

Spectral features of inelastic electron transport via a localized state

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A theory of spectral properties of electron transport via a localized state coupled with a vibrational degree of freedom is presented using a two-channel Newns-Anderson Hamiltonian with a nonequilibrium electron distribution. Our model can be applied to a study of electronic transport through an atomic wire, conductance via a single molecule bridge sandwiched between two electrodes, and also inelastic tunneling spectroscopy of single adsorbates with scanning tunneling microscope. A common key feature expected in these phenomena is an inelastic scattering with lattice or molecular vibration. The density of states ρ_a of the localized level and the second derivative of the total current d^2I/dV^2 with respect to the bias voltage are calculated in order to elucidate how the inelastic scattering manifests itself in ρ_a and d^2I/dV^2 . It is found that two different time scales associated with the *lifetime* of tunneling electrons in the localized state and the *residence time* due to virtual excitation of electrons between two electrodes and the localized state play important roles in various features of d^2I/dV^2 spectra.

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I. INTRODUCTION

Fabrication of nanoscale devices in which quantum effects play a central role has received a great deal of attention for novel atomic and molecular devices. In such systems, contribution to resistance in macroscopic scale such as both an elastic scattering with defects or impurities and an inelastic scattering with the lattice vibrations becomes less influential, because the mean-free path of electrons can be much longer than the length of the size of devices. Recently, Agrait *et al.* studied electronic transport in gold atomic chains of up to seven atoms in length.¹ They found that the electronic transport in a single-mode ballistic atomic wire is nondissipative up to a finite voltage threshold corresponding to the excitation of the atomic vibrations. This threshold showed the evidence of inelastic current accompanied by excitation of vibrational mode. Recently, Smit *et al.* also measured the conductance of a single hydrogen molecule sandwiched between two platinum electrodes.² A sudden drop in the conductance was attributed to the excitation of an intramolecular vibrational mode. Furthermore, inelastic electron tunneling spectroscopy (IETS) combined with scanning tunneling microscope (STM-IETS) has been recognized as a powerful and ultimate tool to identify single adsorbed molecules with atomic spatial resolution.³ A common characteristic of the above-mentioned systems is an inelastic electron transport accompanied with vibrational excitation.

In this paper, we present a theory to elucidate how the localized electronic states involved in the inelastic electron tunneling (IET) processes determine the spectral feature of tunneling current under an effect of the vibrational damping due to electron-hole pair (EHP) excitations in a metal-molecule-metal system. It is found that the spectral shape of the second derivative of the total tunneling current with respect to the bias voltage, d^2I/dV^2 , exhibits a variety of features such as peak, dip, asymmetric, or derivativelike shapes depending on the electronic properties of an adsorbate coupled to a vibrational mode.

II. THEORY

Employing the adsorbate-induced resonance model by Persson and Baratoff⁴ for the STM-IETS, we consider electronic transport through a single localized state coupled with two electrodes (the right electrode may be assumed as a tip and the left electrode as a substrate in the case of the STM-IETS experiment). Temporal occupation of tunneling electrons in the localized state induces vibrational excitation and deexcitation. The Hamiltonian of this system^{4,5} is given by a sum of the following three terms:

$$H_0 = \sum_k \epsilon_k c_k^\dagger c_k + \sum_p \epsilon_p c_p^\dagger c_p + \epsilon_a c_a^\dagger c_a + \hbar\Omega b^\dagger b, \quad (1)$$

$$H' = \sum_k W_{k,a} c_k^\dagger c_a + \sum_p W_{p,a} c_p^\dagger c_a + \text{H.c.}, \quad (2)$$

$$H'' = \chi(c_a^\dagger c_a - \langle c_a^\dagger c_a \rangle)(b + b^\dagger). \quad (3)$$

Annihilation (creation) operator and energy for electrons are denoted by $c(c^\dagger)$ and ϵ , respectively, and k , p , and a label the one-particle eigenstates of the right electrode, the left electrode, and a single orbital, respectively. A molecular vibration is introduced with annihilation (creation) operator $b(b^\dagger)$ and the energy $\hbar\Omega$. In the absence of electron-vibration interaction, H' gives a width $\Delta = \Delta_R + \Delta_L$ induced by electronic shuttling between the adsorbate and two electrodes $\Delta_{R/L} = \pi \sum_{k/p} |W_{k/p,a}|^2 \delta(\epsilon - \epsilon_{k/p})$. The energy dependence of $\Delta_{R/L}$ is neglected in the wide-band limit. The electron-vibration coupling H'' causes vibrational damping and frequency shift through EHP excitations near the Fermi levels in the right and left electrodes. At the same time, this interaction opens IET processes for tunneling electrons via emission and absorption of vibrational phonons.

The right and left electrodes are assumed to be in thermal equilibrium with the same temperature T , and have independent chemical potentials μ_R and μ_L , respectively. The dis-

tribution functions for electrons in the right electrode $n_R(\epsilon)$ and the left electrode $n_L(\epsilon)$ are given by the Fermi distribution function. A bias voltage $eV = \mu_R - \mu_L$ applied between two electrodes gives rise to a nonequilibrium situation for electronic transport due to the hybridization W . The Keldysh-Green function technique is employed to study the nonequilibrium system.^{5,6} The electron is assumed to undergo coherent tunneling through the single energy level.

The *total* stationary current I , which includes both elastic and inelastic currents, is given by

$$I = \frac{2e}{\hbar} \frac{\Delta_R \Delta_L}{\Delta} \int d\epsilon \rho_a(\epsilon) [n_L(\epsilon) - n_R(\epsilon)], \quad (4)$$

where

$$\rho_a(\epsilon) = -\frac{1}{\pi} \text{Im}[\epsilon - \epsilon_a + i\Delta - \Sigma^r(\epsilon)]^{-1} \quad (5)$$

is the density of states (DOS) for electrons in the localized state. The imaginary part of the second-order retarded self-energy for electrons $\Sigma^r(\epsilon)$ is given by

$$\begin{aligned} \text{Im} \Sigma^r(\epsilon) = & -\pi \chi^2 \int_0^\infty d\omega \rho_{\text{ph}}(\omega) \{ \rho_a(\epsilon - \omega) ([1 - n_a(\epsilon - \omega)] \\ & \times [1 + n_{\text{ph}}(\omega)] + n_a(\epsilon - \omega) n_{\text{ph}}(\omega)) \\ & + \rho_a(\epsilon + \omega) ([1 - n_a(\epsilon + \omega)] n_{\text{ph}}(\omega) \\ & + n_a(\epsilon + \omega) [1 + n_{\text{ph}}(\omega)]) \}. \end{aligned} \quad (6)$$

Here, $\rho_{\text{ph}}(\omega)$ is the vibrational DOS. The distribution functions for electrons in the localized state n_a and vibrational phonons n_{ph} are given by

$$n_a(\epsilon) = \frac{\Delta_L}{\Delta} n_L(\epsilon) + \frac{\Delta_R}{\Delta} n_R(\epsilon), \quad (7)$$

$$\begin{aligned} n_{\text{ph}} = & \frac{1}{e^{\omega/kT} - 1} + \frac{\pi \chi^2}{\text{Im} \mathcal{P}^r(\omega)} \frac{\Delta_L \Delta_R}{\Delta^2} \int d\epsilon \rho_a(\epsilon + \omega) \rho_a(\epsilon) \\ & \times [n_R(\epsilon + \omega) - n_L(\epsilon + \omega)] [n_R(\epsilon) - n_L(\epsilon)]. \end{aligned} \quad (8)$$

Here, the retarded self-energy for phonons is denoted as \mathcal{P}^r . Equation (6) gives the electronic energy dissipation due to the coupling with vibrational system. The real and imaginary parts of Σ^r represent the energy-dependent energy shift and the broadening of the adsorbate electronic states due to the electron-vibration coupling, respectively. The first (second) term in the curly bracket in Eq. (6) indicates a process in which an electron (hole) with energy ϵ emits (absorbs) a vibrational energy ω . Transition of an electron (hole) from energy ϵ to energy $\epsilon + \omega$ accompanied with absorption (emission) of a vibrational phonon corresponds to the third (last) term. The first and the last terms give main contribution to energy dissipation at low temperatures. The second-order retarded self-energy for the vibrational phonons $\mathcal{P}^r(\omega)$ determines

$$\rho_{\text{ph}}(\omega) = -\frac{1}{\pi} \text{Im}\{[(\omega^2 - \hbar^2 \Omega^2)/2\hbar \Omega - \mathcal{P}^r(\omega)]^{-1}\}. \quad (9)$$

Here, $\text{Im} \mathcal{P}$ is given by

$$\text{Im} \mathcal{P}^r(\omega) = -\pi \chi^2 \int d\epsilon [n_a(\epsilon) - n_a(\epsilon + \omega)] \rho_a(\epsilon) \rho_a(\epsilon + \omega), \quad (10)$$

which causes the vibrational damping due to the EHP excitations. As described below, $\text{Re} \Sigma^r(\epsilon)$ is found to give an important contribution to characterize the IETS spectrum. The second term of Eq. (8) describes the source of the so-called ‘‘vibrational heating’’ due to the vibrational excitation by tunneling currents and has been shown to play an indispensable role in atom transfer with STM.⁷

Hereafter, we are primarily concerned with the theory of the STM-IETS, where the broadening of the resonance is dominated by the coupling with the substrate, i.e., $\Delta_L \gg \Delta_R$. For $\Delta_R \sim \Delta_L$, the present formulation is applicable for a study of the inelastic electronic transports in atomic chain system and through a single molecule sandwiched between two electrodes. With simplified assumptions of $T=0$ and $n_{\text{ph}}(\omega)=0$ (without the vibrational heating^{5,8}), we obtain the IETS spectrum at $eV \sim \hbar \Omega$ in two limiting cases; one is *resonant* case, $\Delta \gg |\hbar \Omega - \epsilon_a|$, and the other is *far-from-resonance* case, $\Delta \ll |\hbar \Omega - \epsilon_a|$,

$$\frac{d^2 I}{dV^2} \sim \mp \frac{2e^3}{\hbar} \frac{\Delta_L \Delta_R}{\Delta^2} \frac{\Gamma_{\text{ph}}}{\hbar \Omega} \rho_{\text{ph}}(eV), \quad (11)$$

where the upper (lower) sign corresponds to the resonant (far-from-resonance) case and

$$\Gamma_{\text{ph}} \sim \pi \chi^2 \hbar \Omega [\Delta_R \rho_a^2(\mu_R) + \Delta_L \rho_a^2(\mu_L)] / \Delta \quad (12)$$

is the vibrational broadening due to EHP excitations. For these two limiting cases, the IETS spectrum is directly related to $\rho_{\text{ph}}(\omega)$ with opposite signs at a red-shifted vibrational energy $\hbar \Omega' \sim \hbar \Omega - \chi^2 [\Delta_R \rho_a(\mu_R) + \Delta_L \rho_a(\mu_L)] / \Delta$.⁹

III. NUMERICAL CALCULATION

Numerical calculation is performed to study how the IETS spectrum changes as a function of ϵ_a . The chemical potential of the right electrode is chosen as the origin of the energy. The vibrational frequency $\hbar \Omega$ and Δ_L are fixed at 100 meV and 1 eV, respectively. The electron-vibration coupling χ and Δ_R are determined in such a way that the vibrational damping rate is nearly equal to 1 ps and the total current at $eV = \hbar \Omega$ is an order of 1 nA. Figure 1 shows the evolution of the IETS spectra $d^2 I / dV^2$ for $\epsilon_a = 0$ ($\chi = 100$ meV and $\Delta_R = 0.6 \times 10^{-4}$ meV), Δ_L ($\chi = 200$ meV and $\Delta_R = 0.12$ meV), $1.5 \Delta_L$ ($\chi = 320$ meV and $\Delta_R = 0.2$ meV), $2 \Delta_L$ ($\chi = 500$ meV and $\Delta_R = 0.3$ meV). Here, we neglected the redshift of the vibrational frequency. As analytically derived in Eq. (11), in the resonance case, $\epsilon_a = 0$, the IETS spectrum shows a close resemblance to $\rho_{\text{ph}}(\omega)$, that is, a Lorentzian dip (peak) with a width of Γ_{ph} at $|eV| = \hbar \Omega$ for positive (negative) bias voltage. As ϵ_a

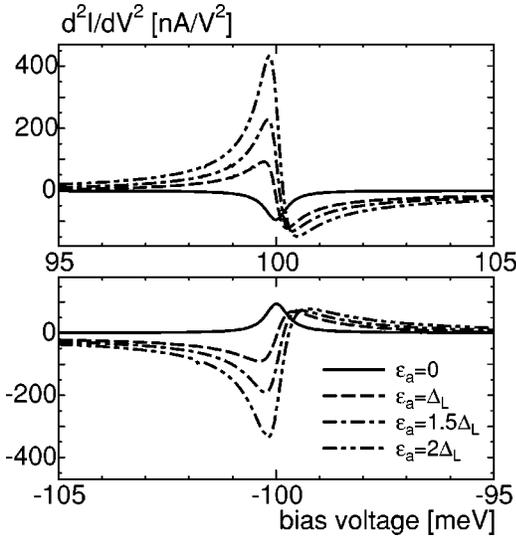


FIG. 1. Evolution of the IETS spectra. The IETS spectra are shown for several positions of ϵ_a . See the parameters in the text. The solid, dashed, dot-dashed, and double-dot-dashed lines represent $\epsilon_a=0$, Δ_L , $1.5\Delta_L$, and $2\Delta_L$, respectively. The upper (lower) figure shows spectra for positive (negative) bias voltage. Here, we neglected the real part of the self-energy for phonons, $\text{Re } \mathcal{P}^r$, which determines the redshift due to coupling with the substrate and the tip.

moves away from the Fermi level, the IETS spectrum changes its shape into “derivativelike” shape at $\epsilon_a=\Delta_L$ and $1.5\Delta_L$, asymmetric one at $\epsilon_a=2\Delta_L$ and exhibits a Lorentzian peak in the far-from-resonance case. Although \hbar/Γ_{ph} is fixed at 1 ps, the broader spectra are observed at off-resonant cases in Fig. 1. The IETS spectrum d^2I/dV^2 does not directly reflect $\rho_{\text{ph}}(\omega)$, but represents the first derivative of $\rho_a(\epsilon)$. A close inspection of $\Sigma^r(\epsilon)$ and $\rho_a(\epsilon)$ reveals how these spectral shapes are determined. Figure 2 shows $\rho_a(\epsilon)$ at $V=0$ for $\epsilon_a=0$. The inset of Fig. 2 depicts the real and imaginary parts of $\Sigma^r(\epsilon)$. Unless the energy of electrons or holes exceeds the vibrational energy, no electronic energy dissipates into the vibrational system. The broadening due to electron-vibration coupling is nearly zero between $-\hbar\Omega$ and $\hbar\Omega$. On the other hand, once an electron has enough energy to excite a vibrational mode, a new channel of energy dissipation becomes available. It produces an additional width $\Delta - \text{Im } \Sigma^r(\epsilon)$ to ρ_a . Upon opening the IET channel, $\text{Re } \Sigma^r(\epsilon)$ shows a sharp peak (dip) at $-\hbar\Omega$ ($\hbar\Omega$) as seen in the inset of Fig. 2.

There are two characteristic time scales which govern the tunneling phenomena. One is the electronic lifetime given by

$$T_{\text{life}}(\epsilon) = \frac{\hbar}{\Delta - \text{Im } \Sigma^r(\epsilon)}, \quad (13)$$

in which electronic energy in the localized state dissipates into the right/left electrode or vibrational mode. The other is the residence time given by

$$T_{\text{res}}(\epsilon) = \frac{\hbar}{|\epsilon_a - \text{Re } \Sigma^r(\epsilon) - \mu_{\text{L/R}}|}. \quad (14)$$

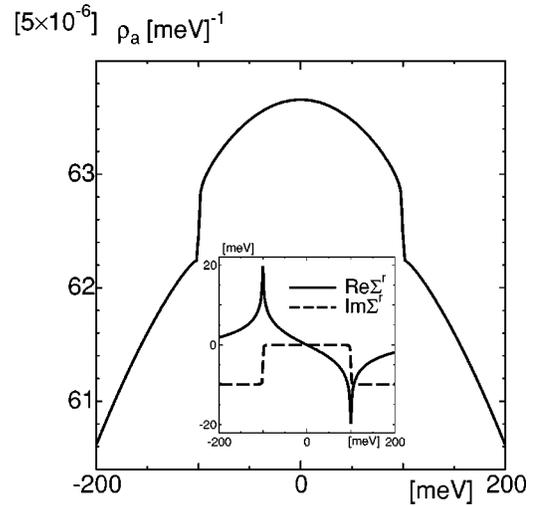


FIG. 2. The electronic DOS for $\epsilon_a=0$, i.e., resonant case, at $V=0$. In the inset, the solid (dashed) line corresponds to the real (imaginary) part of $\Sigma^r(\epsilon)$. The other parameters are the same as in Fig. 1.

The virtual transition from the Fermi levels in the left and right electrodes to the localized state is allowed within $T_{\text{res}}(\epsilon)$.

In the resonant condition, when $T_{\text{life}}(\epsilon)$ is much shorter than $T_{\text{res}}(\epsilon)$, it is plausible to approximate

$$\rho_a(\epsilon) = -\frac{1}{\pi} \text{Im}[\epsilon - \epsilon_a - \Sigma^r(\epsilon)]^{-1} \quad (15)$$

$$\sim \pi^{-1}[\Delta - \text{Im } \Sigma^r(\epsilon)]^{-1} \quad (16)$$

at $\epsilon \sim \hbar\Omega$. The first derivative of ρ_a with respect to the energy, $d\rho_a/d\epsilon \sim d^2I/dV^2$, exhibits a dip ($V>0$) and a peak ($V<0$), whose widths are determined by Γ_{ph} (see Fig. 1). Smit *et al.*² observed a qualitatively similar feature of ρ_a shown in Fig. 2 in the conductance in a Pt/H₂ system. The dip (peak) at 63.5 meV (-63.5 meV) observed in $dG/dV = d^2I/dV^2$ was assigned to the center of mass motion of the H₂ molecule. The width of these structures was found to be much larger than that expected from the thermal and instrumental broadening. As derived in Eq. (11), $dG/dV = d^2I/dV^2$ spectrum is directly related to ρ_{ph} in the resonant case. The large width observed in dG/dV spectrum for the Pt/H₂ system suggests a very short vibrational lifetime due to strong coupling to the Pt electrode. They speculated that conduction through the molecule involves mainly the H₂ anti-bonding states. The present analysis also suggests that the H₂-antibonding orbital participated in the intermediate state for electron transport is located near the Fermi level of the Pt electrode. Agrait *et al.* also observed the same feature of the conductance and differential conductance in the electronic transport in gold atomic chains.¹

In the STM-IETS experiments, Hahn *et al.* observed a dip structure for the O-O stretch mode on Ag(110) for a positive

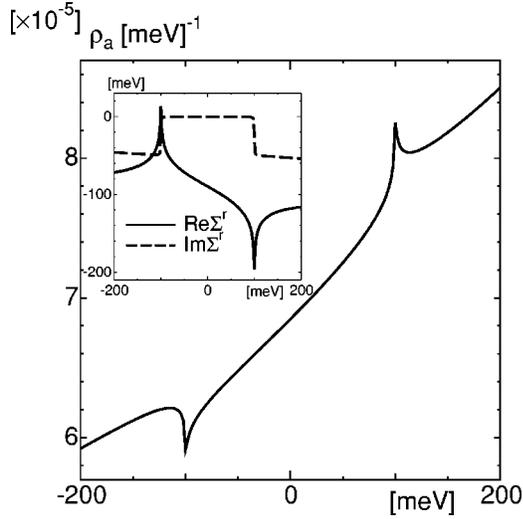


FIG. 3. The electronic DOS for $\epsilon_a = 2\Delta_L$ at $V=0$. In the inset, the solid (dashed) line corresponds to the real (imaginary) part of $\Sigma^r(\epsilon)$. The other parameters are the same as in the Fig. 1.

bias voltage in d^2I/dV^2 spectrum.¹⁰ They suggests that the $1\pi_g^-$ molecular orbital of the O_2 located near the Fermi level of the substrate is responsible for the inelastic tunneling. Since the IETS spectrum is given by the first derivative of $\rho_a(\epsilon)$, it produces a dip (peak) at $eV \sim \hbar\Omega$ ($-\hbar\Omega$) with a width of Γ_{ph} . Inclusion of multiple electron-vibration scattering in Eq. (11) by replacing the denominator of Δ with $\Delta - \text{Im}\Sigma^r(\epsilon)$ gives the following formula in the resonant case:

$$\frac{d^2I}{dV^2} \sim -\frac{2e^3}{\hbar^3} \Delta_L \Delta_R \frac{\Gamma_{ph}}{\hbar\Omega} \rho_{ph}(eV) T_{life}^2(eV). \quad (17)$$

The energy dependence of $T_{life}(eV)$ could be another possible factor to produce the asymmetric shape in the IETS spectrum, even when $\rho_{ph}(eV)$ is a symmetric Lorentzian.

On the other hand, when ϵ_a is away from both the Fermi levels, $T_{res}(\epsilon)$ becomes much shorter than $T_{life}(\epsilon)$. It is not appropriate to assume that tunneling electrons from the left or right electrodes stay in the adsorbate level during $T_{life}(\epsilon)$. In Fig. 3, $\rho_a(\epsilon)$ for $\epsilon_a = 2\Delta_L$ is shown together with the real and imaginary parts of $\Sigma^r(\epsilon)$. In contrast to the resonant case, since $T_{res}(\epsilon) \ll T_{life}(\epsilon)$, $\rho_a(\epsilon)$ is very sensitive to $T_{res}(\epsilon)$ rather than $T_{life}(\epsilon)$, and ρ_a can be approximated as

$$\rho_a(\epsilon) \sim \frac{1}{\pi} \frac{\Delta - \text{Im}\Sigma^r(\epsilon)}{[\epsilon - \epsilon_a - \text{Re}\Sigma^r(\epsilon)]^2}. \quad (18)$$

In this situation, the shift of electronic energy level $\text{Re}\Sigma^r(\epsilon)$ has a crucial influence on the behavior of $\rho_a(\epsilon)$. When the effective energy level $\tilde{\epsilon}_a(\epsilon) = \epsilon_a - \text{Re}\Sigma^r(\epsilon)$ moves closer to the Fermi levels, $T_{res}(\epsilon)$ becomes longer. As a result of larger temporal population in the localized state, this results in the skewed peak structure. The dip (peak) in $\Sigma^r(\epsilon)$ gives a peak (dip) at $\hbar\Omega$ ($-\hbar\Omega$) in $\rho_a(\epsilon)$. By taking the first de-

rivative $d\rho_a(\epsilon)/d\epsilon$, this peak (or dip) produces the derivativelike or asymmetric shape in the IETS spectrum at the vibrational energies $\pm\hbar\Omega$.

This type of singularity of the IETS spectra has been already predicted by Persson.¹¹ However in his analysis $\Sigma^r(\epsilon)$ was not taken into consideration. Inclusion of electronic self-energy may explain the difference of peak height and/or peak positions between the positive and negative bias polarities in the STM-IETS experiment.¹²⁻¹⁴ We also mention the change of the spectral feature for bias polarity. For the resonant (far-from-resonance) case, in which a dip (peak) is observed at a positive bias voltage, the IETS spectrum shows a peak (dip) at a negative bias voltage. However as shown in Fig. 1, the IETS spectra do not give an antisymmetric change for the opposite bias polarity at off-resonant cases. For the derivativelike spectrum such as for $\epsilon_a = \Delta_L$, it gives almost *symmetric* change for the opposite bias polarity. (See the dashed line in Fig. 1.) So far, one of the criteria of an experimental assignment for vibrational signals is based on the antisymmetric change of the IETS spectra for the opposite bias polarity. The present analysis, however, provides another way of assignment for the derivativelike features, which display the symmetric spectrum for both bias polarities.

As discussed by Crljen and Langreth¹⁵ and experimentally observed by Ryberg,¹⁶ the vibrational damping due to the EHP excitations produces an asymmetric Fano shape¹⁷ in the infrared absorption spectra of adsorbates on metal surfaces. Recently, Pascual *et al.* observed an asymmetric line shape in the IETS spectrum for a benzene molecule adsorbed on Ag(110), which was tentatively assigned to the Fano effect.¹⁸ However, the asymmetric feature is not sufficient evidence of the Fano effect. As we have seen here, it is found that the energy dependence of $\tilde{\epsilon}_a(\epsilon)$ produces the asymmetric feature as shown in Fig. 1 for $\epsilon_a = 2\Delta_L$. Even in the resonant/far-from-resonance cases, where the IETS spectrum directly mimics the vibrational DOS, the energy dependence of $T_{life}(\epsilon)$ produces the asymmetric line shape presented in Eq. (17). The present theory proposes that the observation of asymmetric feature in the IETS spectra does not necessarily imply the Fano-type modification of the spectra.

IV. CONCLUDING REMARKS

In summary, we present a general theory for electronic transport accompanying emission and absorption of vibrational phonons. It is shown that a variety of features in the IETS spectra is closely related to the electronic properties of the localized state involved in the electron transport processes. We pointed out the qualitative agreement between our theory and experimental results of the spectral features of the conductance G and the differential conductance dG/dV of hydrogen sandwiched between platinum electrodes² as well as the IETS spectrum of the STM-IETS experiments of adsorbed molecules.³ Only in some specific cases, the resonant and the far-from-resonance cases, the IETS spectrum is directly related to the vibrational DOS. Compared to the available experimental data, the spectral width presented here is much narrower than experimental results. Lauhon and Ho systematically studied the effect of temperature and the bias modulation on the vibrational peak width, the intensity and

the line shape for the C-H stretch mode of a single acetylene molecule on Cu(001).¹³ They reported that the IETS spectra are less influenced by the vibrational damping because of the use of large bias modulation than the vibrational broadening. This may hide the intrinsic features of the IETS spectrum. The present theory proposes that more attention has to be paid on the intrinsic spectral line shape in order to gain deep insight into the electronic and vibrational properties of single adsorbed molecule observed by the STM-IETS.

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