Energy Transfer at Surfaces: Asymmetric Line Shapes and the Electron-Hole–Pair Mechanism

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Rigorous expressions are derived for the line shape for an isolated vibrational mode of an atom or molecule adsorbed on a metallic surface in the presence of electron-hole damping. It is shown that this mechanism necessarily produces an asymmetric line shape with long tails. The experimental presence or absence of such a line shape should therefore play an important role in establishing whether or not electron-hole–pair production is an effective energy-transfer mechanism near metallic surfaces.

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One of the most important problems in surface dynamics is to discover what mechanisms are responsible for energy transfer between an adsorbate or near adsorbate and the host material. One such mechanism, the excitation of electron-hole pairs in a metal substrate, has received a great deal of attention recently,[1] and because of the partial breakdown of adiabaticity which it implies, it is of interest in its own right. However, solid evidence that this is ever the dominant energy-transfer mechanism is sparse.

A particularly favorable case is the damping of adsorbate vibrations.[2] Here one samples an almost harmonic region of the ion potential and for modes of much higher frequency than the phonon continuum, the effects of phonon damping are minimized. One also looks for an adsorbate whose lowest unoccupied level is close to the Fermi level[3]; an electron in this level of an otherwise neutral adsorbate induces an attractive screening cloud in the substrate, so that typically this level will move downward as the adsorbate approaches the surface; in the ideal situation a fairly narrow virtual level on the adsorbate has considerable overlap with the Fermi level. As the adsorbate vibrates, the position of this level also oscillates leading to a breakdown of adiabaticity of order of $\omega\tau$ where ω is the vibrational frequency and $\tau \sim 1/\Gamma$ is the tunneling rate, where Γ is the virtual level width (we choose units where $\hbar = 1$). Calculations based on these assumptions often produce vibrational decay rates γ which are of the same order as those observed experimentally.[2,4,5]

It has apparently been assumed that the line shape associated with this decay is a symmetric Lorentzian[6] with a full width at half maximum equal to γ. I show here that, in fact, an inescapable consequence of the electron-hole decay mechanism is that the line shape (when measured by a probe that couples to the charge) is asymmetric with contributions on a wider scale than γ; this asymmetry becomes greater as the nonadiabatic effects that produce the width itself are increased, and should be substantial if the standard picture (previous paragraph) is correct. Thus if the experimentalists can establish the existence or nonexistence of the type of line shape predicted below, a definitive test of the above picture in specific, and the electron-hole mechanism in general, will be accomplished.

I begin by summarizing and explaining the results. The line shape of a vibrational line in the presence of electron-hole decay processes as measured by a charge-coupled probe is given by the imaginary part of a generalized susceptibility function

$$\alpha = -\mu^2(2\omega_r)/(\omega^2-\omega_r^2+i\omega\gamma), \tag{1}$$

where μ has been termed the "dynamic dipole" of the adsorbed molecule (or atom). In general μ has two components $\mu = \mu^i + \mu^e$, where μ^i is the contribution of the ion cores (or nuclei) and μ^e is the valence electron (or all electron) contribution. The width γ arises because adsorbate electrons and holes can tunnel into the substrate creating real electron-hole pairs. What has not been generally realized, however, is that the very process that allows a nonzero γ also ensures that μ^e has an imaginary part. It takes time for the electrons to tunnel to the substrate so that the oscillations of μ^e from this source are necessarily out of phase with the electric field that drives them. If we let $\mu = \mu_1 + \mu_2 \equiv \mu_1(1+i\omega\tau)$, then (1) becomes

$$\alpha = -(\mu_1)^2 2\omega_r(1+i\omega\tau)^2/(\omega^2-\omega_r^2+i\omega\gamma). \tag{2}$$

The line shape $L(\omega) = +2\alpha_2$ is then[7]

$$L(\omega) = [4\omega_r\tau(\mu_1)^2/\gamma][(1-xy)^2/y(1+x^2)], \tag{3}$$

where $y = \omega\tau$ and $x = (\omega^2-\omega_r^2)/\gamma\omega$. The expression (3) applies to a single harmonic oscillator (mass M) interacting bilinearly with an arbitrary interacting charged Fermi system (mass m). All the frequency dependence is shown explicitly (assuming that $m << M$), that is ω_r, γ, and τ are constants, for which we give exact expressions later.

We note that (3) is a generalization of the well-known Fano line shape.[8] The latter applies when a virtual state, which decays into a single-particle continuum, is excited. Here one has an oscillator which is damped by a particle-hole continuum. The dependence of the variables x and y on frequency is different from the Fano case, but the physical principle, as well as the most important features of the line shape, are the same.

We derive expressions for a reflectivity experiment, although similar considerations would apply for electron energy loss. To lowest order in nonadiabaticity, the effect of the p-polarized incident and reflected waves is merely to set up a quasistatic[5] E field which is normal to the surface at large distances. We should therefore calculate its value and spatial variation in the region of the surface, and finally use this field to calculate the power absorption due to the vibrational mode in question. The change in reflectivity $\delta|R|^2$ due to this process is, to lowest order in q,

$$\delta|R|^2 = -16\pi[(\mathbf{q}\times\hat{\mathbf{n}})^2/(\mathbf{q}\cdot\hat{\mathbf{n}})](N/A)\operatorname{Im}\alpha, \tag{4}$$

where $\hat{\mathbf{n}}$ is a unit vector normal to the surface and $\mathbf{q}$ is the wave vector of the incident radiation; (N/A) is the number of adsorbate molecules (atoms) per unit area and α is a generalized "polarizability" of the system consisting of one adsorbate molecule plus the host system. Equation (4) applies in the zero coverage limit; at finite coverage, one must set $N=1$ in (4) and calculate α for the N-molecule–substrate system. In either case α is given by

$$\alpha = -\int d^3x \int d^3x'\, \hat{\mathbf{n}}\cdot\mathbf{x}\,\delta\chi(\mathbf{x},\mathbf{x}',\omega)\hat{\mathbf{n}}\cdot\mathbf{x}', \tag{5}$$

where $\delta\chi$ is the *change* in the *charge*-density response function of the system (including adsorbate) when the vibrational mode under consideration is unfrozen. The response function $\delta\chi$ has several pieces

$$\delta\chi = \delta\chi_{e-e} + \delta\chi_{e-i} + \delta\chi_{i-e} + \delta\chi_{i-i}, \tag{6}$$

where in a transparent notation e stands for electron and i for ion (or nucleus). One easily finds[5] (assuming harmonicity!) that

$$\delta\chi_{i-i}(\mathbf{x},\mathbf{x}',\omega) = \delta\rho_i(\mathbf{x})\delta\rho_i(\mathbf{x}')D(\omega), \tag{7}$$

where

$$D(\omega) = 2\omega_r/(\omega^2-\omega_r^2+i\omega\gamma). \tag{8}$$

Here $\delta\rho_i(\mathbf{x})$ is the change in the ionic charge density when the normal coordinate Q increases by an amount δQ equal to its transition matrix element, that is $1/(2M\omega_r)^{1/2}$; ω_r is the fully renormalized Born-Oppenheimer vibration frequency, M is the effective reduced mass, and the decay rate γ is given by

$$\gamma = \int d^3x \int d^3x'\, \delta V^{\text{sc}}_{e-i}(\mathbf{x})[-2\operatorname{Im}\tilde{\chi}_e(\mathbf{x},\mathbf{x}',\omega_r)]\delta V^{\text{sc}}_{e-i}(\mathbf{x}'), \tag{9}$$

where δV^{sc} is the fully screened change in the electron-ion potential corresponding to a change δQ in the normal coordinate. χ_e is the (electronic) charge-density response function in the absence of vibrations, and $\tilde{\chi}_e$ is its irreducible part, that is, the response to a fully screened potential. Only the term $\propto\omega$ in $\operatorname{Im}\tilde{\chi}_e$ need be retained. In a one-electron approximation Eq. (9) reduces to Persson and Hellsing's[5] Eq. (1). If we divide α into four pieces as we did $\delta\chi$ in (6), then we have

$$\alpha_{i-i} = -(\mu^i)^2 D(\omega), \tag{10}$$

where

$$\mu^i = \int d^3x\, \delta\rho_i(\mathbf{x})\hat{\mathbf{n}}\cdot\mathbf{x} \tag{11}$$

is the transition dipole of the nuclear motion.

The other terms in (6) are of the same form as (7), that is,

$$\delta\chi_{i-e}(\mathbf{x},\mathbf{x}',\omega) = \delta\rho_i(\mathbf{x})\delta\rho_e(\mathbf{x}',\omega)D(\omega), \tag{12}$$

and similarly for the other two terms. Here $\delta\rho_e(\mathbf{x}',\omega)$ is the electronic charge density induced at $\mathbf{x}$ when the normal coordinate Q vibrates at amplitude δQ and frequency ω. We must keep the frequency dependence in $\delta\rho_e$ to order ω just as we did in the normal mode self-energy to obtain γ. Therefore defining μ^e by

$$\mu^e = \int d^3x\, \delta\rho_e(\mathbf{x},\omega)\hat{\mathbf{n}}\cdot\mathbf{x} \tag{13}$$

and substituting in (5), we immediately obtain Eq. (1), where $\mu = \mu^e + \mu^i$; this is the desired result. However, exact expressions for $\delta\rho_e$ and hence μ^e can be immediately written down:

$$\delta\rho_e(\mathbf{x},\omega) = \int d^3x' \int d^3x''\, \chi_e(\mathbf{x},\mathbf{x}',\omega)|\mathbf{x}'-\mathbf{x}''|^{-1}\delta\rho_i(\mathbf{x}''). \tag{14}$$

If we separate real ($\propto\omega^0$) and imaginary ($\propto\omega^1$) parts $\mu = \mu_1 + i\mu_2$, then

$$\mu_1 = -\int d^3x\, \Phi(\mathbf{x})\delta\rho_i(\mathbf{x}) \tag{15}$$

and

$$\mu_2(\omega) = -\int d^3x \int d^3x' \, \Phi(\mathbf{x}) [\mathrm{Im}\tilde{\chi}_e(\mathbf{x},\mathbf{x}',\omega)] \delta V^{\mathrm{sc}}(\mathbf{x}'), \tag{16}$$

where $\Phi(x)$ is a fully (statically) screened version of the scalar potential $-\hat{\mathbf{n}}\cdot\mathbf{x}$ [Φ would be the true potential in the solid if it were placed in a constant and uniform (at ∞) electric field of unit magnitude; Φ would then give the true local electric field in the sample through $\mathbf{E} = -\nabla\Phi$]. Note the similarity between Eqs. (9) and (16). They each represent the same physical process and both must be included if one is to consistently add corrections to the adiabatic approximation. Equation (16) when evaluated in the single-particle approximation becomes

$$\mu_2(\omega) = 2\pi\omega \int d^3x \int d^3x' \, \Phi^{\mathrm{sp}}(\mathbf{x}) \left| \sum_{k,\epsilon_k=\epsilon_\mathrm{F}} \psi_k^*(\mathbf{x})\psi_k(\mathbf{x}') \right|^2 \delta V^{\mathrm{sp}}(\mathbf{x}'), \tag{17}$$

where ψ_k is the one-electron wave function and Φ^{sp} and δV^{sp} are the full single-particle potentials [which include the possibility for a scattered electron to exchange with one in the screening cloud] corresponding to Φ and δV^{sc}.

I would guess that Eq. (17) is suitable for numerical evaluation in simple cases by groups[2,5] that have already evaluated a similar expression for γ. Here I simply follow Persson and Persson[4] and assume that a single adsorbate molecule can be desribed by an Anderson-type resonant level model. The adsorbate contribution to the electronic charge response in this model is

$$\chi_a(\mathbf{x},\mathbf{x}') = -e^2\rho_a(\epsilon_\mathrm{F})[1 + i\pi\omega\rho_a(\epsilon_\mathrm{F})] \textstyle\sum_i |\phi_i(\mathbf{x})|^2 |\phi_i(\mathbf{x}')|^2 + O(\omega^2), \tag{18}$$

where $\phi_i(\mathbf{x})$ is the orbital wave function for the ith degenerate localized orbital and $\rho_a(\epsilon_\mathrm{F})$ is the adsorbate density of states (of a single orbital). Since this model is incapable of giving the correct substrate charge distribution (even its integral is wrong!), we follow Persson and Persson[4] and pick our origin on the image plane (of the substrate) which we assume is the mean position of all induced substrate charge. Then letting $\delta\epsilon = \int d^3x \, \delta V^{\mathrm{sc}}(\mathbf{x}) |\phi_i(\mathbf{x})|^2$ (which is assumed independent of orbital by symmetry) and

$$\bar{\mu} = \sum_{i=1}^{\mathscr{N}} \int d^3x \, e\hat{\mathbf{n}}\cdot\mathbf{x} |\phi_i(\mathbf{x})|^2, \tag{19}$$

we find immediately that

$$\mu_1^e = -\bar{\mu}\delta\epsilon\rho_a(\epsilon_\mathrm{F}), \tag{20}$$

$$\mu_2 = -\bar{\mu}\delta\epsilon\pi\rho_a^2(\epsilon_\mathrm{F})\omega, \tag{21}$$

$$\gamma = 2\pi\omega_r(\delta\epsilon)^2 \mathscr{N} \rho_a^2(\epsilon_\mathrm{F}). \tag{22}$$

Combining (20) and (22) gives

$$\gamma = 2\pi\omega_r \mathscr{N} (\mu_1^e/\bar{\mu})^2, \tag{23}$$

which is essentially Persson and Persson's result.[4] We obtain in addition

$$\mu_2/\mu_1^e = \pi\rho_a(\epsilon_\mathrm{F})\omega. \tag{24}$$

In general, the τ in Eq. (2) is given by $\tau = (\mu_2/\mu_1\omega) = (\mu_1^e/\mu_1)(\mu_2/\mu_1^e\omega)$ so that in this model

$$\tau = (\mu_1^e/\mu_1)\pi\rho_a(\epsilon_\mathrm{F}). \tag{25}$$

If $\Gamma/2$ is the virtual level width (half width at half maximum) whose position is $\sim\Gamma/2$ above ϵ_F (which is required for the nonnegligible nonadiabatic effects which are assumed), then defining

$$\tau = (\mu_1^e/\mu_1)\tau_t, \tag{26}$$

we see that $\tau_t = \pi\rho_a(\epsilon_\mathrm{F}) \sim 1/\Gamma$. The constraints of the model allow τ to be either positive or negative,

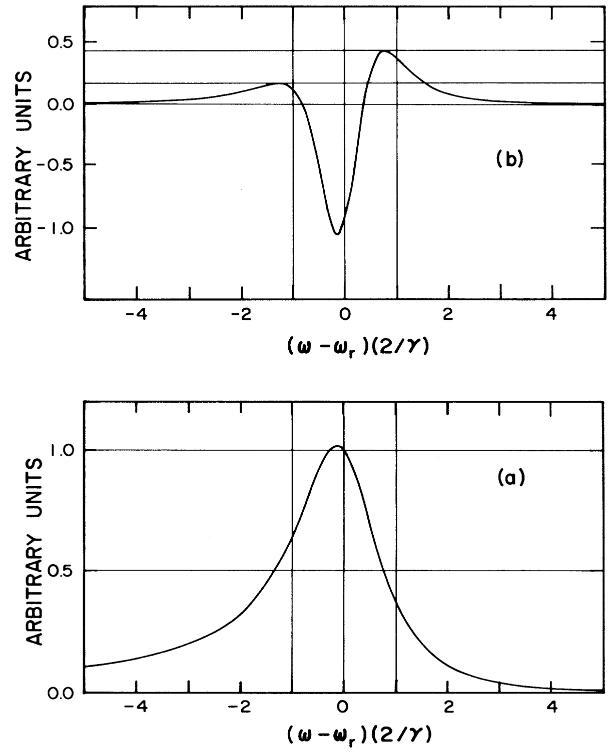

FIG. 1. Plot of the (a) line shape according to Eq. (3) and (b) its second derivative for $\omega_r\tau = 0.13$ and $\gamma/\omega_r << 1$.

depending whether the extra contribution to μ_1 which we have called μ_1^e is parallel or antiparallel to μ_1.

We now specialize to the case of CO on Cu(100). In this case[9] $\omega_r = 0.25$ eV and Persson and Persson[4] and Ryberg[10] have argued that $\mu_1^e/\mu_1 = (+0.12\text{ D})/(+0.22\text{ D}) = 0.54$, and in particular that μ_1^e/μ_1 (and hence τ) is positive. If $1/\tau_t \sim 1$ eV which might be typical[11] of a narrow resonance near the Fermi level, one obtains an asymmetry parameter $\omega_r\tau = +0.13$. In Fig. 1 I plot the resulting line shape and its second derivative. The predicted asymmetry is obviously substantial, and not in agreement with experiment.[9] In fact the *slight* asymmetry of the experiment[9] in the *other direction* suggests that μ_1^e and μ_1 have opposite signs and that τ_t is somewhat smaller.

In summary, I have suggested an asymmetry mechanism which is necessarily present whenever electron-hole–pair creation contributes to the linewidth. Although other mechanisms such as inhomogeneous broadening are capable of producing asymmetric lines, these are not expected to produce the long tails of the present mechanism. Therefore the positive experimental identification of the line shape (3) for vibrational lines well above the phonon continuum would be strong evidence of the importance of electron-hole–pair creation.

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[1] See articles by B. I. Lundqvist and K. Schönhamer, in *Many-Body Phenomena at Surfaces,* edited by D. C. Langreth and H. Suhl (Academic, Orlando, 1984) for a review and recent references.

[2] See B. I. Lundqvist, in *Many-Body Phenomena at Surfaces,* edited by D. C. Langreth and H. Suhl (Academic, Orlando, 1984), p. 453, for references and, more recently, A. G. Equiluz, Phys. Rev. B **30**, 4366 (1984), and J. W. Gadzuk and A. C. Luntz, Surf. Sci. **144**, 429 (1984).

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[6] See Gadzuk and Luntz (Ref. 2), Table I, for a summary of conventional wisdom concerning line shapes.

[7] In writing Eq. (3) we have added a tiny background $4\omega_r(\mu_1\tau)^2\omega/\gamma$ that comes not from Eq. (2), but from the electronic polarizability, a fact most easily verified in the model (18) with use of Eqs. (18)–(22).

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[11] See Ref. 4, Fig. 1, and Ref. 5, Fig. 2. See also J. Stöhr *et al.*, Phys. Rev. Lett. **51**, 2414 (1983).