Vibrations of a molecule in an external force field

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The oscillation frequencies of a molecule on a surface are determined by the mass distribution in the molecule and the restoring forces that occur when the molecule bends. The restoring force originates from the atomic-scale interaction within the molecule and with the surface, which plays an essential role in the dynamics and reactivity of the molecule. In 1998, a combination of scanning tunneling microscopy with inelastic tunneling spectroscopy revealed the vibrational frequencies of single molecules adsorbed on a surface. However, the probe tip itself exerts forces on the molecule, changing its oscillation frequencies. Here, we combine atomic force microscopy with inelastic tunneling spectroscopy and measure the influence of the forces exerted by the tip on the lateral vibrational modes of a carbon monoxide molecule on a copper surface. Comparing the experimental data to a mechanical model of the vibrating molecule shows that the bonds within the molecule and with the surface are weakened by the proximity of the tip. This combination of techniques can be applied to analyze complex molecular vibrations and the mechanics of forming and loosening chemical bonds, as well as to study the mechanics of bond breaking in chemical reactions and atomic manipulation.

AFM | STM-IETS | vibration | CO molecule

The vibrational modes of a molecule on a solid surface are determined by the bonds within the molecule and with the surface, as well as its mass distribution (1, 2). The vibrations of ensembles of molecules can be studied experimentally by inelastic scattering techniques, where particles (e.g., helium atoms or electrons) with a fixed energy are scattered from molecules such as carbon monoxide (CO) adsorbed on surfaces. The energy loss of those particles is related to the excitation of vibrations (1, 2). Isotope-specific vibration spectra of individual molecules have been measured with a combination of scanning tunneling microscopy (STM) and inelastic electron tunneling spectroscopy (IETS), pioneered by Stipe et al. (3), where the excitation of a vibration appears as a peak in the second derivative of the current–voltage curve (4–6). STM-IETS also enables us to measure the vibrational state of a single molecule interacting with a nearby atom or molecule, e.g., the catalytic reaction between a CO molecule and O atoms on a silver surface can be controlled by changing their distance and tracked by STM-IETS (7). However, the presence of the STM tip is an additional perturbation source which can alter the vibrational spectrum of a molecule by the short-range force between them (8–11). For example, in a previous paper (8, 9), the tip-height-dependent vibrational energy of a CO molecule on a Cu(111) surface has been studied by STM-IETS, where the two lateral vibrational modes shown in Fig. 1C were investigated and the vibrational energy shift as a function of the vertical tip position was discussed based on density-functional theory (DFT) calculations (8). Taking into account that the recent works have revealed that the strength and direction of the short-range force exerted by the tip strongly depend on the tip apex structure (12, 13) and chemical element (14), interpretation of the energy shift only by STM-IETS is not straightforward. Force-field measurements by atomic force microscopy (AFM) (15–20) and STM-IETS allow us to precisely interpret the observed vibrational energy and thereby to understand the atomic-scale interactions with high quality. Here, we study a CO molecule adsorbed on an on-top site of a copper (111) surface with a metallic tip as a prototype system (Fig. 1B), and demonstrate that the combination of AFM with STM-IETS enables us to quantitatively connect the force acting on a CO molecule with its vibrational energy.

Results

First, the tip is laterally scanned above a CO molecule at constant height, obtaining a single dip in the current image (Fig. 1C) as well as in the frequency-shift image (Fig. 1D), confirming that the tip apex consists of a single atom (12, 13). Then, to determine the vertical and lateral force acting between the tip and CO molecule, the tip is scanned laterally along the x direction while changing the vertical position of the sensor z by 5 pm between subsequent scans, as shown in Fig. 1E (15, 20). Deconvoluting the frequency-shift distribution Δf(x, z) in the z direction yields the vertical force, which includes both short-range and long-range forces. The short-range force, F\(_x\)(x, z), can be estimated by subtracting the long-range force measured on the Cu surface far from the CO molecule, which is shown in Fig. 1F. Integration of F\(_x\)(x, z) in the z direction yields the potential energy U(x, z) between the CO molecule and the tip, as shown in Fig. 1G. Differentiation of the potential energy with respect to x provides the lateral force F\(_x\)(x, z) shown in Fig. 1H. The zero of the z axis is chosen at the “point contact,” where the tunneling conductance would reach the conductance quantum G\(_0\) = 2\(e^2/h\) ~ (12,906 Ω\(^{-1}\))

Significance

The vibration of a molecule adsorbed on a surface contains essential information on the molecule–surface bond, which is important to understand the surface reactions that occur, e.g., in catalytic reactions. Accessing the vibrational energies of a single molecule is possible by combining scanning tunneling microscopy with inelastic electron spectroscopy. However, the tip of a microscope exerts a force on a nearby molecule, and possibly even induces slight structural changes. To study this problem, we have further incorporated atomic force microscopy. The relationship between the exerted forces and vibrational energies is well reproduced by a classical mechanical model. This combined technique opens the possibility to study the atomic-scale interaction of a molecule on a surface with unprecedented precision.

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with a nonoscillating sensor. In Fig. 1E, z denotes the average vertical position of the oscillating sensor.

Fig. 1 I–K displays the normalized IETS spectra for the frustrated translational (FT) modes and the frustrated rotational (FR) modes for a distance range from z = 270 to 130 pm, where the normalized IETS spectra denote the second derivative of the IV curve (d²V/dV²) divided by the conductance (dI/dV). (During the IETS measurements, the tip oscillates with an amplitude of A = 20 pm. In Fig. 1 I–K, z denotes the average vertical position of the oscillating sensor.) The spectra were taken at the centers of the CO images which coincide with the position of the potential minima (Fig. 1 C and D) and the background IETS, measured on the Cu substrate (21), has been subtracted. Fig. IL displays the energy shifts extracted from Fig. 1 I–K as a function of distance z. While the FT mode increases almost by 30% for the closest tip–sample distances, the FR mode decreases in energy by a few percent only.

**Discussion**

To determine the effect of the tip position on the vibrational modes of the molecule, the effect of the vertical (F_z) and lateral (F_x) forces exerted by the tip on the CO molecule needs to be considered. As elaborated in SI Appendix, these forces are simply related by the action–reaction law to the forces (F_x, F_y) exerted by the molecule on the tip, shown in Fig. 1 F and H.

Fig. 2 A and B shows a schematic model describing CO lateral and vertical vibration modes. In the lateral modes, the vibrations are described by a classical double-pendulum model with arms l₁ and l₂, and the C and O atoms have masses m₁ and m₂. The potential energy of the pendulum is $U = D_10_1^2/2 + D_20_2^2/2$, where $0_1$ is the angle between the Cu–C bond and the surface normal and $0_2$ is the angle between the C–O bond and the surface normal. $D_1$ is the angular force constant that keeps the Cu–C bond upright (at $0_1 = 0$) and $D_2$ is the angular force constant that keeps the bonds Cu–C and C–O in line (at $0_2 = 0$). Using a
Mechanical model describing the oscillation of a CO molecule on a Cu(111) surface under the force field of the tip. The angular force constant $D_1$ keeps the angle between the Cu–C bond and the surface normal, $\theta_1$, close to its potential energy minimum at $\theta_1 = 0$, while $D_2$ straightens the Cu–C–O bond by keeping $\theta_2 - \theta_1$ close to the energy minimum at $\theta_1 = \theta_2$. Analysis of the measured frequency shifts at given external tip forces indicate five different mechanisms of energy shift. First, the lateral gradient of the tip–sample force $F_L$ ($K_L$) directly increases the lateral stiffness, leading to an increased oscillation frequency of the molecule. The vertical force also leads to bond lengthening in $l_1$ and $l_2$ as well as a decrease in $D_1$ and $D_2$. Next, we introduce the perturbation potential induced by the tip. To assess the influence of the tip–sample force on that potential, we assume that the force only acts on the O atom. The reasoning behind this assumption is that while attractive forces between atoms typically decay by a factor of 10 per 100 pm (= 1 Å), repulsive forces decay typically even faster and the O atom is at least 100 pm nearer to the tip’s front atom than the C atom. We discuss the hypothetical case where the force acts only on the C atom in SI Appendix.

The force between the tip and the O atom alters the potential, introducing a perturbation $U_{\text{tip}}$, neglecting terms beyond second order. The left column in Fig. 2C shows the deflection of the CO molecule in the frustrated translational mode and the

Fig. 2. Mechanical model describing the oscillation of a CO molecule on a Cu(111) surface under the force field of the tip. (A) Model for the lateral oscillation modes; the angular force constant $D_1$ keeps the angle between the Cu–C bond and the surface normal, $\theta_1$, close to its potential energy minimum at $\theta_1 = 0$, while $D_2$ straightens the Cu–C–O bond by keeping $\theta_2 - \theta_1$ close to the energy minimum at $\theta_1 = \theta_2$. (B) Model for stretch modes and bond elongations with longitudinal bond stiffness $K_1$ for the Cu–C bond and $K_2$ for the C–O bond. (C) Frustrated translational mode of CO and influence of the tip–sample force on the effective bond stiffness. For the free molecule, our mechanical model finds $\theta_2 = 1.19 \times \theta_1$. Analysis of the measured frequency shifts at given external tip forces indicate five different mechanisms of energy shift. First, the lateral gradient of the tip–sample force $F_L$ ($K_L$) directly increases the lateral stiffness, leading to an increased oscillation frequency of the molecule. The vertical component of the tip–sample force on the effective bond stiffness. For the free molecule, our mechanical model finds $\theta_2 = 2.33 \times \theta_1$. The rotational mode is subject to the same energy-shift mechanisms discussed for the frustrated translation. In contrast to the translational mode where $k_{x}^{\prime}$ and $F_{z}^{\prime}$ and a decrease in $D_1$ are the main causes for energy shifts, the rotational mode is most susceptible to $F_{z}^{\prime}$ and a decrease in $D_2$. A semiclassical approach similar to the calculations of phonons in crystals (22) with the Lagrange formalism (23), we solve the equation of motion for small oscillations of the double pendulum. From the vibrational energies $E_{\text{FT}} = 4.2$ meV and $E_{\text{FR}} = 35.4$ meV (8, 21, 24) and the bonding lengths $l_1 = 187$ pm and $l_2 = 115$ pm (25), the two angular force constants are calculated to be $D_1 = 135$ zNm and $D_2 = 216$ zNm. Quantization must be taken into account to estimate the zero-point amplitude of the vibrations: The FT mode has an energy spectrum given by $\varepsilon(n_{\text{FT}}) = (1/2 + n_{\text{FT}}) \times h\omega_{\text{FT}}$, where $h$ is Planck’s constant and $\omega_0$ is the angular frequency. The excitation number $n_{\text{FT}}$ is an integer and $h\omega_{\text{FT}} = 4.2$ meV. The FR mode is described by an analogous expression with $h\omega_{\text{FR}} = 35.4$ meV. Taking into account that the measured temperature of 4.4 K times Boltzmann’s constant ($k_B T = 0.38$ meV) is considerably smaller than the vibrational energies, the ground state can be assumed to be fully populated. Then the uncertainty in the $x$ position of the CO molecule due to Heisenberg’s uncertainty principle is estimated as $(h/2m_{\text{CO}}\omega_{\text{FT}})^{1/2} = 14$ pm with the CO mass of $m_{\text{CO}} = 28 \times u$, where $u$ is the unified atomic mass unit. The FR mode has an even smaller spatial uncertainty. Thus, the lateral displacement is well below 100 pm for both modes. For these small displacements, the CO molecule approximately feels a linear restoring force with the force constant $k_{x}^{\prime} = -dF_{z}^{\prime}/dx^{\prime}$ from the tip when the tip is located on the potential minimum (see Fig. 1H, Inset) along with vertical force $F_{z}^{\prime}$.

Next, we introduce the perturbation potential induced by the tip. To assess the influence of the tip–sample force on that potential, we assume that the force only acts on the O atom. The reasoning behind this assumption is that while attractive forces between atoms typically decay by a factor of 10 per 100 pm (= 1 Å), repulsive forces decay typically even faster and the O atom is at least 100 pm nearer to the tip’s front atom than the C atom. We discuss the hypothetical case where the force acts only on the C atom in SI Appendix.
corresponding energy scale below. The second column (lateral $F_{\text{L}}$) in Fig. 2C shows the influence of the lateral force gradient between tip and O atom at close distance. As outlined in the energy parabola below, the influence is quite large, comparable to the influence of an attractive vertical force shown in the third column (vertical $F_{\text{V}}$). The fourth column (bond elongation) illustrates the influence of bond lengthening due to the normal force—when the tip pulls at the CO molecule, the bonding lengths $l_1$ and $l_2$ become slightly longer for the vertical spring constants of $K_1 = 208 \text{ N/m}$ and $K_2 = 1,690 \text{ N/m}$ (SI Appendix). This will lower the frequency, but only by a minute amount—the influence on the potential had to be magnified by a factor of 10 to be noticeable in Fig. 2C. A stronger effect occurs when we assume that the presence of the tip directly influences the strength of the bonds between the Cu surface and carbon atom (decrease of $D_1$) and the bond angle of Cu–C–O (decrease of $D_2$). Fig. 2D discusses the various effects of the tip-sample force on the FR mode. While the FT mode is mainly influenced by $k_{\text{F}1}$, $F_{\text{F}1}$ and the decrease of $D_1$, the FR mode is mainly affected by $F_{\text{F}2}$ and the decrease of $D_2$.

Fig. 3 summarizes the experimental results and the comparison with the classical double-pendulum model. In Fig. 3A, the experimental energy-shift values from Fig. 1L are compared with the results from the model with unchanged angular force constants $D_1$ and $D_2$. While the FT mode shows a reasonable agreement between experiment and model, the FR mode experimentally drops slightly in energy, but should rise sharply according to the model. This discrepancy can be explained by the influence of the tip on the bonds between the oxygen atom, the carbon atom, and the substrate. While an ideal spring has a constant spring constant when elongated, a chemical bond is generally weakened when stretched. This bond softening (or hardening for reducing the bonding length) is already modeled in the widely used Morse potential (SI Appendix). Indeed, several previous studies indicate that the proximity of the tip during measurement changes the strength of the bonds between the CO molecule and the Cu surface. Barthes et al. (26) have found experimentally that CO adsorbed on Cu can be picked up by the tip. As the CO molecule has to flip around by 180° during pickup, the bond between CO and Cu surface must become weaker first, probably induced by the proximity of the biased tip and its associated electrostatic field (26). Hofer et al. (27) also find quite substantial relaxations of surface atoms at close tip proximity.

Further, a recent refined measurement of the force needed to move a CO molecule across a Cu surface has shown that this force is only about half as big as expected from the surface diffusion potential (20). Thus, we have to consider that the presence of the tip weakens the bond within the molecule and between the adsorbate and the substrate. To model this effect, we use the vertical force $F_{\text{F}1}$ as a parameter that describes the strength of the perturbation and introduce an empirical parameter $\beta$ that is a measure of the weakening of angular force constants $D_{1/2}$, yielding perturbed angular force constants $D_{1/2}' = D_{1/2} \times (1 - \beta \times F_{\text{F}1})$. The fit to experiment yields $D_1 = 143 \text{ zNm}$, $D_2 = 219 \text{ zNm}$, and $\beta = 0.033\%/\text{pN}$, amounting to a maximal weakening of $-5\%$ for $D_{1/2}$ at the maximal attractive force of $F_{\text{F}1} = 150 \text{ pN}$. As shown in Fig. 3B, the introduction of the bond softening effect yields an excellent fit between theory and experiment.

The tip-induced energy shift and its interpretation are further investigated with a tip presenting a different apex, which we call tip 2. We refer to the tip used for the data in Figs. 1 and 3 as tip 1. The force curves acquired by these two tips are shown in Fig. 4A, where we see that the maximum attractive force for tip 2 is 235 pN, i.e., 50% larger than that of the case of tip 1. In addition, the $z$ position showing the attractive force maximum is larger than that for tip 1 by 30 pm. The $z$-dependent vibrational energies of the FT and FR modes for tip 2 (SI Appendix) is plotted in Fig. 4B with the data by tip 1. Similarly to the case of tip 1, we see a small change in the FR mode energy and a large change in the FT mode energy. In addition, we see a prominent change of the FT mode energy for tip 2 than that of tip 1, which is consistent with the feature of the vertical force in Fig. 4A. The model calculation with and without the bond weakening (SI Appendix) supports the preference of the latter model as shown in Fig. 4C, where the best fitting is acquired by the following parameters: $D_1 = 145 \text{ zNm}$, $D_2 = 219 \text{ zNm}$, and $\beta = 0.029\%/\text{pN}$. These parameters are almost identical to the values in the case of tip 1: The validity of our model considering the bond elongation is confirmed.

The idea of bond elongation also enables us to explain the dependence of normalized IETS intensity on tip height, shown in Fig. 5A: The intensity increases sharply when reducing $z$ from 270 to 170 pm, flattens around $z = 150 \text{ pm}$, and finally decreases again for $z$ approaching 130 pm. To interpret this trend of intensity change, we note the two important factors in the IETS intensity (21): (i) the ratio of current passing through the CO molecule compared with through space tunneling, and (ii) the probability of the inelastic process per electron passing through the CO molecule. In Fig. 5B, the ratio of the tunneling current on the CO molecule to that on the Cu substrate ($I_{\text{CO}}/I_{\text{Cu}}$) is shown. Considering that a CO molecule is less electrically conductive than a vacuum gap (28)—it appears as a dip in a constant-height STM image—the minimum value of $I_{\text{CO}}/I_{\text{Cu}}$ observed at the $z$ position marked by the asterisk indicates that the fraction of electrons tunneling through the CO molecule is maximized. As shown in Fig. 5A, the IETS intensity also reaches its maximum at this $z$ position. The coincidence of the trend between the IETS intensity and $I_{\text{CO}}/I_{\text{Cu}}$ indicates the importance of the first factor (i) outlined above. Why does the ratio $I_{\text{CO}}/I_{\text{Cu}}$ show the dependence of Fig. 5B? One of the reasons is the structural change of the CO molecule by the short-range force shown in Fig. 5C, which can be separated into four distance regimes. In regime I, the tip is so far from the molecule that the force is negligibly small, in II the force is attractive, III indicates maximal attraction, and in IV the force becomes less attractive. When the force from the tip pulls on the CO molecule, the CO molecule and the Cu atom it is bonded to are pulled out of the surface, indicated by the schematic drawings in Fig. 5D (Right), which should contribute to the increase of the solid angle viewed from the tip to the CO molecule and result in the decrease of $I_{\text{CO}}/I_{\text{Cu}}$.

On the other hand, the reason of the increase of $I_{\text{CO}}/I_{\text{Cu}}$ after the
point marked by the asterisk is not known. Further theoretical studies of both elastic and inelastic transport based on combined DFT and nonequilibrium Green’s function calculations (29–31) are needed to fully understand the z-dependent elastic current and IETS intensity.

Finally, we would like to discuss the points which should be addressed in the future. As we described in the Introduction, there are previous studies using STM-IETS that have reported a tip-induced vibrational energy shift for the same CO/Cu(111) system as here. The data of ref. 9 are located between our data by the two different tips (SI Appendix): Both data are consistent. However, the significant decrease of the FT mode and FR mode energies observed in ref. 9 for their smallest z is not confirmed in the present study. This is because the lower limit of z is restricted in our present setup: Large currents induce uncontrolled tip oscillations for the very small z values that are expected to be needed to access the region of very strong energy decrease of FT and FR modes. To avoid the uncontrolled tip oscillation, we intentionally oscillate the tip during the IETS measurements, which leads to additional broadening of the IETS signal on top of the conventional broadening sources of the temperature and the modulation voltage. (Even when the feedback control of the amplitude is active, the uncontrolled oscillation occurs for a very small z.) This broadening prevents us from observing the lifting of the two degenerate vibrational modes of a CO molecule on a Cu(111) surface which is expected to occur when placing the tip on an asymmetrical position of the potential (i.e., off-center). This experimental hurdle should be overcome in the future.

Conclusion

We have measured the potential energy between a CO molecule on a Cu(111) surface and an apex of a metallic tip and its influence on the vibrational energy of the CO molecule. The data clearly show that bond elongation and bond weakening occur, because the mere addition of the perturbation force is insufficient to precisely reproduce the changes of the vibrational energies under the force field of the approaching tip. This finding indicates that if we use a CO functionalized tip as an atomically sized “cantilever” without an external oscillation source, we have to consider that this cantilever (32, 33) does alter its stiffness k due to tip-sample interaction. This is not the case for mesoscopic or macroscopic cantilevers that show a constant

Fig. 4. Vibrational energy shift for different tip apexes. (A) Short-range vertical force for the tip used in Fig. 1 (tip 1) and for a tip with a different apex (tip 2). Thin lines are acquired by sweeping the tip along the z direction, whereas thick lines are derived from 2D force-field measurements (Fig. 1E). In the latter case, both the vertical and the lateral components of the force are measured; however, the feasible z range is limited by the occurrence of CO manipulation. (B) The energies of the FT and FR modes for both tips as a function of the vertical tip position. (C) Experimental data (open squares), together with the model calculation with softened angular force constants (thick lines). The best-fit values for tip 2 are $D_1 = 145 \text{ zNm}$, $D_2 = 219 \text{ zNm}$, and $\beta = 0.029\%/\text{pN}$, which are almost identical to the values for tip 1.

Fig. 5. Bond elongation and IETS intensity. (A) IETS intensity for the FR (blue) and FT (red) modes as a function of z. (B) Ratio of the tunneling current over the CO molecule to the current over the Cu substrate. (C) Short-range force between CO and tip, indicating four characteristic regimes: (C, I) Large distance, weak attraction; (C, II) Shorter distance, stronger attraction; (C, III) Maximal attraction; and (C, IV) Weak attraction due to the onset of tip-sample repulsion. The dotted line is extrapolated. (D) Schematic of the four regimes and the corresponding stretch of the CO-surface bond.

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stiffness $k$ independent of the tip–sample interaction. The combination of AFM with STM-IETS allows us to precisely quantify these interactions.

**Methods**

All measurements were carried out at 4.4 K by an ultrahigh vacuum low-temperature STM and AFM (LT-SPM by ScientaOmicron GmbH) with custom-made qPlus force sensors (34) and custom-made filters for radio-frequency noise attenuation in spectroscopy measurements and for the frequency shift measurements. The qPlus sensor has a stiffness of $k = 1,800$ N/m, a resonant frequency of $f_0 = 55,031$ Hz, and is oscillated with a zero-to-peak amplitude of $A = 20$ pm. The sample substrate was a Cu(111) surface that was cleaned by repeated sputtering and annealing. The clean sample was then dosed with CO gas to create a low coverage of CO molecules.

The tip was made from a cut iridium wire, cleaned by field evaporation and poked into the copper surface several times in situ to prepare the tip, which was sharp and consisted of a single atom on its apex as confirmed by constant-height current and $\Delta f$ images (SI Appendix, Figs. 51 and 59) (carbon monoxide front atom identification) (12, 13). When the oscillating tip comes close to the sample, an average force gradient $<\Delta z>/\Delta x$ acts between tip and sample that shifts the resonant frequency of the sensor by $\Delta f = f_0<\Delta z>/2k$ (35). When this frequency shift $\Delta f$ is measured from a minimal $z$ value ($z_{min}$) up to a $z$ value where $\Delta f$ is essentially zero (a few nanometers are usually sufficient), the vertical force can be recovered from $\Delta f$ by first calculating the force gradient $<\Delta z>/\Delta x$ and, then, e.g., by using the Sader–Jarvis method (36), taking into account recent limitations of its applicability (37). The short-range force between the tip and the CO molecule, $F_z(z)$, is derived by subtracting the force curve on the Cu(111) surface from that on the CO molecule. Further integral of $F_z(z)$ yields the potential energy $U(z)$.

The 2D force components along the vertical ($z$) and lateral ($x$) direction were measured by consecutively scanning the tip along the $x$ direction, and decreasing the vertical distance for every scanline by 5 pm (SI Appendix, Fig. 52). The resulting 2D distribution of frequency shift $\Delta f(x, z)$ is converted to the 2D distribution of the vertical force by the Sader–Jarvis method (36). The 2D short-range vertical force, $F_z(x, z)$, is acquired by subtracting the vertical force on the Cu(111) away from the CO molecule. The integration of $F_z(x, z)$ along the $z$ direction results in the 2D distribution of the potential energy $U(x, z)$ (15, 20). Differentiation of the potential energy with respect to $x$ provides the 2D distribution of the lateral force $F_x(x, z)$.

The tunneling current $I$ is averaged over many cycles of the sensor oscillation, as the bandwidth of the current acquisition is smaller than $f_0$. To measure the conductance (dIdV) and IET signal (d$^2$I/d$^2$V), a modulation voltage (2,338 Hz and 1-mV$_{rms}$ amplitude) is added to the sample bias, and the first and second harmonics in the current are detected by a lock-in amplifier (HF2LI; Zurich Instruments). In the text, the IETS signal is normalized to the conductance ($6, 21$), i.e., (d$^2$I/d$^2$V)/dIdV has been plotted. The complete set of the IETS are shown in SI Appendix, Figs. 53, 54, and 510.

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