hand, a dynamic dipole oriented normal to the surface causes a mirror dipole aligned in the same direction, leading to double sensitivity to infrared light. As a result, vibrations of the adsorbate system belonging to totally symmetric modes can absorb the injected infrared light and appear as peaks in the RAIR spectrum.

2.1.3 Principles of EELS

Electron energy loss spectroscopy (EELS)³ is a typical vibrational spectroscopy for molecules adsorbed onto a surface [62], in addition to RAIRS. When electrons with energies of several electron-volts are injected into a metal surface, most electrons are scattered elastically; however, several electrons are scattered after exciting the vibrational modes of the adsorbates or phonon modes of the substrate. Because the inelastically scattered electrons lose energies equivalent to the vibrational eigenenergies, the loss energy distribution of scattered electron intensities corresponds to the vibrational spectra of the surface. Owing to its high sensitivity, EELS can provide spectra at lower frequencies than RAIRS. However, the energy resolution of EELS is about $20\text{--}30\text{ cm}^{-1}$ in general ($\sim 5\text{ cm}^{-1}$ at the most), which is worse than that of RAIRS.

At a metal surface, incident electrons can be scattered inelastically by the following three processes: (i) dipole scattering, (ii) impact scattering, and (iii) negative-ion resonance scattering. In (i), vibrational modes are excited by the long-range interactions between the electronic field of the incident electrons and the dynamic dipole of adsorbates. This excitation mechanism complies with the same surface selection rules as those of RAIRS (Fig. 2.8c, d), and active modes should have a surface-normal component of the dynamic dipole moment. For the vibrational modes excited by this process, the peak intensities in the EEL spectrum are maximized when the exit angle is equal to the incident angle, i.e., in specular geometry. By comparing this specular spectrum with off-specular spectra, contributions to the process (i) can be discriminated from the contributions of the other mechanisms. In (ii), vibrational modes are excited by the dynamic impact of incident electrons. This scattering cross-section is

³Vibrational spectroscopy with EELS is often described as high-resolution electron energy loss spectroscopy (HREELS) to be clearly distinguished from EELS measured with transmission electron microscope (TEM). In this thesis, HREELS is described simply as EELS.

much smaller than that of (i). The peak intensities ascribed to this process are independent of the exit angle. In (iii), vibrational modes are excited by trapping incident electrons in empty states of adsorbates. This scattering cross-section is extremely large. Peak intensities ascribed to this process strictly depend on the energy of the incident electrons.

2.2 Methods

2.2.1 STM Methods

The STM experiments were conducted in an UHV chamber at Kyoto University. The pressure in the chamber was kept below 5×10^{-11} Torr during the STM measurements. An STM tip was made from a tungsten wire (with a diameter of 0.2 mm) etched electrochemically with NaOH solution (~ 2 mol/L) [63]. The STM images were acquired in constant-current mode at 6 K or 79–92 K. A sample bias V of 30 mV and a tunneling current I of 0.5–5 nA were used as typical scanning parameters and modified as required.

The surface was exposed to sample gasses (NO, CO, H₂O, methanol (CH₃OH), and ethanol (CH₃CH₂OH)) via a tube doser positioned ~ 1 cm from the surface maintained less than 15 K through a variable leak valve.

2.2.1.1 Preparation of Clean Surfaces

Single-crystalline Cu(110), Cu(001), and Cu(111) surfaces were cleaned by repeated cycles of Ar⁺ sputtering and annealing at ~ 650 K. The cleanness of the surfaces was checked by STM observation. The upper panels of Fig. 2.9 show the STM images of the clean Cu surfaces. Atomically resolved images of the surfaces are only observed when the tip apex is specially sharpened or when a molecule on the surface is attached to the tip apex (i.e., a molecule-functionalized tip) [64]. On the Cu(110) surface, the topmost Cu atoms aligned in the $[1\bar{1}0]$ direction (i.e., the atomic Cu rows) were observed as a striped pattern (Fig. 2.9a). Here, a_0 denotes the lattice distance along the Cu row (2.56 Å) whereas the atomic distance along the $[001]$ direction is defined as b_0 (3.61 Å). The lower panel of Fig. 2.9a shows the atomic structure of Cu(110) schematically, together with the typical adsorption sites. Adatoms and admolecules are bonded to the top of a topmost Cu atom (atop site), to a twofold bridge site in the $[1\bar{1}0]$ or $[001]$ directions (short-bridge and long-bridge sites, respectively), or on top of a Cu atom in the second layer (hollow site). In the STM image of Cu(001) (upper panel in Fig. 2.9b), each topmost Cu atom is visualized as a round protrusion. This surface has three kinds of typical adsorption sites: the atop, bridge, and hollow sites (lower panel in Fig. 2.9b).

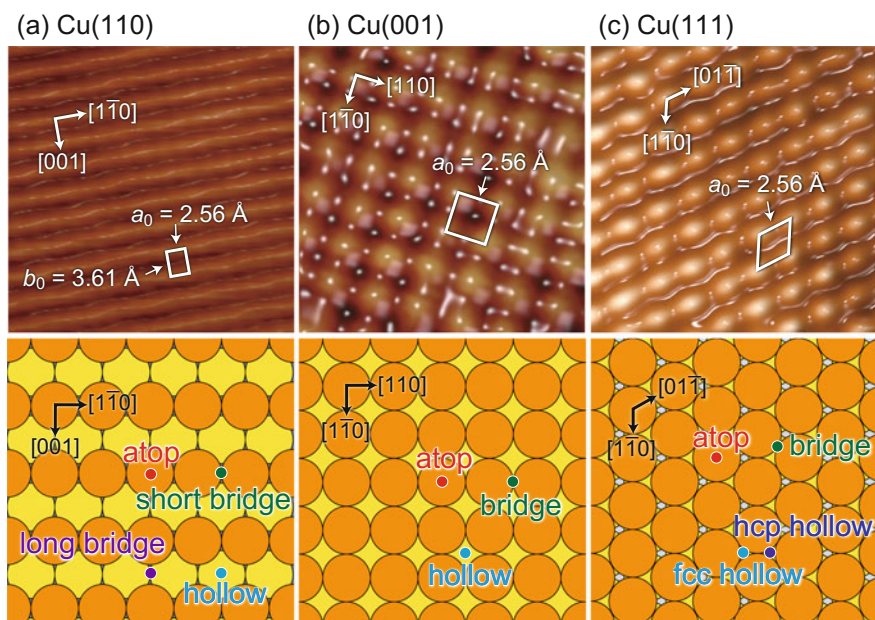


Fig. 2.9 STM images of clean **a** Cu(110), **b** Cu(001), and **c** Cu(111) surfaces at 6 K ($V = \mathbf{a}$ 20, **b** 30, and **c** 30 mV, $I = \mathbf{a}$ 0.05, **b** 5, and **c** 5 nA). The image sizes are **a** $40 \text{ \AA} \times 40 \text{ \AA}$, **b** $17 \text{ \AA} \times 17 \text{ \AA}$, and **c** $20 \text{ \AA} \times 20 \text{ \AA}$. The schematic illustrations of typical adsorption sites are also shown at the *bottom* of each image

For Cu(111), two kinds of threefold sites exist; one is on top of a Cu atom at the third layer (fcc hollow site), whereas the other is on top of a Cu atom in the second layer (hcp hollow site). Although the two hollow sites cannot be distinguished in the STM image shown in Fig. 2.9c, the positional relationship was clarified by STM images of Cu adatoms on the surface [65]. Figure 2.10a shows an STM image of a Cu adatom on the Cu(111) surface. The Cu atom was dropped from the tip apex by point contact between the tip and the clean surface [66]. Further point contact of the tip to another place induced another Cu atom of the tip apex to move onto the surface (Fig. 2.10b). It is known that on Cu(111), Cu adatoms are preferably located at the fcc hollow sites rather than the hcp hollow sites [65]. By using STM manipulation, the two Cu adatoms were made to approach each other, forming a Cu dimer (Cu_2) on the surface (Fig. 2.10c). The STM image of the dimer appears shredded because the Cu atoms are hopping between the hollow sites and rotating around the atop site [65]. Therefore, STM images of the adatoms and the dimer should be centered at the fcc hollow sites and the atop site, respectively, which uniquely specifies the positional relation between the fcc and hcp hollow sites, as shown in Fig. 2.10c.

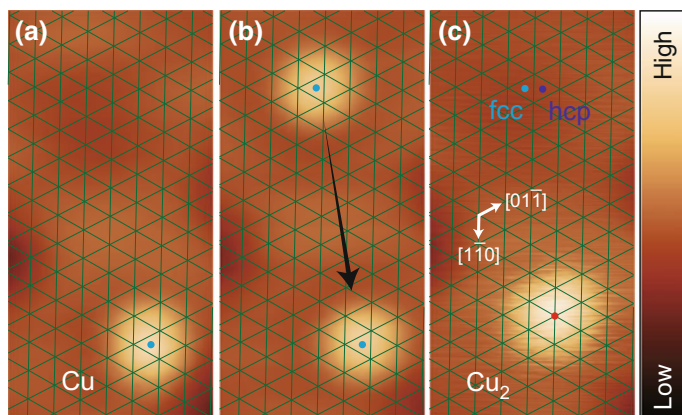


Fig. 2.10 **a** STM image of a Cu adatom on Cu(111) at 6 K ($V = 30$ mV, $I = 5$ nA, $15 \text{ \AA} \times 30 \text{ \AA}$). **b** Image of the same area as **a** after point contact between the tip and the bare surface to drop another Cu adatom onto the surface. **c** Image of the same area as **b** after manipulation of the upper adatom to make a Cu dimer ($V = 100$ mV). The *green lines* represent the lattice of the topmost Cu atoms. *Cyan* and *red dots* represent the locations of Cu adatoms and the center of the STM image of the Cu dimer, respectively

2.2.1.2 STS and IETS Measurements

For STS, dI/dV spectra were recorded in constant-height mode using a lock-in amplifier with a modulation voltage of $1\text{--}12 \text{ mV}_{\text{rms}}$ at 590 Hz according to the following procedure.⁴ When the tip was fixed over the target, the dI/dV signals were recorded during sweeping sample bias voltages with the current feedback loop open. After the measurements, the tip was moved to the bare Cu surface at the same tip height, and then, dI/dV spectrum was recorded for use as a background spectrum. Several spectra were recorded over the same target, and these were accumulated and averaged to improve the signal-to-noise ratio. The spectrum over the target is displayed after subtraction of the background spectrum. The reproducibility of the detected structure was confirmed by recording the spectra of several target molecules on the surface and by recording the spectra using different STM tip.

To visualize the spatial distributions of the LDOS, two-dimensional dI/dV spatial maps were recorded. A map was obtained in constant-height mode using a lock-in amplifier with a modulation voltage of $4\text{--}12 \text{ mV}_{\text{rms}}$ at 590 Hz . After the feedback loop was open, the bias voltage was fixed to a set value, and the dI/dV signals were recorded during the lateral movement of the tip.

For IETS, d^2I/dV^2 spectra were recorded in constant-current mode using a lock-in amplifier with a modulation voltage of $6\text{--}12 \text{ mV}_{\text{rms}}$ at 590 Hz using the following procedure. When the tip was fixed over the target, the d^2I/dV^2 signals were recorded while sweeping sample bias voltages with the current feedback loop open. After

⁴STS of NO/Cu(111) is an exception. The details of the method are described in Chap. 8.

the measurements, the tip was moved to the bare Cu surface with the feedback loop closed. The feedback was turned off again, and then, d^2I/dV^2 spectrum was recorded to be used as a background spectrum. Several spectra were recorded over the same target, and these were accumulated and averaged to improve the signal-to-noise ratio. The spectrum over the target is displayed after the subtraction of the background spectrum.⁵

Spatial maps of the d^2I/dV^2 signals were recorded in a similar manner to the STS maps mentioned above. A map was obtained in constant-current mode using a lock-in amplifier, and a topographic image was simultaneously obtained.

2.2.1.3 STM Manipulation

To induce molecules and adatoms on surfaces to move parallel on the surface, I carried out STM manipulation as follows. The tip-sample distance was set closer than usual parameters for scanning: $V = 10$ mV and $I = 20$ – 90 nA, leading to tunneling gap resistances of 0.1 – 0.5 M Ω . After that, the tip was shifted laterally at a speed of ~ 1 Å/s with the feedback loop closed. The successful manipulation was confirmed by a line profile of the tip-sample distance recorded during the tip motion; if a target molecule/atom is induced to move by the tip, a characteristic saw-tooth (or zigzag) wave is observed in the line profile [67, 68].

2.2.2 RAIRS Methods

The RAIRS experiments were carried out in an UHV chamber at the University of Tokyo. The RAIR spectra were obtained by using a Fourier-transform infrared spectrometer (Bruker IFS66v/S) with a mercury cadmium telluride (HgCdTe) detector (700 – 7500 cm^{-1}). The spectra were taken at 23 K with 2 – 4 cm^{-1} resolution and 500 – 1000 scans. A single-crystalline Cu(110) substrate was cleaned by repeated cycles of Ne^+ sputtering and annealing. The cleanness of the surface was checked by the low-energy electron diffraction (LEED) pattern and RAIR spectra of CO/Cu(110) at 80 K [69, 70]. NO molecules were introduced through a pulse gas dosing system. By referring to temperature-programmed desorption (TPD) and X-ray photoelectron spectroscopy (XPS) data of cyclohexane/Rh(111) as a function of pulse shot number [71, 72], the exposure per shot was estimated to be 6.5×10^{-3} L for NO.

⁵For IETS shown in Chap. 4, the background spectrum recorded over the bare surface was not removed, but it was confirmed that no characteristic structure was observed in the background.

2.2.3 EELS Methods

The EELS experiments were conducted in an UHV chamber at Kyoto University. The EEL spectra were obtained at 110 K with a primary energy of 7.0 eV at the incidence and reflection angles of 60° from the surface normal (LK-5000, LK Technologies, Inc.). The typical energy resolution was 25 cm^{-1} . A single-crystalline Cu(110) surface was cleaned by repeated cycles of Ar^+ sputtering and annealing. The cleanness of the surface was checked by the resonance phonon peak at 170 cm^{-1} [73]. NO molecules were introduced through a variable-leak valve to adsorb onto a clean surface at 110 K.

2.2.4 DFT Methods

Electronic structure calculations for NO molecules on Cu(110) and Cu(001) surfaces were performed with DFT and the GGA-PBE exchange-correlation functional [74] as implemented in the VASP code [75]. The projected-augmented-wave (PAW) method was used to describe the atomic cores [76, 77]. One or two NO molecules were placed on a 5-layer Cu slab exposing either the (110) or the (001) surface, using a lattice constant of $a = 3.64 \text{ \AA}$. Each slab was separated by about $11 \text{ \AA}$ of vacuum along the surface normal to reduce the interaction between periodic cells. Similarly, the single-adsorbate(s) limit was modeled with 4×5 surface cells, except for NO/Cu(001) for which a 4×4 cell was used to improve the symmetry of the low-frequency vibrational modes. The following parameters were used: an energy cutoff of 515 eV in the plane-wave basis set, a $4 \times 4 \times 1$ Monkhorst–Pack sampling of the Brillouin zone, and a first-order Methfessel–Paxton scheme [78] with a smearing of 50 meV for the orbital occupancies. Forces on the molecule(s) and on the two topmost layers were relaxed to $0.02 \text{ eV/\AA}$. Vibrational frequencies and modes were computed using finite displacements of $0.02 \text{ \AA}$ and a stringent electronic convergence criterion for accurate forces (total energies were converged to 10^{-6} eV). The adsorption energy per NO molecule is defined as $E_{\text{ads}} = (n \times E_{\text{NO}} + E_{\text{surf}} - E_{\text{system}})/n$, where E_{NO} is the energy of a single gas-phase NO, E_{surf} is the energy of the clean surface, and E_{system} the energy of the combined system with n NO molecules.

Spin-resolved projected density of states (PDOS) were computed using the implementation of Ref. [79] by projecting for each spin-state s the wave functions of the full system $\psi_{n,s,k}^{\text{TOT}}$ onto the wave functions of the free monomer or dimer $\varphi_{m,s}^{\text{MO}}$, i.e.,

$$\text{PDOS}_{m,s}(\varepsilon) = \sum_{n,k} |\langle \varphi_{m,s,k}^{\text{MO}} | \psi_{n,s,k}^{\text{TOT}} \rangle|^2 \delta(\varepsilon - \varepsilon_{n,s,k}). \quad (2.11)$$

In this expression $\sum_{n,k} \delta(\varepsilon - \varepsilon_{n,s,k})$ is the DOS of all $(n, \mathbf{k})$ states with spin s , where n and $\mathbf{k}$ refer to the band index and $\mathbf{k}$ points, respectively. The delta function is numerically approximated by a Gaussian function with smearing $\sigma = 0.2 \text{ eV}$. To

facilitate comparison to experiments, the PDOS shown in the figures below include a summation over spin.

Constant-current STM images were simulated with the Tersoff–Hamann approximation as the LDOS integrated within an energy window $[E_F, E_F + W]$ ($[E_F + W, E_F]$) for positive (negative) W values, where E_F denotes the Fermi level of the sample. IETS maps were computed using the theoretical model developed by Lorente et al., which is based on the many-body extension of the Tersoff–Hamann theory for the STM [27, 38, 80, 81]. The expressions used here take into account finite values of the vibrational quanta and voltage in evaluating the DOS [32, 34]. Specifically, the relative change in conductance $\Delta\sigma/\sigma$ is evaluated as the sum of the inelastic $\Delta\sigma_{\text{ine}}$ and elastic $\Delta\sigma_{\text{ela}}$ components normalized to the conductance σ , which are given for positive sample bias ($V > 0$) by

$$\frac{\Delta\sigma_{\text{ine}}}{\sigma} = \frac{1}{\rho(\mathbf{r}_0, E_F + eV)} \sum_{n,k} \left| \sum_m \frac{\langle \psi_{m,k} | \nu | \psi_{n,k} \rangle \psi_{m,k}(\mathbf{r})}{\varepsilon_{n,k} - \varepsilon_{m,k} + i0^+} \right|^2 \times [1 - f(\varepsilon_{n,k})] \delta(E_F + eV - \hbar\Omega - \varepsilon_{n,k}), \quad (2.12)$$

and

$$\frac{\Delta\sigma_{\text{ela}}}{\sigma} = \frac{-2\pi^2}{\rho(\mathbf{r}_0, E_F + eV)} \sum_{n,k} \left| \sum_m \langle \psi_{m,k} | \nu | \psi_{n,k} \rangle \psi_{m,k}(\mathbf{r}_0) \right|^2 \times [1 - f(\varepsilon_{m,k})] \delta(\varepsilon_{m,k} - \hbar\Omega - \varepsilon_{n,k})^2 \times [1 - f(\varepsilon_{n,k})] \delta(E_F + eV - \hbar\Omega - \varepsilon_{n,k}), \quad (2.13)$$

respectively, where σ denotes the differential conductance, $\rho(\mathbf{r}_0, E_F + eV)$ is the local DOS at the position $\mathbf{r}_0$ of the tip apex, and ν is the local electron-vibration potential for a vibrational mode with energy $\hbar\Omega$. Note that within the Tersoff–Hamann approximation, the change in conductance is interpreted as the change in the sample DOS at the tip apex caused by the vibration [27, 38, 80, 81]. Equations (2.12) and (2.13) give positive and negative d^2I/dV^2 signals, respectively, when $V > 0$. In practice, the change in the sample DOS and the LDOS $\rho(\mathbf{r}_0, E_F + eV)$ are integrated within an energy window $[E_F, E_F + W]$ in order to avoid the numerical limitation of having a finite number of states. All simulated topographies and IETS maps correspond to constant density contours of $\rho = 5 \times 10^{-9} \text{ e/\AA}^3$.

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