

# Inelastic Electron Tunneling from a Metal Tip: The Contribution from Resonant Processes

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We present a simple model calculation for electron tunneling between a metal probe tip and a metal surface with a chemisorbed molecule. It is shown that under suitable conditions, *resonant* tunneling via interaction with a molecule vibration can give a *decrease* of 10% or more in the total tunneling conductance. Adsorbate systems are suggested where our predictions may be tested.

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The scanning tunneling microscope (STM) has proven to be very useful for the study of surface structure.<sup>1</sup> Another unique capability of the STM would be to perform inelastic-electron-tunneling (IET) spectroscopy on molecules adsorbed on readily accessible and controllable surfaces, as done until now with molecules incorporated in oxide junctions.<sup>2</sup> The spatial resolution of the STM should allow one to *probe individual adsorbates*, their bonding environments, and, with IET, their vibrational properties. Such *local* elastic and inelastic tunneling measurements could provide a unique insight into surface properties not possible with other techniques such as high-resolution electron-energy-loss (EEL) or infrared-reflectance spectroscopy. The ability to study adsorbates locally is especially attractive since it is widely believed that many catalytic reactions involve only a few active surface sites, such as steps or foreign atoms (e.g., promoters or inhibitors).

Earlier, Persson and Demuth calculated the contribution from dipole coupling to the inelastic tunneling current.<sup>3</sup> In the favorable case of CO on Cu(100), the increase in tunneling conductance at the excitation threshold for stretch vibrations was found to be only 1% of the elastic background contribution. Such changes are difficult to detect even with cryogenic rigid STM's currently available.<sup>1</sup> In the present work we show that *resonant tunneling* can give a relative change  $\eta$  in tunneling conductance which is 10% or more. This is particularly important because it appears easier to identify adsorbed molecules via their internal vibration frequencies rather than via their electronic levels which are significantly broadened and shifted.

The model we study is the simplest one which contains what we believe is the essential physics. It provides useful estimates of the resonant contribution and predicts a fingerprintlike decrease in conductance ( $\eta < 0$ ) in the optimum situation of an electronic resonance overlapping the Fermi level  $\bar{\epsilon}_F$  of the substrate. In that case  $\eta$  can be related to quantities derivable from independent mea-

surements.

We consider tunneling from a single atom (from now on called the tip atom), located at the apex of a metal tip, to a molecule adsorbed on a metal surface [see Fig. 1(a)]. The molecule is assumed to have an electronic resonance as shown schematically in Fig. 1(b). This resonance is derived from an orbital  $|a\rangle$  of the molecule. Extensive spectroscopic investigations and electronic structure calculations, e.g., Lang and Williams,<sup>4</sup> have shown that such adsorbate-induced resonances frequently occur in the vicinity of  $\bar{\epsilon}_F$ . Tunneling between the metal tip and  $|a\rangle$  occurs most effectively when  $|a\rangle$  has  $s$  or  $p_z$  symmetry (more generally,  $Y_{10}$  symmetry). Wave functions with  $m \neq 0$  (e.g.,  $p_x$ ) have a nodal plane or axis perpendicular to the substrate; as a consequence their overlap with the probe tip and their contributions to the tunneling current are much smaller than those for  $m=0$ .<sup>3,5</sup> For simplicity, we assume that tunneling occurs via a single resonance derived from an  $m=0$  orbital  $|b\rangle$  associated with the tip atom. Figure 1(b) shows the densities of states projected onto orbitals  $|a\rangle$

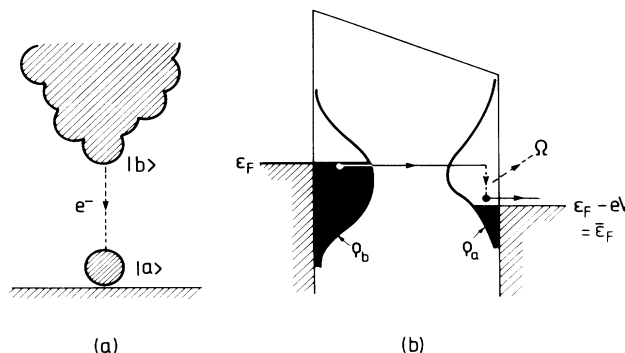


FIG. 1. (a) Electron tunneling from a metal-tip atom with an orbital  $|b\rangle$  to an adsorbed molecule with an orbital  $|a\rangle$ . (b) Densities of states  $\rho_a(\epsilon)$  and  $\rho_b(\epsilon)$  projected onto the orbitals  $|a\rangle$  and  $|b\rangle$ .

and  $|b\rangle$ :

$$\rho_a(\epsilon) = \sum_{\alpha} |\langle a | \alpha \rangle|^2 \delta(\epsilon - \epsilon_{\alpha}),$$

$$\rho_b(\epsilon) = \sum_{\beta} |\langle b | \beta \rangle|^2 \delta(\epsilon - \epsilon_{\beta}).$$

Here, and in what follows,  $|\alpha\rangle$ ,  $|\alpha'\rangle$ ,  $\dots$ , and  $|\beta\rangle$ ,  $|\beta'\rangle$ ,  $\dots$ , denote one-particle electronic eigenstates of the molecule-metal system and of the tip which decay away from the respective electrodes.

The basic physical process we want to model is as follows: When a potential  $V$  is applied, a net electron tunnel current flows between the two electrodes. If the tip is centered above the molecule, then an effective tunnel channel will be via the resonance  $\rho_a$ . When an electron has tunneled into the orbital  $|a\rangle$ , it is on the average trapped in this orbital for a time  $\tau \approx \hbar/\Gamma$ , where  $\Gamma$  is the width of the resonance  $\rho_a(\epsilon)$ . This leads to a change of the internuclear potential which induces a relaxation of the molecule. For example, when an electron is trapped temporarily in the antibonding  $2\pi^*$  level of CO, the C—O bond distance tends to increase. Thus, when the electron hops from  $|a\rangle$  to the conduction band of the substrate via the hybridization interaction  $U_{ak}$ , the molecule can be left in a vibrational excited state. This kind of process is well documented in inelastic electron scattering from gas-phase molecules.<sup>6</sup>

The following Hamiltonian contains the process described above:

$$H = \epsilon_a(Q) \hat{n}_a + \sum_k \epsilon_k \hat{n}_k + \sum_k U_{ak} (c_a^\dagger c_k + \text{H.c.}) + \epsilon_b \hat{n}_b + \sum_k \epsilon_k \hat{n}_k + \sum_k U_{bk} (c_b^\dagger c_k + \text{H.c.}) + \Omega v^\dagger v + t_{ab} (c_a^\dagger c_b + c_b^\dagger c_a). \quad (1)$$

Here,  $Q$  is the displacement associated with a vibrational mode of the adsorbed molecule,  $\epsilon_a(Q)$  is the resonance level of the molecule calculated for fixed  $Q$ ,  $v^\dagger$  and  $v$  are the creation and annihilation operators for the molecular vibration, and  $\Omega/\hbar$  its frequency. Furthermore,  $k$  and  $k'$  label the one-particle eigenstates of the substrate and of the metal tip, respectively. The last term in  $H$  allows an electron to tunnel between the tip atom and the adsorbed molecule. We expand  $\epsilon_a(Q)$  to first order in  $Q$ :

$$\epsilon_a(Q) \approx \epsilon_a(0) + \epsilon'_a(0)Q = \epsilon_a + \delta\epsilon(v + v^\dagger),$$

where

$$\delta\epsilon = \epsilon'_a(0)Q_0 = \epsilon'_a(0)\hbar/(2m^*\Omega)^{1/2}, \quad (2)$$

and  $m^*$  is the reduced mass of the vibrational mode under consideration. We can now write Eq. (1) as

$$H = H_0 + \delta\epsilon(v + v^\dagger)c_a^\dagger c_a + t_{ab}(c_a^\dagger c_b + c_b^\dagger c_a) \equiv H_0 + U.$$

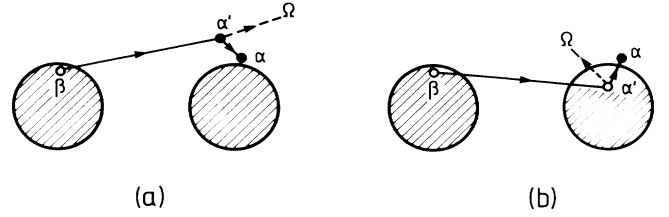


FIG. 2. Two processes which contribute to inelastic electron tunneling. The shaded circles represent Fermi spheres associated with the metal tip (left) and the molecule-metal system (right). (a) An electron in a level  $\beta$  on the metal tip tunnels to a level  $\alpha'$  of the molecule-metal system. This electron next makes a transition to level  $\alpha$  while emitting a phonon (a molecular vibration quantum). (b) An electron-hole pair is first (virtually) created (hole in  $\alpha'$  and electron in  $\alpha$ ) in the molecule-metal system simultaneously with a phonon. Next, the electron in level  $\beta$  on the metal tip tunnels to the molecule-metal system and recombines with the  $\alpha'$  hole.

Since  $H_0$  is quadratic in creation and annihilation operators, it can be diagonalized,

$$H_0 = \sum_{\alpha} \epsilon_{\alpha} c_{\alpha}^{\dagger} c_{\alpha} + \sum_{\beta} \epsilon_{\beta} c_{\beta}^{\dagger} c_{\beta} + \Omega v^{\dagger} v, \quad (3)$$

to include resonances in nonperturbative fashion from the outset. Next we use perturbation theory with respect to  $U = U_1 + U_2$ , where

$$U_1 = \delta\epsilon(v + v^{\dagger}) \sum_{\alpha, \alpha'} \langle \alpha' | a \rangle \langle a | \alpha \rangle c_{\alpha}^{\dagger} c_{\alpha}, \quad (4)$$

$$U_2 = t_{ab} \sum_{\alpha, \beta} (\langle b | \beta \rangle \langle \alpha | a \rangle c_{\alpha}^{\dagger} c_{\beta} + \text{H.c.}), \quad (5)$$

to calculate the rates of elastic ( $w_{\text{el}}$ ) and inelastic ( $w_{\text{inel}}$ ) electron tunneling. Since the final states in those processes are orthogonal they do not interfere. Assuming  $k_B T \ll \Omega \sim eV$ , we get the resonant inelastic tunneling rate associated with single-phonon emission:

$$w_{\text{inel}} = (2\pi/\hbar) \sum_{\alpha, \beta} f(\epsilon_{\beta}) [1 - f(\epsilon_{\alpha} + eV)] \delta(\epsilon_{\alpha} + \Omega - \epsilon_{\beta}) |\langle \alpha, n=1 | U (H_0 - \epsilon_{\beta} - i0)^{-1} U | \beta, n=0 \rangle|^2, \quad (6)$$

where  $i0$  denotes an infinitesimal positive imaginary part and  $f(\epsilon) \equiv \Theta(\epsilon_F - \epsilon)$  is the Fermi-Dirac distribution function. The factor  $f(\epsilon_{\beta})[1 - f(\epsilon_{\alpha} + eV)]$  guarantees that an electron tunnels from an occupied state of the metal tip to an empty state of the molecule-metal system. This formula accounts for the two processes shown in Fig. 2. With use of Eqs. (3)–(5), assuming that the tip density of states projected on the orbital  $|b\rangle$  is broad so that  $\rho_b(\epsilon_F) \approx \rho_b(\epsilon_F - \Omega)$  to a good approximation, and neglecting the distortion of the barrier by the applied voltage, we obtain after some simplifications the corresponding tunneling conductance

$$\frac{\partial I_{\text{inel}}}{\partial V} \approx \frac{4\pi e^2}{\hbar} \delta\epsilon^2 |t_{ab}|^2 \rho_b(\epsilon_F) \rho_a(\bar{\epsilon}_F + \Omega - eV) \left| \int d\epsilon' \frac{\rho_a(\epsilon')}{\epsilon' - \bar{\epsilon}_F - eV - i0} \right|^2 \Theta(eV - \Omega). \quad (7)$$

The elastic channel also contains contributions of order  $\delta\epsilon^2$  due to phonon emission and reabsorption. Most of these vary smoothly with  $eV$  but, because of restrictions on the occupancy of available states, one term exhibits (at  $T=0$ ) a logarithmic singularity and another one a step-function decrease at  $eV=\Omega$ .<sup>7</sup> Near threshold the contribution to the total tunneling conductance normalized to its zero-order elastic background is found to be<sup>8</sup>

$$\frac{\partial I^{(2)}/\partial V}{\partial I^{(0)}/\partial V} \approx \delta\epsilon^2 \left\{ \frac{\rho_a(\bar{\epsilon}_F)}{\rho_a(\bar{\epsilon}_F + \Omega)} \left| \int d\epsilon' \frac{\rho_a(\epsilon')}{\epsilon' - \bar{\epsilon}_F - \Omega - i0} \right|^2 \Theta(eV - \Omega) \right. \\ \left. - 2\rho_a(\bar{\epsilon}_F) \left[ \pi^2 \rho_a(\bar{\epsilon}_F + \Omega) \Theta(eV - \Omega) + \ln \left( \frac{|eV - \Omega|}{\Delta} \right) \right] \rho_a(\bar{\epsilon}_F) \right\}, \quad (8)$$

where  $\Delta$  is a cutoff energy much smaller than  $\Gamma$ . The logarithmic term will influence the line shape but not the net change  $\eta$  in the normalized conductance, defined as its difference between  $eV=\Omega+\delta$  and  $eV=\Omega-\delta$ , because it is symmetric about  $eV=\Omega$ . In an actual measurement,  $\delta$  should be chosen larger than the combined thermal and vibrational lifetime broadening, but small enough for background variations to be negligible.

If we ignore the logarithmic term and approximate  $\rho_a(\epsilon)$  by a Lorentzian of width  $\Gamma$  (FWHM) centered at  $\epsilon=\epsilon_a$ , Eq. (8) gives

$$\eta_{\text{res}} \approx \frac{\delta\epsilon^2}{(\bar{\epsilon}_F - \epsilon_a)^2 + (\Gamma/2)^2} \frac{(\bar{\epsilon}_F + \Omega - \epsilon_a)^2 - (\Gamma/2)^2}{(\bar{\epsilon}_F + \Omega - \epsilon_a)^2 + (\Gamma/2)^2}. \quad (9)$$

Equations (8) and (9) are the main results of this work. If  $\Omega \ll \Gamma$  and  $(\delta\epsilon/\Gamma)^2 \ll 1$ , then multiphonon contributions, which can be important for free molecules,<sup>6</sup> are negligible. Both conditions are satisfied for chemisorbed molecules (see below) to which we restrict our attention from now on. Although resonantly enhanced,  $|\eta_{\text{res}}|$  remains smaller than unity in that case.

When  $V$  is reversed, electrons tunnel from the molecule-metal system to the tip;  $\eta_{\text{res}}$  is still given by Eq. (8) but with the opposite sign in front of  $\Omega$  and the logarithm. Together with the asymmetry in the barrier transmissivity, this produces a stronger asymmetry in  $\partial I/\partial V$  than dipole coupling.<sup>2</sup>

The dipole contribution to the inelastic tunneling conductance is given approximately by  $\eta_{\text{dip}} \approx (\mu/ea_0)^2$ , where  $\mu$  is the dynamic dipole moment of the vibrational mode, and  $a_0$  is the Bohr radius.<sup>3</sup> The corresponding inelastic  $\delta\epsilon^2$  contribution is negligible compared with the elastic one.<sup>7,8</sup> Assume that the main contribution to  $\mu$  also comes from the charge oscillations occurring between the molecular and the metal substrate as the resonance oscillates about  $\bar{\epsilon}_F$  while the molecule vibrates. We can then write  $\mu = ed\delta n \approx ed\delta\epsilon\rho_a(\bar{\epsilon}_F)$ , where  $d$  is the distance between the positive and negative centroids of the oscillating distributions (for large molecule-metal separation this would be the distance between the centroid of  $|a\rangle$  and the static image-plane position), and obtain

$$\eta_{\text{dip}} \approx (d/a_0)^2 [\delta\epsilon\rho_a(\bar{\epsilon}_F)]^2 \quad (10)$$

or, using Eqs. (8)–(9),

$$\eta_{\text{dip}}/\eta_{\text{res}} \approx (d/\pi a_0)^2/C,$$

where  $C = -1 + (\bar{\epsilon}_F - \epsilon_a)^2/(\Gamma/2)^2$ . For most chemisorbed atoms<sup>4</sup> or small molecules,  $d \lesssim a_0$  so that, unless  $|\epsilon_a - \bar{\epsilon}_F| \approx \Gamma/2$ ,  $|\eta_{\text{dip}}/\eta_{\text{res}}| \lesssim 1/\pi^2$ . Thus, when the conditions stated above prevail, resonant tunneling is still expected to dominate over the dipole contribution by roughly a factor of 10.

As discussed elsewhere,<sup>9</sup> damping of the vibrational mode via electron-hole pair excitation accompanies the charge fluctuation  $\delta n$  discussed above. A model calculation, essentially based on the same model Hamiltonian as used above, predicts a damping rate<sup>9</sup>

$$\tau^{-1} = 2\pi\Omega(\delta n)^2 = 2\pi\Omega[\delta\epsilon\rho_a(\bar{\epsilon}_F)]^2. \quad (11)$$

Therefore, we can rewrite Eq. (9) as

$$\eta_{\text{res}} \approx \pi C/2\Omega\tau. \quad (12)$$

Equation (12), apart from being of interest in its own right, should be useful for estimating  $\eta_{\text{res}}$  when  $\Omega$  and  $\tau$  are known from, e.g., infrared reflectance or EEL measurements.

Let us estimate  $\eta_{\text{res}}$  for some small molecules, for example,  $\text{O}_2$ ,  $\text{N}_2$ ,  $\text{NO}$ , and  $\text{CO}$ . From calculations on the free molecules and their negative ions one can deduce  $\epsilon'_{2\pi^*} \approx 10$  eV/Å; since, furthermore,  $Q_0 \approx 0.03$ – $0.04$  Å,  $\delta\epsilon \approx 0.3$ – $0.4$  eV.<sup>6</sup> Upon chemisorption, the  $2\pi^*$  level of these molecules forms a resonance located in the vicinity of  $\bar{\epsilon}_F$  (usually above).<sup>10</sup> If this resonance has a realistic FWHM  $\Gamma \lesssim 2$  eV, and if it is centered at  $\bar{\epsilon}_F$ , we get from Eq. (8)  $|\eta_{\text{res}}| \approx (2\delta\epsilon/\Gamma)^2 \gtrsim 0.1$ . Typically,  $|\eta_{\text{res}}|$  is smaller than estimated above because the  $2\pi^*$  resonance is centered somewhat away from  $\bar{\epsilon}_F$ . However, it can be forced closer to  $\bar{\epsilon}_F$  via coadsorption with an electron promoter or inhibitor. Thus, when optimum conditions prevail, the contribution from resonant tunneling can be unusually large.

An additional contribution arises from modulation of the tunneling distance by vibrational motion, and can be accounted for by expanding  $t_{ab}(Q) \approx t_{ab}(0) + t'_{ab}(0)Q$ . This gives  $\eta = |\alpha Q_0|^2 \approx 10^{-3}$  because

$$\alpha = t'_{ab}/t_{ab} \approx (2m\phi/\hbar^2)^{1/2} \approx 1 \text{ Å}^{-1}$$

( $\phi$  is the metal work function) in typical cases.<sup>1</sup>

For  $|\epsilon_a - \bar{\epsilon}_F| < \Gamma/2$ , Eq. (9) predicts a decrease in  $\partial I/\partial V$  at  $eV = \Omega$ . A decrease was in fact observed at the C—N stretch vibration threshold in the IET spectrum of CNCH<sub>3</sub> (an electronic analog of CO) chemisorbed on small rhodium particles incorporated into an oxide junction.<sup>11</sup> Including thermal broadening and the logarithmic term in Eq. (8), we can quantitatively fit the observed line shape.<sup>8</sup> Most IET measurements on oxide junctions have been performed on molecules which interact weakly with the electrodes. In such cases one expects a resonance to occur near  $\bar{\epsilon}_F$  only by coincidence. Thus  $\partial I/\partial V$  usually exhibits increases at vibrational excitation thresholds, and the corresponding intensities often correlate well with those of peaks in infrared spectra, thus indicating predominant dipole coupling.<sup>2</sup>

We close by discussing an especially interesting system where resonant tunneling could be important, namely, O<sub>2</sub> chemisorbed on Pt(111).<sup>12</sup> The O—O stretch frequency, 1556 cm<sup>-1</sup> in the gas phase drops to 875 cm<sup>-1</sup> upon chemisorption (at  $T \lesssim 90$  K). This reduction has been attributed to a significant weakening of the O—O force constant by a large electron transfer from the metal to the antibonding  $2\pi^*$  orbitals of O<sub>2</sub>, and back donation from the corresponding bonding  $1\pi$  orbitals. The O—O stretch vibration is infrared inactive in the gas phase because of symmetry, but upon chemisorption this mode acquires a large perpendicular dipole moment  $\mu \approx 0.1ea_0$ , as can be deduced from EEL measurements. This indicates that, although the molecule lies parallel to the surface,<sup>12</sup> large charge rearrangements occur during vibrational motion. Associated with this should be a strong electron-hole pair damping. Indeed, from EEL measurements one can deduce that  $1/\tau \approx 20$  cm<sup>-1</sup> and also that the line profile is asymmetric as expected for this damping process.<sup>13</sup> Hence, if tunneling occurs via the O<sub>2</sub>  $1\pi$  or  $2\pi^*$  resonances and  $|C| \approx 1$ , then Eq. (12) suggests that  $|\eta_{\text{res}}| \approx 0.04$  which should be possible to

detect experimentally. Although the  $2\pi^*$  resonance perpendicular to the surface has overall  $m = \pm 1$  symmetry, tunneling should be effective if the tip is centered above one of the O atoms rather than at their midpoint. Finally, we note that in this case  $\eta_{\text{dip}} \approx 0.01$ .

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