Microscopic origin of molecule excitation via inelastic electron scattering in scanning tunneling microscope

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Abstract
The scanning-tunneling-microscope-induced luminescence emerges recently as an incisive tool to measure the molecular properties down to the single-molecule level. The rapid experimental progress is far ahead of the theoretical effort to the observed phenomena. Such incompetence leads to a significant difficulty in quantitatively assigning the observed feature of the fluorescence spectrum to the structure and dynamics of a single molecule. This work is devoted to revealing the microscopic origin of the molecular excitation via inelastic scattering of the tunneling electrons in the scanning tunneling microscope. The theory proposed here excludes the inelastic electron scattering as the origin of the observed larger photon-counting rate at the positive bias than that at the negative bias voltage.

1. Introduction
The physical limitation of conventional semiconductor devices spurs the recent development of single-molecule photoelectronics [1–3] where incisive tools to probe single molecular structure and dynamics are of great demand. Combining the high resolution of scanning tunneling microscope (STM) with the specificity of fluorescence spectroscopy of molecules, STM-induced luminescence (STML) provides an ideal tool for studying the photon emission and dynamics on the single-molecule level [4, 5]. By introducing an insulating film, one decouple the molecule and metal substrate to avoid fluorescence quenching [6, 7]. Experimental breakthroughs have allowed direct observations of the single-molecule properties, e.g., the control of electron transport in the single-molecule junction [8], the dipole–dipole coupling between molecules [9–11], the energy transfer in molecular dimers [12], and the Fano-like lineshape [13–15]. However, the retarded theoretical followup prevents us from conclusively understanding the single-molecule properties through the quantitative analyses of experimental data.

Such a lack of the corresponding theoretical effort has led to inconsistency between experimental explanations. The underlying origin of the asymmetric emission intensity at positive and negative bias between the tip and substrate was assigned to the carrier-injection mechanism [9], while it was also understood as inelastic electron tunneling (probably mediated by the localized surface plasmon) [16] for the same molecule, i.e., the single ZnPc molecule. The question exists even on the asymmetry with larger tunneling current at positive bias or vice versa [9, 16]. The inconsistency remains unresolved mainly due to the absence of microscopic theory which can determine the properties of the different tunneling mechanisms that are mixed in the \textit{ab initio} calculations [17, 18].

In this work, we reveal the underlying microscopic origin of the inelastic electron scattering down to the basic Coulomb interaction between the tunneling electron and the single molecule. Our theory shows the asymmetry with a larger tunneling current as well as a larger photon-counting rate at negative bias, in turn, excludes the possibility of the opposite asymmetry to be attributed to the inelastic electron scattering. Such an attempt shall initiate the understanding of the experimental feature from its microscopic origin and stimulate the theoretical studies of the STML.
2. Model for the inelastic tunneling electron scattering mechanism

For the clarity of the notation, we sketch the design of the single-molecule STML in figure 1(a). As a demonstration, we show a single molecule as a dipole with a positive (red) and negative (blue) charge on a salt-covered metal substrate. The later discussion is performed on the multi-electron molecule for the general purpose. A metal tip is positioned above the substrate plane. Both the tip and substrate are typically made of a noble metal, e.g., silver (Ag). To reduce the nonradiative energy transfer between the molecule and metal substrate, the thin NaCl film is applied to decouple molecule and substrate. With a nonzero bias voltage, an electron (black) from one electrode excites the molecule via the Coulomb interaction during its tunneling through the vacuum and then enters into the other electrode (see figure 1(b)). Subsequently, the excited molecule emits a photon via the spontaneous emission, which is measured by the photon counting to reveal molecular properties.

The Hamiltonian is divided into three parts as $\hat{H} = \hat{H}_d + \hat{H}_m + \hat{H}_{d-m}$, where $\hat{H}_d$ is the Hamiltonian of the tunneling electron between the tip and substrate, $\hat{H}_m$ is the Hamiltonian of the molecule, and $\hat{H}_{d-m}$ is the interaction between the tunneling electron and the single molecule. The Hamiltonian of the tunneling electron is $\hat{H}_d = -\nabla^2/2m_e + V(\vec{r})$, where $V(\vec{r})$ is the potential for the tunneling electron at position $\vec{r} = (x, y, z)$ and $m_e$ is the mass of an electron. The wave functions are written for different regions [19, 20] as

$$\hat{H}_d \phi_k \simeq \tilde{\xi}_k \phi_k,$$

$$\hat{H}_d \phi_n \simeq \tilde{E}_n \phi_n,$$

where $\hat{H}_d$ ($\hat{H}_{d,s}$) is the Hamiltonian of the free tip (substrate) obtained by neglecting the potential in the substrate (tip) region. $|\phi_k\rangle(|\phi_n\rangle)$ is the eigenstate of free tip (substrate) with $\tilde{\xi}_k \equiv \xi_k + eV_b(\tilde{E}_n \equiv E_n)$ where $\xi_k$ ($E_n$) is the eigenenergy with zero bias voltage. The detailed forms of the wave functions are discussed in appendix A. The Hamiltonian of the molecule is simplified as a two-level system [21, 22]

$$\hat{H}_m = E_c |\chi_c\rangle\langle\chi_c| + E_b |\chi_b\rangle\langle\chi_b|,$$

where $|\chi_c\rangle(|\chi_b\rangle)$ is its excited (ground) state with energy $E_c$ ($E_b$). This simplification is reasonable since only two levels are accessible for one particular bias. More spectral features can be explained by adding energy levels for different bias voltages and the electron–phonon coupling [23]. To demonstrate the coupling mechanism and for clarity, we make the simplification of the two-level molecule.

The key element to understand the mechanism is the interaction between the molecule and the tunneling electron. The interaction between the single tunneling electron and the molecule, simplified from the Coulomb interaction, resembles the electron–dipole interaction as (see appendix B)

$$\hat{H}_{d-m} \simeq -\frac{\hat{\mu} \cdot \vec{r}}{r^3},$$

where $\hat{\mu} = -Ze\vec{r}_0$ denotes the effective electric dipole moment operator of the molecule. $Z$ is the effective charge number, and $\vec{r}_0$ stands for the vector of the center of the electrons in the molecule. Here, we have
chosen the central position of the positive charge of the molecule as the origin of the coordinate system.

The interaction is rewritten explicitly with the basis of the wave functions of the single molecule and tunneling electron as

\[
\hat{H}_{\text{el-m}} \simeq \sum_{n,k} \mathcal{N}_{nk\lambda}\ket{V_{b,\lambda} - \xi_G} \hat{\sigma}_x \bra{\phi_k} \langle \varphi_n \rangle \\
\simeq \sum_{n,k} \mathcal{N}_{nk\lambda}\ket{V_{b,\lambda} - E_n} \hat{\sigma}_x \bra{\varphi_n} \langle \phi_k \rangle.
\]

(3)

We have defined the transition matrix element \( \mathcal{N}_{nk\lambda}\ket{V_{b,\lambda} - \xi_G} \equiv -e \vec{\mu} \cdot \langle \phi_k \rangle \hat{\vec{r}} / |\vec{r}| |\varphi_n \rangle \) from substrate’s state \( \ket{\varphi_n} \) to tip’s state \( \ket{\phi_k} \) and \( \mathcal{N}_{nk\lambda}\ket{V_{b,\lambda} - E_n} \equiv -e \vec{\mu} \cdot \langle \varphi_n \rangle \hat{\vec{r}} / |\vec{r}| |\phi_k \rangle \) from tip’s state \( \ket{\phi_k} \) to substrate’s state \( \ket{\varphi_n} \). \( \hat{\sigma}_x \equiv |\chi_e \rangle \langle \chi_e| + |\chi_b \rangle \langle \chi_b| \) is the transition matrix between molecular ground and excited states and \( \vec{\mu} \equiv \langle \chi_e| \hat{\vec{r}} |\chi_b \rangle \) is the transition dipole. The electron–dipole interaction in equation (3) will induce energy transfer between the tunneling electron and the molecule (the state of the two-level molecule is flipped).

Tip’s wave function in the vacuum region has the asymptotic spherical form \( \phi_k (\vec{r}) = A_k e^{-\kappa_{\lambda}\sqrt{x^2+y^2}} / \sqrt{\kappa_{\lambda}} (\vec{r} - \vec{a}) \) where \( \sqrt{x^2+y^2} \) is the position of tip’s center of curvature, and \( \kappa_{\lambda} = \sqrt{-2m_{e}\nu_{e}^{2}} \) is its decay factor. The normalized coefficient \( A_k \) can be determined by first-principles calculations. This wave function is typical known as the s wave, which is the simplest case for the tip [24]. The surface wave function of the bare metal substrate in the vacuum region takes the form \( \sim B_n e^{-\kappa_{\lambda}|\vec{r}|} \) with \( \kappa_{\lambda} = \sqrt{-2m_{e}\nu_{e}^{2}} \) being the decay factor and \( B_n \) the normalization factor [25, 26].

Experiments have shown that the insulating layer on the metal surface does not change the lineshape of the substrate-photon-emission spectrum but only reduces its intensity [9]. Therefore, in our model, we write the substrate’s wave function as \( \varphi_n (\vec{r}) = B_n e^{-\kappa_{\lambda}|\vec{r}|} \) which decays along the +z direction with decay factor \( \kappa_{\lambda} \) and the normalization constant \( B_n \). With the wave functions for the tip and substrate, the transition matrix element is explicitly written as

\[
\mathcal{N}_{nk\lambda}\ket{V_{b,\lambda} - \xi_G} \simeq -A_k B_n \sum_{l=n,k} \int_{V_{nm}} \frac{dV}{\nu_{m}} \kappa_{n} \sqrt{(x-a_{\lambda})^2 + y^2 + (z - d - R)^2(x^2 + y^2 + z^2)^{3/2}},
\]

where \( \mu_{\lambda}(x,y,z) \) is the \( x(y,z) \) component of the molecular dipole moment. And without loss of generality, we have chosen the position of tip’s center of curvature along z axis, i.e., \( \vec{a} = (a_{\lambda}, 0, d + R) \). In the later discussion, we ignore the dependence of \( \mathcal{N}_{nk\lambda}\ket{V_{b,\lambda} - \xi_G} \) on the normalization constants \( A_k \) and \( B_n \) by taking them to be independent on the index \( k \) and \( n \).

3. The asymmetry of the photon-counting rate

To interpret the asymmetry of the photon-counting rate, we calculate the tunneling rate at negative bias \( (V_b < 0) \), illustrated in figure 1(b), where the Fermi level of tip is lower than that of substrate. The molecule is initially in its ground state and the tunneling electron in one of substrate’s eigenstates, i.e., \( |\Psi (t = 0)\rangle = |\chi_{b}\rangle |\varphi_n\rangle \). To the first order of \( \hat{H}_e \sim \hat{H}_{dls} \) and \( \hat{H}_{el-m} \), we obtain the time evolution of the system as

\[
|\Psi (t)\rangle = e^{-i(\widetilde{E}_b + \nu_{e})t} |\chi_{b}\rangle |\varphi_n\rangle + \sum_{k} \xi_{g,k}(t) |\chi_{b}\rangle |\phi_k\rangle + \sum_{k} \xi_{c,k}(t) |\chi_{e}\rangle |\phi_k\rangle,
\]

(5)

where the second and third terms stand for elastic and inelastic tunneling, respectively. In order to obtain the above result, we have applied the rotating-wave approximation for Hamiltonian in equation (3).

The corresponding tunneling amplitudes read

\[
\xi_{g,k}(t) = e^{-i\tilde{E}_b t} e^{-\xi_{g,k} t} / \tilde{E}_n - \xi_k, \mathcal{M}_{nk},
\]

(6a)

\[
\xi_{c,k}(t) = e^{-i(\widetilde{E}_b + \nu_{e})t} - e^{-i(\xi_{g,k} + \nu_{e})t} / \tilde{E}_n - \xi_k - E_{eg} \mathcal{N}_{nk\lambda}\ket{V_{b,\lambda} - \xi_G},
\]

(6b)

where \( \mathcal{M}_{nk} \equiv \langle \phi_k | (\hat{H}_d - \hat{H}_{dls}) |\varphi_n\rangle \) is the transition matrix element of the elastic tunneling and \( E_{eg} \equiv E_e - E_g \) is the optical gap of the single molecule.
We will focus on the inelastic tunneling process instead of the elastic tunneling which has been well explored in the earlier development [19, 24–26] of STM. The inelastic tunneling rate \( \mathcal{J}_{\text{inel}} \) from \( |\phi_k\rangle \) to \( |\phi_n\rangle \) is \( \mathcal{J}_{\text{inel}} = \frac{d|c_{\xi,k}(t)|^2}{dt} \). The overall inelastic electron current at negative voltage \( I_{-\text{inel}} = e \sum_k \sum_n \mathcal{J}_{\text{inel}} (E_n) (1 - F_{\mu_0,T}(\xi_k)) \) is exactly rewritten as

\[
I_{-\text{inel}} = 2\pi e \int dE_n \rho_n(E_n) \rho_k(\xi_k) F_{\mu_0,T}(E_n) \times (1 - F_{\mu_0,T}(\xi_k)) \left| \mathcal{N}_{\xi\xi_k}|V_{\mu_0}\xi_k-E_{\xi_k}|^2 \right| |\xi_k=E_n-eV_0-E_{\text{eg}},
\]

where \( \rho_k(E) (\rho_n(E)) \) is the density of state of tip (substrate) at the energy \( E \). \( F_{\mu_0,T}(E) \) is the Fermi–Dirac distribution of electrons in tip or substrate state at energy \( E \) with chemical potential \( \mu_0 \) and temperature \( T \). Notice that two of the model parameters, i.e., the chemical potential and density of state, depend on the electrode material. The constraint \( \xi_k = E_n - eV_0 - E_{\text{eg}} \) rules out all the tunneling processes whose energy does not conserve and allows the simplification of the molecule as a two-level system for one particular voltage. We consider here the tip and substrate are of the same metal (Ag).

In STM experiment, the temperature of the ultrahigh-vacuum chamber is low enough, typically lower than 10 K [9–16, 27, 28], that the Fermi–Dirac distribution function is approximately a Heaviside function, i.e., \( F_{\mu_0,T}(E) = 1 \) for \( E < \mu_0 \) and \( F_{\mu_0,T}(E) = 0 \) for \( E > \mu_0 \). The inelastic tunneling current becomes

\[
I_{-\text{inel}} \approx 2\pi e \int_{\mu_0+eV_0+E_{\text{eg}}}^{\mu_0} dE_n \rho_n(E_n) \rho_k(\xi_k) \times \left| \mathcal{N}_{\xi\xi_k}|V_{\mu_0}\xi_k-E_{\xi_k}|^2 \right| |\xi_k=E_n-eV_0-E_{\text{eg}},
\]

Equation (8) suggests that the current for inelastic tunneling is nonzero only at the condition \( eV_0 < -E_{\text{eg}} \) for the negative bias case.

For the positive bias \( V_0 > 0 \), the current for the inelastic tunneling is obtained with the similar method as

\[
I_{+\text{inel}} \approx 2\pi e \int_{\mu_0}^{\mu_0+eV_0-E_{\text{eg}}} dE_n \rho_n(E_n) \rho_k(\xi_k) \times \left| \mathcal{N}_{\xi\xi_k}|V_{\mu_0}\xi_k-E_{\xi_k}|^2 \right| |\xi_k=E_n-eV_0+E_{\text{eg}}.
\]

Similar to the negative bias case, the condition for a nonzero inelastic current is \( eV_0 > E_{\text{eg}} \). The equal bias voltage for nonzero inelastic current at negative and positive bias is an important feature different from the carrier-injection mechanism where the electron injection requires different voltage for the negative and positive bias [9, 29]. With equations (8) and (9), we obtain the inelastic tunneling current as

\[
I_{\text{inel}} = \begin{cases} 
I_{-\text{inel}}, & V_0 < -E_{\text{eg}}, \\
0, & -E_{\text{eg}} \leq V_0 \leq \frac{e}{e}, \\
I_{+\text{inel}}, & V_0 > \frac{e}{e}.
\end{cases}
\]

The photon-counting rate of molecular fluorescence is a quantity relevant for probing the properties of the single molecule. Once excited, the molecule will decay to its lower state spontaneously with rate \( \gamma \). The photon-counting rate \( \Gamma \) is proportional to the inelastic current

\[
\Gamma = I_{\text{inel}}/e.
\]

The detailed derivation can be found in the appendix C. In figure 2, we plot the photon-counting rate as the function of the bias voltage between tip and substrate. The blue solid and black dashed lines show the relative emission intensity for the tip-substrate distance \( d = 0.5 \text{ nm} \) and 1 nm, respectively. The Fermi energy of silver is \( \mu_0 = -4.64 \text{ eV} \), and the density of state of silver can be found in [30]. For simplicity, we choose the tip right above the molecule \( (a_z = 0) \) in which case the transition matrix elements corresponding to \( \mu_0 \) and \( \mu_0 \) vanish due to symmetry (see equation (4)). The tip’s center of curvature is \( R = 0.5 \text{ nm} \). As predicted in equation (10), the bias voltages for nonzero inelastic current at negative and positive bias are the same, i.e., \( |eV_0| > E_{\text{eg}} = 2 \text{ eV} \). Insets in figure 2 describe the mechanism of the inelastic electron scattering.

Another important feature is the asymmetry of the larger photon counting at negative bias than that at positive bias, as illustrated in figure 2. This intensity asymmetry stems from the eigenfunction asymmetry of tip and substrate. The tip’s wave function \( \phi_k(\mathbf{r}) \) decays spherically with factor \( \kappa_k \), and substrate’s wave function \( \phi_n(\mathbf{r}) \) decays along the +z direction with factor \( \kappa_n \). The relation between the elements of the transition matrix at positive bias \( V_0 \) and that at negative bias \( -V_0 \) reads \( (R = 0.5 \text{ nm}, \text{see the appendix D for more details})

\[
\mathcal{N}_{\xi\xi_k}|V_{\mu_0}\xi_k-E_{\xi_k}|^2 \approx \frac{\kappa_n}{\kappa_k} \left[ 1 + (\kappa_k - \kappa_n - \sqrt{2} \left( \sqrt{n^2} - \sqrt{k^2} \right)) \frac{e^{-\kappa_k d}}{e^{-\kappa_n d}} \mathcal{N}_{\xi\xi_k}|V_{\mu_0}\xi_k-E_{\xi_k}|^2. \right]
\]
Figure 2. Asymmetric photon intensity in inelastic electron scattering mechanism. The blue solid (black dashed) line represents the emission intensity for the tip-substrate distance \( d = 0.5 \) nm (1 nm). Two insets show the inelastic electron scattering mechanism for a two-level molecule at the negative and positive bias. The molecular optical gap is \( E_{\text{eg}} = 2 \) eV, and the Fermi energy of silver is \( \mu_0 = -4.64 \) eV. The tip’s center of curvature is \( R = 0.5 \) nm. Here, we choose the case where the tip is positioned right above the molecule and the molecular transition dipole is along the \( z \)-axis.

Figure 3. (a) The ratio \( R \) between the photon counting at the positive and negative voltages versus the tip-substrate distance for \( R = 0.5 \) nm. (b) The ratio \( R \) versus the bias voltage for \( d = 1 \) nm. The solid lines show the ratio calculated with the exact tunneling rate from equations (8) and (9), and the dashed lines show the analytical formula for the ratio in equation (13). The other parameters are the same as that in figure 2.

The ratio between the transition matrix element at positive bias \( V_b \) and that at negative bias \(-V_b\) depends on the tip-substrate distance and the bias voltage. Inserting equation (12) into equation (9), we obtain the ratio of the emission intensity as

\[
R = \frac{I_{+\text{inela}}}{I_{-\text{inela}}} = \frac{V_b}{E_{\text{eg}}} \left[ 1 + \ln \left( \frac{|\mu_0| + |eV_b - E_{\text{eg}}|}{|\mu_0|} \right) \right]^{1/4} \times \left[ \frac{|eV_b - E_{\text{eg}}| + |\mu_0|}{2|\mu_0|} \right]^{1/4} \left[ \frac{2|m_e| |\mu_0|}{4} \right]^{1/4} \left( 2|m_e| |\mu_0| \right)^{1/4} \left( -\frac{\sqrt{\pi}}{4} \right) d \right]^{1/4}. 
\]

The current equation shows the characteristic asymmetry with a larger current at negative bias induced by the inelastic electron scattering. And the asymmetry feature grows with increasing bias and tip-substrate distance. Such asymmetry for inelastic electron scattering is caused by the geometry shape of the tip and the substrate and persists with different materials.

In figure 3, we show the dependence of the asymmetric ratio \( R \) on the tip-substrate distance and the bias voltage with both the analytical formula (blue dashed line) in equation (13) and the numerical result (blue solid line) calculated with equations (8) and (9). The analytical formula shows an agreement with the numerical result on the trend that the asymmetry of the photon counting increases with increasing tip-substrate distance and bias voltage. The decay of the ratio \( R \) as a function of tip-substrate distance and bias voltage is predicted in equation (13) and can be tested with the experimental data.
4. Photon counting rate of a molecule with a large planer transition dipole

In most of the STML experiments, the molecule lies flat on the substrate surface and thus possesses a large planer transition dipole along the symmetric axis of the molecule [9, 15, 16]. And experimental results also showed that the STML intensity at the molecular lobe was much stronger than that above the molecular center. This effect can be explained with our theory pretty well. We consider a molecule with a large transition moment along the $x$-axis, e.g., $\mu_x = 100\mu_z$. When the tip is right over the molecular center, i.e., $a_x = 0$, as a result of symmetry, only the dipole $\mu_z$ contributes to the inelastic transition matrix element (see equation (4)). When the tip is displaced along the $x$-axis for a short distance (smaller than the molecular size), the large transition dipole $\mu_x$ plays an important role in the transition matrix element. The photon-counting rate in the latter case can be larger than that in the former case.

Figure 4 shows the photon-counting rate with the tip’s lateral displacement. The blue solid line shows the photon intensity at $a_x = 0.5$ nm, and the black dashed line shows the photon intensity for a zero lateral displacement $a_x = 0$ nm. The data shows that the photon-counting rate above the molecular lobe is almost three orders of magnitude larger than that right over the molecule center. The inset shows the schematic diagram in the $xz$ plane.

With the theoretical predictions above, we revisit the important features observed in recent experiments [9, 15, 16]. In the single-hydrocarbon fluorescence induced by STM [15], the phenomenon that the emission intensity at negative bias was larger than that at positive bias is in line with our prediction. Though such an asymmetric intensity feature (the intensity at negative bias was much larger than that at positive bias) of a single ZnPc molecule was attributed to the carrier-injection mechanism [9], we emphasize that the inelastic electron scattering mechanism may also play an important role in this feature. By changing the tip and substrate material from Ag to Au (which changes the Fermi energy and the density of state of electrodes in our model), Doppagne et al. [16] observed a phenomenon that was opposite to the feature in [9]. The emission of a single neutral ZnPc molecule at positive bias was 30 times more intense than that at negative bias. Our theory definitely excludes the inelastic electron scattering mechanism as the origin of such asymmetric luminescence [16].

5. Conclusions and outlook

In conclusion, we have derived the microscopic origin of the molecular excitation via the inelastic electron scattering mechanism in single-molecule STML. We obtain the emission intensity in the inelastic electron scattering mechanism and find that the inelastic electron scattering mechanism requires a symmetric bias voltage for a nonzero inelastic current. It also implies that the energy window between the Fermi levels of two electrodes should at least equal the optical gap of the molecule [29]. Importantly, we reveal an asymmetric emission intensity at negative and positive bias which is due to the asymmetric forms of wave functions at two electrodes and show that the ratio of such asymmetry decays with tip-substrate distance and bias voltage. Our model offers us a theoretical insight into the molecular excitation in the inelastic electron scattering process which has never been explored before.

Before closing, it is worthy to mention that the inelastic scattering mechanism is one of the three mechanisms proposed now and the photon counting obtained here is one small part of the total emission intensity according to most of the experimental results in existence. Further research is needed for
elucidating the competition of these three mechanisms and finding the dominant one under certain conditions.

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Appendix A. Electronic wave functions on the tip and substrate

In this section, we show the details of the wave function of the tunneling electron Hamiltonian, 

\[ \hat{H}_{el} = -\frac{1}{2m_e} \nabla^2 + V(\vec{r}). \]  

(A.1)

The total potential \( V(\vec{r}) \), illustrated in figure A1(a), is divided into two parts: the tip \( V_t(\vec{r}) \) (subfigure (b)), and the substrate part \( V_s(\vec{r}) \) (subfigure (c)). We use the approximate method proposed by Bardeen in 1961 [19, 20]. The Hamiltonian of the free tip and substrate is \( \hat{H}_{el,t} = -\frac{1}{2m_e} \nabla^2 + V_t(\vec{r}) \) and \( \hat{H}_{el,s} = -\frac{1}{2m_e} \nabla^2 + V_s(\vec{r}) \), respectively. For zero bias \( V_b = 0 \), the eigenstates of the free tip and substrate are

\[ \hat{H}_{el,t,0} |\phi_k\rangle = \xi_k |\phi_k\rangle, \]  

(A.2a) 

\[ \hat{H}_{el,s,0} |\varphi_n\rangle = E_n |\varphi_n\rangle, \]  

(A.2b) 

where \( \hat{H}_{el,t,0} \) represents the free tip (substrate) Hamiltonian at zero bias and \( |\phi_k\rangle \) \((|\varphi_n\rangle)\) is the eigenstate of free tip (substrate) with energy \( \xi_k \) \((E_n)\). As the tip apex has been modeled as a metal sphere, its wave function in the vacuum region has the asymptotic spherical form

\[ |\phi_k(\vec{r})\rangle = A_k e^{-\kappa_k |\vec{r} - \vec{a}|}, \]  

(A.3) 

where \( \vec{a} \) is the position of tip’s center of curvature and \( \kappa_k = \sqrt{-2m_e\xi_k} \) is its decay factor. \( A_k \) can be determined by the first-principles calculations. On the other hand, in the vacuum region, we take substrate’s wave function as

\[ |\varphi_n(\vec{r})\rangle = B_n e^{-\kappa_n |z|}, \]  

(A.4) 

where \( \kappa_n = \sqrt{-2m_eE_n} \) is the decay factor.

Figure A1. The schematic diagrams of the potential along z-axis. (a) The potential \( V(\vec{r}) \) of the tip and substrate. (b) The potential \( V_t(\vec{r}) \) for the tip. (c) The potential \( V_s(\vec{r}) \) for the substrate.
For a nonzero bias $V_b \neq 0$, we take the potential change induced by bias voltage as a perturbation and obtain the solution up to the first-order correction,

$$
\hat{H}_{\text{el}} |\phi_k\rangle \simeq \tilde{\xi}_k |\phi_k\rangle ,
$$

(A.5a)

$$
\hat{H}_{\text{ele}} |\varphi_n\rangle \simeq \tilde{E}_n |\varphi_n\rangle ,
$$

(A.5b)

where $\hat{H}_{\text{el}}(s)$ represents the free tip (substrate) Hamiltonian at bias $V_b$ and $\tilde{\xi}_k \equiv \xi_k + eV_b \left( \tilde{E}_n \equiv E_n \right)$ is the corrected energy of state $|\phi_k\rangle \left(|\varphi_n\rangle \right)$. Here we neglect the change of the wave function of the tip induced by the applied voltage $[24]$.

**Appendix B. The electron–molecule interaction**

In this section, we show the detailed derivation of the effective electron–dipole interaction between a tunneling electron and a single molecule. The Coulomb interaction between a tunneling electron and the molecule is written as

$$
H_{\text{el–m}} = \sum_{n=1}^{N} \left( \frac{Z_n e^2}{|\vec{r} - \vec{r}_n|} + \frac{Z_e e^2}{|\vec{r} - \vec{r}_{nj}|} \right),
$$

(A.6)

where $\vec{r}$ is the position of the tunneling electron. The molecule contains $N$ atoms. For the $n$th atom, there is one atomic nucleus (effective charge $Z_n$) and $Z_e$ electrons. $\vec{r}_n$ ($\vec{r}_{nj}$) is the position of nucleus ($j$th electron). $\vec{R}_0 \equiv \sum_{n=1}^{N} \vec{r}_n Z_n / \sum_{n=1}^{N} Z_n$ denotes the center of the positive charge. For the case where the distance between the tunneling electron and the molecule is much larger than the size of the molecule, i.e., $|\vec{r} - \vec{R}_0| \gg |\vec{R}_n - \vec{R}_0|, |\vec{r}_{nj} - \vec{R}_0|$ for all $n,j$, the coupling in equation (A.6) becomes

$$
H_{\text{el–m}} = \sum_{n=1}^{N} \sum_{j=1}^{Z_n} \left( \frac{e^2}{|\vec{r} - \vec{r}_n|} - \frac{e^2}{|\vec{r} - \vec{r}_{nj}|} \right)
$$

$$
= \sum_{n=1}^{N} \sum_{j=1}^{Z_n} \frac{e^2}{|\vec{r} - \vec{R}_0|} \left( 1 + \frac{2 (\vec{r} - \vec{R}_0) \cdot (\vec{R}_0 - \vec{r}_n)}{|\vec{r} - \vec{R}_0|^2} + \frac{|\vec{R}_0 - \vec{r}_n|^2}{|\vec{r} - \vec{R}_0|^2} \right)^{-1/2}
$$

$$
- \sum_{n=1}^{N} \sum_{j=1}^{Z_n} \frac{e^2}{|\vec{r} - \vec{R}_0|} \left( 1 + \frac{2 (\vec{r} - \vec{R}_0) \cdot (\vec{R}_0 - \vec{r}_n)}{|\vec{r} - \vec{R}_0|^2} + \frac{|\vec{R}_0 - \vec{r}_n|^2}{|\vec{r} - \vec{R}_0|^2} \right)^{-1/2}
$$

$$
\approx \sum_{n=1}^{N} \sum_{j=1}^{Z_n} \frac{e^2}{|\vec{r} - \vec{R}_0|^3} \left( 1 - \frac{\vec{r}_n \cdot (\vec{r}_n - \vec{R}_0)}{|\vec{r} - \vec{R}_0|^2} \right) = \left( 1 - \frac{\vec{r} \cdot (\vec{R}_0 - \vec{R}_0)}{|\vec{r} - \vec{R}_0|^2} \right)
$$

$$
= -\frac{e (\vec{r} - \vec{R}_0) \cdot \vec{\mu}}{|\vec{r} - \vec{R}_0|^3},
$$

(A.7)

where $\vec{\mu} = \sum_{j=1}^{Z_n} e (\vec{r}_n - \vec{r}_{nj}) = Ze (\vec{R}_n - \vec{R}_0)$, $Z \equiv \sum_{n=1}^{N} Z_n r_n \equiv \sum_{n=1}^{N} \sum_{j=1}^{Z_n} \vec{r}_{nj}/Z$ denotes the total electric dipole moment of the molecule. We set the position of the positive charge as the origin of the coordinate axes, i.e., $\vec{R}_0 = 0$. The electron–molecule interaction is expressed as

$$
H_{\text{el–m}} \simeq -\frac{\vec{r} \cdot \vec{\mu}}{|\vec{r}|^3}.
$$

(A.8)
Appendix C. The photon count rate

Once excited to its excited state, the molecule will decay to its lower state and emit a photon spontaneously. Its photon-counting rate is proportional to the probability in excited state, \( p_e (t) \equiv \sum_n |c_{n,k} (t)|^2 \). Taking the molecular excitation and the spontaneous emission process together, we obtain the master equation for the excitation probability

\[
\frac{d}{dt} p_e (t) = -\gamma p_e (t) + \frac{I_{\text{inela}}}{e},
\]

where \( \gamma \) is the molecular spontaneous emission rate. In the steady state, the excitation probability becomes \( p_e (t) = \frac{I_{\text{inela}}}{e\gamma} \). The photon-counting rate becomes

\[
\Gamma = \frac{\gamma I_{\text{inela}}}{e\gamma} = \frac{I_{\text{inela}}}{e}.
\]

Appendix D. The ratio of emission intensity

The wavefunction \( \varphi_n (\mathbf{r}) \) of the substrate decays along the +z direction [25, 26]. At the positive bias \( V_b > 0 \), the transition matrix element of the inelastic tunneling reads

\[
\mathcal{N}_{k,s}|\psi_n\rangle = \langle \phi_k | \hat{H}_{e-m} | \varphi_n \rangle,
\]

where \( \xi_k = \gamma + eV_b \) is the energy of substrate and tip at zero bias. Here we define the function \( \text{Erf}(x) = \frac{2}{\sqrt{\pi}} \int_0^x e^{-t^2} \, dt \) is the error function. We consider the radius \( R = 0.5 \text{ nm} \) and obtain the ratio of positive transition amplitude over the negative one up to the first order of the distance \( d \),

\[
\frac{\mathcal{N}_{k,s}|\psi_n\rangle}{\mathcal{N}_{k,s}|\psi_n\rangle} \approx e^{-\kappa_a d}\frac{K_a}{K_s} \left[ 1 + \left( \kappa_a - \kappa_s - \frac{\pi}{2} (\sqrt{K_a} - \sqrt{K_s}) \right) d \right],
\]

where \( \mathcal{N}_{k,s}|\psi_n\rangle \) is the transition matrix element of the inelastic tunneling from tip’s state \( \phi (\mathbf{r}) \) with energy \( \xi_k + eV_b \) to substrate’s state \( \varphi (\mathbf{r}) \) with energy \( E_n \) at bias \( V_b \) and \( \mathcal{N}_{k,s}|\psi_n\rangle \) is the transition matrix element of the inelastic tunneling from substrate’s state \( \varphi (\mathbf{r}) \) with energy \( \xi_k \) to tip’s state \( \phi (\mathbf{r}) \) with energy \( E_n - e |V_b| \). We have chosen the tip right above the molecule \( (\mu_z = 0) \) and the molecular dipole in the z direction \( (\mu_z \neq 0) \). The inelastic tunneling current at the positive bias is

\[
I_{\text{inela}} = 2\pi e \int_{E_n}^{E_n + eV_b - E_{\text{eg}}} dE_n \rho_t (E_n) \rho_t (\xi_k) |\mathcal{N}_{k,s}|\psi_n\rangle^2|\xi_k = E_n - eV_b + E_{\text{eg}}\rangle,
\]

\[
\simeq 2\pi e \int_{E_n}^{E_n + eV_b - E_{\text{eg}}} dE_n \rho_t (E_n) \rho_t (\xi_k) A (E_n, d)
\]

\[
\times \left| \mathcal{N}_{k,s}|\psi_n\rangle \right|^2|\xi_k = E_n - eV_b + E_{\text{eg}}\rangle^*,
\]

where \( \rho_t (E) (\rho_t (E)) \) denotes the density of state of tip (substrate) at the energy \( E \) and \( \mu_0 \) is the Fermi energy of substrate and tip at zero bias. Here we define the function
For the noble metal, the density of state is approximated as a constant around its Fermi energy [30]. Thus, the dependence on the radius is small. For a small bias which satisfies $(eV_b - E_{eq}) / \mu_0 \ll 1$, equation (A.13) can be further simplified as

$$I_{+\text{inel}} \approx 2\pi e \int_{\mu_0}^{\mu_0 + eV_b - E_{eq}} dE_n \rho_s (E_n) \rho_t (\xi_k) A (E_n, d)$$

$$= \left[ N_{\xi_k \mid -V_b, \xi_k = \mu_0} \right] \left| \xi_k = -eV_b + E_{eq} \right|$$

$$\approx \frac{1}{eV_b - E_{eq}} \int_{\mu_0}^{\mu_0 + eV_b - E_{eq}} dE_n A (E_n, d)$$

$$\times 2\pi e \int_{\mu_0}^{\mu_0 + eV_b - E_{eq}} dE_n \rho_s (E_n) \rho_t (\xi_k) \left[ N_{\xi_k \mid -V_b, \xi_k = \mu_0} \right] \left| \xi_k = -eV_b + E_{eq} \right|$$

$$\approx e^{-2m_e|\mu_0|/\mu_0} \left( \frac{|\mu_0| - E_{eq}}{|\mu_0| + |eV_b - E_{eq}|} \right) \left[ 1 + \ln \left( \frac{|\mu_0| + |eV_b - E_{eq}|}{|\mu_0| - |eV_b - E_{eq}|} \right) \right] I_{-\text{inel}} \mid -V_b.$$  

(A.15)

For the noble metal, the density of state is approximated as a constant around its Fermi energy [30]. Thus, in deriving equation (A.15), we have extracted the density of state function from the integral.

The dependence of the ratio on the distance $d$ is plotted in the main text of the current paper. Its dependence on the radius $R$ of the tip is illustrated in figure A2 which is obtained by the numerical calculation of the integral in equations (8) and (9) in our manuscript.
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