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Analysis of lateral hopping of a single CO molecule on Pd(110)

H. Ueba
Division of Nano and New Functional Materials Science, Graduate School of Science and Engineering, University of Toyama, Toyama, 930-8555 Japan

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Lateral hopping of a single CO molecule on Pd(110) by Komeda *et al.* [Science **295**, 2055 (2002)] is revisited using a recently proposed formula of reaction yield $Y(V)$ as a function of bias voltage V. The calculated $Y(V)$ using a Lorentzian vibrational density of states (DOS) for the C-O stretch mode meets with a better agreement with the experimental data than using a Gaussian DOS. It is also found that the broadening used in the fitting to the experimental result is very close to the intrinsic vibrational lifetime of the C-O stretch mode on Pd (110). Using the fitting parameters of the transition rate to excite the frustrated translation mode above the barrier, the anharmonic coupling of the C-O stretch mode to the frustrated translation mode is determined for the first time from the analysis of the experimental result.

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Tunneling electrons from a tip of a scanning tunneling microscope (STM) can be used as an atomic size source of electrons for electronic or vibrational excitations and to manipulate individual atoms and molecules in a controlled manner across a surface.[1] In a concluding remark of an ultimate switching device whose function utilizes a Xe atom shuttling between a tip of an STM and a substrate, Eigler *et al.*[2] delivered a message: "We are intrigued by the idea that atom switches might already exist in the form of single cage-like molecules which derive their switching function from an atom that is trapped in the cage." Such a perspective has been recently achieved in "four-level conductance switch based on single proton transfer in a free-base tetraphenyl-porphyrin molecule,"[3] "molecular switch of an encapsulated cluster within a fullerene cage,"[4] and "four-wheel-drive nanocar" that undergoes continuous and conformational and directional motions upon sequential electronic and vibrational excitation with STM.[5] In these recent milestone works, the action spectra, i.e., the reaction rate as a function of bias voltage, provide indispensable information required to deepen an understanding of their microscopic mechanisms, such as how the vibrational mode Sc_3N cluster in C_{80} fullerene cage transfer energy from the tunneling electrons into the cluster rotation, how a change of single hydrogen atom position inside in the cavity of the ring porphyrin molecule leads to distinct conductance states, how the threshold bias corresponding to the excitation of the C=C double bond stretching vibration induces the helix inversion of the rotor unit, and how the threshold suggesting resonant tunneling into the LUMO of the molecule and resultant formation of transient negative ion state is responsible for the directional movement of the four-wheel-drive nanocar. All of these answers needed to be clarified by a novel and very sophisticated theoretical works to understand the molecular potential-energy surface, the associated electronic and vibrational excitations, and the coupling of electrons to nuclear motion of single molecules.[6]

Going back to 1998, Stipe *et al.*[7] opened a new avenue of "single molecule vibrational spectroscopy and microscopy using an STM." They observed that vibrational spectrum (defined as the second derivative of tunneling current I with respect to the applied bias V, i.e., d^2I/dV^2 named as inelastic electron tunneling spectrum: IETS) of a single acetylene [$C_2H(D)_2$] molecule adsorbed on the Cu(100) surface. Immediately after this pioneering work of "scanning tunnel microscopy-inelastic electron tunneling spectroscopy (STM-IETS)," they have completed the first comprehensive and systematic experiments for a reversible rotation of single $C_2H(D)_2$ molecule on Cu(100).[8] Almost all the experimental data collections [reaction rate $R(V)$ or yield $Y(R) = R(V)/I$, $\Delta\log(R)/\Delta V$ plot compared to the IETS] reported there have now been established as indispensable experimental method in order to gain insights into the vibrationally mediated motions and reactions of single molecules with an STM.

One of the pioneering works in a single molecule manipulation includes a lateral hopping of a CO molecule on Pd(110).[9] The experimental result of the hopping rate $R(I)$ as a function of tunneling current I indicates a single electron process and the yield $Y(V)$ as a function of a bias voltage V indicates excitation of the C-O stretch mode is a trigger for hopping motions. A simple but transparent theory developed by Persson and Ueba[9,10] proved that anharmonic mode coupling between the C-O stretch mode excited by tunneling electrons and the frustrated translation mode [the reaction coordinate (RC) mode] plays a key role. Their theory allowed us to estimate the branching ration, which describes how the energy stored in the excited high-frequency mode is used to activate the RC mode from the ground state to above the reaction barrier, in competing with its efficient energy dissipation into a heat bath of electron-hole pair excitations in a metal. Ueba and Persson[11] also proposed that the second derivative of $R(V)$ with respect to V is related to the vibrational DOS, which usually cannot be directly observed in IETS when a molecule motion is induced by vibrational excitation. Knowing a relation between inelastic tunneling current $I_{\text{in}}(V)$ and the vibrational density of states (DOS), $d^2I_{\text{in}}/dV^2 \sim \rho_{\text{ph}}(V)$,[11] Motobayashi *et al.*[12] proposed an empirical form of $I_{\text{in}}(V)$ without relying on explicit formula of $I_{\text{in}}(V)$ derived using a nonequilibrium Keldysh Green's function method.[13] This formula allows a fitting of the observed action spectrum $Y(V)$ over whole bias voltage using three parameters (vibrational energy, broadening of the Gaussian vibrational DOS, and prefactor characterized by the microscopic elementary processes). Their formula has been successfully applied to reproduce the experimental $Y(V)$ for CO hopping on Pd(110) and the configurational change of the *cis*-2-butene molecule on Pd(110). This permitted us to determine the vibrational energy, reaction order (number of electrons required), and transition rate associated with anharmonic coupling between the modes excited by tunneling electrons and the RC modes.

Here we apply a recently developed formal theory of $R(V)$ and $Y(V)$, which successfully reproduced the experimental results of H-atom relay reaction in a molecular chain of H(D)$_2$O-OH(D)-OH(D) on Cu(100),[14] to a detailed analysis of a lateral hopping of a single CO molecule on Pd(100).[9] It has been well established that the hopping is induced by anharmonic mode coupling between the C-O stretch mode excited by tunneling electron and the frustrated translation mode in a single electron process. In this case, the reaction rate $R(V)$ is given by[1,13,14]

$$R(V) = \frac{\gamma_{\nu,\rm RC}}{\gamma_{\rm eh}}\Gamma_{\rm iet}(V,\Omega), \tag{1}$$

where $\gamma_{\nu,\rm RC}$ is an activation rate of the reaction coordinate (RC) mode over a barrier via an intermode coupling between a vibrational mode ν (with the energy larger than a reaction barrier) in competing with its damping $\gamma_{\rm eh}$ due to electron-hole pair excitations in a metal, and $\Gamma_{\rm iet}(V,\Omega)$ is the generation (emission) rate of the vibrational mode ν.[15] Here $\Gamma_{\rm iet}(V,\Omega)/\gamma_{\rm eh}$ represents the source of the vibrational heating of the mode ν by tunneling electrons, while $P = \gamma_{\nu,\rm RC}/\gamma_{\rm eh}$ represents the branching ratio, which gives a probability that a vibrationally excited molecule by $\Gamma_{\rm iet}$ decays by performing a molecular reaction in competing with its energy dissipation into the substrate.[10] Note also that $I_{\rm in} = e\Gamma_{\rm iet}(V,\Omega)$ is a good approximation of the inelastic tunneling current $I_{\rm in}$.[16]

We consider a given vibrational mode to be characterized by a vibrational density of states (DOS) $\rho_{\rm ph}(\omega)$ and define $\Gamma_{\rm iet}(V)$ in terms of a spectral representation[13]

$$\Gamma_{\rm iet}(V) = \int_0^\infty d\omega \rho_{\rm ph}(\omega)\Gamma_{\rm in}(\omega,V), \tag{2}$$

where $\Gamma_{\rm in}(\omega,V)$ is the spectral vibrational generation rate. It was confirmed that Eqs. (1) and (2) lead to $d^2R(V)/dV^2 \propto \rho_{\rm ph}(V)$ as shown before.[11] Here we assume a Gaussian distribution for the phonon DOS around a characteristic value Ω, i.e.,

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

where the full width at half maximum is given by $2\sqrt{2\ln 2}\sigma_{\rm ph}$. The motivation for a Gaussian distribution is to take into account all broadening effects in a single parameter $\sigma_{\rm ph}$, including several sources of inhomogeneous broadening, intrinsic vibrational lifetime broadening, and instrumental ones. At low temperatures $k_BT \ll \hbar\Omega$, and at tunneling conditions $\Gamma_t \ll \Gamma_s$, the spectral generation rate is given by

$$\Gamma_{\rm in}(\omega,V) \simeq \frac{\gamma_{\rm eh}(\Omega)}{\hbar\Omega}\frac{\Gamma_t}{\Gamma_s}(|eV|-\hbar\omega)\theta(|eV|/\hbar\omega - 1), \tag{4}$$

where Γ_s and Γ_t are the tunneling couplings (wide-band limit) to substrate and tip sides, respectively. Here $\gamma_{\rm eh}(\Omega) = 4\pi\Omega\chi^2\rho_a^2(\varepsilon_F)$ is the electron-hole pair damping rate with χ being the electron-vibration coupling and $\rho_a(\varepsilon_F)$ the adsorbate density of states (DOS) at the Fermi energy ε_F. $\theta(x)$ is the Heaviside step function. Expressing the current $I(V) = \sigma_0 V$ in terms of the elastic conductance σ_0 (inelastic current $I_{\rm in}$ is orders of magnitude smaller than the elastic current), the reaction yield $Y(V)$ is given by

$$Y(V) = K_{\rm eff}\frac{F(V)}{V}, \tag{5}$$

where

$$F(V) = \int_0^{|eV|} d\omega\ \rho_{\rm ph}(\omega)(|eV| - \hbar\omega), \tag{6}$$

and the effective prefactor is given by

$$K_{\rm eff} = \frac{\gamma_{\nu,\rm RC}}{\sigma_0\hbar\Omega}\frac{\Gamma_t}{\Gamma_s}, \tag{7}$$

and the analytical form of $F(V,\omega)$ is obtained as

$$F(V) = \sqrt{\frac{2}{\pi}}\sigma_{\rm ph}\left[e^{-(V-\Omega)^2/(2\sigma_{\rm ph}^2)} - e^{-\Omega^2/(2\sigma_{\rm ph}^2)}\right] + (V-\Omega)\left[\mathrm{Erf}\left(\frac{V-\Omega}{\sqrt{2}\sigma_{\rm ph}}\right) + \mathrm{Erf}\left(\frac{\Omega}{\sqrt{2}\sigma_{\rm ph}}\right)\right]. \tag{8}$$

This slightly differs from a previous one,[12] which cannot be used for a low-energy vibrational mode whose broadening extends the vibrational DOS below $V = 0$; otherwise, it is confirmed that both formulas give the same result. For a Lorentzian DOS $\rho_{\rm ph}(\omega) = (\sigma_{\rm ph}/\pi)/[(\omega-\Omega)^2 + \sigma_{\rm ph}^2]$, we obtain

$$F(V) = \frac{2}{\pi}(V-\Omega)\left[\arctan\left(\frac{V-\Omega}{\sigma_{\rm ph}}\right) + \arctan\left(\frac{V}{\Omega}\right)\right] + \frac{\sigma_{\rm ph}}{\pi}\log\frac{\Omega^2+\sigma_{\rm ph}^2}{(V-\Omega)^2+\sigma_{\rm ph}^2}. \tag{9}$$

It is well known that a main difference of a Lorentzian and Gaussian function manifests itself in the tail feature. For more fundamental broadening work in the electron transport, i.e., inelastic phonon scattering in atomic- and molecular-wire junctions, see Refs. 17 and 18.

In what follows we attempt to reproduce the experimental result of $Y(V)$ for CO hopping using the Gaussian or Lorentzian DOS with a set of parameters $(\hbar\Omega,\sigma_{\rm ph},K_{\rm eff})$. Figure 1(a) compares the experimental (the red circles[9]) and the calculated (black curve) using the Gaussian DOS with parameters (236 meV, 6 meV, 6.9×10^{-12}). The Gaussian broadening of 6 meV is quite large compared to that expected from the intrinsic lifetime of 0.5 ps (=1.3 meV) for the C-O stretch mode on Pd(100).[19,20] Such large $\sigma_{\rm ph}$ could be attributed to unknown inhomogeneous broadening caused by a combination of instrumental factors, statistical errors, and effects of an unstable tip-surface junction.[12] We need to know the coupling ratio Γ_t/Γ_s to evaluate $\gamma_{\nu,\rm RC}$ from $K_{\rm eff} = 6.9 \times 10^{-12}$. In doing so we use a formula of the elastic conductance $\sigma_0 = G_0\Gamma_s\Gamma_t/[(\epsilon_F - \epsilon_a)^2 + (\Gamma_s + \Gamma_t)^2]$ for a single adsorbate level ϵ_a, where $G_0 = 2e^2/h$ is a quantum conductance. The tunneling gap set point condition $:I = 1$ nA at $V = 100$ mV (before increasing V over 220 mV to observe CO hopping) gives $\sigma_0 = 10$ nA/V.[9] The inverse

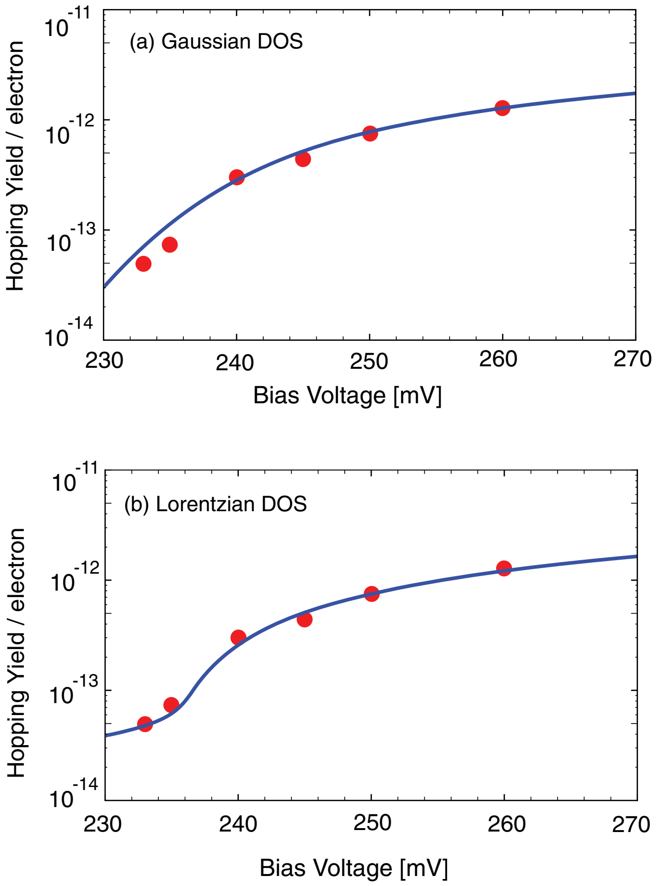

FIG. 1. (Color online) CO hopping yield. The red circles and curves are the experimental result from Ref. 9, and the calculated one using a Gaussian (a) and a Lorenztian (b) DOS with the sets of parameters described in the text.

photoemission experiment for CO on Pd(111) exhibits the $2\pi^*$ state ϵ_a with the width Γ_s of 1 eV at about 0.9 eV above the Fermi level.[21] Since $\Gamma_s \gg \Gamma_t$, we roughly estimate $\Gamma_t/\Gamma_s = 2.6 \times 10^{-4}$. Note that this ratio sounds reasonable in view of STM experiment for chemisorbed molecules. Thus determined Γ_t/Γ_s, however, should only be viewed as a rough estimate because the projected density of states of the $2\pi^*$ level of CO molecules on metal surfaces is not always a Lorentzian shape. Also, it should be noted that in $Y(V)$ experiment as a function of V, the tip-sample distance d is under control in order to keep a constant tunneling current I. Strictly speaking, this means $\Gamma_t \sim \mathrm{e}^{-\alpha d}$ (α: constant). In the experiments of the present concern, V varies between 230 and 270 mV so that the elastic current changes just a factor, not an order. This permits us to assume the same Γ_t even in the constant current mode to measure $Y(V)$. Using thus determined coupling ratio of $\Gamma_t/\Gamma_s = 2.6 \times 10^{-4}$, we obtain $\gamma_{\nu,\mathrm{RC}} = 3.6 \times 10^2$/s for the mode coupling between the C-O stretch mode ($\hbar\Omega = 236$ meV) and the frustrated translation mode ($\hbar\Omega = 25$ meV). This gives the branching ratio (a fraction of the vibrational excited molecules which decay by transferring enough energy into the reaction coordinate to overcome the barrier) $P = \gamma_{\nu,\mathrm{RC}}/\gamma_{\mathrm{eh}} = 2.9 \times 10^{-10}$.

Figure 1(b) shows a similar fitting using a Lorentzian DOS. The fitting (blue curve) using a Lorentzian DOS with a set of parameters (236 meV, 0.8 meV, 6.5 $\times 10^{-12}$) shows a better agreement with the experimental result in the low bias region below $V \simeq 240$ mV. Of particular interest here is that such a nice fitting is achieved using $\sigma_{\mathrm{ph}} = 0.8$ meV, which gives the lifetime of 0.83 ps, which is very close to the theoretical[19] and the experimental value measured in the line-width of the infrared absorption spectrum.[20] Recently we have demonstrated that the experimental result $Y(V)$ of H-atom relay reaction in a molecular chain of H(D)$_2$O-OH(D)-OH(D) on Cu(100)[14] has been nicely reproduced using a Gaussian DOS with large σ_{ph}. A unique property of this system is the existence of two types of the O-H mode, i.e., free O-H and shared O-H mode. The detailed calculation of vibrational energies of these modes as well as the scissor mode as a function of the O-O distance ($d_{\mathrm{O-O}}$) belonging to H$_2$O and OH shows that, while the free O-H mode and the scissor mode remain unchanged against sub-Å change of $d_{\mathrm{O-O}}$, the energy of the shared O-H mode changes over more than 10 meV.[22] This causes inhomogeneous broadening so that a Gaussian DOS works pretty well in this system. In the case of a single CO molecule adsorbed on a bridge site on Pd(110), the C-O stretch mode has the stable vibrational energy and lifetime so that a description of the damped harmonic oscillator gives a Lorentzian DOS whose width is determined by the intrinsic lifetime of 0.8 ps. Using again $\sigma_0 = 10$ nA/V and $\Gamma_t/\Gamma_s = 2.6 \times 10^{-4}$, we obtain $\gamma_{\nu,\mathrm{RC}} = 3.5 \times 10^2$/s and $P = 2.8 \times 10^{-10}$. It is remarked that in both cases of Gaussian and Lorentzian DOS, we obtain an order of magnitude agreement of P with that estimated in our first analytical formula of the branching ratio.[9,10] This permits us to estimate the anharmonic coupling λ between the mode ν and RC mode with the energy $\hbar\omega_0$ from[10]

$$P \simeq \frac{8\eta^2}{\sqrt{2\pi}} \frac{(1-\varepsilon_{\mathrm{B}}/\hbar\Omega)}{(2-\varepsilon_{\mathrm{B}}/\hbar\Omega)^2} \left(\frac{\lambda}{\varepsilon_{\mathrm{B}}}\right)^2 n^{3/2}\mathrm{e}^{-2n}, \tag{10}$$

where η (=0.01 used below in an order estimate) takes care of the reduced weight of a plane wave function for a continuum state above the potential barrier[10,23] and $n = \varepsilon_{\mathrm{B}}/\hbar\omega_0$. Using $\hbar\Omega = 236$ meV, $\hbar\omega_0 = 25$ meV, and the barrier height $\varepsilon_{\mathrm{B}} = 150$ meV (this gives $n = 6$) and $P = 2.8 \times 10^{-10}$ we obtain $\lambda = 3.6$ meV. On the basis of a similarity of the bridge bonding configuration and electronic structure between CO/Ni(111) and CO/Pd(110), and considering a simplicity of our model and many approximations to obtain the formula of $Y(V)$ and P, thus estimated anharmonic coupling λ through the full analysis of a lateral hopping of CO on Pd(110) is very close to $\lambda = 4.3$ meV, determined by the temperature dependence of the infrared absorption spectra of the bridge-bonded CO molecule[24] and theoretically calculated as an origin of a vibrational dephasing brought about by energy exchange between anharmonically coupled low and high frequency modes of CO on Ni(111).[25,26]

As described above $I_{\mathrm{in}}(V) = \mathrm{e}\Gamma_{\mathrm{iet}}(V)$, which is shown in Fig. 2 as a blue curve together with the vibrational DOS given by $d^2I_{\mathrm{in}}(V)/dV^2 \sim \rho_{\mathrm{ph}}(V)$ as a red curve (in arb. unit). Since $I_{\mathrm{in}}(V)$ is linear in V except near $\mathrm{e}V \simeq \hbar\Omega$, it is a good approximation to define $I_{\mathrm{in}}(V) \simeq \sigma_{\mathrm{in}} V$ in terms of the inelastic conductance σ_{in}. From the linear part of $dI_{\mathrm{in}}(V)/dV$ as shown in the green curve, we obtain $\sigma_{\mathrm{in}} = 0.46$ [nA/V], which yields

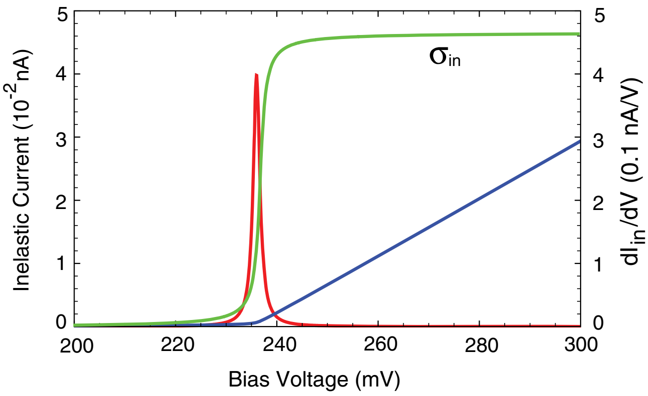

FIG. 2. (Color online) Inelastic tunneling current (blue curve) exciting the C-O stretch mode at 236 meV. Also shown are the Lorentzian DOS of this mode (red curve) in arb. unit and dI_{in}/dV (green curve), where the constant part gives the inelastic conductance σ_{in} as described in the text.

the change of conductance $\Delta\sigma = \sigma_{\mathrm{in}}/\sigma_0 = 4.6 \times 10^{-2}$ due to excitation of the C-O stretch mode.

STM allows the real-space observation of site-resolved single-molecule motions and reaction. The reaction rate as a function of bias voltage and tunneling current provides important informations to gain deep insight into the elementary processes of reactions induced by vibrational excitation by tunneling electrons. The identification of the vibrational mode responsible for various surface motions and reactions of single molecules is essential for achieving mode-selective control of chemical reactions at surfaces. While $R(I)$ only tells us how many electrons are required to induce reaction, a reproduction of a experimental $Y(V)$ using a formula presented here provides almost all the key quantities in vibrationally mediated reactions of single molecules. An important and novel finding in this work is not the determination of the C-O stretch mode energy and its damping rate. That is an estimate of the anharmonic coupling from the transition rate $\gamma_{\nu,\mathrm{RC}}$ used in the full and excellent reproduction of the experimental result for the first time since we assumed in Ref. 9. The present analysis not only completes our understanding of the elementary process for CO hopping on Pd(110) but can also be applied to investigate any vibrationally mediated motions and reactions induced by vibrational mode coupling. In particular, the explicit analytical formula proposed here provides a versatile tool to analyze experimental data of $R(V)$ or $Y(V)$ in order to deepen an understanding of the elementary processes responsible for single molecule reactions.

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