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Damping in the vibrational spectroscopy of adsorbates with STM

M. A. Gata* and P. R. Antoniewicz
Department of Physics, The University of Texas at Austin, Austin, Texas 78712

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The damping of vibrationally excited adsorbates on metal surfaces may be an important issue in the observability of their vibrational spectra with a scanning tunneling microscope. In the present paper, we discuss these effects in the framework of two-particle Green's functions, following a method originally employed to describe inelastic scattering in heterostructures [N. S. Wingreen, K. W. Jacobson, and J. W. Wilkins, Phys. Rev. B **40**, 11 834 (1989)]. By dressing the phonon lines, one can take into account the finite lifetime of the oscillations and obtain an expression for the total transition probability, through all the possible phonon channels. We also show, in the no-damping limit, and for a single vibrating coordinate, the analytical correspondence between the present method and the one presented in a previous related work [M. A. Gata and P. R. Antoniewicz, Phys. Rev. B **47**, 13 797 (1993)]. [S0163-1829(99)02036-6]

I. INTRODUCTION

Vibrational spectroscopy of chemisorbed species using a low-temperature scanning tunneling microscope should provide a particularly convenient technique of identifying atoms and molecules on surfaces and in the study of their adsorption properties and mutual interactions. Experimental evidence of this kind of spectroscopy has been, however, scarce. More than a decade ago, Smith *et al.*[1] obtained $\partial I/\partial V$ spectra that could possibly be interpreted along the lines of our model in Ref. 2. But the instability of the tip-sample distance, as well as other factors have a large impact on the fluctuations of the total tunneling current (see, for example, Ref. 3), precluding an unambiguous observation of the inelastic effects we are seeking. Extrinsic factors, such as noise, mechanical instabilities and others, have been progressively reduced in recent experiments. However, one should also take into consideration some of the inescapable, intrinsic, sources of signal degradation.

Two different inelastic tunneling coupling mechanisms have been suggested by workers in this field: the electron-dipole coupling, and the tunneling through an adsorbate resonance. Both may be, in principle, susceptible to be used for vibrational spetroscopy. However, for electron-dipole coupling, a change of conductance of at most 1% is expected,[4] whereas the tunneling through an adsorbate could provide, in principle, relative changes of about 10 % in the conductance, especially when the resonance density of states is centered at the Fermi level of the metal substrate.[5,6,2] Note, however, that Persson and Baratoff[5] predict a decrease in conductance, whereas we expected an increase,[2] due to the opening of more tunneling channels.

Most recently, Stipe, Rezaei, and Wo[7–10] observed inelastic electron tunneling spectra, with a relative increase in the junction conductance, at the excitation energies of the vibrational modes, of up to 12% for the case of C_2H_2 on Cu(100),[8] but not so large for the same molecule on Ni(100).[10] These landmark results were achieved with an ultra-stable homemade scanning tunneling microscopy (STM)[7] at a temperature of 8 K, by placing the tip above a single, isolated acetylene molecule adsorbed on metal surfaces (Cu and Ni), in conditions that favor a resonant tunneling transition such as the one we are concerned with, both presently and in the previous work.[2]

What interests us here are the obstacles to experimental observation, which are intrinsic to chemisorption itself. Also, among other possibilities, we choose the damping of the adsorbate oscillations due to the excitation of electron-hole pairs in the adsorbate-metal substrate system, as the main channel for the dissipation of the oscillator energy. The importance of this particular process has been emphasized by a number of workers, in particular Gadzuk,[11] Ueba,[12] Persson and Persson,[13] Persson and Hellsing,[14] Persson and Ryberg,[15] among others. One of the main results of these works is the predicted dependence of the lifetime of the vibrational excitation on the inverse square of the adsorbate projected density of states at the Fermi energy, $\rho_a(\epsilon_F)$, as well as on the inverse square of the electron-oscillator (''local phonon'') coupling constant, denoted here by χ_A^0. Other predicted characteristics of the electron-hole pair excitation mechanism are a lorentzian lineshape (but see Ref. 16), weak temperature dependence and a strong isotopic effect.[17]

Unfortunately, these results indicate that the condition for the largest change in the resonant tunneling conductance coincides with the condition for the strongest damping of the oscillation, with the possible result that the anticipated vibrational sidebands in the first derivative $\partial I/\partial V$ will be greatly reduced. Furthermore, since the total tunneling current is given by the convolution of the transition rate with the densities of electronic states (DOS) of the tip[18] and of the substrate, it may very well happen that their structure will dominate the observed conductance as a function of bias voltage precluding, for reasons intrinsic to the chemisorption phenomenon, the attainment of this kind of vibrational spectroscopy. It should be mentioned, however, that Stipe *et al.*[8] were able to minimize this problem by subtracting off the the DOS-dependent spectra obtained at a clean surface site, away from any adsorbed molecule.

Our aim in the present paper is to develop a model describing these effects and making a direct comparison with a previous description[2] based on the resolvent formulation of the chemisorption problem. As an outcome of this connection we show, in the Appendix, that there is an analytical correspondence, at least in the case of a single vibrational coordinate, between scattering in the gas phase,[19] chemisorption in the Newns-Anderson approach as presented in review papers, e.g., by Grimley[20] or Muscat and Newns[21] and resonant tunneling in heterostructures as, e.g., in Ref. 22. This was shown explicitly some time ago,[23] for the zero and one-phonon channels. Gadzuk[24] has pointed out the general correspondence between the descriptions of Domcke and Cederbaum[19] and Wingreen *et al.*,[22] using numerical simulations but without establishing explicitly, however, that analytical connection.

This paper is organized as follows. In Sec. II we start with the same Hamiltonian as before[2] and follow Wingreen *et al.*,[22] expressing the total current, elastic and inelastic, in terms of a Fourier transform of a two-particle Green's function. This Green's function is solved for, leading to a current as a sum over all possible phonon channels. Next, in Sec. III, we review the results of Ueba,[12] of interest to the present problem, concerning the electron-hole damping of the adsorbate motion. In particular we extract the expression for the dressed phonon propagator and, by inserting this modified propagator in the perturbation expansion for the aforementioned two-particle Green's function, we rederive, in Sec. IV, the total current. This current reduces to the previous expression in the no-damping limit. We then compute the related resonant transition rate as a function of the incoming (tip) electron energy relative to the shifted adsorbate orbital energy. This shows the main point of our present argument, the possible disappearance of the conductance vibrational sidebands, which, as we argued previously, should provide information on the adsorbate vibration quantum. In Sec. V, we draw some conclusions pertinent to the observation of these spectra and, in the Appendix, we prove the consistency of our two approaches by showing that, at least for a single vibration mode and in the absence of damping, the present many-body method and the simpler one we used previously give the same analytical result for the transition rate.

II. TUNNELING CURRENT

We aim at describing the resonant tunneling transition as a scattering event in the more general formalism of many-body Green's functions, with the restriction of a single vibration coordinate (''local phonon''). In this section we obtain, without damping, an expression for the total current (elastic plus inelastic). We only highlight the main points in this section because we follow Ref. 22 quite closely and because the final result is, in fact, the same as in Ref. 2, using a resolvent technique.

Our starting Hamiltonian is the same as in Ref. 2, $H=H_0+H_1$, where

$$H_0=\epsilon_A^0 c_A^\dagger c_A+\sum_l \epsilon_l c_l^\dagger c_l+\sum_k \epsilon_k c_k^\dagger c_k+\Omega(B^\dagger B+1/2) \tag{2.1}$$

and

$$H_1=\chi_A^0(c_A^\dagger c_A-\langle n_A\rangle)(B+B^\dagger)+\sum_l (V_{Al}c_A^\dagger c_l+V_{lA}c_l^\dagger c_A) +\sum_k (V_{Ak}c_A^\dagger c_k+V_{kA}c_k^\dagger c_A). \tag{2.2}$$

In H_0 the first term describes the atom (or molecule) to be adsorbed, the second and third terms describe the substrate and tip states, respectively, and the last term represents the unperturbed adsorbate-oscillator. H_1, on the other hand, describes the various interactions—the first term couples the state of occupation of the adsorbate orbital with its position coordinate, the second and third terms couple the adsorbate orbital with the substrate and tip states, respectively. The constant factor $\langle n_A\rangle$ represents the self-consistent equilibrium occupancy of the adsorbate orbital, i.e., without tunneling current. As before, tunneling between tip and adsorbate will be assumed to be represented by the matrix element $V_{Ak}=\langle A|H|k\rangle=\langle A|H|t\rangle\langle t|k\rangle$, where $|t\rangle$ is the orbital of the last tip atom from/to which electrons tunnel and $\langle A|H|t\rangle$ is Bardeen's tunneling matrix element.[25,26]

Introducing a coordinate displacement through the new phonon operators b such that $B^{(\dagger)}=b^{(\dagger)}+\chi_A^0\langle n_A\rangle/\Omega$, we rewrite the Hamiltonian thus: $H=H_0+H_1$, with

$$H_0=\epsilon_A^0 c_A^\dagger c_A+\sum_l \epsilon_l c_l^\dagger c_l+\sum_k \epsilon_k c_k^\dagger c_k+\Omega(b^\dagger b+1/2)+\alpha \tag{2.3}$$

and

$$H_1=\chi_A^0(c_A^\dagger c_A-\langle n_A\rangle)(b+b^\dagger)+\sum_l (V_{Al}c_A^\dagger c_l+V_{lA}c_l^\dagger c_A) +\sum_k (V_{Ak}c_A^\dagger c_k+V_{kA}c_k^\dagger c_A), \tag{2.4}$$

where we have defined a renormalized adsorbate energy given by $\epsilon_A=\epsilon_A^0+2(\chi_A^0)^2\langle n_A\rangle/\Omega$ (and which may include image effects) and the constant factor $\alpha\equiv-(\chi_A^0\langle n_A\rangle)^2/\Omega$.

From S-matrix theory, the electronic transmission probability between an initial state $|k_i\rangle$ in the tip and a final state $|l_f\rangle$ in the substrate, here through the intermediate resonance $|A\rangle$, is given by the thermal average[22,27]

$$T^2(l_f,k_i)=\sum_{n_f}\sum_{n_i}\frac{e^{-\beta E_{n_i}}}{Z_{phonon}}|\langle l_f;n_f|S|k_i;n_i\rangle|^2, \tag{2.5}$$

where $\beta=(k_BT)^{-1}$, $E_{n_i}=\Omega(n_i+1/2)$ is the energy of the oscillator in state $|n_i\rangle$ and Z_{phonon} is the localized oscillator partition function.

The S matrix operator above is expressed by[27]

$$S=1-i\int_{-\infty}^{+\infty}\frac{dt_1}{\hbar}e^{iH_0t_1/\hbar}H_1e^{-iH_0t_1/\hbar} -i\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty}\frac{dt_1dt_2}{\hbar^2}e^{iH_0t_2/\hbar}H_1G_{ret.}(t_2-t_1)H_1e^{-iH_0t_1/\hbar} \tag{2.6}$$

where

$$G_{ret.}(t_2-t_1)=-i\Theta(t_2-t_1)e^{-iH(t_2-t_1)} \tag{2.7}$$

is the retarded Green's function operator, in the present case to be applied to the intermediate resonant orbital $|A\rangle$. H is the total Hamiltonian operator, $H=H_0+H_1$, and the initial and final electron-phonon states are defined by their occupancies

$$|k_i;n_i\rangle=|0_A;(1_{k_i});n_i\rangle \quad |l_f;n_f\rangle=|0_A;+1_{l_f};n_f\rangle. \tag{2.8}$$

The initial electron-phonon state describes an empty adsorbate orbital, n_i adsorbate-oscillator phonons and the ground states of both the tip, from which the tunneling electron $|k_i\rangle$ is highlighted, and the substrate. The final electron-phonon state describes an empty adsorbate orbital, n_f adsorbate-oscillator phonons and the ground state of the tip minus one electron and of the substrate plus one electron, $|l_f\rangle$. The transition we are considering carries one electron from an occupied tip state (below the tip Fermi level) to the empty adsorbate resonance, to an empty state above the substrate Fermi level. In fact, the intermediate resonant state has a fractional occupancy, but that occupancy is taken into account by affecting the total current by the correspondent vacancy factor so that we will be able, from now on, to perform the calculation of the transition rates as if the intermediate state were vacant.

The transition probability for a tip electron of energy ϵ_{k_i} to be transmitted to the substrate with energy ϵ_{l_f} is given by the Fourier transform

$$\begin{aligned}T^2(l_f,k_i)=|V_{Ak_i}|^2|V_{l_fA}|^2\int\int\int\int\frac{dt_1dt_2ds_1ds_2}{\hbar^4}\\ \times\Theta(t_2-t_1)\Theta(s_2-s_1)\\ \times e^{i\epsilon_{l_f}(t_2-s_2)/\hbar}e^{-i\epsilon_{k_i}(t_1-s_1)/\hbar}\\ \times\langle c_A(s_1)c_A^{\dagger}(s_2)c_A(t_2)c_A^{\dagger}(t_1)\rangle,\end{aligned} \tag{2.9}$$

and the transmission probability per unit time, $W(l_f,k_i)$, for all the possible final phonon excitations of the resonant orbital oscillator, is given by (see, e.g., Ref. 27)

$$\begin{aligned}W(l_f,k_i)[sec^{-1}]=\frac{T^2(l_f,k_i)}{\int_{-\infty}^{+\infty}dt_1}=\frac{1}{\hbar}|V_{Ak_i}|^2|V_{l_fA}|^2\\ \times\int\int\int\frac{d\tau ds dt}{\hbar^3}\\ \times e^{i[(\epsilon_{k_i}-\epsilon_{l_f})\tau+\epsilon_{l_f}t-\epsilon_{k_i}s]/\hbar}G_A(\tau,s,t)\end{aligned} \tag{2.10}$$

where

$$G_A(\tau,s,t)=\Theta(t)\Theta(s)\langle c_A(\tau-s)c_A^{\dagger}(\tau)c_A(t)c_A^{\dagger}(0)\rangle \tag{2.11}$$

is the two-particle, four-time thermodynamic Green's function containing all information on electron-phonon as well as on adsorbate-electrodes interactions. The expansion of this Green's function according to the usual rules of many-body perturbation theory[22,28] leads to a transmission rate, at 0 K, given by

$$W(l_f,k_i)=\sum_{m=0}^{\infty}W_m(\epsilon_{k_i})\delta(\epsilon_{k_i}-\epsilon_{l_f}-m\Omega), \tag{2.12}$$

where

$$W_m(\epsilon_{k_i})=2\pi/\hbar|V_{Ak_i}|^2|V_{l_fA}|^2e^{-2g}\frac{g^m}{m!}|B_m[z(\epsilon_{k_i})]|^2, \tag{2.13}$$

$$B_m[z(\epsilon_{k_i})]=\sum_{j=0}^{m}(-1)^j\binom{m}{j}\sum_{l=0}^{\infty}\frac{g^l}{l!}[z(\epsilon_{k_i})-(j+l)\Omega]^{-1} \tag{2.14}$$

and also $g=(\chi_A^0/\Omega)^2$, $z(\epsilon_{k_i})=\epsilon_{k_i}-(\epsilon_A'-g\Omega)+i\Gamma/2$. Here $\epsilon_A'=\epsilon_A+\Sigma^R+\alpha$, Σ^R being the chemical shift of the adsorbate level upon hybridization, given by the Hilbert transform of the level (full) width Γ which, in turn, is given by $\Gamma(\epsilon)=2\pi\Sigma_k|V_{Ak}|^2\delta(\epsilon-\epsilon_k)+2\pi\Sigma_l|V_{Al}|^2\delta(\epsilon-\epsilon_l)$. One expects the interaction with the tip to have a negligible contribution both to the chemical shift and to the level width, due to its much weaker coupling to the adsorbate. In what follows we shall take Γ to be a constant independent of the energy, implying that Σ^R is null.

The total resonant tunneling current, for any number of vibration excitations (‘‘phonons’’) excited in the process, can be written

$$J_{total}=e\sum_k\sum_l W(l,k)[1-f_{subs.}(\epsilon_l)](1-\langle n_A\rangle)f_{tip}(\epsilon_k), \tag{2.15}$$

where $f_{tip}(\epsilon)$ and $f_{subs.}(\epsilon)$ are the Fermi-Dirac occupancy factors, which are simple step functions for $T=0K$, and $(1-\langle n_A\rangle)$ is the equilibrium vacancy factor associated with the adsorbate orbital. Since, in the absence of damping, we can separate this transition rate according to the number of phonons produced and introduce the densities of electronic states for the tip and for the substrate, we can also write the total current as a function of the applied bias voltage V (tip negative, in the process we have been considering) thus

$$\begin{aligned}J_{total}(V)=(1-\langle n_A\rangle)e\Omega_{tip}\Omega_{subs.}\sum_{m=0}^{\infty}\Theta(eV-m\Omega)\\ \times\int_{m\Omega}^{+eV}W_m(\epsilon)\rho_{tip}(\epsilon-eV)\rho_{subs.}\\ \times(\epsilon-m\Omega)d\epsilon\end{aligned} \tag{2.16}$$

in which the electronic energies are being measured with respect to the substrate Fermi level, Ω_{tip} and $\Omega_{subs.}$ are the tip and substrate volumes, respectively, and each m component defines the number of phonons excited in the transition ($m=0$ corresponds to the elastic current, $m=1$ to the one-phonon inelastic current, etc). This expression for the total resonant current reduces to expressions (55) and (56) in our previous model, Ref. 2, for $m=0$ and for $m=1$.

As a consequence of the equality of the two results for the no-damping total current, elastic and (any-phonon) inelastic, which is proven in the Appendix below, our previous conclusions concerning the possible ratio between inelastic and elastic resonant currents remain the same—although varying widely with the adsorption conditions, that ratio could, in principle, become of the order of 10%.[2,5,29,8]

III. DAMPED OSCILLATOR PROPAGATOR

Ueba[12] considered the phenomenon of adsorbate vibrational damping on metal surfaces, due to the excitation of electron-hole pairs in the overall electronic system. In particular, he used a finite temperature propagator approach that is especially suitable for our present purposes. In fact, he was able to arrive at final results for the self-energy $\Pi_{ret}(\omega)$, to be associated with the ''local phonon.'' The real and imaginary components of this self energy represent the shift in frequency and the width (finite lifetime) of the vibration. Specifically, the approximate expression for the redshift due to adsorption is given by

$$\mathrm{Re}[\Pi_{ret}(\omega)] \simeq -2|\lambda|^2 \rho_A(\epsilon_F), \tag{3.1}$$

whereas the width Δ is given by

$$\Delta \simeq -2\,\mathrm{Im}[\Pi_{ret}(\omega=\Omega/\hbar)] = 2\pi|\lambda|^2 \Omega \rho_A^2(\epsilon_F) \tag{3.2}$$

and gives the vibrational lifetime, $\hbar/\Delta$. In the above expressions, λ is the electron-phonon coupling constant (presently denoted by χ_A^0), Ω the unshifted vibration quantum and $\rho_A(\epsilon_F)$ the value of the adsorbate density of states at the Fermi level of the substrate. We assume a Lorentzian density of states, so damping will be strongest if the Lorentzian is centered at the Fermi level.

From the above results, we can determine the perturbed phonon correlation function $\langle A(t_2)A(t_1)\rangle = iD_>(t_2-t_1)$, where $A(t)=b(t)+b^\dagger(t)$. It is this perturbed propagator that we shall need to determine first and then to insert in the perturbative expansion of the new Green's function $G_A(\tau,s,t)$, which will then include the effect of the oscillator damping.

In order to pursue this objective, we start from Dyson's equation

$$D_{ret}(\omega) = \{[D_{ret}^0(\omega)]^{-1} - \Pi_{ret}(\omega)\}^{-1}, \tag{3.3}$$

where the unperturbed phonon propagator is

$$D_{ret}^0(\omega) = \frac{2\Omega}{(\hbar\omega)^2 - \Omega^2 + i\delta} \tag{3.4}$$

and, by way of the spectral density function $B(\omega) = -2\,\mathrm{Im}[D_{ret}(\omega)]$, take advantage of the relation $D_>(\omega) = -i[n_B(\omega)+1]B(\omega)$, which gives, at 0 K

$$D_>(\omega) = -iB(\omega). \tag{3.5}$$

Fourier transforming $D_>(\omega)$ to the time domain, we obtain the final result under the restrictions of zero temperature and weak damping (i.e., damping time $\hbar/\Delta$ much longer than vibration period, or $\Delta \ll \Omega, \Omega'$),

$$D_>(t_1-t_2) = -i\left(\frac{\Omega}{\Omega'}\right) e^{-\Delta|t_1-t_2|/\hbar} e^{-i\Omega'(t_1-t_2)/\hbar} \tag{3.6}$$

where the shifted adsorbate-oscillator vibration quantum Ω' is given by the relation

$$(\Omega')^2 = \Omega^2 + 2\Omega\,\mathrm{Re}[\Pi_{ret}] - \Delta^2. \tag{3.7}$$

The above expression for $D_>(t_1-t_2)$ reduces to the previously used result, $D_>(t_1-t_2) = -i\exp[-i\Omega(t_1-t_2)/\hbar]$, in the limit of no damping ($\Delta \to 0, \Omega' \to \Omega$).

IV. CHANGED TRANSITION RATE AND CONDUCTANCE

It was shown, in Eq. (2.10) above, that the transmission rate is given by a triple Fourier transform of the two-particle propagator $G_A(\tau,s,t)$, associated with the adsorbate orbital. The perturbative expansion of this propagator, according to the usual diagrammatic methods, introduces electron and phonon lines representing the respective correlation functions. Our approach consists in dressing the phonon lines in the second-order diagrams (the zeroth order diagrams do not contain phonon lines and the first-order diagrams are null) and to determine the new $G_A(\tau,s,t)$ to all orders, once again by a exponential resummation.[28,22] As before, the ''bare'' electron lines already include, in fact, hybridization of the adsorbate orbital, so that the corresponding propagators also decay in time. These are given by

$$G_{A,ret}^{(0)}(t) = -i\Theta(t) e^{-(i\epsilon_A' + \Gamma/2)t/\hbar} \tag{4.1}$$

where ϵ_A' and Γ are defined as above, and Θ is the step function.

According to this method, the perturbed propagator $G_A(\tau,s,t)$ is given by

$$G_A(\tau,s,t) = G_A^{(0)}(\tau,s,t) \times \exp\left[\frac{G_{A,1}^{(2)}(\tau,s,t) + G_{A,2}^{(2)}(\tau,s,t) + G_{A,3}^{(2)}(\tau,s,t)}{G_A^{(0)}(\tau,s,t)}\right]. \tag{4.2}$$

$G_A^{(0)}(\tau,s,t)$ is represented by a diagram with two electron lines, $G_{A,1}^{(2)}(\tau,s,t)$ is represented by two electron lines connected by a dressed phonon line, $G_{A,2}^{(2)}(\tau,s,t)$ and $G_{A,3}^{(2)}(\tau,s,t)$ are represented by two electron lines in which one or the other is straddled by a dressed phonon line, as in Ref. 22. The new results for these zeroth and second-order propagators are

$$G_A^{(0)}(\tau,s,t) = [G_{A,ret}^{(0)}(s)]^* G_{A,ret}^{(0)}(t), \tag{4.3}$$

$$\begin{aligned} G_{A,1}^{(2)}(\tau,s,t) = {} & G_A^{(0)}(\tau,s,t)(\chi_A^0)^2 \frac{\Omega}{\Omega'} \left\{ \frac{2\Delta}{(\Delta)^2 + (\Omega')^2} \right. \\ & \times \Theta(t-\tau+s)[\tau\Theta(\tau) - (\tau-t)\Theta(\tau-t) \\ & - (\tau-s)\Theta(\tau-s)]/\hbar + e^{-\Delta|\tau|/\hbar} e^{-i\Omega'\tau/\hbar} \\ & \times [V - iW\,\mathrm{sgn}(\tau)] - e^{-\Delta|\tau-t|/\hbar} e^{-i\Omega'(\tau-t)/\hbar} \\ & \times [V - iW\,\mathrm{sgn}(\tau-t)] \end{aligned}$$

$$-e^{-\Delta|\tau-s|/\hbar}e^{-i\Omega'(\tau-s)/\hbar}[V-iW\,\mathrm{sgn}(\tau-s)]$$
$$+e^{-\Delta|\tau-s-t|/\hbar}e^{-i\Omega'(\tau-s-t)/\hbar}$$
$$\left.\times[V-iW\,\mathrm{sgn}(\tau-s-t)]\right\}, \tag{4.4}$$

$$G^{(2)}_{A,2}(\tau,s,t)=G^{(0)}_{A}(\tau,s,t)\frac{(\chi^0_A)^2\Omega/\Omega'}{\Delta+i\Omega'}$$
$$\times\left\{-t/\hbar+\frac{1}{\Delta+i\Omega'}[1-e^{-(\Delta+i\Omega')t/\hbar}]\right\}, \tag{4.5}$$

$$G^{(2)}_{A,3}(\tau,s,t)=G^{(0)}_{A}(\tau,s,t)\frac{(\chi^0_A)^2\Omega/\Omega'}{\Delta-i\Omega'}$$
$$\times\left\{-s/\hbar+\frac{1}{\Delta-i\Omega'}[1-e^{-(\Delta-i\Omega')s/\hbar}]\right\}. \tag{4.6}$$

In $G^{(2)}_{A,1}(\tau,s,t)$ we defined the factors

$$V=\frac{\Delta^2-(\Omega')^2}{[\Delta^2+(\Omega')^2]^2}, \tag{4.7}$$

$$W=\frac{2\Delta\Omega'}{[\Delta^2+(\Omega')^2]^2}. \tag{4.8}$$

In the above we also have the step function Θ and the function

$$\mathrm{sgn}(x)=\begin{cases}-1 & \text{if } x<0\\ 0 & \text{if } x=0\\ +1 & \text{if } x>0.\end{cases}$$

The final result for the perturbed two-particle Green's function $G_A(\tau,s,t)$ is somewhat involved:

$$G_A(\tau,s,t)=G^{(0)}_{A,ret}(t)[G^{(0)}_{A,ret}(s)]^*\exp\Bigg((\chi^0_A)^2\frac{\Omega}{\Omega'}D^2\Bigg\{2F^R-\frac{F^I}{D}\Theta(t-\tau+s)[\tau\Theta(\tau)-(\tau-t)\Theta(\tau-t)-(\tau-s)\Theta(\tau-s)]/\hbar$$
$$+(1/2)\frac{F^I}{D}(t+s)/\hbar$$
$$+i\frac{1}{D}(t-s)/\hbar-Fe^{-\Delta t/\hbar}e^{-i\Omega' t/\hbar}-F^*e^{-\Delta s/\hbar}e^{i\Omega' s/\hbar}+F(\tau)e^{-\Delta|\tau|/\hbar}e^{-i\Omega'\tau}-F(\tau-t)e^{-\Delta|\tau-t|/\hbar}e^{-i\Omega'(\tau-t)/\hbar}$$
$$-F(\tau-s)e^{-\Delta|\tau-s|/\hbar}e^{-i\Omega'(\tau-s)/\hbar}+F(\tau-s-t)e^{-\Delta|\tau-s-t|/\hbar}e^{-i\Omega'(\tau-s-t)/\hbar}\Bigg\}\Bigg), \tag{4.9}$$

where we have defined the factors

$$D=\frac{\Omega'}{\Delta^2+(\Omega')^2}, \tag{4.10}$$

$$F(x)=F^R+iF^I\ \ \mathrm{sgn}(x), \tag{4.11}$$

$$F^R=\frac{(\Delta)^2-(\Omega')^2}{(\Omega')^2}, \tag{4.12}$$

$$F^I=-\frac{2\Delta}{\Omega'}. \tag{4.13}$$

All these results are consistent with the ones in Sec. II (and with Ref. 2) in the limit with no damping ($\Delta\rightarrow 0$ and $\Omega'\rightarrow\Omega$) and considering only a single vibration coordinate. We also note that the decay law for an electron put at time $t=0$ in the adsorbate orbital is still the same as without damping, viz., $P(t)=G_A(t,t,t)=|G^{(0)}_{A,ret}(t)|^2 \propto \exp[-(\Gamma/2)t/\hbar]$. We can explain this result by noting that nothing in the present formalism allows for an interference between the two distinct lifetime associated processes that take place, namely the decay of the localized phonon, due to energy dissipation to the electron-hole continuum, and the width of the electronic resonance, due to its interaction with the electronic degrees of freedom of the underlying substrate. These processes occur independently in the present model because of the assumption that the Green's function of the electronic resonance takes an exponential form, a step necessary in order to keep the problem soluble.

Having obtained the result for $G_A(\tau,s,t)$, the modified transition rate and resonant current are of the same general form as given by Eqs. (2.10) and (2.15), respectively, even though $W(l_f,k_i)$ is now different from Eq. (2.12).

In expression (2.15) above we first transform the summations over electronic states to integrals in the electronic energies, through the use of the density of states in energy, $\rho(\epsilon)$, along with the volumes Ω of tip and sample, for each side of the tunneling junction. Taking Fermi-distribution functions at zero K as step functions Θ, the result is, for any number of excited phonons,

$$J_{total}=(1-\langle n_A\rangle)e\int_{-\infty}^{+\infty}d\epsilon_k\Omega_{tip}\rho_{tip}(\epsilon_k)\Theta(\epsilon_{F_{tip}}-\epsilon_k)\times\int_{-\infty}^{+\infty}d\epsilon_l\Omega_{subs.}\rho_{subs.}(\epsilon_l)\Theta(\epsilon_{F_{subs.}}-\epsilon_l)W(\epsilon_l,\epsilon_k), \tag{4.14}$$

where

$$W(\epsilon_l,\epsilon_k)[sec^{-1}]=\frac{1}{\hbar}|V_{A,k}|^2|V_{l,A}|^2\times\int\int\int\frac{d\tau ds dt}{\hbar^3}e^{i[(\epsilon_k-\epsilon_l)\tau+\epsilon_l t-\epsilon_k s]/\hbar}\times G_A(\tau,s,t), \tag{4.15}$$

as in Eq. (2.10) (writing ϵ_{k_i} as ϵ_k and ϵ_{l_f} as ϵ_l), but with a different $G_A(\tau,s,t)$. The applied bias voltage displaces the scale of values taken by ϵ_k and $\epsilon_{F_{tip}}$. Instead of attempting to perform a triple Fourier transform and a double energy integration in order to compute the total current, we turn to the calculation of the integrated transition rate $W(\epsilon_k)$, defined by

$$W(\epsilon_k)=\int_{-\infty}^{+\infty}d\epsilon_l W(\epsilon_l,\epsilon_k) \tag{4.16}$$

and representing the transition probability per unit time for an electron to transfer from a tip state of energy ϵ_k, through the resonance, to any substrate state, but without taking into account either the electronic statistical distributions or the densities of states in the electrodes. In fact, the integrated transition rate should suffice for our present purpose, of assessing the effect damping may have on the vibrational spectra.

We use the approximation of taking the electronic transition-matrix elements to be constant, independent of the energies in the physically important ranges and, after changing the order of the integrations and using the result $\int_{-\infty}^{+\infty}d\epsilon_l e^{i\epsilon_l(t-\tau)/\hbar}=2\pi\hbar\,\delta(t-\tau)$, we simplify $W(\epsilon_k)$ to

$$W(\epsilon_k)=\frac{2\pi}{\hbar}|V_{A,k}|^2|V_{l,A}|^2\times\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty}\frac{ds dt}{\hbar^2}e^{i\epsilon_k(t-s)/\hbar}G_A(t,s,t). \tag{4.17}$$

However, $G_A(t,s,t)$ itself can now be considerably simplified, resulting in

$$W(\epsilon_k)=\frac{4\pi}{\hbar}|V_{A,k}|^2|V_{l,A}|^2\frac{e^{[(\chi_A^0)^2(\frac{\Omega}{\Omega'})D^2F^R]}}{\Gamma'}\mathrm{Re}\int_0^{+\infty}\frac{d\sigma}{\hbar}\times\exp\{-[A-iB(\epsilon_k)]\sigma/\hbar\}\exp[-Ce^{-(\Delta+i\Omega')\sigma/\hbar}], \tag{4.18}$$

in which σ is a new dummy integration variable and Re extracts the real part of the integral. On the other hand, besides the already defined parameters D and F^R, we have introduced a larger electronic resonance width, denoted Γ', and, for compactness, the three new factors A, $B(\epsilon_k)$, both real, and C, complex, defined thus

$$\Gamma'=\Gamma+2(\chi_A^0)^2\left(\frac{\Omega}{\Omega'}\right)\frac{\Delta}{\Delta^2+(\Omega')^2}, \tag{4.19}$$

$$A=\Gamma/2+2(\chi_A^0)^2\left(\frac{\Omega}{\Omega'}\right)\frac{\Delta}{\Delta^2+(\Omega')^2}, \tag{4.20}$$

$$B(\epsilon_k)=(\epsilon_k-\epsilon_A')+(\chi_A^0)^2\frac{\Omega}{\Delta^2+(\Omega')^2}, \tag{4.21}$$

$$C=(\chi_A^0)^2\left(\frac{\Omega}{\Omega'}\right)[V-iW], \tag{4.22}$$

V and W having been defined in Eqs. (4.7) and (4.8) above. Now it turns out that the remaining integral above can be conveniently expressed by an incomplete gamma function $\gamma(\alpha,\beta)$, with complex arguments, and we obtain the final expression for the integrated transition rate:

$$W(\epsilon_k)=\frac{4\pi}{\hbar}|V_{A,k}|^2|V_{l,A}|^2\frac{e^{[(\chi_A^0)^2(\frac{\Omega}{\Omega'})D^2F^R]}}{\Gamma'}\times\mathrm{Re}\left\{\frac{C^{(-)\frac{A-iB(\epsilon_k)}{\Delta+i\Omega'}}}{\Delta+i\Omega'}\gamma\left[\frac{A-iB(\epsilon_k)}{\Delta+i\Omega'},C\right]\right\}. \tag{4.23}$$

From this result, we may be able to estimate the effect that the existence of damping, here caused by the excitation of electron-hole pairs, has on the tunneling transition rate. The two main effects due to an increase in Δ are the washing out of the first derivative vibrational sidebands and the general lowering of the transition rate. As before,[2] these peaks are expected to become visible for a sufficiently large resonance lifetime and their separation in energy is equal to the value of the oscillation quantum.

In order to make the effect clearly visible, we chose a suitable range of adsorption parameters, keeping in mind the condition of small damping, $\Delta\ll\Omega,\Omega'$. Even though we do not attempt to apply the present results to a specific tip-adsorbate-substrate system, our range of adsorption parameters should be representative of real experimental situations. Since our main concern at present is the influence of damping on the conductance curves ($\partial I/\partial V$), and since this observable is a convolution of the transition rate $W(\epsilon_l,\epsilon_k)$ with the densities of states and electronic distributions (4.14), the graphs below have the axes: (1) the incoming electron energy, in eV, with a range of -1 to $+1$ volt around an origin coincident with the adsorbate shifted resonance center (ϵ_A'), (2) the the damping energy parameter Δ, also in eV, ranging from zero (the no-damping situation) up to a maximum of 0.02 eV (except in one graph), corresponding to a minimum time damping constant of around 3.3×10^{-14} s, and (3) the

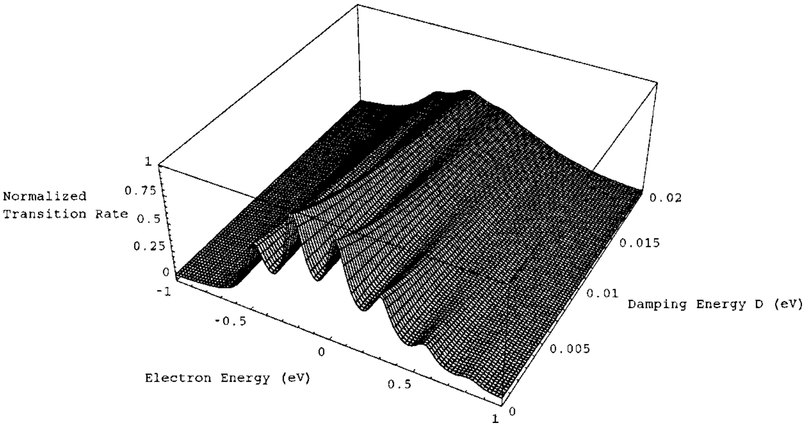

FIG. 1. Tunneling transition rates for $\Gamma = 0.15$ eV, $\chi_A^0 = 0.30$ eV, $\Omega' = 0.30$ eV, $\Omega' = 0.25$ eV, Δ values from 0.00 to 0.02 eV.

integrated transition rate, $W(\epsilon)$, normalized to its maximum value in each run. Furthermore, taking a typical value of the observed (redshifted) oscillation quanta of $\Omega' \sim 250$ meV, which gives an (unobservable) unshifted quantum Ω of around 300 meV,[12] the ratio Δ/Ω' varies between zero and a maximum of the order of 0.08, i.e., a minimum ratio between the oscillator damping time constant and its ''period'' of around 12.5 (or a minimum quality factor of $Q = 6.25$).

The remaining adsorption parameters are the electronic resonance width, Γ, in eV, and the electron-oscillator coupling constant, χ_A^0, also in eV. Their chosen values are meant mainly to illustrate our results in the (ϵ, Δ, W) graphs, but should be typical of real chemisorption situations. On the other hand, we have not included, in the computations, the prefactor $(4\pi/\hbar)|V_{A,k}|^2|V_{l,A}|^2$ in expression (4.23) above, under the simplifying assumption that the hopping and tunneling matrix elements are constant.

V. DISCUSSION

Even though one can see that the existence of damping will increase the difficulty in detecting the presence of the inelastic channel due to the lowering of the total transition rate and the smoothing of the (possible) first derivative peaks, an immediate conclusion is the importance of the interplay between Δ, χ_A^0, and Γ. That is, a relatively large value of the damping constant Δ by itself is not sufficient to prevent the appearance of structure in the spectra. As to be expected, it has to be combined with a relatively large electron-oscillator coupling constant. In other words, even short oscillation decay times will not affect the junction conductance, unless the electron-oscillator coupling constant, χ_A^0 is sufficiently strong. And, of course, the reverse is also true, even for large values of χ_A^0, Δ has to attain a sufficiently large value for any damping effects to become visible, as all the graphs show.

However, a combination of strong electron-oscillator coupling (large χ_A^0), i.e., strong variations of the resonance position with the vibration coordinate, together with a strong oscillation damping (large Δ), here due to the creation of electron-hole pairs, can effectively lead to a rapid smoothing of the spectra, especially for long-lived, narrow electronic resonances (small Γ). These circunstances seem to indicate the advantage of using weakly chemisorbed species in attempting to observe vibration spectra of adsorbates with the STM. Another possibility would consist in tunneling (from the tip) through a mostly unoccupied antibonding orbital of a strongly chemisorbed system, in the so-called ''surface molecule limit.''[30,31,21,32]

In the figures, we try to convey what we believe are the essential components of the present results. In Fig. 1, we show the decrease of the vibrational structure as we decrease the oscillation decay time, from infinity to the 3.3×10^{-14} s minimum value. As in Ref. 2, in the absence of damping, the vibrational sidebands, a quantum Ω' apart, are clearly visible due to the relative high value of the coupling constant χ_A^0. This high value also clearly redshifts the position of the first phonon emission peak (no absorption peaks are present since we are at 0 K).

In Fig. 2, with a slightly larger electronic width Γ but a particularly small coupling constant χ_A^0, we extend the Δ

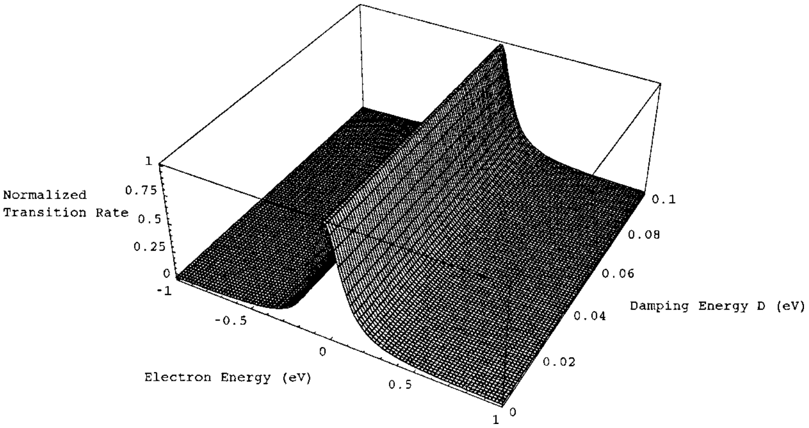

FIG. 2. Tunneling transition rates for $\Gamma = 0.20$ eV, $\chi_A^0 = 0.01$ eV, $\Omega' = 0.30$ eV, $\Omega' = 0.25$ eV, Δ values from 0.00 to 0.10 eV.

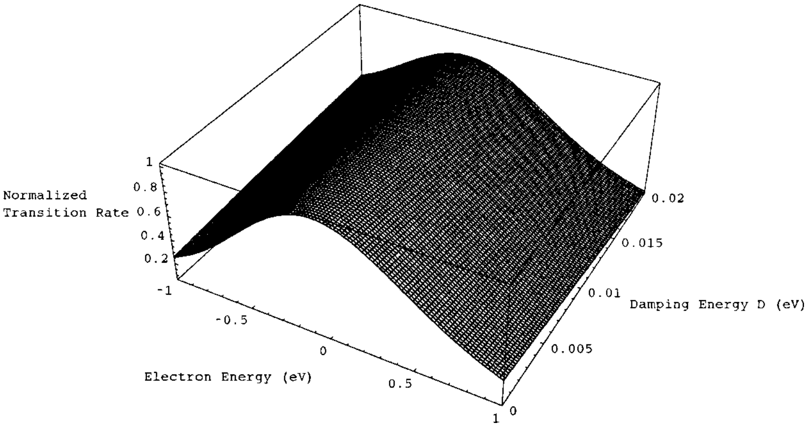

FIG. 3. Tunneling transition rates for $\Gamma=0.75$ eV, $\chi_A^0=0.35$ eV, $\Omega'=0.30$ eV, $\Omega'=0.25$ eV, Δ values from 0.00 to 0.02 eV.

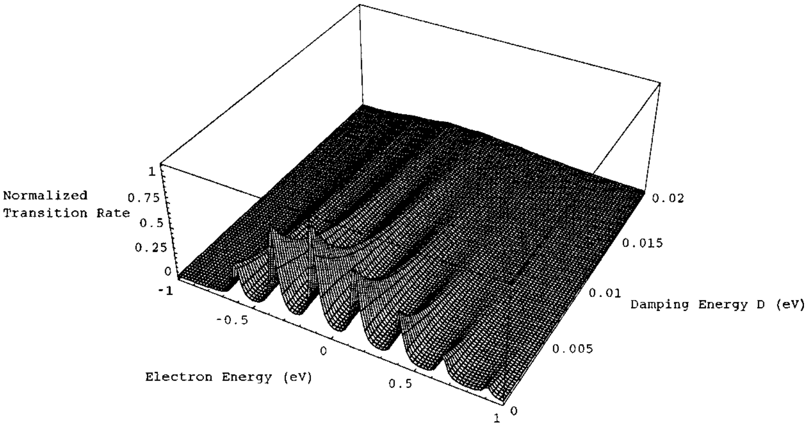

FIG. 4. Tunneling transition rates for $\Gamma=0.05$ eV, $\chi_A^0=0.35$ eV, $\Omega'=0.3$ eV, $\Omega'=0.25$ eV, Δ values from 0.00 to 0.02 eV.

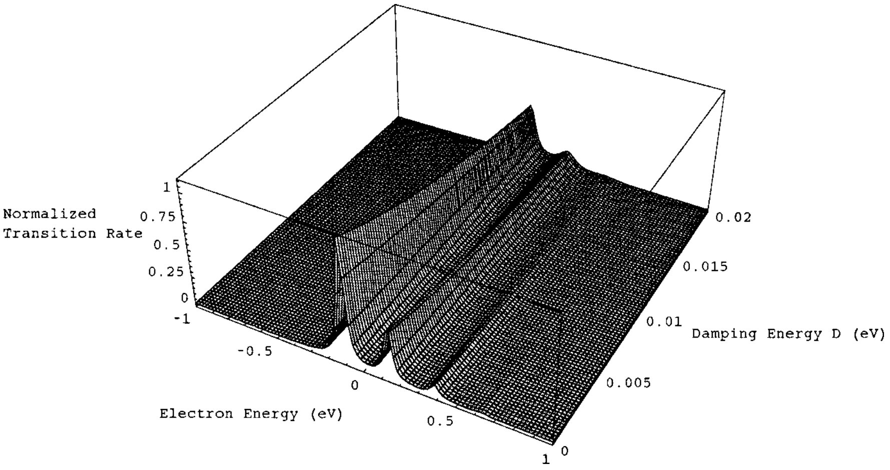

FIG. 5. Tunneling transition rates for $\Gamma=0.05$ eV, $\chi_A^0=0.15$ eV, $\Omega'=0.3$ eV, $\Omega'=0.25$ eV, Δ values from 0.00 to 0.02 eV.

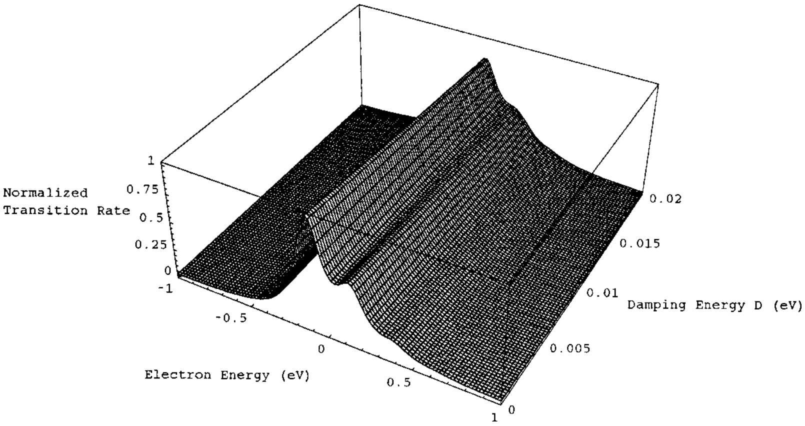

FIG. 6. Tunneling transition rates for $\Gamma=0.20$ eV, $\chi_A^0=0.15$ eV, $\Omega'=0.3$ eV, $\Omega'=0.25$ eV, Δ values from 0.00 to 0.02 eV.

values up to 0.10 eV, reaching an unphysical damping ratio Δ/Ω' of 0.40, with the intention of showing that even exaggerated damping constants do not lead, by themselves, to visible effects on the junction conductance. Also, no vibrational sidebands are present.

In Fig. 3, the spectrum just reproduces the electronic resonance profile with almost no lowering of the transition rate, even though the coupling constant is relatively strong. But the width of the electronic level, upon chemisorption, imposes a fairly stable and wide, shapeless bump across the voltage axis, with no vibrational sidebands present.

In contrast, Fig. 4 shows a rather structured spectrum, with the same value for the coupling constant as in Fig. 3, but with a much narrower electronic width. This is the combination of adsorption parameters, considered above, that leads to the fastest disappearance of variations in the conductance spectra.

In Fig. 5 we keep the electronic width from the previous figure but decrease the coupling constant, reducing both the redshift of the spectrum and the number of visible vibrational sidebands. The reduction in the transition rate is also much less pronounced.

Finally, in Fig. 6, we again use moderate values for both Γ and χ_A^0 and the result is similar to Fig. 1 but with a reduced damping effect, due to the smaller value of the coupling constant.

Another consequence of damping is the fact that, having acquired an imaginary component, the possible frequency values of the adsorbate/oscillator are no longer eigenvalues of the Hamiltonian and, therefore, the opening of the inelastic channel is not a step-function as before, but instead by a function that increases smoothly from zero to one. This reduces the inelastic channel peak that one usually looks for. As the inelastic signal becomes weaker, the particular structure of the density of states, of both substrate and tip, becomes more important and may, by itself, cause variations in conductance that will be hard to distinguish from the ones due to the electron-phonon coupling.

Further work on this problem will necessarily deal with a better description of the physical situation specific to surface phenomena in scanning tunneling microscopy, for example, by going beyond the tunneling Hamiltonian. One will also need to adopt a more sophisticated approach to the description of the nonequilibrium occupancy of the intermediate resonant state. A more realistic description of the physical situation should be able to account for the observed dependence of the height of the conductance peaks on the sharpness of the microscope tip.[8]

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APPENDIX: RELATIONSHIP BETWEEN THE TWO METHODS

In this appendix, we show the analytical consistency between the present approach, in the no-damping version of Sec. II, and the one we followed previously, in Ref. 2. This comparison also concerns the relationship between the gas-phase inelastic scattering model of Domcke and Cederbaum[19] and inelastic resonant tunneling in heterostructures in the model of Wingreen, Jakobsen and Wilkins.[22] The existence of such a connection has been pointed out by Gadzuk.[24] and ourselves[23,2,29] The previous results for the elastic and one-phonon inelastic components of the tunneling current [expressions (55) and (56), respectively, in Ref. 2, but neglecting the imaginary component of the electron-phonon coupling constant] are particular cases of the general, any-phonon, result. In that resolvent formalism, this general result could be written

$$J_{total}(V)=(1-\langle n_A\rangle)e\Omega_{tip}\Omega_{subs.}\sum_{m=0}^{\infty}\Theta(eV-m\Omega)\times\int_{m\Omega}^{+eV}W_m(\epsilon)\rho_{tip}(\epsilon-eV)\rho_{subs.}(\epsilon-m\Omega)d\epsilon \tag{A1}$$

as well, but the included transition rate $W_m(\epsilon)$(m being the number of excited phonons) would be given by

$$W_m(\epsilon)=2\pi/\hbar|V_{Ak}|^2|V_{Al}|^2e^{-2g}\frac{g^m}{m!}|A_m[z(\epsilon)]|^2, \tag{A2}$$

where

$$A_m[z(\epsilon)]=\sum_{n=0}^{\infty}\sum_{j=max\{0,m-n\}}^{m}(-1)^j\binom{m}{j}\frac{g^{j-m+n}}{(j-m+n)!}\times\{z(\epsilon)-n\Omega\}^{-1}\tag{A3}$$

and $z(\epsilon)$ and g are defined as above. The $e^{-g}g^{m/2}/(m)^{1/2}A_m[z(\epsilon)]$ factor is basically the same as in the original model of Domcke and Cederbaum,[19,23,24] for the gas-phase inelastic resonant scattering, but considering a single vibration coordinate and an electronic resonance width independent of the vibration coordinate. It also results from the calculation of the product of the Frank-Condon overlaps between the oscillator initial, ground state and all possible, intermediate, displaced oscillator vibration states, here represented by the index n, with the overlaps between these intermediate states and the final vibrational state, here represented by the index m.[33]

Since, in the present paper, the corresponding expressions we got for $J_{total}(V)$ and for $W_m(\epsilon)$, Eqs. (2.16) and (2.13) respectively, are formally identical to the ones above, Eqs. (A1) and (A2), what remains to be proven is, in fact, the equality

$$|B_m[z(\epsilon)]|^2=|A_m[z(\epsilon)]|^2,\tag{A4}$$

with

$$B_m[z(\epsilon)]=\sum_{j=0}^{m}(-1)^j\binom{m}{j}\sum_{l=0}^{\infty}\frac{g^l}{l!}\{z(\epsilon)-(j+l)\Omega\}^{-1}.\tag{A5}$$

This $B_m[z(\epsilon)]$ factor is basically the same as in the original model of Wingreen *et al.*,[22] for the inelastic resonant tunneling in quantum well structures, but again with a single-vibration coordinate.

It will be convenient to start by separating out $A_m(z)$ as

$$A_m(z)=\left(\sum_{n=0}^{m-1}\sum_{j=m-n}^{m}+\sum_{n=m}^{\infty}\sum_{j=0}^{m}\right)(-1)^j\binom{m}{j}\frac{g^{j-m+n}}{(j-m+n)!}\times\{z-n\Omega\}^{-1},$$

the first double summation including the terms for which $n<m$ and the second double summation the ones for which $n\geqslant m$. Leaving A_m as it stands, we will get an equivalent result starting from the above expression for $B_m(z)$. Decomposing it according to the values of $j=0,1,2,\ldots,m-2,m-1,m$, we can write

$$B_m(z)=(-1)^0\binom{m}{0}\sum_{l=0}^{\infty}\frac{g^l}{l!}\{z-l\Omega\}^{-1}+(-1)^1\binom{m}{1}\sum_{l=0}^{\infty}\frac{g^l}{l!}\times\{z-(1+l)\Omega\}^{-1}+(-1)^2\binom{m}{2}\sum_{l=0}^{\infty}\frac{g^l}{l!}\times\{z-(2+l)\Omega\}^{-1}+\cdots+(-1)^{m-2}\binom{m}{m-2}\sum_{l=0}^{\infty}\frac{g^l}{l!}\{z-(m-2+l)\Omega\}^{-1}$$

$$+(-1)^{m-1}\binom{m}{m-1}\sum_{l=0}^{\infty}\frac{g^l}{l!}\{z-(m-1+l)\Omega\}^{-1}+(-1)^m\binom{m}{m}\sum_{l=0}^{\infty}\frac{g^l}{l!}\{z-(m+l)\Omega\}^{-1}.$$

We pick up the last term, for $j=m$, and rewrite the summation index as $l'=l+m$,

$$(-1)^m\binom{m}{m}\sum_{l=0}^{\infty}\frac{g^l}{l!}\{z-(m+l)\Omega\}^{-1}=(-1)^m\binom{m}{m}\sum_{l'=m}^{\infty}\frac{g^l}{l!}\{z-l'\Omega\}^{-1}.$$

For the $j=m-1$ term, we first separate out the $l=0$ part and then take $l'=l+m-1$ in the remaining part, obtaining

$$(-1)^{m-1}\binom{m}{m-1}\left(\frac{g^0}{0!}\{z-(m-1)\Omega\}^{-1}+\sum_{l'=m}^{\infty}\frac{g^{l'-m+1}}{(l'-m+1)!}\{z-l'\Omega\}^{-1}\right).$$

For the $j=m-2$ term, we group the $l=0$ and $l=1$ parts, introduce $l'=l+m-2$ in the remaining and obtain

$$(-1)^{m-2}\binom{m}{m-2}\left(\sum_{l'=m-2}^{l'=m-1}\frac{g^{l'-m+2}}{(l'-m+2)!}\{z-l'\Omega\}^{-1}+\sum_{l'=m}^{\infty}\frac{g^{l'-m+2}}{(l'-m+2)!}\{z-l'\Omega\}^{-1}\right).$$

Of course, l' is a dummy index and, introducing first $l'=l+m-p$ and using the fact that $\binom{m}{m-p}=\binom{m}{p}$, we can write down the general $j=m-p$ term as (grouping equal factors under the two summation signs)

$$(-1)^{m-p}\binom{m}{p}\left(\sum_{l=m-p}^{m-1}+\sum_{l=m}^{\infty}\right)\frac{g^{l-m+p}}{(l-m+p)!}\{z-l\Omega\}^{-1},$$

where, in the first summation, $l<m$ and $1\leqslant p\leqslant m$ and, in the second, $m\leqslant l,\quad 0\leqslant p\leqslant m$.

We now sum over all possible p values, ranging from 1 to m in the first summation and from 0 to m in the second summation and rewrite B_m as a sum over p, instead of j:

$$B_m(z)=(-1)^m\left(\sum_{p=1}^{m}\sum_{l=m-p}^{m-1}+\sum_{p=0}^{m}\sum_{l=m}^{\infty}\right)\times(-1)^p\binom{m}{p}\frac{g^{l-m+p}}{(l-m+p)!}\{z-l\Omega\}^{-1},$$

the first term for $l<m$ and the second term for $l\geqslant m$. In order to prove our point, we still have to show that the first term in B_m above corresponds to the first term in A_m, that is to say, that

$$\sum_{p=1}^{m}\sum_{l=m-p}^{m-1}F_m(p,l)=\sum_{l=0}^{m-1}\sum_{p=m-l}^{m}F_m(p,l),$$

where the matrix element $F_m(p,l)$ is being defined in an obvious way. But, in fact, these two double-summations span the same set of elements of this matrix, the ones below its main diagonal, including this diagonal. On the lhs of the above equality, for each line p, we sum all the column elements leftwards, until we reach the first column. On the rhs, we cover exactly the same elements, this time summing, for each column l, all the line elements downwards, until we reach the last line. Recognizing this fact, we may write

$$B_m(z)=(-1)^m\left(\sum_{l=0}^{m-1}\sum_{p=m-l}^{m}+\sum_{p=0}^{m}\sum_{l=m}^{\infty}\right)\times(-1)^p\binom{m}{p}\frac{g^{l-m+p}}{(l-m+p)!}\{z-l\Omega\}^{-1},$$

and comparing this result with the last expression above for $A_m(z)$, we conclude that $B_m(z)=(-1)^m A_m(z)$ or that $|B_m(z)|^2=|A_m(z)|^2$, as required for the equality of the total tunneling currents, according to the two methods.

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*On leave from DCTD, Universidade dos Açores, 9500 Ponta Delgada, Portugal.

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