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Optical properties of adsorbate atoms

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We calculate the dielectric response of adsorbate atoms on a metal surface assuming an Anderson model of the system. The dielectric function is then used to predict the change in the surface optical reflectance caused by the adsorbates. General results are obtained for substrates with one and two electron bands with and without the assumption of momentum conservation in the band-to-band optical transitions. A detailed analysis is carried out for the single-band momentum-conserving case. Here, the model is the same as that studied by Caroli and Kjollerstrom if the substrate density of states and various matrix elements are taken to be constants. However, we find an additional nonnegligible contribution omitted in their analysis. In other single-band cases, we show the wide variety of behavior which may be obtained for different parameter ranges and provide expressions to be used in data analyses.

I. INTRODUCTION

A number of recent experimental investigations have used optical-reflectance techniques to probe the electronic properties of atoms chemisorbed on solid surfaces. Changes in reflectance due to chemisorption are measured as functions of adsorbate coverage and frequency. McIntyre[1] has pioneered the use of *in situ* modulation spectroscopy to study adsorption at the electrode-electrolyte interface. Rubloff *et al.*[2] have more recently studied adsorption at the metal-vacuum interface. In the electrochemical case, these techniques provide a unique probe of the surface electronic structure. At the vacuum interface, such studies are a useful supplement to the by now conventional photoemission, field-emission, and ion-neutralization spectroscopies which unlike optical reflectance yield information only on filled electronic levels.

All of these experiments have been analyzed using an approach introduced by McIntyre and Aspnes.[3] The metal-adsorbate system is modeled by a semi-infinite substrate, characterized by a bulk dielectric function, which is covered with a monoatomic layer with modified dielectric properties. The chemisorption-induced changes in reflectivity can then be associated with differences between the surface layer and bulk dielectric functions. Although obviously a considerable oversimplification, this model has been useful in rationalizing a variety of experimental data.

McIntyre suggested that resonance levels associated with the adsorbed atoms might be crucial in determining the relevant dielectric properties. Rubloff *et al.*[2] used somewhat arbitrary Lorentzian parametrizations to represent such effects in order to fit their experimental data. When account was taken of adsorbate-induced elimination of surface states, and it was assumed that optical transitions occurred from the adsorbate levels to the metal's Fermi level, many of the fitted adsorbate level positions agreed with those found using other spectroscopic techniques.

In this paper, we use an Anderson model of the chemisorption system in order to obtain better expressions for the adsorbate-layer dielectric function. Such expressions are suitable for use in future fits to experimental data. This approach also provides an expression for the dielectric function of a dilute alloy which can be used to interpret the recent optical-reflection experiments of Callendar and Schnatterly[4] and Drew *et al.*[5] as well as a number of others.[6] In this context, Caroli[7] and Kjollerstrom[8] have performed similar dielectric-functions, assuming a one-band model, infinite bandwidth, constant matrix elements and substrate density of states, and momentum conservation. Here we relax those restrictions. In the special case studied by Caroli[7] and Kjollerstrom[8] we obtain their results plus an additional term which they overlooked. Our approach is similar to one used earlier by Penn to treat the effect of adsorbates on photoemission[9] and field emission.[10] We use Fermi's Golden Rule and a many-body formalism to calculate the imaginary part of the dielectric function. Under certain circumstances, a consideration of the required analytical properties of the dielectric function permits us to immediately obtain the real part from the imaginary part of that function. In general, however, a Kramers-Kronig transform must be performed.

We obtain general results for the adsorbate-layer dielectric function ϵ when the substrate k vector is a good quantum number and when it is not due,

e.g., to surface or final-state effects. Multiband and single-band substrates are treated separately.

In general, the calculated adsorbate-layer dielectric function together with the known substrate dielectric function can be used in the McIntyre and Aspnes (MA) expression to predict $\Delta R(\omega)/R$ or for parametric analyses. We make some convenient approximations in order to use our calculated dielectric function to predict characteristic frequency-dependent differential reflectances. In the low-frequency limit, the MA formula for $\Delta R/R$ can be approximated by $\omega^2\epsilon_1$. For higher frequencies, assuming a constant substrate dielectric function, there are contributions to $\Delta R/R$ of the form $\omega\epsilon_1$ and $\omega\epsilon_2$.

In the single-band case, detailed analysis is possible. One simple approximation consists of assuming that all matrix elements are real constants, the metal density of states is constant, and the bandwidth is infinite. This corresponds to the approach of Caroli[7] and Kjollerstrom.[8] We find, however, that they have omitted one of three terms in the dielectric function. Within this real-constant-matrix-element approximation, a single parameter in addition to the level position E_A and width Γ_A characterizes the frequency dependence of ϵ. This parameter α is essentially the ratio of the strength of the excitations which consist of an adsorbate electron jumping to a substrate state and then being raised in energy to the strength of the direct excitation of an adsorbate electron to an excited substrate state. If $|E_A|/\Gamma$, the absolute value of the adsorbate level energy with respect to the Fermi level in units of the adsorbate level width, is $\gtrsim 1$, then structure in $\Delta R/R$ appears at $\omega \sim E_A$. The nature of the structure, i.e., a minimum or maximum, depends, however, on the magnitude of α.

In the more general single-band case, where the band has a finite width, more than one parameter is required to characterize ϵ and $\Delta R/R$. Then we analyze the frequency dependence of each contributing term. For $|E_A|/\Gamma \gtrsim 1$ there is, in general, structure at $\omega \sim E_A$ in the contribution to $\Delta R/R$ which is lowest order in ω^{-1}. High-order terms have structure only for larger values of $|E_A|/\Gamma$. Structure in ϵ_2 appears in general only for $|E_A|/\Gamma > 3$, which should be contrasted with the use by Rubloff *et al.* of a Lorentzian approximation to ϵ_2 in fitting experimental data. Finite bandwidths reduce but do not eliminate structure in $\Delta R/R$, while additional structure is often introduced at values of ω given very approximately by the sum of $|E_A|$ and the bandwidth. These results should be used in future detailed parametric analyses of experimental data.

There are a number of terms in the dielectric function which exist only for multiband substrates, e.g., transition metals. These terms are not simply characterized and depend in detail on the form of the energy bands. We present general expressions which can be used in their future analysis. At present it is difficult to assess their importance.

We concentrate on adsorbates with a single virtual level as opposed to the miltilevel system sometimes found in practice. Furthermore, some levels are probably more closely associated with the substrate than with the adsorbate, a situation not normally accounted for within the Anderson model. However, if the adsorbate and the nearest substrate atoms are taken as forming a complex which itself interacts with the rest of the substrate electrons, then the Anderson model may be adequate.

In Sec. II, we derive various expressions for the dielectric function. Formal results for ϵ_2 are given in Sec. II A. Section II B considers ϵ_2 in the one- and two-band cases when momentum is conserved. In Sec. II C, we obtain expressions for ϵ_2 valid when momentum is not conserved. Section II D briefly treats ϵ_2 for two-level adsorbates and Sec. II E describes how the real part of the dielectric function can be obtained from its imaginary part. Finally, in Secs. III A and III B we present a variety of results for the intraband momentum-conserving case, and in Sec. III C the momentum-nonconserving case is considered. In Sec. III D the reflectivity is related to the dielectric function and numerical results are presented.

II. CALCULATION OF ϵ_2, ϵ_1

A. Formal expression for ϵ_2

The imaginary part of the dielectric function associated with the optical absorption of photons of energy $\hbar\omega_0$ by a system of electrons is

$$\epsilon_2(\omega_0) = \int_{-\infty}^{\infty} \gamma(\omega)\, d\omega \,, \tag{1}$$

where $\gamma(\omega)$ is related to the number of electrons excited to final states of energy ω per unit time and is given by

$$\gamma(\omega) = \beta(1/\omega_0^2) \sum_{mm'} f(\epsilon_m)[1 - f(\epsilon_{m'})] \times |\langle m|\tau|m'\rangle|^2 \delta(\epsilon_{m'} - \epsilon_m - \omega_0)\delta(\epsilon_{m'} - \omega) \,. \tag{2a}$$

Here ϵ_m, $|m\rangle$ are eigenvalues and eigenfunctions of the Hamiltonian H for the system, $f(\epsilon)$ is the Fermi function, $\tau = P_z = -i\hbar\,\partial/\partial z$ and

$$\beta = (4\pi e^2/\Omega)(\hbar/m)^2 \,, \tag{2b}$$

where Ω is the volume of the metal. Equations (2) take spin degeneracy into account. γ can also be written in the form

$$\gamma(\omega)=F(\omega)\sum_{mm'}|\langle m|\tau|m'\rangle|^2\langle m|\mathcal{G}^I(\omega-\omega_0)|m\rangle \times\langle m'|\mathcal{G}^I(\omega)|m'\rangle\,, \tag{3a}$$

where

$$F(\omega)=\beta(\omega_0\pi)^{-2}f(\omega-\omega_0)[1-f(\omega)] \tag{3b}$$

and

$$\mathcal{G}^I(\omega)=(1/2i)[\mathcal{G}(\omega-i0^+)-\mathcal{G}(\omega+i0^+)]\,,$$
$$\mathcal{G}=(1/2i)[(\omega-i0^+-H)^{-1}-(\omega+i0^+-H)^{-1}]\,. \tag{3c}$$

It will be convenient to use a basis set $\{|k\rangle\}$ which does not diagonalize H rather than the set $\{|m\rangle\}$ which does. Equation (3a) becomes

$$\gamma(\omega)=F(\omega)\sum_{kk'k''k'''}\langle k|\tau|k'\rangle\langle k''|\tau|k'''\rangle \times\langle k'|\mathcal{G}^I(\omega-\omega_0)|k''\rangle\langle k'''|\mathcal{G}^I(\omega)|k\rangle\,. \tag{4}$$

We are specifically interested in calculating ϵ_2 for the case of a metal with adsorbates on the surface. It will be assumed that the adsorbate-adsorbate interaction is weak compared to the adsorbate-metal interaction and that the system is adequately described by the Anderson model.[11] The usual form of the Anderson model[11] makes use of an overcomplete set of states: the metal states which are themselves complete and the adsorbate state. This leads to an incorrect expression for the density of states. This problem is treated by Anderson and McMillian[12] (AM). Their result for the Green's function that describes the metal-adsorbate system and takes overcompleteness into account is

$$\mathcal{G}_{kk'}(E\pm i0^+)=(E\pm i0^+-H)^{-1}_{kk'}=g_k(E\pm i0^+)\delta_{k,k'} +[g_k(E\pm i0^+)\nu_{ka}-\langle k|a\rangle]\Lambda^{-1}(E\pm i0^+) \times[\nu_{ak'}g_{k'}(E\pm i0^+)-\langle a|k'\rangle]\,, \tag{5}$$

where H is the metal-adsorbate Hamiltonian expressible as the sum of a metallic part, H_0, and the change in potential caused by the adsorbate, ΔV; and $|a\rangle$ is the wave function associated with the adsorbate. The complete set of electron states of the metal denoted by $\{|k\rangle\}$ is such that $H_0|k\rangle=\epsilon_k|k\rangle$. It is understood that k includes all the quantum numbers required to specify a metal state. Here

$$g_k(E\pm i0^+)=(E-H_0\pm i\lambda)^{-1}_{kk}=(E-\epsilon_k\pm i\lambda)^{-1}\,, \tag{6a}$$

where $\hbar/\lambda$ represents the lifetime of an electron. We assume λ to be very small but finite. The purpose of assuming λ to be finite is primarily to facilitate obtaining $\epsilon_1(\omega_0)$ by means of the Kramers-Kronig relation. This will be described in detail later in the paper. Also

$$\nu_{ka}=\langle k|E-H|a\rangle\,, \tag{6b}$$

$$\Lambda^{-1}(E\pm i0^+)=\left(E-\epsilon_a-\sum_k\nu_{ak}g_k(E\pm i0^+)\nu_{ka}\right)^{-1}\,, \tag{6c}$$

where ϵ_a is the energy associated with the state $|a\rangle$. Equation (5) is obtained from Eqs. (2.34) and (2.36) of the AM paper only after taking some notational errors into account. Beginning with AM (2.36), H_{ka} and G' are referred to as V_{ka} and G.

In Eq. (5), Λ^{-1} represents the Green's function that describes the adsorbate. Thus the resonant energy of the adsorbate, ω_r, is given by $\mathrm{Re}\Lambda(\omega_r-i0^+)=0$ and from (6c)

$$\omega_r=\epsilon_a+\mathrm{Re}\left(\sum_k\nu_{ak}g_k(\omega_r-i0^+)\nu_{ka}\right)\,, \tag{7}$$

where $\nu_{ka}=\langle k|\omega_r-H|a\rangle$. The width of the resonant level is $\mathrm{Im}[\sum_k\nu_{ak}g(\omega_r-i0^+)\nu_{ka}]$. The approximation of Eq. (5) for $(E-H)^{-1}$ is similar to that of the original Anderson model but the effective metal-adsorbate interaction is $-\nu_{ak}=(H-E)_{ak}$ rather than H_{ak}.

We show in Appendix A that use of Eq. (5) in Eq. (4) yields

$$\gamma(\omega)\simeq\gamma_0(\omega)+F(\omega)\sum_k g_k^I(\omega)\{[|u_k(\omega-\omega_0)|^2 -|v_k(\omega-\omega_0)|^2]\Lambda^I(\omega-\omega_0) +[2\,\mathrm{Re}u_k(\omega-\omega_0)v_k^*(\omega-\omega_0)]\Lambda^R(\omega-\omega_0)\} +F(\omega)\sum_k g_k^I(\omega-\omega_0)\{[u_k(\omega)|^2-|v_k(\omega)|^2]\Lambda^I(\omega) +[2\,\mathrm{Re}u_k(\omega)v_k^*(\omega)]\Lambda^R(\omega)\}\,, \tag{8a}$$

where

$$u_k(\omega)=\sum_{k'}\tau_{kk'}g_{k'}^R(\omega)(\Delta V)_{k'a}\,, \tag{8b}$$

$$v_k(\omega)=\sum_{k'}\tau_{kk'}g_{k'}^I(\omega)(\Delta V)_{k'a}\,, \tag{8c}$$

$$g_{k'}^R(\omega)=\mathrm{Re}[g_{k'}(\omega-i0^+)]=(\omega-\epsilon_{k'})/[(\omega-\epsilon_{k'})^2+\lambda^2]\,, \tag{8d}$$

$$g_{k'}^I(\omega)=\mathrm{Im}[g_{k'}(\omega-i0^+)]=\lambda/[(\omega-\epsilon_{k'})^2+\lambda^2]\,, \tag{8e}$$

$$\Lambda^R(\omega)=\mathrm{Re}[\Lambda^{-1}(\omega-i0^+)]\,, \tag{8f}$$

$$\Lambda^I(\omega)=\mathrm{Im}[\Lambda^{-1}(\omega-i0^+)]\,, \tag{8g}$$

$$\Delta V=H-H_0\,. \tag{8h}$$

We have neglected the contribution of the last term on the right-hand side of (A4a) since it represents intra-adsorbant transitions, i.e., transitions from the filled portion of a virtual adsorbate level to its unfilled portion. In most cases of interest the adsorbate level is either almost entirely filled or has a smaller width than the photon energy ω_0 so the transition probability is very small. We will consider intra-adsorbate transitions in the

case when there are two different adsorbate levels later in the paper.

It will be convenient to define the "wave functions" $|a'\rangle$ and $|a''\rangle$ by

$$|a'(\omega)\rangle = g^R(\omega)\Delta V|a\rangle \equiv |a\rangle - g^R(\omega)\nu|a\rangle\,, \tag{9a}$$

$$|a''(\omega)\rangle = g^I(\omega)\Delta V|a\rangle \simeq -g^I(\omega)\nu|a\rangle\,, \tag{9b}$$

where we have used the fact that λ in (8d) and (8e) is small. The wave function $|a'\rangle$ represents the wave function of the adsorbate including the effect of the metal-adsorbate interaction $-\nu = H - E$. $|a''\rangle$ represents the hopping of an electron from the adsorbate to the metal under the influence of the potential ΔV. With the above definitions of $|a'\rangle$ and $|a''\rangle$ we find from Eqs. (8b) and (8c)

$$u_k(\omega) = \langle k|\tau|a'(\omega)\rangle\,, \tag{10a}$$

$$v_k(\omega) = \langle k|\tau|a''(\omega)\rangle\,. \tag{10b}$$

Use of (10) in (8) yields

$$\begin{aligned}\gamma(\omega) &= \gamma_0 + \gamma_{12} + \gamma_{21} \\ &= \gamma_0(\omega) + \pi F(\omega)[(\alpha_1 - \beta_1)\Lambda^I(\omega-\omega_0) + \gamma_1\Lambda^R(\omega-\omega_0)] \\ &\quad + \pi F(\omega)[(\alpha_2 - \beta_2)\Lambda^I(\omega) + \gamma_2\Lambda^R(\omega)]\,,\end{aligned} \tag{11a}$$

with

$$\alpha_1 = \sum_k \delta_\lambda(\omega - \epsilon_k)\left|\langle k|\tau|a'(\omega-\omega_0)\rangle\right|^2\,, \tag{11b}$$

$$\beta_1 = \sum_k \delta_\lambda(\omega - \epsilon_k)\left|\langle k|\tau|a''(\omega-\omega_0)\rangle\right|^2\,, \tag{11c}$$

$$\gamma_1 = \sum_k \delta_\lambda(\omega - \epsilon_k)2\,\mathrm{Re}[\langle k|\tau|a'(\omega-\omega_0)\rangle\langle a''(\omega-\omega_0)|\tau|k\rangle] \tag{11d}$$

$$\alpha_2 = \sum_k \delta_\lambda(\omega - \omega_0 - \epsilon_k)\left|\langle k|\tau|a'(\omega)\rangle\right|^2\,, \tag{11e}$$

$$\beta_2 = \sum_k \delta_\lambda(\omega - \omega_0 - \epsilon_k)\left|\langle k|\tau|a''(\omega)\rangle\right|^2\,, \tag{11f}$$

$$\gamma_2 = \sum_k \delta_\lambda(\omega - \omega_0 - \epsilon_k)2\,\mathrm{Re}[\langle k|\tau|a'(\omega)\rangle\langle a''(\omega)|\tau|k\rangle]\,, \tag{11g}$$

where

$$\delta_\lambda(\omega) = \pi^{-1}\lambda/(\omega^2 + \lambda^2) \tag{11h}$$

and δ_λ is a delta function as $\lambda \to 0$.

γ_0 is the usual expression which describes transitions between metal wave functions. The remaining terms involve adsorbate levels and are the ones of interest here. γ_{12} and γ_{21} describe electron transitions from the adsorbate to the metal and from the metal to the adsorbate, respectively. More precisely the first term in γ_{12}, $\gamma_{12}^{(1)} = \pi F(\omega)\alpha_1\Lambda^I(\omega-\omega_0)$, is the probability that an electron is optically excited directly from the adsorbate state $|a'(\omega-\omega_0)\rangle$ to a metal state with energy ω. The second term in γ_{12}, $\gamma_{12}^{(2)} = \pi F(\omega)\beta_1\Lambda^I(\omega-\omega_0)$, is the probability that an electron on the adsorbate with energy $\omega - \omega_0$ jumps to a metal state of energy $\omega - \omega_0$ and is subsequently excited to a metal state of energy ω by a photon. Finally the last term in γ_{12} represents an interference between the two excitation processes. The terms in γ_{21} have an analogous interpretation.

B. ϵ_2 when momentum is conserved

In order to evaluate $\gamma(\omega)$ as given by Eq. (8) we will assume the metal states $\{|\vec{k}\rangle\}$ are adequately approximated by Bloch states $\{|\vec{k}, n\rangle\}$, where now $\vec{k}$ is a reduced wave vector. This is consistent with the assumption of a long electron lifetime, which implies that surface effects are relatively small. For simplicity we will assume that there are only two metal bands of importance.

It is shown in Appendix B that use of Eq. (8) in Eq. (1) now yields for the intraband contribution to $\epsilon_2(\omega_0)$

$$\epsilon_2(\omega_0) = \epsilon_2^{(0)}(\omega_0) + \epsilon_2^{(1)}(\omega_0)$$

$$\begin{aligned}\epsilon_2^{(1)}(\omega_0) = \frac{1}{\omega_0^2}\Bigg[&\sum_n\Bigg(\langle|\tau_{kn,a}|^2\rangle_{\mathrm{av}} \\ &+\langle|\tau_{kn,kn}|^2|\nu_{kn,a}|^2\rangle_{\mathrm{av}}\frac{\omega_0^2 - 4\lambda^2}{(\omega_0^2+4\lambda^2)^2}\Bigg)\phi_1(\omega_0) \\ &+\sum_n 2\,\mathrm{Re}\langle\tau_{kn,kn}\nu_{kn,a}\tau_{a,kn}\rangle_{\mathrm{av}} \\ &\times\left(\frac{\omega_0}{\omega_0^2+4\lambda^2}\phi_2(\omega_0) - \frac{2\lambda}{\omega_0^2+4\lambda^2}\phi_3(\omega_0)\right) \\ &-\sum_n\langle|\tau_{kn,kn}|^2|\nu_{kn,a}|^2\rangle_{\mathrm{av}}\frac{4\omega_0\lambda}{(\omega_0^2+4\lambda^2)^2}\phi_4(\omega_0)\Bigg],\end{aligned} \tag{12a}$$

$$\phi_1(\omega_0) = (\beta/\pi^2)\int_0^{\omega_0} d\omega\,[\rho(\omega)\Lambda^I(\omega-\omega_0) + \rho(\omega-\omega_0)\Lambda^I(\omega)] \tag{12b}$$

$$\phi_2(\omega_0) = (\beta/\pi^2)\int_0^{\omega_0} d\omega\,[\rho(\omega)\Lambda^I(\omega-\omega_0) - \rho(\omega-\omega_0)\Lambda^I(\omega)]\,, \tag{12c}$$

$$\phi_3(\omega_0) = (\beta/\pi^2)\int_0^{\omega_0} d\omega\,[\rho(\omega)\Lambda^R(\omega-\omega_0) + \rho(\omega-\omega_0)\Lambda^R(\omega)]\,, \tag{12d}$$

$$\phi_4(\omega_0) = (\beta/\pi^2)\int_0^{\omega_0} d\omega\,[\rho(\omega)\Lambda^R(\omega-\omega_0) - \rho(\omega-\omega_0)\Lambda^R(\omega)]\,, \tag{12e}$$

where $\epsilon_2^{(0)}(\omega_0)$ is the imaginary part of the dielectric function in the absence of adsorbates and $\langle\rangle_{\mathrm{av}}$ is defined in (B6b). In the limit that $\lambda \to 0$ we have

$$\begin{aligned}\epsilon_2^{(1)}(\omega_0) = (\beta/\omega_0^2)(&\langle|\tau_{kn,a}|^2\rangle_{\mathrm{av}} \\ &+\langle|\tau_{kn,kn}|^2|\nu_{kn,a}|^2\rangle_{\mathrm{av}}\omega_0^{-2})\,\phi_1(\omega_0)\end{aligned}$$

$$+\langle 2\,\mathrm{Re}\,\tau_{kn,kn}\nu_{kn,a}\tau_{a,kn}\rangle_{\mathrm{av}}\,\omega_0^{-1}\phi_2(\omega_0)\ . \quad (12f)$$

If the metal has a constant density of states and $\Lambda(\omega)=\Lambda^R(\omega)+i\Lambda^I(\omega)=(\omega-E_a+i\Gamma)^{-1}$, the terms on the right-hand sides of (12f) and (12a) which involve ϕ_1 and ϕ_4 are the same as those obtained by Caroli and Kjollerstrom, respectively. These authors considered only intraband terms. The terms in (12f) and (12a) that involve ϕ_2 and ϕ_3 have been incorrectly omitted by those authors because they assumed $\tau_{kn,a}$ but not $\tau_{kn,kn}$ to be a constant independent of k whereas $\tau_{-kn,-kn}=-\tau_{kn,kn}$. Then the term $\langle 2\,\mathrm{Re}\tau_{kn,kn}\nu_{kn,a}\tau_{a,kn}\rangle_{\mathrm{av}}$ in (12f) and (12a) vanishes by symmetry and thus ϕ_2 and ϕ_3 do not contribute to $\Delta\epsilon_2$. Various authors[4,5] have experimentally determined the Anderson-model parameters V_{ka}, ϵ_a, and the level width Γ for several dilute alloy systems by fitting their experimental optical data to the Caroli-Kjollerstrom expressions. We have attemped to determine more accurate values for the Anderson-model parameters than those obtained in Ref. 4 by fitting their experimental curves to $\epsilon_2^{(1)}$ as given by (12f) with the matrix elements regarded as adjustable parameters. This is the same procedure as adopted in Ref. 4 except the term in ϕ_2 was omitted there. We found that the additional term does not allow for a better fit of the experimental data and consequently the Anderson-model parameters determined in Ref. 4 remain unchanged. The reason for this is not clear at present.

In Appendix B we show that the contribution of $\epsilon_2(\omega_0)$ from interband terms is

$$\Delta\epsilon_2(\omega_0)=\sum_n 2\,\mathrm{Re}\,[\,\tau_{a,kn}\tau_{kn,k\bar{n}}\nu_{k\bar{n},a}\,]_0\,\phi_{1,n}+\sum_n 2\,\mathrm{Re}\,[\,\tau_{a,k\bar{n}}\tau_{k\bar{n},kn}\tau_{kn,kn}\nu_{kn,a}\,]_0\,\phi_{2,n}+\sum_n |\,\tau_{kn,k\bar{n}}|^2\,|\,\nu_{k\bar{n},a}|^2\,\phi_{3,n}\ , \quad (13a)$$

where the brackets $[\ ]_0$ mean the term is taken as constant and where n denotes one metal band and $\bar{n}$ the other;

$$\phi_{1,n}=(\beta/\omega_0^2)\,\mathrm{Im}\left(\int_0^{\omega_0}d\omega\,\Lambda(\omega)M^{(1)}(\omega,\omega_0)+\int_0^{\omega_0}d\omega\,\Lambda(\omega-\omega_0)N^{(1)}(\omega,\omega_0)\right)\ , \quad (13b)$$

$$\phi_{2,n}=(\beta/\omega_0^2)\,\mathrm{Im}\left(-(\omega_0-2i\lambda)^{-1}\int_0^{\omega_0}d\omega\,\Lambda(\omega)M^{(1)}(\omega,\omega_0)+(\omega_0+2i\lambda)^{-1}\int_0^{\omega_0}d\omega\,\Lambda(\omega-\omega_0)N^{(1)}(\omega,\omega_0)\right), \quad (13c)$$

$$\phi_{3,n}=(\beta/\omega_0^2)\,\mathrm{Im}\left(\int_0^{\omega_0}d\omega\,\Lambda(\omega)M^{(2)}(\omega,\omega_0)+\int_0^{\omega_0}d\omega\,\Lambda(\omega-\omega_0)N^{(2)}(\omega,\omega_0)\right), \quad (13d)$$

$$M^{(1)}(\omega,\omega_0)=\sum_k\frac{\delta(\omega-\omega_0-\epsilon_{kn})}{\omega-\epsilon_{k\bar{n}}}+i\pi\sum_k\delta(\omega-\omega_0-\epsilon_{kn})\times\delta(\omega-\epsilon_{k\bar{n}})\ , \quad (13e)$$

$$N^{(1)}(\omega,\omega_0)=\sum_k\frac{\delta(\omega-\epsilon_{kn})}{\omega-\omega_0-\epsilon_{k\bar{n}}}+i\pi\sum_k\delta(\omega-\epsilon_{kn})\,\delta(\omega-\omega_0-\epsilon_{k\bar{n}})\ , \quad (13f)$$

$$M^{(2)}(\omega,\omega_0)=\sum_k\frac{\delta(\omega-\omega_0-\epsilon_{kn})}{(\omega-\epsilon_{k\bar{n}}-i0^+)^2}\ , \quad (13g)$$

and

$$N^{(2)}(\omega,\omega_0)=\sum_k\frac{\delta(\omega-\epsilon_{kn})}{(\omega-\omega_0-\epsilon_{k\bar{n}}-i0^+)^2}\ . \quad (13h)$$

Clearly the terms $\phi_{i,n}$ have a very complicated dependence on band structure owing to the form of the $M^{(i)}$ and $N^{(i)}$.

C. ϵ_2 when momentum is not conserved

If momentum conservation as defined by $\tau_{kn,k'n'}=\Delta_{k,k'}\tau_{kn,kn'}$ is not valid then $\gamma(\omega)$ is given by Eq. (11). This might be the case if the electron that is excited by the incident photon interacts strongly with the hole it leaves behind. Taking the matrix elements $\langle k|\tau|k'\rangle$, $\langle k|\tau|a\rangle$ and ν_{ka} as constants and $\lambda\to 0$ we can rewrite Eqs. (11b)–(11h) as

$$\alpha_1=A\rho(\omega)\ , \quad (14a)$$

$$\alpha_2=A\rho(\omega-\omega_0)\ , \quad (14b)$$

$$\gamma_i=G\rho(\omega)\rho(\omega-\omega_0),\quad i=1,2 \quad (14c)$$

$$\beta_1=B\rho(\omega)\rho(\omega-\omega_0)^2\ , \quad (14d)$$

$$\beta_2=B\rho(\omega-\omega_0)\rho(\omega)^2\ , \quad (14e)$$

where A, B, and G are constants given by

$$A=|\langle k|\tau|a'\rangle|^2\ , \quad (14f)$$

$$G=2\pi\,\mathrm{Re}(\langle k|\tau|a'\rangle\langle a|\tau|k\rangle)\ , \quad (14g)$$

$$B=\pi|\langle k|\tau|a\rangle|^2|\nu_{ka}|^2\ , \quad (14h)$$

and we have assumed $\lambda\to 0^+$ in (11).

D. ϵ_2 for adsorbates with two resonant levels

We wish to allow for the possibility that there are two resonant levels associated with the adsorbate and that there can consequently be optical transitions between them. In the absence of the metal-adsorbate interaction, the adsorbate states obey a Hamiltonian H_a and have energies ϵ_1, ϵ_2 and wave functions $|a_1\rangle$, $|a_2\rangle$ which satisfy

$$H_a|a_i\rangle=\epsilon_i|a_i\rangle,\quad i=1,\ 2\ . \quad (15)$$

A straightforward application of the AM approach[12] yields the generalization of Eq. (A2) to this case of two resonant adsorbate levels:

$$\mathcal{G}_{kk'} = g_k\delta_{kk'} + \sum_{i,j=1}^{2} (g_k\nu_{ka_i} - \langle k|a_i\rangle)(\Lambda^{-1})_{i,j}(\nu_{a_jk'} - \langle a_j|k'\rangle) \tag{16a}$$

and

$$\Lambda_{i,j} = (E-\epsilon_i)\delta_{i,j} - \sum_k \nu_{a_i,k}g_k\nu_{k,aj}\,. \tag{16b}$$

We denote the linear combinations of $|a_i\rangle$ that diagonalize Λ^{-1} by $|a_L\rangle$, $|a_U\rangle$. The $|a_L\rangle$, $|a_U\rangle$ are related to $|a_1\rangle$, $|a_2\rangle$ by a unitary transformation. We have

$$\mathcal{G}_{kk'} = g_k\delta_{kk'} + \sum_{i=L,U}(g_k\nu_{k,a_i} - \langle k|a_i\rangle)\Lambda_{ii}^{-1}(\nu_{a_ik'}g_{k'} - \langle a_i|k'\rangle), \tag{17a}$$

$$\Lambda_{ii} = E - \epsilon_i - \sum_k \nu_{a_i,k}g_k\nu_{k,a_i}\,, \quad i=L,U \tag{17b}$$

and ϵ_i is given by

$$\epsilon_i = \langle a_i|H_a|a_i\rangle\,, \quad i=L,U\,. \tag{17c}$$

The positions of the resonant levels E_L, E_U are given by

$$\mathrm{Re}[\Lambda_{ii}(E_i - i0^+)] = 0\,, \quad i=L,U\,. \tag{18}$$

The dielectric function associated with adsorbate-adsorbate transitions is obtained from

$$\epsilon_{aa}(\omega_0) = \int_{-\infty}^{\infty}\gamma_{aa}(\omega)\,d\omega\,, \tag{19a}$$

with

$$\begin{aligned}\gamma_{aa}(\omega_0) = -\tfrac{1}{2}F(\omega_0)\{&\Lambda_i^I(\omega)\Lambda_j^I(\omega-\omega_0)(|\Phi_{ij}^{II}|^2 \\ &+ |\phi_{ij}^{RR}|^2 - |\phi_{ij}^{RI}|^2 - |\Phi_{ij}^{IR}|^2) \\ &+ \Lambda_I^R(\omega)\Lambda_j^R(\omega-\omega_0)[2\,\mathrm{Re}(\Phi_{ij}^{RR}\Phi_{ij}^{II*}) \\ &+ 2\,\mathrm{Re}(\phi_{ij}^{RI}\phi_{ij}^{IR*})] \\ &+ \Lambda_i^I(\omega)\Lambda_j^R(\omega-\omega_0)[2\,\mathrm{Re}(\phi_{ij}^{IR}\phi_{ij}^{RR*}) \\ &- 2\,\mathrm{Re}(\phi_{ij}^{RI}\Phi_{ij}^{II*})] \\ &+ \Lambda_i^R(\omega)\Lambda_j^I(\omega-\omega_0)[2\,\mathrm{Re}(\phi_{ij}^{RI}\phi_{ij}^{RR*}) \\ &- 2\,\mathrm{Re}(\phi_{ij}^{IR}\phi_{ij}^{II*})]\}\,,\end{aligned} \tag{19b}$$

where

$$\Phi_{ij}^{MN} = [\Delta V g^M(\omega-\omega_0)\tau g^N(\omega)\Delta V]_{j,i} \tag{19c}$$

and M, N are either R or I and i, j denote $|a_L\rangle$ or $|a_U\rangle$. Equations (19) are derived in Appendix C.

E. ϵ_1 via the Kramers-Kronig formula

Having obtained $\epsilon_2(\omega_0)$ we may now calculate $\epsilon_1(\omega_0)$ using the Kramers-Kronig equation

$$\epsilon_1(\omega_0) = (1/\pi)P\int_{-\infty}^{\infty}\frac{d\omega}{\omega-\omega_0}\,\epsilon_2(\omega)\,, \tag{20}$$

where P denotes the principal part, and for the cases of interest to us $\epsilon_1(\infty) = 0$. Clearly (20) is valid only if $\epsilon_2(\omega)$ is no more singular than $1/\omega$ as $\omega \to 0$. From Eqs. (12) it is apparent that if $\lambda = 0$ only the first term in $\epsilon_2^{(1)}(\omega_0)$ satisfies this condition. Consequently we have used a small but finite λ in all our numerical calculations with Eq. (20). A somewhat different approach for the intraband contribution is also possible. The intraband contribution to the dielectric function is, from (12a)

$$\begin{aligned}\epsilon_2^{(1)}(\omega) = \mathrm{Im}\{(A/\omega^2)\{&ai\Phi_1(\omega) + b(\omega+2i\lambda)^{-1} \\ &\times[\Phi_3(\omega) + i\Phi_2(\omega)] \\ &+ c(\omega+2i\lambda)^{-2}[\Phi_4(\omega) + i\Phi_1(\omega)]\}\}\,,\end{aligned} \tag{21}$$

where A, a, b, and c are constants. In Appendix D we show that in the limit of small λ the real part of $\epsilon^{(1)}$ is given by

$$\epsilon_1^{(1)}(\omega) = A\left(\left(\frac{a+c}{\omega^2}\right)\frac{\Phi_1^K(\omega)}{\omega^2} + \left(\frac{b}{\omega}\right)\frac{\Phi_2^K(\omega)}{\omega^2}\right) + \frac{B}{\omega^2} + \frac{C}{\omega}\,, \tag{22a}$$

where

$$\frac{\Phi_i^K(\omega)}{\omega^2} = \left(\frac{1}{\pi}\right)P\int_{-\infty}^{\infty}\frac{d\omega'}{\omega'-\omega}\,\frac{\Phi_i(\omega')}{\omega'^2}\,, \quad i=1,2 \tag{22b}$$

and B, C are constants given by

$$B = -Ac\left(\frac{\Phi_1^K(\omega)}{\omega^2} - \frac{\Phi_4(\omega)}{\omega^2}\right)_{\omega=0}\,, \tag{22c}$$

$$C = -Ab\left(\frac{\Phi_2^K(\omega)}{\omega^2} - \frac{\Phi_3(\omega)}{\omega^2}\right)_{\omega=0} \tag{22d}$$

Thus we can determine $\epsilon_1^{(1)}(\omega)$ in the limit of small λ simply by calculating $\Phi_1^K(\omega)$, $\Phi_2^K(\omega)$ as given by (22b) and (12) and $[\Phi_3(\omega)/\omega^2]_{\omega=0}$, $[\Phi_4(\omega)/\omega^2]_{\omega=0}$ as given by (12) without having to calculate the Kramers-Kronig transform of every term in (12a).

III. MODEL CALCULATIONS OF ϵ AND NUMERICAL RESULTS

We now consider the frequency dependence of the dielectric function when the following conditions hold: (i) Only intraband terms are considered, (ii) matrix elements are considered constant, (iii) the metal density of states is constant with the metal bandwidths defined in Fig. 1.

A. Calculations of $\epsilon_2(\omega)$ assuming momentum conservation as well as conditions (i)–(iii)

ϵ_2 is given by Eq. (12f) which can be written in the form

$$\epsilon_2^{(\mathrm{con})}(\omega) = A_0[\omega^{-2}(1 + A_1\omega^{-2})\Phi_1 + \omega^{-3}A_2\phi_2]\,, \tag{23a}$$

$$\phi_{1,2} = \int_{l_1}^{l_2}[\Lambda^I(\omega'-\omega) \pm \Lambda^I(\omega')]\,d\omega'\,, \tag{23b}$$

$$l_2 = \begin{cases}\omega\,, & \omega < \omega_T \\ \omega_T\,, & \omega > \omega_T\end{cases} \tag{23c}$$

$$l_1 = \begin{cases} 0 , & \omega < \omega_B \\ -\omega_B + \omega , & \omega > \omega_B \end{cases} \tag{23d}$$

$$\Lambda^I(\omega) = [(\omega - E_a)^2 + 1]^{-1} , \tag{23e}$$

and all energies are in units of the level width Γ_A. ϕ_i in (23b) differs from ϕ_i as defined earlier in the paper by a constant factor β/π^2 which is adsorbed into A_0. A_0 and A_1 are always positive while A_2 can be negative. If we assume that the expressions for the A_i are real constants then (12f) has the form

$$\epsilon_2(\omega) = A_0[\omega^{-2}(1 + \omega^{-2}\alpha^2)\phi_1 - 2\omega^{-3}\alpha\phi_2] . \tag{24}$$

$\phi_{1,2}$ are simply evaluated. Thus for $\omega_T > \omega_B > 0$.

$$\phi_{1,2} \equiv \alpha_{1,2} = \pm \arctan(\omega - E_A) + \arctan(\omega + E_A) + (-1 \pm 1)\arctan(E_A), \quad 0 < \omega < \omega_B \tag{25a}$$

$$= -\arctan(E_A) \pm \arctan(\omega - E_A) + \arctan(\omega_B + E_A) \pm \arctan(\omega - E_A - \omega_B), \quad \omega_B < \omega < \omega_T \tag{25b}$$

$$\equiv \beta_{1,2} = \mp \arctan(\omega - E_A - \omega_B) - \arctan(\omega + E_A - \omega_T) \pm \arctan(\omega_T - E_A) + \arctan(E_A + \omega_B) , \quad \omega_T < \omega \tag{25c}$$

and for $\omega_B > \omega_T > 0$,

$$\phi_{1,2} = \alpha_{1,2}, \quad 0 < \omega < \omega_T \tag{26a}$$

$$= -\arctan(\omega + E_A - \omega_T) + \arctan(\omega + E_A) \pm \arctan(E_A) \pm \arctan(\omega_T - E_A), \quad \omega_T < \omega < \omega_B \tag{26b}$$

$$= \beta_{1,2}, \quad \omega_B < \omega . \tag{26c}$$

When $\omega_T, \omega_B \to \infty$, the term in Eq. (23a) proportional to ϕ_1 agrees with the expression for ϵ_2 derived by Kjollerstrom[8] and Caroli.[7] The term in Eq. (23a) proportional to ϕ_2 was overlooked by those authors.

B. Calculation of $\epsilon_1(\omega)$ assuming momentum conservation as well as conditions (i)–(iii)

In the limit $\omega_T, \omega_B \to \infty$ the real part of the dielectric function follows immediately from (23a) and (25a):

$$\epsilon_1^{(\mathrm{con})}(\omega) = \omega^{-2}(A_0 + \omega^{-2}A_2) L_1 + \omega^{-3}A_1 L_2 \tag{27a}$$

or for the case of real matrix elements

$$\epsilon_1^{(\mathrm{con})}(\omega) = A_0[\omega^{-2}(1 + \omega^{-2}\alpha^2) L_1 - 2\alpha\omega^{-3}L_2] , \tag{27b}$$

where

$$L_1 = -\tfrac{1}{2} \ln\left(\frac{[(\omega - E_a)^2 + 1][(\omega + E_a)^2 + 1]}{(E_A^2 + 1)^2}\right), \tag{27c}$$

$$L_2 = \tfrac{1}{2} \ln\left(\frac{(\omega - E_a)^2 + 1}{(\omega + E_a)^2 + 1}\right). \tag{27d}$$

The term in (27a) proportional to L_1 agrees with the expression for ϵ_1 given by Kjollerstrom, the term in L_2 was overlooked.

For finite ω_T, ω_B, ϵ_1 must be obtained by the Kramers-Kronig integral of (12). As discussed in Sec. II, ϵ_1 cannot be obtained from (12f) by numerical integration of the Kramers-Kronig equation because of the singular nature of some of the terms in (12f). Consequently, it is necessary to use Eq. (12a) for ϵ_2, from which ϵ_1 can be calculated numerically, or alternatively Eq. (22). Equation (12a) contains the terms ϕ_3, ϕ_4 in addition to ϕ_1, ϕ_2 which appear in (12f). From (12d) and (12e)

$$\phi_{3,4} = \int_{l_1}^{l_2} [\Lambda^R(\omega' - \omega) \pm \Lambda^R(\omega')] d\omega' \tag{28a}$$

and

$$\Lambda^R(\omega) = \frac{\omega - E_A}{(\omega - E_A)^2 + 1} . \tag{28b}$$

Thus for $\omega_T > \omega_B > 0$,

$$\phi_3 = L_2, \quad 0 < \omega < \omega_B \tag{29a}$$

$$= \tfrac{1}{2} \ln\left(\frac{(E_A^2 + 1)[(\omega - E_A)^2 + 1]}{[(E_A + \omega_B)^2 + 1][(\omega - E_A - \omega_B)^2 + 1]}\right), \quad \omega_B < \omega < \omega_T \tag{29b}$$

$$\equiv R = \tfrac{1}{2} \ln\left(\frac{[(\omega + E_A - \omega_T)^2 + 1][(\omega_T - E_A)^2 + 1]}{[(E_A + \omega_B)^2 + 1][(\omega - E_A - \omega_B)^2 + 1]}\right), \quad \omega_T < \omega \tag{29c}$$

and for $\omega_B > \omega_T > 0$,

$$\phi_3 = L_2 , \quad 0 < \omega < \omega_T \tag{30a}$$

$$= \tfrac{1}{2} \ln\left(\frac{[(\omega + E_A - \omega_T)^2 + 1][(\omega_T - E_A)^2 + 1]}{[(\omega + E_A)^2 + 1](E_A^2 + 1)}\right),$$

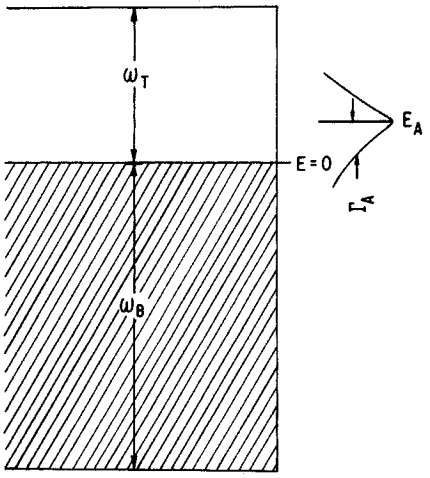

FIG. 1. Schematic energy diagram used in obtaining the results of Sec. III.

$$\omega_T < \omega < \omega_B \tag{30b}$$

$$= R, \quad \omega_B < \omega . \tag{30c}$$

Thus for $\omega_T > \omega_B > 0$,

$$\phi_4 = L_1, \quad 0 < \omega < \omega_B \tag{31a}$$

$$= \tfrac{1}{2} \ln\left(\frac{[(\omega - \omega_B - E_A)^2 + 1](E_A^2 + 1)}{[(\omega - E_A)^2 + 1][(\omega_B + E_A)^2 + 1]}\right),$$

$$\omega_B < \omega < \omega_T \tag{31b}$$

$$\equiv T = \tfrac{1}{2} \ln\left(\frac{[(\omega - \omega_T + E_A)^2 + 1][(\omega - \omega_B - E_A)^2 + 1]}{[(\omega_B + E_A)^2 + 1][(\omega_T - E_A)^2 + 1]}\right),$$

$$\omega_T < \omega \tag{31c}$$

and for $\omega_B > \omega_T > 0$,

$$\phi_4 = L_1, \quad 0 < \omega < \omega_T \tag{32a}$$

$$= \tfrac{1}{2} \ln\left(\frac{[(\omega - \omega_T + E_A)^2 + 1](E_A^2 + 1)}{[(\omega + E_A)^2 + 1][(\omega_T - E_A)^2 + 1]}\right),$$

$$\omega_T < \omega < \omega_B \tag{32b}$$

$$= T, \quad \omega_B < \omega . \tag{32c}$$

From Eqs. (28)–(32) we can obtain $\epsilon_2^{(1)}$ as given by Eq. (12a) and $\epsilon_1^{(1)}$ can then be found by a numerical integration of the Kramers-Kronig equation.

The interband k-conserving terms corresponding to Eq. (13) cannot be characterized by a quantity as simple as a density of states. These terms are very sensitive to $\epsilon_n(k)$ and $\epsilon_\pi(k)$. Consequently, we do not attempt to calculate them since any results would clearly be very dependent on the model band structure assumed.

C. Calculation of the dielectric function in the absence of momentum conservation again assuming conditions (i)–(ii)

From Eqs. (11) and (14) we find

$$\epsilon_2^{(\text{noncons})} = \frac{C_0 \phi_1}{\omega^2} + \frac{D_0 \phi_3}{\omega^2} , \tag{33}$$

where C_0 and D_0 may be either positive or negative. The contribution of the first term to the real part of the dielectric function is given by $C_0 L_1/\omega^2$ in the limit $\omega_T, \omega_B \to \infty$. In this limit the analytical properties of $\epsilon(\omega)$ permit us to write down the Kramers-Kronig transform of Eq. (33) using

$$P = -\alpha_2 = \arctan(\omega - E_a) - \arctan(\omega + E_a) + 2\arctan(E_a) \tag{34}$$

as

$$\epsilon_1^{(\text{noncons})} = \frac{C_0 L_1}{\omega^2} + \frac{D_0 P}{\omega^2} , \tag{35}$$

where L_1 is given by (27c).

Recall that the Kramers-Kronig transform of $\omega^{-n} \phi_{1,2}$ is given by $\omega^{-n} L_{1,2}$ in the limit $\omega_T, \omega_B \to \infty$. In what follows we will define $L_{1,2}(\omega_T, \omega_B)$ to be such that the actual Kramers-Kronig transform of $\omega^{-n} \phi_{1,2}$ is $\omega^{-n} L_{1,2}(\omega_T, \omega_B)$ for finite ω_T, ω_B.

D. Calculation of the reflectivity

As discussed above, we use the McIntyre expression to relate the fractional change in reflectance to the dielectric properties of the substrate and adsorbate layer. Then

$$\frac{\Delta R}{R}(\omega) = -\frac{4d\omega}{c}\left(\frac{\epsilon_2^b \epsilon_1^{(1)} - (\epsilon_1^b - 1)\epsilon_2^{(1)}}{(\epsilon_1^b - 1)^2 + (\epsilon_2^b)^2}\right) , \tag{36}$$

where $\epsilon_{1,2}^b$ refer to the real and imaginary parts of the substrate dielectric function, $\epsilon_{1,2}^{(1)}$ refer to the analogous effective-adsorbate-layer-dielectric-function parts calculated above, d is the effective thickness of the adsorbate, and c is the speed of light.

If we ignore the frequency dependence of ϵ^b, then

$$\frac{\Delta R}{R}(\omega) = -\alpha' \omega \epsilon_1^{(1)} + \beta' \omega \epsilon_2^{(1)} . \tag{37}$$

Since ϵ_2^b is in general positive, α' is a positive constant while β' can be of either sign. A full treatment would use the known frequency dependence of ϵ^b, as Rubloff *et al.* did in their Lorentzian fit to reflectance data. Some frequency dependence of ϵ^b can be conveniently included by noting that, in many metals at low frequencies, $\epsilon_2^b \gg \epsilon_1^b - 1$ and $\epsilon_2^b \propto 1/\omega$. Hence in such cases $\beta' \ll \alpha'$ and

$$\frac{\Delta R}{R}(\omega) = -\delta \omega^2 \epsilon_1^{(1)} , \tag{38}$$

where δ is a positive constant.

From the various expressions for $\epsilon_1^{(1)}$ and $\epsilon_2^{(1)}$ it is clear that, for the intraband k-conserving case case, the coefficients of the terms involving L_1 and ϕ_1 are positive. Hence structure in those terms is directly reflected in the dielectric function. In the interband case the coefficients of the various terms in the dielectric-function expression can be of either sign and hence their structure may or may not be inverted in the dielectric function.

From the $\Delta R/R$ equations, the sign of the $\epsilon_1^{(1)}$ structure is inverted when used in the reflectivity expressions. Thus, for the intraband k-conserving case, structure in L_1 is always inverted in $\Delta R/R$. The ϵ_2 contributions may or may not be inverted depending on the frequency regime involved.

Note also that the ϕ_1 and L_1 contributions are even under the interchange $E_A, \omega_B, \omega_T \to -E_A, \omega_T, \omega_B$ while the ϕ_2, L_2, ϕ_3, and P contributions are odd under that interchange.

In the case of the real-constant-matrix-element approximation, intraband transitions, and k con-

servation the real and imaginary parts of the dielectric function, $\epsilon_1^{(1)}$ and $\epsilon_2^{(1)}$, are given by Eqs. (27b) and (24), respectively. From Eqs. (37) and (38) it is seen that $\Delta R/R$ is determined by $\omega\epsilon_2^{(1)}$, $\omega\epsilon_1^{(1)}$, and $\omega^2\epsilon_1^{(1)}$. For various positive values of α, the quantities $\omega\epsilon_2$, $\omega\epsilon_1$, and $\omega^2\epsilon_1$ are shown in Figs. 2, 3, and 4 for $E_A=-3$. Analogous results are shown in Figs. 5–7 for $E_A=-1$. For $E_A=-3$, structure appears at $\omega\sim|E_A|$ for $\alpha\lesssim 2$. The structure persists at even higher values of α for $E_A=+3$. Little, if any, characteristic structure appears in the $E_A=-1$ curves.

In summary, for infinite bandwidths, the lowest-order contribution in ω^{-1} to $\Delta R/R$ exhibits structure at $\omega\sim|E_A|>1$. When higher-order contributions are present, they have in general structure only for larger values of $|E_A|$. It is however, these higher-order contributions which were found to be most important in alloy experiments. Structure in $\epsilon_2^{(1)}$ appears in general only for $|E_A|\gtrsim 3$, and the $\epsilon_2^{(1)}$ are not Lorentzian. This should be contrasted with the use by Rubloff *et al.* of a Lorentzian approximation in fitting their experimental data.

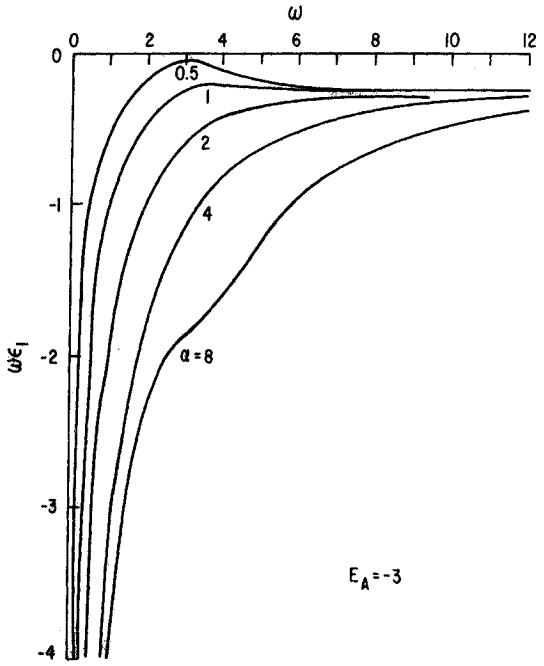

FIG. 3. $\omega\epsilon_1$ [$\omega\times$Eq. (27b)] in the real-constant-matrix-element approximation for $E_A=-3$.

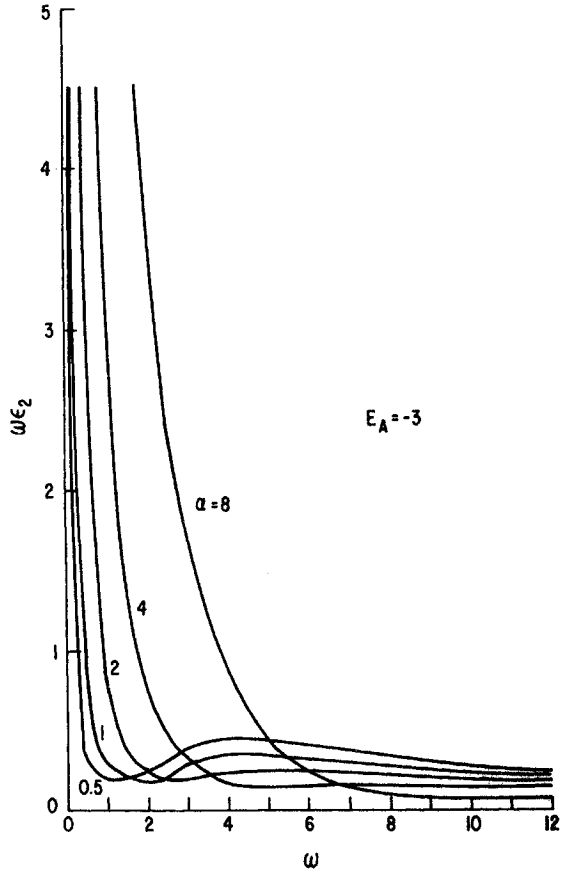

FIG. 2. $\omega\epsilon_2$ [$\omega\times$Eq. (24)] in the real-constant-matrix-element approximation for $E_A=-3$.

In general the unoccupied bandwidth must be taken as finite. For finite ω_T, structure in $\Delta R/R$ is reduced in magnitude but remains, while additional structure is often introduced at values of ω given very approximately by ω_T+E_A. Such struc-

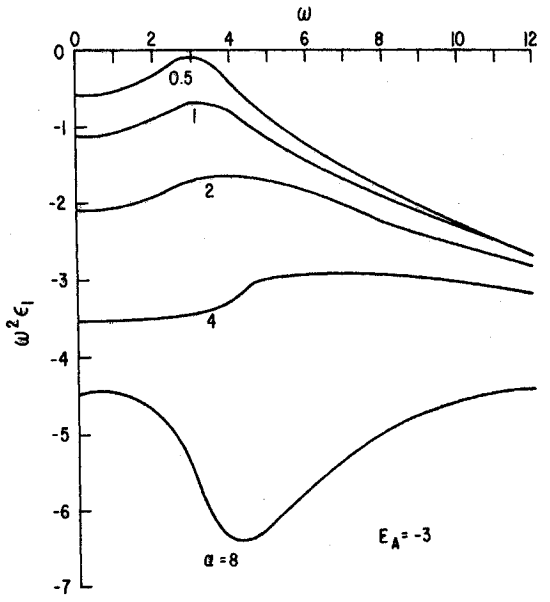

FIG. 4. $\omega^2\epsilon_1$ [$\omega^2\times$Eq. (27b)] in the real-constant-matrix-element approximation for $E_A=-3$.

ture often appears even when no structure was present in the infinite-bandwidth case.

APPENDIX A

We show here that use of Eq. (5) in Eq. (4) yields Eq. (8). We note that if

$$\Delta V = H - H_0 \tag{A1a}$$

then

$$\begin{aligned}\langle k|(E\pm i0^+)\Delta V|a\rangle &= \langle k|g(E\pm i0^+)(E-H_0)|a\rangle - \langle k|g(E\pm i0^+)v|a\rangle \\ &= [1\mp i\lambda g_k(E\pm i0^+)]\langle k|a\rangle - g_k(E\pm i0^+)\,v_{ka} \\ &\simeq \langle k|a\rangle - g_k(E\pm i0^+)v_{ka}\,. \end{aligned} \tag{A1b}$$

Equation (5) can thus be written as

$$\mathcal{G}_{kk'}(E\pm i0^+) = g_k(E\pm i0^+)\delta_{kk'} + [\Delta\mathcal{G}(E\pm i0^+)]_{kk'}\,, \tag{A2a}$$

where

$$[\Delta\mathcal{G}(E\pm i0^+)]_{kk'} = \langle k|g(E\pm i0^+)\Delta V|a\rangle \times\Lambda^{-1}(E\pm i0^+)\langle a|\Delta V g(E\pm i0^+)|k'\rangle. \tag{A2b}$$

From (A2) and (3c) we have

$$\mathcal{G}^I_{kk'}(\omega) = g^I_k(\omega)\delta_{kk'} + \Delta\mathcal{G}^I_{kk'}(\omega'), \tag{A3a}$$

where

$$g^I(\omega) = (1/2i)[\,g(\omega - i0^+) - g(\omega + i0^+)\,], \tag{A3b}$$

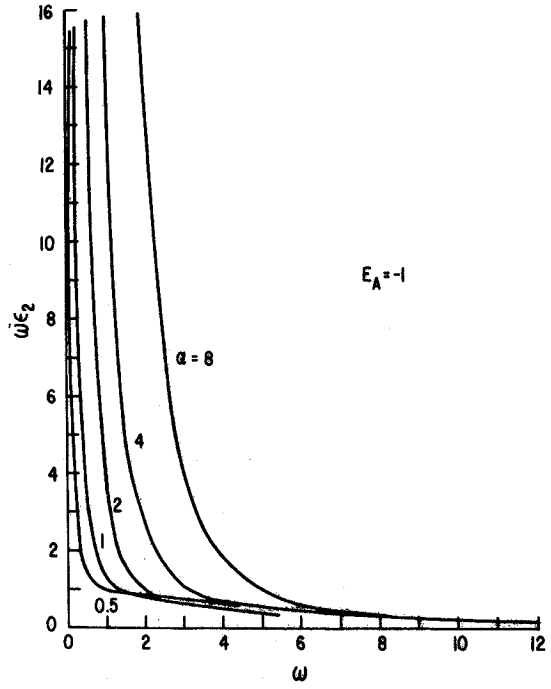

FIG. 5. $\omega\epsilon_2$ [$\omega\times$Eq. (24)] in the real-constant-matrix-element approximation for $E_A=-1$.

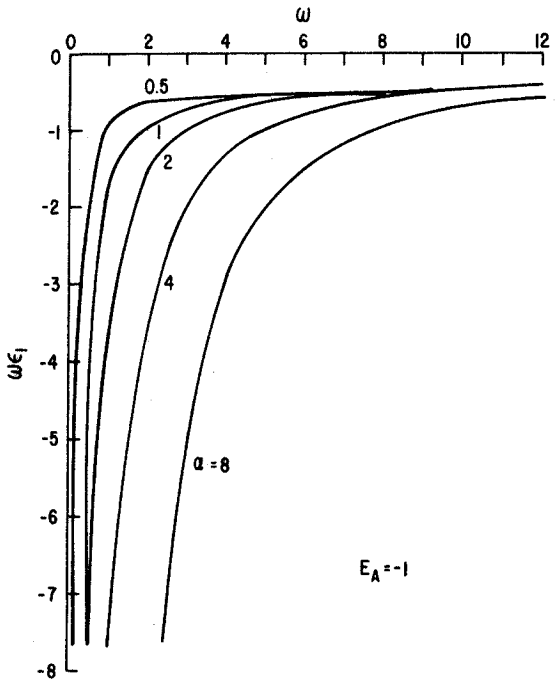

FIG. 6. $\omega\epsilon_1$ [$\omega\times$Eq. (27b)] in the real-constant-matrix-element approximation for $E_A=-1$.

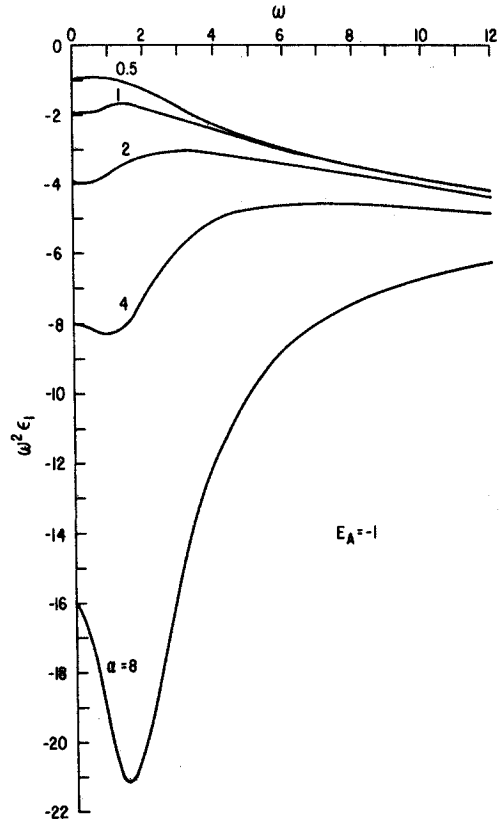

FIG. 7. $\omega^2\epsilon_1$ [$\omega^2\times$Eq. (27b)] in the real-constant-matrix-element approximation for $E_A=-1$.

$$\Delta \mathcal{G}^I(\omega) = [g(\omega)\Delta V \Lambda_{0P}^{-1}(\omega)\Delta V g(\omega)]^I + (1/2i)\,[g(\omega - i0^+)\Delta V \Lambda_{0P}^{-1}(\omega - i0^+) \times \Delta V g(\omega - i0^+) - g(\omega + i0^+)\Delta V \Lambda_{0P}^{-1}(\omega + i0^+) \times \Delta V g(\omega + i0^+)]\,, \tag{A3c}$$

$$\Lambda_{0P}^{-1}(\omega \pm i0^+) = |a\rangle\left(\omega - \epsilon_a - \sum_k \nu_{ak}(\omega)\, g_k(\omega \pm i0^+)\nu_{ka}(\omega)\right)^{-1}\langle a| \tag{A3d}$$

and from (6a)

$$g(\omega \pm i0^+) = (\omega - H_0 \pm i\lambda)^{-1}\,. \tag{A3e}$$

Use of (A3a) in (4) yields

$$\gamma(\omega) = \gamma_0(\omega) + F(\omega)\sum_{kk'k''} \tau_{kk'} g^I_{k'}(\omega)\tau_{k'k''}\Delta \mathcal{G}^I_{k''k}(\omega - \omega_0) + F(\omega)\sum_{kk'k''} \tau_{kk'} g^I_{k'}(\omega - \omega_0)\tau_{k'k''}\Delta \mathcal{G}^I_{k''k}(\omega) + F(\omega)\sum_{kk'k''k'''} \tau_{kk'}\Delta \mathcal{G}^I_{k'k''}(\omega)\tau_{k''k'''} \times \Delta \mathcal{G}_{k'''k}(\omega - \omega_0)\,, \tag{A4a}$$

where $\tau_{kk'} = \langle k|\tau|k'\rangle$ and

$$\gamma_0(\omega) = F(\omega)\sum_k \tau_{kk'} g^I_{k'}(\omega)\tau_{k'k} g^I_k(\omega - \omega_0) \tag{A4b}$$

is the value $\gamma(\omega)$ takes in the absence of adsorbates.

Use of (A3c) in (A4) and neglect of the last term on the right-hand side of (A4a) yields Eq. (8).

APPENDIX B

In this appendix we derive Eqs. (12) and (13). Use of Bloch states $\{|\vec{k},n\rangle\}$ for the metal states $\{|\vec{k}\rangle\}$ in Eqs. (12)–(14) gives

$$u_{kn}(\omega) = \sum_{k'n'} \tau_{kn,k'n'}(\omega - \epsilon_{k'n'})^{-1}_{\lambda}(\Delta V)_{k'n',a} = \tau_{kn,a} - \sum_{k'\bar{n}'} \tau_{kn,k'n'}(\omega - \epsilon_{k'n'})^{-1}_{\lambda}\nu_{k'n',a}\,, \tag{B1a}$$

$$v_{kn}(\omega) = \pi \sum_{k'n'} \tau_{kn,k'n'}\,\delta_{\lambda}(\omega - \epsilon_{k'n'})(\Delta V)_{k'n',a} \simeq -\pi \sum_{k'n'} \tau_{kn,k'n'}\,\delta_{\lambda}(\omega - \epsilon_{k'n'})\,\nu_{k'n',a}\,, \tag{B1b}$$

where

$$(\omega - \epsilon_{kn})^{-1}_{\lambda} = (\omega - \epsilon_{kn})/[(\omega - \epsilon_{kn})^2 + \lambda^2]\,, \tag{B1c}$$

$$\delta_{\lambda}(\omega - \epsilon_{kn}) = \pi^{-1}\lambda/[(\omega - \epsilon_{kn})^2 + \lambda^2]\,. \tag{B1d}$$

It is clear that as $\lambda \to 0^+$, $(\omega - \epsilon_{kn})^{-1}_{\lambda} \to P(\omega - \epsilon_{kn})^{-1}$, where P denotes the principal part and $\delta_{\lambda}(\omega - \epsilon_{kn}) \to \delta(\omega - \epsilon_{kn})$. Equation (8a) can now be written in the form

$$\gamma(\omega) = \gamma_0(\omega) + \pi F(\omega)\,\mathrm{Im}\Big(\sum_{kn} \delta_{\lambda}(\omega - \epsilon_{kn}) \times [\,|u_{kn}(\omega - \omega_0)|^2 - |v_{kn}(\omega - \omega_0)|^2 + 2i\,\mathrm{Re}u_{kn}(\omega - \omega_0)\,v^*_{kn}(\omega - \omega_0)]\,[\Lambda^R(\omega - \omega_0) + i\Lambda^I(\omega - \omega_0)]\Big) + \pi F(\omega)\,\mathrm{Im}\Big(\sum_{kn} \delta_{\lambda}(\omega - \omega_0 - \epsilon_{kn}) \times [\,|u_{kn}(\omega)|^2 - |v_{kn}(\omega)|^2 + 2i\,\mathrm{Re}u_{kn}(\omega)\,v^*_{kn}(\omega)]\,[\Lambda^R(\omega) + i\Lambda^I(\omega)]\Big)\,. \tag{B2}$$

From Eq. (16) we have

$$|u_{kn}(\omega)|^2 - |v_{kn}(\omega)|^2 + 2i\,\mathrm{Re}u_{kn}(\omega)\,v^*_{kn}(\omega) = |\tau_{kn,a}|^2 - \sum_{n'} (\omega - \epsilon_{kn'} - i\lambda)^{-1} 2\,\mathrm{Re}(\tau_{a,kn}\tau_{kn,kn'}\nu_{kn',a}) + \sum_{n'n''} \nu_{a,kn'}\tau_{kn',kn}\tau_{kn,kn''}\nu_{kn'',a}(\omega - \epsilon_{kn'} - i\lambda)^{-1} \times (\omega - \epsilon_{kn''} - i\lambda)^{-1}\,, \tag{B3}$$

where we have used the fact that $\tau_{kn,kn'} = \Delta_{k,k'}\tau_{kn,kn'}$. An identical result analogous to (B3) holds for $|u_{kn}(\omega - \omega_0)|^2 - |v_{kn}(\omega - \omega_0)|^2 + 2i\,\mathrm{Re}u_{kn}(\omega - \omega_0) \times v^*_{kn}(\omega - \omega_0)$ when ω in (B3) is replaced by $\omega - \omega_0$.

For simplicity we will assume that at most two metal bands are of importance, n and $\bar{n}$. In this case (B3) becomes

$$|u_{kn}(\omega)|^2 - |v_{kn}(\omega)|^2 + 2i\,\mathrm{Re}u_{kn}(\omega)\,v^*_{kn}(\omega) = |\tau_{kn,a}|^2 - (\omega - \epsilon_{kn} - i\lambda)^{-1} 2\,\mathrm{Re}(\tau_{a,kn}\tau_{kn,kn}\nu_{kn,a}) + (\omega - \epsilon_{kn} - i\lambda)^{-2}\,|\tau_{kn,kn}|^2\,|\nu_{kn,a}|^2 - (\omega - \epsilon_{k\bar{n}} - i\lambda)^{-1} 2\,\mathrm{Re}(\tau_{a,kn}\tau_{kn,k\bar{n}}\nu_{k\bar{n},a}) + (\omega - \epsilon_{k\bar{n}} - i\lambda)^{-2}\,|\tau_{kn,k\bar{n}}|^2\,|\nu_{k\bar{n},a}|^2 + (\omega - \epsilon_{kn} - i\lambda)^{-1}(\omega - \epsilon_{k\bar{n}} - i\lambda)^{-1} \times 2\,\mathrm{Re}(\nu_{a,k\bar{n}}\tau_{k\bar{n},kn}\tau_{kn,kn}\nu_{kn,a})\,, \tag{B4}$$

and a similar expression is valid if in (B4) we replace ω by $\omega - \omega_0$.

In order to evaluate $\gamma(\omega)$ from (B2) we require

$$\sum_{kn} \delta_{\lambda}(\omega - \omega_0 - \epsilon_{kn})[\,|u_{kn}(\omega)|^2 - |v_{kn}(\omega)|^2 + 2i\,\mathrm{Re}u_{kn}(\omega)\,v^*_{kn}(\omega)]$$

of Eq. (B4) as well as the analogous result with $\omega - \omega_0 \to \omega$.

1. Intraband terms

We will first evaluate these quantities for the intraband terms; those terms on the right-hand side of (B4) which involve only kn. We set

$$I_1=\sum_{kn}\delta_\lambda(\omega-\omega_0-\epsilon_{kn})[\,|\tau_{kn,a}|^2-(\omega-\epsilon_{kn}-i\lambda)^{-1}2\,\mathrm{Re}(\tau_{a,kn}\tau_{kn,kn}\nu_{kn,a})+(\omega-\epsilon_{kn}-i\lambda)^{-2}|\tau_{kn,kn}|^2|\nu_{kn,a}|^2] \tag{B5a}$$

and

$$I_2=\sum_{kn}\delta_\lambda(\omega-\epsilon_{kn})[\,|\tau_{kn,a}|^2-(\omega-\omega_0-\epsilon_{kn}-i\lambda)^{-1}2\,\mathrm{Re}(\tau_{a,kn}\tau_{kn,kn}\nu_{kn,a})+(\omega-\omega_0-\epsilon_{kn}-i\lambda)^{-2}|\tau_{kn,kn}|^2|\nu_{kn,a}|^2]\,. \tag{B5b}$$

In evaluating I_1 and I_2 we note that only those terms in the summation $\sum_{kn}$ with $\epsilon_{kn}\simeq\omega-\omega_0$ or $\epsilon_{kn}\simeq\omega$ are large since $\delta_\lambda(\omega-\omega_0-\epsilon_{kn})$ and $\delta_\lambda(\omega-\epsilon_{kn})$ are Lorentzians of width λ. Noting that

$$\sum_{kn}\equiv\frac{V}{(2\pi)^3}\sum_n\int dS_{k,n}\,d\epsilon_{k,n}\,|\nabla_k\epsilon_{kn}|^{-1}$$

we have

$$\begin{aligned}I_1\simeq{}&\frac{V}{(2\pi)^3}\sum_n\int_{\epsilon_{kn}=\omega-\omega_0}dS_{kn}\,|\nabla_k\epsilon_{kn}|^{-1}|\langle kn|\tau|a\rangle|^2\int d\epsilon_{kn}\,\pi^{-1}\lambda[(\omega-\omega_0-\epsilon_{kn})^2+\lambda^2]^{-1}\\
&-\frac{V}{(2\pi)^3}\sum_n\int_{\epsilon_{kn}=\omega-\omega_0}dS_{kn}\,|\nabla_k\epsilon_{kn}|^{-1}2\,\mathrm{Re}(\tau_{a,kn}\tau_{kn,kn}\nu_{kn,a})\int d\epsilon_{kn}\,\pi^{-1}\lambda[(\omega-\omega_0-\epsilon_{kn})^2+\lambda^2]^{-1}(\omega-\epsilon_{kn}-i\lambda)^{-1}\\
&+\frac{V}{(2\pi)^3}\sum_n\int_{\epsilon_{kn}=\omega-\omega_0}dS_{kn}\,|\nabla_k\epsilon_{kn}|^{-1}|\tau_{kn,kn}|^2|\nu_{kn,a}|^2\int d\epsilon_{kn}\,\pi^{-1}\lambda[(\omega-\omega_0-\epsilon_{kn})^2+\lambda^2]^{-1}(\omega-\epsilon_{kn}-i\lambda)^{-2}\\
\simeq{}&\rho(\omega-\omega_0)\sum_n[\langle(\tau_{kn,a})_{\omega-\omega_0}\rangle_{\mathrm{av}}-\langle 2\,\mathrm{Re}(\tau_{a,kn}\tau_{kn,kn}\nu_{kn,a})_{\omega-\omega_0}\rangle_{\mathrm{av}}(\omega_0-2i\lambda)^{-1}\\
&+\langle(|\tau_{kn,kn}|^2|\nu_{kn,a}|^2)_{\omega-\omega_0}\rangle_{\mathrm{av}}(\omega_0-2i\lambda)^2]\,,\end{aligned} \tag{B6a}$$

where

$$\langle[g(kn)]_{\omega-\omega_0}\rangle_{\mathrm{av}}=\frac{\int_{\epsilon_{kn}=\omega-\omega_0}dS_{kn}\,|\nabla_k\epsilon_{kn}|^{-1}g(kn)}{\int_{\epsilon_{kn}=\omega-\omega_0}dS_{kn}\,|\nabla_k\epsilon_{kn}|^{-1}}\,. \tag{B6b}$$

Similarly,

$$\begin{aligned}I_2\simeq{}&\rho(\omega)\sum_n[\langle(|\tau_{kn,a}|^2)_\omega\rangle_{\mathrm{av}}+\langle 2\mathrm{Re}(\tau_{a,kn}\tau_{kn,kn}\nu_{kn,a})_\omega\rangle_{\mathrm{av}}\\
&\times(\omega_0+2i\lambda)^{-1}+\langle(|\tau_{kn,kn}|^2|\nu_{kn,a}|^2)_\omega\rangle_{\mathrm{av}}(\omega_0+2i\lambda)^{-2}]\,.\end{aligned} \tag{B7}$$

Thus the contribution to $\epsilon_2(\omega)$ from intraband terms is given by

$$\begin{aligned}\epsilon_2(\omega_0)=\epsilon_2^{(0)}(\omega_0)+{}&\beta(\pi\omega_0)^{-2}\,\mathrm{Im}\Big(\int_0^{\omega_0}\rho(\omega)\Lambda^{-1}(\omega-\omega_0)\\
&\times\sum_n[\langle(|\tau_{kn,a}|^2)_\omega\rangle_{\mathrm{av}}\\
&+(\omega_0+2i\lambda)^{-1}\langle 2\,\mathrm{Re}(\tau_{kn,kn}\nu_{kn,a}\tau_{a,kn})_\omega\rangle_{\mathrm{av}}\\
&+(\omega_0+2i\lambda)^{-2}\langle(|\tau_{kn,kn}|^2|\nu_{kn,a}|^2)_\omega\rangle_{\mathrm{av}}]\Big)\\
&+\beta(\pi\omega)^{-2}\,\mathrm{Im}\Big(\int_0^{\omega_0}\rho(\omega-\omega_0)\Lambda^{-1}(\omega)\\
&\times\sum_n[\langle(|\tau_{kn,a}|^2)_{\omega-\omega_0}\rangle_{\mathrm{av}}\\
&-(\omega_0-2i\lambda)^{-1}\langle 2\,\mathrm{Re}(\tau_{kn,kn}\nu_{kn,a}\tau_{a,kn})_{\omega-\omega_0}\rangle_{\mathrm{av}}\\
&+(\omega_0-2i\lambda)^{-2}\langle(|\tau_{kn,kn}|^2|\nu_{kn,a}|^2)_{\omega-\omega_0}\rangle_{\mathrm{av}}]\Big)\,,\end{aligned} \tag{B8a}$$

where $\epsilon_2^{(0)}$ (ω_0) is the dielectric function in the absence of the adsorbate,

$$\Lambda^{-1}(\omega)=\Lambda^R(\omega)+i\Lambda^I(\omega)\,, \tag{B8b}$$

and $\langle\,\rangle_{\mathrm{av}}$ is defined in (B6b).

If we regard the matrix elements in (B8a) as being independent of ω then we obtain Eq. (12).

2. Interband terms

We next evaluate the contribution to $\epsilon_2(\omega_0)$ from the interband terms in (B4), those that involve kn and $k\bar{n}$. We define

$$\begin{aligned}I_3=\sum_{kn}\delta_\lambda(\omega-\omega_0-\epsilon_{kn})[&-(\omega-\epsilon_{k\bar{n}}-i\lambda)^{-1}\\
&\times 2\,\mathrm{Re}(\tau_{a,kn}\tau_{kn,k\bar{n}}\nu_{k\bar{n},a})\\
&+(\omega-\epsilon_{k\bar{n}}-i\lambda)^{-2}|\tau_{kn,k\bar{n}}|^2|\nu_{k\bar{n},a}|^2\end{aligned}$$

$$+(\omega-\epsilon_{kn}-i\lambda)^{-1}(\omega-\epsilon_{k\bar{n}}-i\lambda)^{-1}$$
$$\times 2\,\mathrm{Re}(\nu_{a,k\bar{n}}\tau_{k\bar{n},kn}\tau_{kn,kn}\nu_{kn,a})] \quad \text{(B9a)}$$

and

$$I_4=\sum_{kn}\delta_\lambda(\omega-\epsilon_{kn})[-(\omega-\omega_0-\epsilon_{k\bar{n}}-i\lambda)^{-1}$$
$$\times 2\,\mathrm{Re}(\tau_{a,k\bar{n}}\tau_{k\bar{n},kn}\nu_{k\bar{n},a})$$
$$+(\omega-\omega_0-\epsilon_{k\bar{n}}-i\lambda)^{-2}|\tau_{kn,k\bar{n}}|^2|\nu_{k\bar{n},a}|^2$$
$$+(\omega-\omega_0-\epsilon_{kn}-i\lambda)^{-1}(\omega-\omega_0-\epsilon_{k\bar{n}}-i\lambda)^{-1}$$
$$\times 2\,\mathrm{Re}(\nu_{a,k\bar{n}}\tau_{k\bar{n},kn}\tau_{kn,kn}\nu_{kn,a})] \,. \quad \text{(B9b)}$$

In treating this expression we will assume that all the matrix elements are constants; $\tau_{a,kn}\to\bar{\tau}_{a,kn}$ = const. Furthermore in the first two terms on the right-hand side of (B9a) and (B9b) we replace λ with 0^+; this cannot be done in the third term as the substitution would lead to a denominator proportional to ω. This produces difficulties when we use the Kramers-Kronig transform to obtain ϵ_1 from ϵ_2. The third term on the right-hand side of (B9a) becomes

$$I_3^{(3)}=2\sum_n \mathrm{Re}[\nu_{a,k\bar{n}}\tau_{k\bar{n},kn}\tau_{kn,kn}\nu_{kn,a}]_0$$
$$\times\int d\epsilon_{kn}dS_{kn}\,|\nabla_k\epsilon_{kn}|^{-1}\frac{\lambda}{(\omega-\omega_0-\epsilon_{kn})^2+\lambda^2}$$
$$\times(\omega-\epsilon_{kn}-i\lambda)^{-1}(\omega-\epsilon_{k\bar{n}}-i\lambda)^{-1}$$
$$\simeq 2\sum_n \mathrm{Re}[\nu_{a,k\bar{n}}\tau_{k\bar{n},kn}\tau_{kn,kn}\nu_{kn,a}]_0$$
$$\times\int d\epsilon_{kn}\frac{\lambda}{(\omega-\omega_0-\epsilon_{kn})^2+\lambda^2}(\omega-\epsilon_{kn}-i\lambda)^{-1}$$
$$\times\int\frac{dS_{kn}|\nabla_k\epsilon_{kn}|^{-1}}{\omega-\epsilon_{k\bar{n}}-i\lambda} \,. \quad \text{(B10)}$$

We now assume the integral $\int dS_{kn}$ may be replaced by $\int_{\epsilon_{nk}=\omega-\omega_0}dS_{kn}$ to obtain

$$I_3^{(3)}\simeq\sum_n 2\,\mathrm{Re}[\nu_{a,k\bar{n}}\tau_{k\bar{n},kn}\tau_{kn,kn}\nu_{kn,a}]_0$$
$$\times(\omega_0-2i\lambda)^{-1}\sum_k\delta(\omega-\omega_0-\epsilon_{kn})(\omega-\epsilon_{k\bar{n}}-i0^+)^{-1} \,. \quad \text{(B11)}$$

Similarly the third term on the right-hand side is

$$I_4^{(3)}=\sum_{kn}\delta_\lambda(\omega-\epsilon_{kn})(\omega-\omega_0-\epsilon_{kn}-i\lambda)^{-1}(\omega-\omega_0-\epsilon_{k\bar{n}}-i\lambda)$$
$$\times 2\,\mathrm{Re}(\nu_{a,k\bar{n}}\tau_{k\bar{n},kn}\tau_{kn,kn}\nu_{kn,a})$$
$$\simeq-\sum_n 2\,\mathrm{Re}[\nu_{a,k\bar{n}}\tau_{k\bar{n},kn}\tau_{kn,kn}\nu_{kn,a}]_0(\omega_0+2i\lambda)^{-1}$$
$$\times\sum_k\delta(\omega-\epsilon_{kn})(\omega-\omega_0-\epsilon_{k\bar{n}}-i0^+)^{-1} \,. \quad \text{(B12)}$$

Consequently the contribution of the interband terms to $\epsilon_2(\omega_0)$ is from (B9), (B11), and (B12) given by Eq. (13).

APPENDIX C

We derive here the dielectric function associated with adsorbate to adsorbate electronic transitions when the adsorbate has two levels, Eq. (19). As discussed in the text the Green's function for the metal-adsorbate system when the adsorbate has two virtual levels is

$$G(\omega)=g(\omega)+g(\omega)\Delta V[\Lambda_a^{-1}(\omega)+\Lambda_b^{-1}(\omega)]\Delta Vg(\omega). \quad \text{(C1)}$$

From Eq. (4) we have that portion of $\gamma(\omega_0)$ associated with adsorbate-to-adsorbate transitions as

$$\gamma_{aa}(\omega)=F(\omega)\sum_{\substack{kk'k''k'''\\ i,j}}\tau_{kk'}\tau_{k''k'''}[g(\omega)\Delta V\Lambda_i^{-1}(\omega)\Delta Vg(\omega)]^I_{k'k''}$$
$$\times[g(\omega-\omega_0)\Delta V\Lambda_j^{-1}(\omega-\omega_0)\Delta Vg(\omega-\omega_0)]_{k'''k} \,, \quad \text{(C2a)}$$

where

$$[h(\omega)]^I\equiv(1/2i)[h(\omega-i0^+)-h(\omega+i0^+)] \quad \text{(C2b)}$$

and

$$(g\Delta V\Lambda_a^{-1}\Delta Vg)_{kk'}\equiv g_k\Delta V_{ka}\Lambda_a^{-1}\Delta V_{ak'}g_{k'} \,. \quad \text{(C2c)}$$

Assuming momentum conservation as in Eq. (19) and using (A2b) in (A2a) yields

$$\gamma_{aa}(\omega)=F(\omega)(1/2i)^2$$
$$\times\sum_{i,j;k,k'}\{[\tau g^-(\omega)\Delta V]_{k,i}\Lambda_i^-(\omega)[\Delta Vg^-(\omega)\tau]_{i,k'}$$
$$-[\tau g^+(\omega)\Delta V]_{k,i}\Lambda_i^+(\omega)[\Delta Vg^+(\omega)\tau]_{ik'}\}$$
$$\times\{[g^-(\omega-\omega_0)\Delta V]_{k'j}\Lambda_j^-(\omega-\omega_0)[\Delta Vg^-(\omega-\omega_0)]_{jk}$$
$$-[g^+(\omega-\omega_0)\Delta V]_{k'j}\Lambda_j^+(\omega-\omega_0)[\Delta Vg^+(\omega-\omega_0)]_{jk}\} \,, \quad \text{(C3a)}$$

where

$$h^\pm(\omega)=h(\omega\pm i0) \,. \quad \text{(C3b)}$$

Carrying out the summations over k, k' in (A3a) yields

$$\gamma_{aa}(\omega_0)=F(\omega)(-\tfrac{1}{2})$$
$$\times\Big(\sum_{i,j}\mathrm{Re}\{[\Delta Vg^+(\omega-\omega_0)\tau g^+(\omega)\Delta V]_{j,i}$$
$$\times[\Delta Vg^+(\omega)\tau g^+(\omega-\omega_0)\Delta V]_{i,j}\Lambda_i^+(\omega)\Lambda_j^+(\omega-\omega_0)\}$$
$$-\mathrm{Re}\{[\Delta Vg^+(\omega-\omega_0)\tau g^-(\omega)\Delta V]_{i,j}$$
$$\times[\Delta Vg^-(\omega)\tau g^+(\omega-\omega_0)\Delta V]_{j,i}\Lambda_j^+(\omega-\omega_0)\Lambda_i^-(\omega)\}\Big) \,. \quad \text{(C4)}$$

Noting

$$g^+(\omega)=g^R(\omega)+ig^I(\omega) \,, \quad \text{(C5)}$$

$$[\Delta V g^+(\omega-\omega_0)\tau g^+(\omega)\Delta V]_{j,i}[\Delta V g^+(\omega)\tau g^+(\omega-\omega_0)\Delta V]_{i,j} = |X|^2 - |Y|^2 + 2i\,\mathrm{Re}(XY^*)\ , \tag{C6a}$$

where

$$X=\{\Delta V[g^R(\omega-\omega_0)\tau g^R(\omega)-g^I(\omega-\omega_0)\tau g^I(\omega)]\Delta V\}_{j,i}\ , \tag{C6b}$$

$$Y=\{\Delta V[g^R(\omega-\omega_0)\tau g^I(\omega)+g^I(\omega-\omega_0)\tau g^R(\omega)]\Delta V\}_{j,i}\ . \tag{C6c}$$

Also

$$[\Delta V g^+(\omega-\omega_0)\tau g^-(\omega)\Delta V]_{j,i}[\Delta V g^-(\omega)\tau g^+(\omega-\omega_0)\Delta V]_{i,j} = |S|^2 - |T|^2 + 2i\,\mathrm{Re}(ST^*)\ , \tag{C7a}$$

where

$$S=\{\Delta V[g^R(\omega-\omega_0)\tau g^R(\omega)+g^I(\omega-\omega_0)\tau g^I(\omega)]\Delta V\}_{j,i}\ , \tag{C7b}$$

$$T=\{\Delta V[g^I(\omega-\omega_0)\tau g^R(\omega)-g^R(\omega-\omega_0)\tau g^I(\omega)]\Delta V\}_{j,i}\ . \tag{C7c}$$

APPENDIX D

In this appendix we derive Eq. (22) for $\epsilon_1^{(1)}(\omega)$, where $\epsilon_1^{(1)}$ is the real part of the dielectric function arising from intraband transitions. Equation (21) for the imaginary part of the intraband dielectric function may be written as

$$\epsilon_2^{(1)}(\omega)=A\,\mathrm{Im}\{[a+c(\omega+2i\lambda)^{-2}][\phi_1^K(\omega)+i\phi_1(\omega)]/\omega^2 + b(\omega+2i\lambda)^{-1}[\phi_2^K(\omega)+i\phi_2(\omega)]/\omega^2\}+\bar{\epsilon}_2(\omega)\ , \tag{D1a}$$

$$\bar{\epsilon}_2(\omega)=A\,\mathrm{Im}\{b(\omega+2i\lambda)^{-1}[\phi_3(\omega)-\phi_2^K(\omega)]/\omega^2 + c(\omega+2i\lambda)^{-2}[\phi_4(\omega)-\phi_1^K(\omega)]/\omega^2\}\ , \tag{D1b}$$

where $\phi_i^K(\omega)$ is given by Eq. (22b). The quantities $[\phi_i^K(\omega)+i\phi_i(\omega)]/\omega^2$ for $i=1,2$ themselves represent valid dielectric functions since $\phi_i(\omega)/\omega^2$ is the imaginary part of a dielectric function and $\phi_i^K(\omega)/\omega^2$ is its Kramers-Kronig transform. Consequently the quantities $[a+c(\omega+2i\lambda)^{-2}][\phi_1^K(\omega)+i\phi_1(\omega)]/\omega^2$ and $b(\omega+2i\lambda)^{-1}[\phi_2^K(\omega)+i\phi_2(\omega)]/\omega^2$ are valid dielectric functions, since the terms $(\omega+2i\lambda)^{-n}$ are analytic in the upper half plane and go to zero as $\omega\to\infty$. Therefore the real part of the dielectric function $\epsilon^{(1)}=\epsilon_1^{(1)}+i\epsilon_2^{(1)}$ is given by

$$\epsilon_1^{(1)}(\omega)=A\,\mathrm{Re}\{[a+c(\omega+2i\lambda)^{-2}][\phi_1^K(\omega)+i\phi_1(\omega)]/\omega^2 + b(\omega+2i\lambda)^{-1}[\phi_2^K(\omega)+i\phi_2(\omega)]/\omega^2\}+\bar{\epsilon}_1(\omega)\ , \tag{D2a}$$

where

$$\bar{\epsilon}_1(\omega)=(1/\pi)P\int_{-\infty}^{\infty}\frac{d\omega'}{\omega'-\omega}\,\bar{\epsilon}_2(\omega')\ . \tag{D2b}$$

Using (B1)

$$\bar{\epsilon}_1(\omega)=(A/\pi)\int_{-\infty}^{\infty}\frac{d\omega'}{\omega'-\omega}\,\frac{1}{\omega'^2}\left(\frac{2b\lambda}{(\omega'^2+4\lambda^2)}[\phi_2^K(\omega')-\phi_3(\omega')] + \frac{4c\lambda\omega'}{(\omega'^2+4\lambda^2)^2}[\phi_1^K(\omega')-\phi_4(\omega')]\right)\ . \tag{D3}$$

In the limit $\lambda\to 0$

$$\bar{\epsilon}_1(\omega)\to\frac{Ab}{\omega}\left(\frac{\phi_3(\omega')}{\omega'^2}-\frac{\phi_2^K(\omega')}{\omega^2}\right)_{\omega'=0} + \frac{Ac}{\omega^2}\left(\frac{\phi_4(\omega')}{\omega'^2}-\frac{\phi_1^K(\omega')}{\omega'^2}\right)_{\omega'=0} \equiv c/\omega+B/\omega^2\ , \tag{D4}$$

where we have used the fact that $\phi_i^K(\omega')$, $\phi_3(\omega')$, and $\phi_4(\omega')$ are even functions of ω'. From (B2a) and (B4) we have

$$\epsilon_1^{(1)}(\omega)\xrightarrow[\lambda\to 0]{} A\left(a+\frac{c}{\omega^2}\right)\frac{\phi_1^K(\omega)}{\omega^2}+\frac{Ab}{\omega}\,\frac{\phi_2^K(\omega)}{\omega^2}+\frac{c}{\omega}+\frac{B}{\omega^2}\ . \tag{D5}$$

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