# Quantum theory of IR spectroscopy for dipole-forbidden vibrational modes of adsorbed molecules on the surface of a metal in the frequency range of the anomalous skin effect

A. I. Volokitin

*Samara State Technical University, 443010 Samara, Russia*

B. N. J. Persson

*Institut für Festkörperforschung, Jülich, Germany*

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A completely quantum-mechanical calculation of the IR spectrum for the dipole-forbidden vibrational modes of adsorbed molecules on a metal surface is performed. It is shown for broad-band metals with a simple band structure that the asymmetry of the line shape is determined by nonlocal effects, while the nonadiabaticity makes a small contribution. In the region of the limiting anomalous skin effect ($\omega/\omega_1 \ll 1$, where $\omega$ is the frequency of the IR radiation, $\omega_1 = \nu_F/\delta$, $\nu_F$ is the Fermi velocity, $\delta = c/\omega_p$ is the depth of the skin layer, and $\omega_p$ is the plasma frequency) the broad-band absorption spectrum caused by the adsorbed molecules has an asymptotic limit $\omega^0$. The theory is compared with new absolute measurements of the IR spectrum of the CO/Cu(100) system.

## 1. INTRODUCTION

The remarkable discovery of the possibility of detecting formally dipole-forbidden vibrational modes of adsorbed molecules using IR spectroscopy[1–4] has led to considerable progress in understanding this phenomenon.[5–9] We have proposed a theory based on the concept of "surface conductivity."[10–13]

According to that theory, the scattering of electrons on the potential of adsorbed molecules results in the broad-band absorption of IR radiation. When the frequency $\omega$ of the IR radiation coincides with the resonant frequency $\omega_0$ of dipole-forbidden modes of adsorbed molecules, the molecules move in resonance with the collective motion of the conduction electrons. This causes the added resistance to disappear, and the reflection coefficient becomes equal to its value for a clean surface. Therefore, dipole-forbidden modes produce an antiabsorption peak at the resonant frequency when the reflection coefficient at the resonant frequency is greater than the off-resonance values. At the same time, the reverse picture is observed for dipole-active modes.

The theory developed in Refs. 9 and 10 is valid only in the range of frequencies $\omega \gg \omega_1 = v_F/\delta$, where $v_F$ is the Fermi velocity, $\delta = c/\omega_p$ is the depth of the skin layer, and $\omega_p$ is the plasma frequency. The frequency of the frustrated rotations for CO/Cu(100) is $\omega_0 = 285\ \mathrm{cm}^{-1}$, and for copper we have $\omega_1 \approx 500\ \mathrm{cm}^{-1}$; therefore, the condition for the validity of local optics is not satisfied. In Refs. 12 and 13 we expanded the region of applicability of the original theory to the entire range of IR radiation. For adsorbate modes which are parallel to the surface this theory predicts an antiabsorption peak with asymmetry, which is uniquely determined by the ratio $\omega/\omega_1$ (we assume that the bulk value of the Drude relaxation time is equal to infinity).

However, the theory presented in Refs. 12 and 13 is not complete. First, we used an approach based on the semiclassical Boltzmann equation to obtain the change in the reflection coefficient caused by adsorbates. As a result, all the quantum interference effects are lost, and, more importantly, the theory is valid only for modes of an atomic adsorbate which are parallel to the surface. It is difficult to extend the theory so as to also include the frustrated rotations of molecules for which experimental data have been obtained, since it is not clear which boundary conditions should be used in this case to solve the Boltzmann equation.

In this paper we present a general theory of the IR spectrum of dipole-forbidden modes based on the Kubo formalism. We previously used such an approach only in the region where local optics are valid, i.e., where $\omega \gg \omega_1$ (Ref. 13). The present theory is valid for an arbitrary type of vibrational mode and for the entire range of IR frequencies, and it includes all quantum interference phenomena. The theory can be generalized to superconductors in the same manner as was done in the investigation of the anomalous skin effect without consideration of the modes of the adsorbed molecules in Refs. 14 and 15.

The only restriction on the theory stems from the fact that the final equations are obtained in the "jellium" model; therefore, it is rigorously valid only for metals with a simple band structure. In principle, the theory can be generalized to metals with a complicated band structure. However, this requires considerably more elaborate calculations.

## 2. THEORY

We consider a semi-infinite metal with a low concentration $n_a$ of adsorbates randomly distributed over the surface. We shall treat the metal in the jellium model, i.e., the charge of the metal ions is assumed to be smeared uniformly in a semi-infinite positive background. Let $x$, $y$, and $z$ denote a coordinate system with the $xy$ plane in the plane of the surface and the positive $z$ axis directed into the metal. We shall

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consider vibrational modes of adsorbed molecules which are dipole-forbidden with respect to the normal component of the electric field $\mathbf{E}_\perp$, so that there is no direct interaction between $\mathbf{E}_\perp$ and modes of the adsorbed molecules. As was shown in Refs. 12 and 13, the parallel component of the electric field $\mathbf{E}_\parallel$ is extremely small on a surface; therefore, the direct interaction between $\mathbf{E}_\parallel$ and modes of adsorbates can also be neglected. However, there is an important interaction between $\mathbf{E}_\parallel$ and the "free" conduction electrons of the metal. The latter interaction is more significant than the former due to the high polarizability of the "free" electrons. Within the metal (in the IR frequency range) the parallel component of the electric field $\mathbf{E}_\parallel$ is considerably greater than the normal component $\mathbf{E}_\perp$; therefore, we can neglect the interaction between $\mathbf{E}_\perp$ and the conduction electrons within the metal. Assuming that $\mathbf{E}_\parallel$ is aligned parallel to the $x$ axis, after averaging of the current density in the $xy$ plane, we can write the Hamiltonian of the system with consideration of the interaction of the conduction electrons with the external electromagnetic radiation in the form

$$H=H_0+H_{\text{el-ph}}+H_{\text{int}}, \tag{1}$$

$$H_0=\sum_{a\sigma} \varepsilon_0 c_{a\sigma}^{+}c_{a\sigma}+\sum_{k\sigma} \varepsilon_{k0} c_{k\sigma}^{+}c_{k\sigma}+\sum_{ka\sigma} (V_{ak}c_{a\sigma}^{+}c_{k\sigma}+\text{h.c.})+\sum_{a} \omega_0 b_a^{+} b_a, \tag{2}$$

$$H_{\text{el-ph}}=\sum_{ka\sigma} (W_{ak}c_{a\sigma}^{+}c_{k\sigma}+\text{ h.c.})\hat{Q}_{a}, \tag{3}$$

$$H_{\text{int}}=\frac{i}{\omega}\int_0^\infty dz\ \hat{j}_x(z)E_x(z)e^{-i\omega t}+\text{h.c.}, \tag{4}$$

where $c_{k\sigma}^{+}$ and $c_{a\sigma}^{+}$ are the creation operators for electrons in the $|k\rangle$ and $|a\rangle$ states with spin $\sigma$ of the metal and the adsorbate, respectively, $b_a^{+}$ is the creation operator of a phonon for the dipole-forbidden modes of the adsorbates, $\hat{Q}_a=Q_0(b_a^{+}+b_a)$ is the operator of the normal coordinate of a mode, $W_{ak}=dV_{ak}/dQ_a$ for $Q_a=0$, $E_x(z)$ is the parallel component of the electric field, and $\hat{j}_x(z)$ is the parallel component of the current-density operator, which we shall write in a basis of wave functions in the jellium model in the absence of adsorbates. At distances of several angstroms from the surface, the one-electron wave functions have the form

$$\Psi_k(\mathbf{x})=\frac{1}{\sqrt{A}}u_p(z)\exp(i\mathbf{k}_\parallel\cdot\mathbf{x}), \tag{5}$$

$$u_p(z)=\sqrt{\frac{2}{L}}\sin(pz+\Phi_p), \tag{6}$$

where we have normalized the wave functions to a parallelepiped with an area of the upper face $A$ and a thickness $L$, $\Phi_p$ is the phase shift, $k=(\mathbf{k}_\parallel,p)$, and $\mathbf{k}_\parallel=(k_x,k_y)$ is the component of the wave vector parallel to the surface. In a thin layer with a thickness of several angstroms near the surface of the metal ($z=0$) the wave function differs from (5)–(6). However, this spatial region makes a negligible contribution to the change in the reflection coefficient, since the electron–photon interaction extends several hundred angstroms into the metal (the depth of the skin layer is $\delta\approx c/\omega$). In the basis of wave functions (5)–(6) the current-density operator has the form

$$\hat{j}_x(z)=\frac{e}{m}\sum_{\mathbf{k}_\parallel,p_1,p_2,\sigma} k_x c_{k_1\sigma}^{+}c_{k_2\sigma}u_{p_1}(z)u_{p_2}(z), \tag{7}$$

where $k_1=(\mathbf{k}_\parallel,p_1)$ and $k_2=(\mathbf{k}_\parallel,p_2)$. According to the Kubo formula,[16] the relation between an electric field and the induced electrical current density can be written in the form

$$j_x(z)=\int_0^\infty dz'\sigma_{xx}(z,z',\omega)E_x(z')e^{-i\omega t}, \tag{8}$$

$$\sigma_{xx}(z,z',\omega)=\frac{ine^2}{m\omega}\,\delta(z-z')+\frac{i}{\pi}\,\Pi(z,z',\omega), \tag{9}$$

where $\Pi(z,z',\omega)$ is specified by the retarded form of the "current–current" Green's function, which, in turn, can be defined using the temperature Green's function by means of analytical continuation from a discrete set of points $\omega_n=2\pi inT$ on the positive imaginary axis to the real axis. The "current–current" temperature Green's function has the form

$$\Pi(z,z',i\omega_n)=-\frac{1}{A}\int_0^\beta d\tau\,\exp(i\omega_n\tau)\langle T_\tau\hat{j}_x(z,\tau)\hat{j}_x(z',0)\rangle. \tag{10}$$

After plugging (7) into (10), we obtain

$$\Pi(z,z',\omega_n)=\frac{1}{A}\left(\frac{e}{m}\right)^2\sum_{\mathbf{k}_\parallel,p_1,p_2,\mathbf{k}'_\parallel,p'_1,p'_2} \times k_x k'_x u_{p_1}(z)u_{p_2}(z) \times u_{p'_1}(z')u_{p'_2}(z')M_{k_1k_2}^{k'_1k'_2}(i\omega_n), \tag{11}$$

where

$$M_{k_1k_2}^{k'_1k'_2}(i\omega_n)=-\sum_\sigma \int_0^\beta d\tau\,\exp(i\omega_n\tau) \times\langle T_\tau\, c_{k_1\sigma}^{+}(\tau)c_{k_2\sigma}(\tau)c_{k'_1\sigma}^{+}(0)c_{k'_2\sigma}(0)\rangle. \tag{12}$$

In the present work we shall calculate the change in the reflectivity due to adsorbates in a linear approximation with respect to the adsorbate concentration $n_a$. In this approximation the indirect interaction of the adsorbed molecules through electronic states of the metal can be neglected. Diagrammatic representations of the various Green's functions for this case are shown in Fig. 1. The analytical expressions corresponding to these diagrams have the form

$$M_{k_1k_2}^{k'_1k'_2}(i\omega_n)=\Pi_{k_1k_2}^{k'_1k'_2}(i\omega_n)+\Sigma_{k_1k_2}(i\omega_n)D(i\omega_n)\Sigma_{k'_1k'_2}(i\omega_n), \tag{13}$$

$$\Pi_{k_1k_2}^{k'_1k'_2}(i\omega_n)=2T\sum_{\omega'_n} G_{k_2k'_1}(i\omega'_n)G_{k'_2k_1}(i\omega'_n+i\omega_n), \tag{14}$$

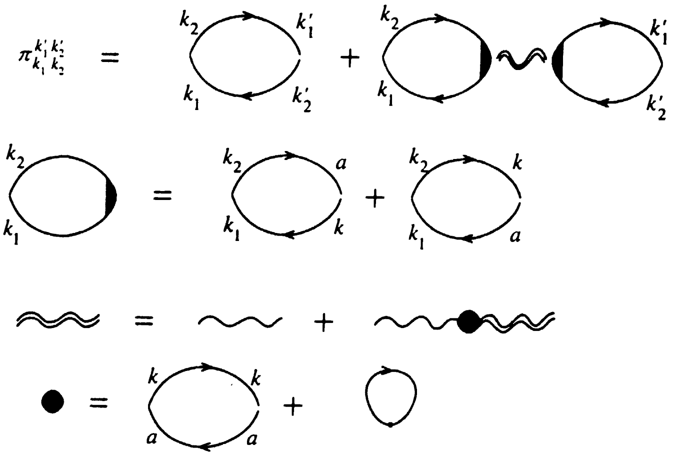

FIG. 1. Feynman diagrams which were taken into account in the calculations of the conductivity. The wavy lines represent the phonon Green's functions and the lines with arrows represent the electronic Green's functions.

$$\Sigma_{k_1k_2}(i\omega_n)=2T\sum_{k\omega_n'}[W_{ak}G_{k_2a}(i\omega_n')G_{kk_1}(i\omega_n'+i\omega_n)+W_{ak}^*G_{ak_1}(i\omega_n')G_{k_2k}(i\omega_n'-i\omega_n)], \qquad (15)$$

where the Fermi and Bose frequencies are $\omega_n'=(2n+1)\pi T$ and $\omega_n=2\pi nT$, respectively with $n=0,\pm 1,\cdots$, and $G_{kk'}$, $G_{ak}$, $G_{ka}$, and $D$ are the one-particle temperature Green's functions

$$G_{kk'}(i\omega_n')=-\int_0^\beta d\tau\,\exp(i\omega_n'\tau)\langle T_\tau\, c_{k\sigma}(\tau)c^+_{k'\sigma}(0)\rangle=\frac{\delta_{kk'}}{i\omega_n'-\varepsilon_k}+\frac{V^*_{ak}}{i\omega_n'-\varepsilon_k}G_{aa}(i\omega_n')\frac{V_{ak'}}{i\omega_n'-\varepsilon_k}, \qquad (16)$$

$$G_{ak}(i\omega_n')=-\int_0^\beta d\tau\,\exp(i\omega_n'\tau)\langle T_\tau c_{a\sigma}(\tau)c^+_{k\sigma}(0)\rangle=\frac{V_{ak}}{i\omega_n'-\varepsilon_k}G_{aa}(i\omega_n'), \qquad (17)$$

$$G_{ka}(i\omega_n')=G^*_{ak}(-i\omega_n'), \qquad (18)$$

$$G_{aa}(i\omega_n')=-\int_0^\beta d\tau\, e^{i\omega_n'\tau}\langle T_\tau c_{a\sigma}(\tau)c^+_{a\sigma}(0)\rangle=\frac{1}{i\omega_n'-\varepsilon_0-\Sigma(i\omega_n')}, \qquad (19)$$

$$D(i\omega_n)=-\int_0^\beta d\tau\,\exp(i\omega_n\tau)\langle T_\tau\hat{Q}_a(\tau)\hat{Q}_a(0)\rangle/Q_0^2=\frac{2\omega_0}{(i\omega_n)^2-\omega_0^2-2\omega_0\Sigma_{\rm ph}(i\omega_n)}, \qquad (20)$$

$$\Sigma(i\omega_n')=\sum_k\frac{|V_{ak}|^2}{i\omega_n'-\varepsilon_k}, \qquad (21)$$

$$\Sigma_{\rm ph}(i\omega_n)=-Q_0^2\int_0^\beta d\tau\,\exp(i\omega_n\tau)\langle T_\tau\hat{F}(\tau)\hat{F}(0)\rangle=2TQ_0^2\sum_{\omega_n'}G_{aa}(i\omega_n')[\mu(i\omega_n'+i\omega_n)+\mu(i\omega_n'-i\omega_n)], \qquad (22)$$

$$\hat{F}=\sum_{ka\sigma}(W_{ak}c^+_{a\sigma}c_{k\sigma}+\text{h.c.}), \qquad (23)$$

$$\mu(i\omega_n')=\sum_k\frac{|W_{ak}|^2}{i\omega_n'-\varepsilon_k}. \qquad (24)$$

The summation over the Fermi frequencies can be performed using the spectral representations for the Green's functions

$$G_{ij}(i\omega_n')=\int_{-\infty}^{\infty}d\varepsilon\,\frac{\rho_{ij}(\varepsilon)}{i\omega_n'-\varepsilon}, \qquad (25)$$

$$\rho_{ij}(\varepsilon)=\frac{1}{\pi}\,\text{Im}\,G_{ij}(\varepsilon-i\delta) \qquad (26)$$

and the well known rules for such summation.[17] After summation and analytical continuation from a discrete set of points on the imaginary axis to the upper section along the real axis, we obtain

$$\Pi^{k_1'k_2'}_{k_1k_2}(\omega)=2\int_{-\infty}^{\infty}d\varepsilon\int_{-\infty}^{\infty}d\varepsilon'\rho_{k_2k_1'}(\varepsilon)\rho_{k_2'k_1}(\varepsilon')\times\frac{f(\varepsilon)-f(\varepsilon')}{\omega+i\delta+\varepsilon-\varepsilon'}, \qquad (27)$$

$$\Sigma_{k_1k_2}(\omega)=2Q_0\sum_k \int_{-\infty}^{\infty} d\varepsilon \int_{-\infty}^{\infty} d\varepsilon' [W_{ak}\rho_{k_2a}(\varepsilon)\rho_{kk_1}(\varepsilon') + W^*_{ak}\rho_{ak_1}(\varepsilon')\rho_{k_2k}(\varepsilon)] \frac{f(\varepsilon)-f(\varepsilon')}{\omega+i\delta+\varepsilon-\varepsilon'}, \tag{28}$$

$$\Sigma_{\text{ph}}(\omega)=2Q_0^2\int_{-\infty}^{\infty} d\varepsilon \int_{-\infty}^{\infty} d\varepsilon' \rho_{aa}(\varepsilon)\mu''(\varepsilon')[f(\varepsilon) - f(\varepsilon')]\left[\frac{1}{\omega+i\delta+\varepsilon-\varepsilon'} - \frac{1}{-\omega-i\delta+\varepsilon-\varepsilon'}\right], \tag{29}$$

$$\mu''(\varepsilon)=\text{Im } \mu(\varepsilon-i\delta)/\pi, \tag{30}$$

where $f(\varepsilon)$ is the Fermi distribution function. For $\omega \ll \Gamma = \pi\Sigma_k|V_{ak}|^2\delta(\varepsilon_F-\varepsilon_k)$ we can restrict ourselves in the expansion of $\Sigma_{\text{ph}}(\omega)$ in powers of $\omega$ to the linear term, i.e.,

$$\Sigma_{\text{ph}}(\omega)=\Sigma_{\text{ph}}(0)+\frac{i\omega\eta_0}{2\omega_0}, \tag{31}$$

$$\eta_0=\frac{8\omega_0}{\pi} Q_0^2 \frac{\Gamma^2}{(\varepsilon_F-\varepsilon_0)^2+\Gamma^2} \frac{\langle|W_{ak}|^2\rangle_{\varepsilon_F}}{\langle|V_{ak}|^2\rangle_{\varepsilon_F}}, \tag{32}$$

where $\langle\cdots\rangle_{\varepsilon_F}=\Sigma_k\cdots\delta(\varepsilon_F-\varepsilon_k)$. The zero-order term $\Sigma_{\text{ph}}(0)$ can be included in the definition of $\omega_0$ and will henceforth be omitted. Equation (11) contains a product of four rapidly oscillating functions, which can be represented in the form

$$\begin{aligned} u_{p_1}(z)u_{p_2}(z)u_{p_1'}(z')u_{p_2'}(z') &= \left(\frac{2}{L}\right)^2 \sin(p_1z+\Phi_{p_1})\sin(p_2z+\Phi_{p_2}) \\ &\quad \times \sin(p_1'z'+\Phi_{p_1'})\sin(p_2'z'+\Phi_{p_2'}) \\ &= \frac{1}{L^2}\cos(qz+\Phi_{p_1}-\Phi_{p_2}) \\ &\quad \times\cos(q'z'+\Phi_{p_1'}-\Phi_{p_2'}) \\ &\quad +\text{rapidly oscillating terms,} \end{aligned} \tag{33}$$

where $q=p_1-p_2$ and $q'-p_1'-p_2'$.

After summation with respect to the momenta in Eq. (11), the rapidly oscillating terms in Eq. (33) give an interference term, which vanishes after averaging with respect to the short-wavelength oscillations. The most important contribution to the sum in (11) is made by the first term in Eq. (33) with $q\approx 1/\delta \ll k_F$, where $k_F$ is the Fermi momentum. For such $q$ we have $\Phi_{p_1}-\Phi_{p_2}\approx 0$, $V_{a\mathbf{k}}V^*_{a\mathbf{k}+\mathbf{q}}\approx|V_{ak}|^2$, $V_{a\mathbf{k}}W^*_{a\mathbf{k}+\mathbf{q}}\approx V_{ak}W^*_{ak}$, etc. Substituting (13), (27), and (28) into Eq. (11), neglecting the interference terms with short-wavelength oscillations, and taking into account that only with terms with $\mathbf{k}_\parallel=\mathbf{k}_\parallel'$ make a nonzero contribution during the summation with respect to the momenta, we obtain

$$\Pi(z,z',\omega)=\left(\frac{e}{m}\right)^2\left(\Pi_0(z-z')+\Pi_0(z+z') + n_a\left[\Pi_{\text{imp}}(z,z',\omega) + \frac{M}{2\omega_0}L(z)D(\omega)L(z')\right]\right), \tag{34}$$

where

$$\Pi_0(z)=\int_{-\infty}^{\infty}\frac{dq}{\pi}\cos qz\,\pi_0(q), \tag{35}$$

$$\pi_0(q)=\frac{1}{V}\sum_k k_x^2\frac{f(\varepsilon_{k+q})-f(\varepsilon_k)}{\omega+i\delta+\varepsilon_{k+q}-\varepsilon_k}, \tag{36}$$

$$\Pi_{\text{imp}}(z,z',\omega)=\int_{-\infty}^{\infty}\frac{dq}{\pi}\int_{-\infty}^{\infty}\frac{dq'}{\pi}\cos qz\cos q'z'\,\pi_{\text{imp}}(q,q'). \tag{37}$$

$$\begin{aligned} \pi_{\text{imp}}(q,q') &= \sum_k k_x^2|V_{ak}|^2\int_{-\infty}^{\infty}\frac{d\varepsilon}{\pi} \\ &\quad \times\text{Im}\left[\frac{G_{aa}(\varepsilon-i\delta)}{(\varepsilon-\varepsilon_{k+q}-i\delta)(\varepsilon-\varepsilon_{k+q'}-i\delta)}\right] \\ &\quad \times[f(\varepsilon)-f(\varepsilon_k)]\left(\frac{1}{\omega+i\delta+\varepsilon-\varepsilon_k} + \frac{1}{\varepsilon-\varepsilon_k-\omega-i\delta}\right), \end{aligned} \tag{38}$$

$$L(z)=\int_{-\infty}^{\infty}\frac{dq}{\pi}\cos qz\,l(q), \tag{39}$$

$$\begin{aligned} l(q) &= 4\omega_0Q_tQ_0\sum_k k_xV_{ak}W^*_{ak}\int_{-\infty}^{\infty}\frac{d\varepsilon}{\pi}\text{Im}\left[\frac{G_{aa}(\varepsilon-i\delta)}{\varepsilon-\varepsilon_{k+q}-i\delta}\right] \\ &\quad \times[f(\varepsilon)-f(\varepsilon_k)]\left(\frac{1}{-\omega-i\delta+\varepsilon-\varepsilon_k} - \frac{1}{\omega+i\delta+\varepsilon-\varepsilon_k}\right), \end{aligned} \tag{40}$$

and $Q_t=(2M\omega_0)^{-1/2}$. For $q\ll k_F$ we have

$$f(\varepsilon_{k+q})-f(\varepsilon_k)=\frac{\partial f}{\partial\varepsilon_k}\mathbf{v}_F\cdot\mathbf{q}=-\delta(\varepsilon_F-\varepsilon_k)\mathbf{v}_F\cdot\mathbf{q}. \tag{41}$$

Substituting this expression into (36) we obtain

$$\begin{aligned} \pi_0(q) &= -\int\frac{d^3k}{(2\pi)^3}\left[1-\frac{\omega}{\omega+i\delta+\mathbf{v}_F\cdot\mathbf{q}}\right]\delta(\varepsilon_k-\varepsilon_F) \\ &= -\frac{mn_0}{2}+\frac{3}{8}mn_0\omega\int_{-1}^{1}\frac{(1-x^2)dx}{\omega+i\delta+v_Fqx} \\ &= -\frac{mn_0}{2}+\frac{3}{8}mn_0\omega\left(\frac{1}{v_Fq}\right)^3\left[2v_Fq\omega+((v_Fq)^2 - \omega^2)\ln\left(\frac{\omega+i\delta+v_Fq}{\omega+i\delta-v_Fq}\right)\right]. \end{aligned} \tag{42}$$

In Eq. (42) the branch of the logarithm which vanishes when $q=0$ is taken. The first term in Eq. (42) gives the local term, which cancels out with the first term in Eq. (9) when $n(z)=n_0$ holds, where $n_0$ is the electron density in the metal without adsorbates averaged over the short-wavelength oscillations. In our calculations we use the approximation of a metal with an infinite band-gap width. In this approximation the width of the electronic level for an adsorbate $\Gamma(\varepsilon)=\pi\Sigma_k|V_{ak}|^2\delta(\varepsilon-\varepsilon_k)$ does not depend on the energy $\varepsilon$, and with consideration of Anderson's compensation theorem,[17] even in the presence of adsorbates the averaged electron density is equal to $n_0$, i.e., the contribution of the adsorbates to the averaged electron density vanishes.

In calculating $\pi_{\text{imp}}(q,q')$ we can deform the contour of integration with respect to $\varepsilon$ and $\varepsilon_k$ so that it consists of paths around the poles at $\varepsilon=\varepsilon_k\pm\omega$ and sections in which $|\varepsilon-\varepsilon_k|\gg\omega,\ \nu_F q$. The paths about the poles make the following contribution

$$-\sum_k k_x^2|V_{ak}|^2 \times\left\{\frac{G_{aa}(\varepsilon_k-\omega-i\delta)(f(\varepsilon_k-\omega)-f(\varepsilon_k))}{(\varepsilon_k-\omega-i\delta-\varepsilon_{k+q})(\varepsilon_k-\omega-i\delta-\varepsilon_{k+q'})} + \frac{G_{aa}(\varepsilon_k+\omega+i\delta)(f(\varepsilon_k+\omega)-f(\varepsilon_k))}{(\varepsilon_k+\omega+i\delta-\varepsilon_{k+q})(\varepsilon_k+\omega+i\delta-\varepsilon_{k+q'})}\right\}. \tag{43}$$

When approximation (41) is used for $\omega\ll\Gamma$, (43) takes on the form

$$-2\pi i\omega\rho_{aa}(\varepsilon_F)\sum_k \frac{k_x^2|V_{ak}|^2\delta(\varepsilon_k-\varepsilon_F)}{(\omega+i\delta-\bar{\upsilon}_F\bar{q})(\omega+i\delta-\bar{\upsilon}_F\bar{q}')}. \tag{44}$$

In the integration region far from the poles the dependence on $q$ and $\omega$ in the integrand can be neglected. In this case the contribution from this integration region is given by the expression

$$\sum_k k_x^2|V_{ak}|^2\int_{-\infty}^{\infty}\frac{d\varepsilon}{\pi}\,\text{Im}\left[\frac{G_{aa}(\varepsilon-i\delta)}{(\varepsilon-\varepsilon_k-i\delta)^3}\right]f(\varepsilon). \tag{45}$$

With consideration of the fact that for a metal with an infinite band ($\Gamma=\text{const}$)

$$\int_{-\infty}^{\infty}\frac{\varepsilon'\Gamma(\varepsilon')d\varepsilon'}{(\varepsilon-\varepsilon'-i\delta)^3}=0, \tag{46}$$

we find that the contribution from the regions far from the poles vanishes in this approximation.

Thus, in the infinite-band approximation $\pi_{\text{imp}}(q,q')$ is determined by the contribution (44).

The calculation of $l(q)$ is performed similarly. The contribution from the paths around the poles at $\varepsilon=\varepsilon_k\pm\omega$ is given by the formula

$$8\pi\omega_0\omega iQ_0Q_{\iota}\rho_{aa}(\varepsilon_F)\sum_k\frac{k_xV_{ak}W_{ak}^*\delta(\varepsilon_F-\varepsilon_k)}{\omega+i\delta-\bar{\upsilon}_F\bar{q}}, \tag{47}$$

and the contribution from the parts of the contour far from the poles is given by the formula

$$8\omega_0Q_0Q_{\iota}\omega\sum_k k_xV_{ak}W_{ak}^*\int\frac{d\varepsilon}{\pi}\left[\frac{G_{aa}(\varepsilon-i\delta)}{(\varepsilon-\varepsilon_k-i\delta)^3}\right]f(\varepsilon). \tag{48}$$

When Eq. (46) is taken into account, the last expression will be equal to zero in the infinite-band limit. We note that the contribution (48) is determined by the polarization current, which is related to the adiabatic oscillations of the polarization charge of the adsorbate. As follows from Anderson's theorem,[17] in the infinite-band limit the polarization charge is equal to zero; therefore, the polarization current associated with its motion will also be equal to zero.

The reflection coefficient is defined by the formula[12]

$$R=1+\frac{4}{\cos\theta}\frac{\omega}{c}\,\text{Im}\,\frac{E_x(0)}{E_x'(0)}, \tag{49}$$

where $E_x'(0)$ is the derivative of the parallel component of the electric field along a normal to the surface and $\theta$ is the angle of incidence. If the length is measured in units of $\delta=c/\omega_p$, the reflection coefficient is given by the formula

$$R=1+\frac{4}{\cos\theta}\frac{\omega}{\omega_p}\,\text{Im}\,\frac{g(0)}{g'(0)}, \tag{50}$$

where $g(\xi)=E_x(\delta\xi)$.

The function $g(\xi)$ is determined from the solution of Maxwell's equation

$$g''(\xi)=-\frac{4\pi i\omega}{\omega_p^2}J(\delta\xi)=\int_0^{\infty}d\xi'(\tilde{\Pi}_0(\xi-\xi')+\tilde{\Pi}_0(\xi+\xi'))g(\xi')+\int_0^{\infty}d\xi'\,\tilde{\Pi}_{\text{imp}}(\xi,\xi')g(\xi'), \tag{51}$$

where

$$\tilde{\Pi}_0(\xi)=\tfrac{3}{8}\int_{-\infty}^{\infty}\frac{dq}{\pi}\cos q\xi\int_0^{\pi}\frac{\sin^3\theta d\theta}{\varphi_q(\theta)}, \tag{52}$$

$$\varphi_q(\theta)=1+i\delta-\frac{q\cos\theta}{\beta}, \tag{53}$$

$$\tilde{\Pi}_{\text{imp}}(\xi,\xi')=-\frac{M}{m}\frac{n_a}{n}\frac{\omega_p}{c}\int_{-\infty}^{\infty}\frac{dq}{\pi}\int_{-\infty}^{\infty}\frac{dq'}{\pi}\cos q\xi\cos q'\xi' \times\left\{\frac{i\eta}{\omega}\int_0^{\pi}d\theta\,\frac{\sin^3\theta a(\theta)}{\varphi_q(\theta)\varphi_{q'}(\theta)} + \frac{\eta_m^2}{\omega^2-\omega_0^2+i\omega\eta_0}\left(\int_0^{\pi}d\theta\,\frac{\sin^2\theta b(\theta)}{\varphi_q(\theta)}\right) \times\left(\int_0^{\pi}d\theta\,\frac{\sin^2\theta b(\theta)}{\varphi_{q'}(\theta)}\right)\right\}, \tag{54}$$

$$\eta=\frac{4}{\pi M}\frac{\Gamma^2}{(\varepsilon_F-\varepsilon_0)^2+\Gamma^2}\frac{\langle k_x^2|V_{ak_F}|^2\rangle_{\varepsilon_F}}{\langle|V_{ak_F}|^2\rangle_{\varepsilon_F}}, \tag{55}$$

$$\eta_m=\frac{8\omega_0}{\pi}\frac{\Gamma^2}{(\varepsilon_F-\varepsilon_0)^2+\Gamma^2}Q_{\iota}Q_0\frac{\langle ik_xV_{ak}W_{ak}^*\rangle_{\varepsilon_F}}{\langle|V_{ak}|^2\rangle_{\varepsilon_F}}, \tag{56}$$

$$a(\theta)=\frac{\int_0^{2\pi}d\varphi\cos^2\varphi|V_{ak_F}(\theta,\varphi)|^2}{\int_0^{\pi}d\theta\int_0^{2\pi}d\varphi\sin^3\theta\cos^2\varphi|V_{ak_F}(\theta,\varphi)|^2}, \qquad (57)$$

$$b(\theta)=\frac{\int_0^{2\pi}d\varphi\cos\varphi V_{ak_F}W^*_{ak_F}(\theta,\varphi)}{\int_0^{\pi}d\theta\int_0^{2\pi}d\varphi\sin^2\theta\cos\varphi V_{ak_F}W^*_{ak_F}(\theta,\phi)}, \qquad (58)$$

$\beta=\omega/\omega_1$. It is convenient to solve Eq. (51) by means of the even continuation of $g(\xi)$ into the region $-\infty<\xi<0$. For such a continuation $g(\xi)=g(-\xi)$, and the first derivative $g'(\xi)$ has a discontinuity at $\xi=0$. In the range $-\infty<\xi<+\infty$ the function $g(\xi)$ satisfies the equation

$$g''(\xi)=A\delta(\xi)+\int_{-\infty}^{\infty}d\xi'\tilde{\Pi}_0(\xi-\xi')g(\xi')$$
$$+\int_0^{\infty}\tilde{\Pi}_{\text{imp}}(\xi,\xi')g(\xi'). \qquad (59)$$

After the replacement $g\rightarrow A\tilde{g}$ the constant $A$ vanishes from the equation. The solution of the equation obtained as a result of such a replacement in the linear approximation of $n_a$ has the form

$$g(\xi)=\tilde{g}_0(\xi)+\int_{-\infty}^{\infty}d\xi'\int_0^{\infty}d\xi''\tilde{g}_0$$
$$\times(\xi-\xi')\tilde{\Pi}_{\text{imp}}(\xi',\xi'')\tilde{g}_0(\xi''), \qquad (60)$$

where $\tilde{g}_0(\xi)$ satisfies Eq. (59) for $\tilde{\Pi}_{\text{imp}}=0$ and $A=1$. This solution can easily be obtained using a Fourier technique,[12] and it has the form

$$g_0(\xi)=-\int_{-\infty}^{\infty}\frac{dq}{2\pi}\frac{\cos q\xi}{\varepsilon(q)}, \qquad (61)$$

$$\varepsilon(q)=q^2+\tfrac{3}{4}\int_0^{\pi}\frac{\sin^3\theta d\theta}{\varphi_q(\theta)}. \qquad (62)$$

As a result of the calculations with consideration of the fact that $\tilde{g}'(+0)=1/2$, for the change in the reflection coefficient upon adsorption we obtain

$$\Delta R=-\frac{4}{\cos\theta}\frac{M}{m}\frac{n_a}{n}\frac{\eta}{c}\operatorname{Re}G, \qquad (63)$$

$$G=\int_0^{\pi}d\theta\sin^3\theta a(\theta)f^2(\theta)$$
$$-\frac{i\eta_m^2\omega}{\eta(\omega^2-\omega_0^2+i\omega\eta_0)}\left(\int_0^{\pi}d\theta\sin^2\theta b(\theta)f(\theta)\right)^2, \qquad (64)$$

$$f(\theta)=\int_{-\infty}^{\infty}\frac{dq}{\pi}\frac{1}{\varepsilon(q)}\frac{1}{\varphi_q(\theta)}. \qquad (65)$$

Let us consider the limiting cases. The case of $\beta\gg1$ corresponds to the region where local optics are valid. In this case $\varphi_q(\theta)$ can be set equal to unity, $\varepsilon(q)=q^2+1$, and $f(\theta)=1$. As a result we find that in this limit

$$\Delta R=-\frac{4}{\cos\theta}\frac{M}{m}\frac{n_a}{n}\frac{\eta}{c}\operatorname{Re}\left[\frac{\eta(\omega^2-\omega_0^2)+i\omega(\eta\eta_0-\eta_m^2)}{\eta(\omega^2-\omega_0^2+i\omega\eta_0)}\right]. \qquad (66)$$

For oscillations of an adatom parallel to the surface, we have $\eta=\eta_0=\eta_m$ and

$$\Delta R=-\frac{4}{\cos\theta}\frac{M}{m}\frac{n_a}{n}\frac{\eta}{c}\frac{(\omega^2-\omega_0^2)^2}{(\omega^2-\omega_0^2)^2+\omega^2\eta^2}. \qquad (67)$$

We previously obtained this result in Refs. 10–13.

The case of $\beta\ll1$ corresponds to the limiting anomalous skin effect. In this case it is convenient to introduce a new variable $x=\cos\theta$ and to perform the integration first with respect to $x$. Here we must note that in the limit $\beta\ll1$ the main contribution to the integral is associated with the paths around the poles at $x=\beta/q\pm i\delta$. Physically this means that in the case of the limiting anomalous skin effect, only electrons moving at grazing angles to the surface make a significant contribution to the reflection coefficient. This stems from the fact that only these electrons experience the effect of the external electromagnetic field over the course of a complete oscillation period of the electromagnetic field. At the same time, electrons moving along a normal to the surface experience the effect of the external field over the course of a time which is small compared with the oscillation period of the electromagnetic field.

As a result of the calculations we obtain

$$\varepsilon(q)=q^2-\frac{3}{4}\frac{\pi i\beta}{|q|}, \qquad (68)$$

$$G\rightarrow\frac{16a(\pi/2)}{3\pi^2}\int_0^{\infty}dx\int_0^{\infty}dx'\frac{xx'}{x+x'}\frac{1}{x^3+1}\frac{1}{x'^3+1}. \qquad (69)$$

It follows from (69) that the background absorption tends to a constant as $\omega\rightarrow0$. This result differs from the result obtained in the quasiclassical treatment, in which the background absorption varies according to a $\omega^{2/3}$ law.[12] However, since electrons moving at grazing angles to the surface interact considerably less strongly with the adsorbates than do electrons moving at angles close to a normal to the surface, because $a(\pi/2)\ll a(0)$, holds the constant to which the background absorption tends will be very small, and it will be very difficult to determine it in an experiment.

## 3. NUMERICAL RESULTS AND DISCUSSION

It follows from the results obtained that the reflectivity depends in the general case on the angular dependence of the matrix element $V_{ak_F}(\theta,\varphi)$. However, inasmuch as this dependence appears under an integral sign, it should be expected that the final results will depend weakly on the details of the behavior of $V_{ak_F}(\theta,\varphi)$. Therefore, in analogy to the representations of diffuse reflection from a surface,[12,18] we approximate the functions $a(\theta)$ and $b(\theta)$ by their mean values $\bar{a}(\theta)$ and $\bar{b}(\theta)$. Since the functions $a(\theta)$ and $b(\theta)$ satisfy the normalization conditions

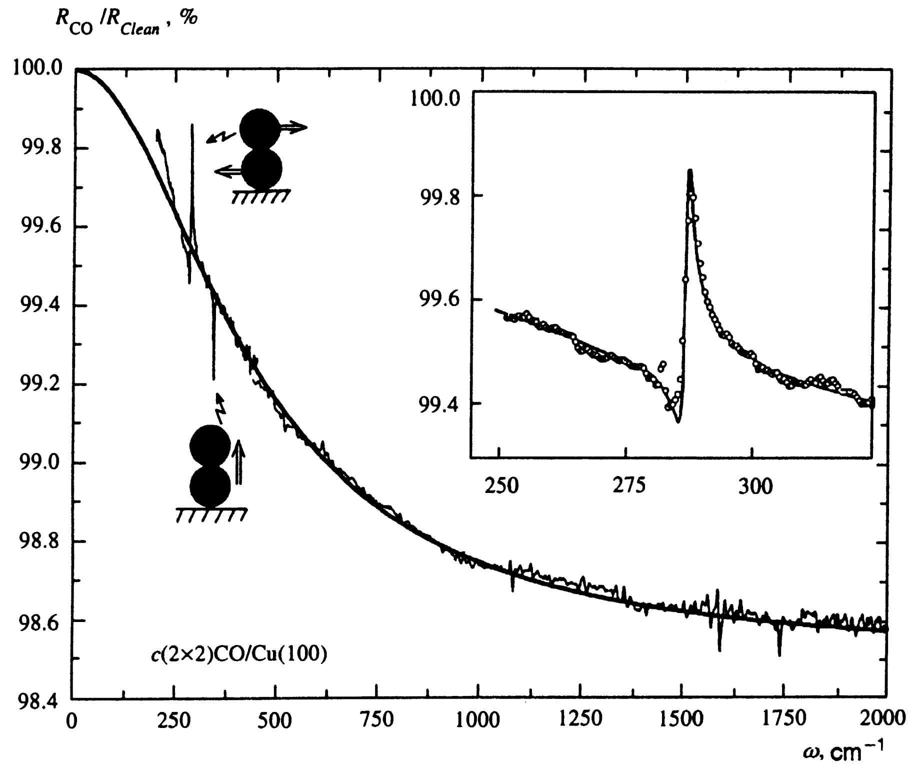

FIG. 2. Results of measurements of the change in the broad-band reflectivity caused by the $c(2\times2)$ CO structure on Cu(100) (the thin solid line and the circles in the inset) and the calculations described in the text. The inset shows the magnified region of dipole-forbidden frustrated rotations.

$$\int_0^\pi d\theta \sin^3\theta a(\theta) = 1, \tag{70}$$

$$\int_0^\pi d\theta \sin^2\theta b(\theta) = 1, \tag{71}$$

the mean values will be equal to $\bar{a}=3/4$ and $\bar{b}=2/\pi$. We introduce the quantity

$$r=\frac{\eta_m^2}{\eta_0\eta}=\frac{\langle ik_x V_{ak} W_{ak}^*\rangle_{\varepsilon_F}^2}{\langle k_x^2 |V_{ak}|^2\rangle_{\varepsilon_F}\langle |W_{ak}|^2\rangle_{\varepsilon_F}}. \tag{72}$$

If we introduce the notations $ik_xV_{ak}=\Phi(k)$ and $W_{ak}=\varphi(k)$, we have

$$r=\frac{\langle\Phi\varphi^*\rangle^2}{\langle\Phi\Phi^*\rangle\langle\varphi\varphi^*\rangle}. \tag{73}$$

Since $\langle\Phi\varphi^*\rangle$ is a real quantity, it follows from Schwarz's inequality that $0\leq r\leq 1$. For parallel modes of anatomic adsorbate

$$V_{ak}(Q_a)=V_{ak}(0)\exp(ik_xQ_a); \tag{74}$$

therefore,

$$W_{ak}=V'_{ak}(0)=ik_xV_{ak}(0), \tag{75}$$

and from (72) we have $r=1$. The multiplier $r$ has a simple physical meaning. The multiplier $r$ takes into account the fact that in the general case, in which $r<1$, it is impossible to eliminate the relative motion between different points of a vibrating adsorbed molecule and the drift of the conduction electrons.[12]

Figure 2 presents a comparison of the calculated reflection coefficient with the experimental data obtained in Ref. 19 for the $c(2\times2)$ CO/Cu(100) system.

The reflection coefficient is calculated from Eq. (63) with the parameters $\omega_1=400$ cm$^{-1}$, $\eta=0.07$ cm$^{-1}$, $r=0.5$, and $\eta_0=1.7$ cm$^{-1}$. We note that the frequency dependence of the background absorption and the asymmetry of the resonance curve in the inset are determined by the single parameter $\omega_1$, and it is remarkable that both curves agree well with the experimental data at the same value of $\omega_1$, which, moreover, is close to the value obtained in the jellium model for Cu with one conduction electron per Cu atom: $\omega_1(\text{theory})=(v_F/c)\omega_p\approx440$ cm$^{-1}$. The friction coefficient $\eta$ corresponds to a lifetime of ≈70 ps for parallel modes of CO on Cu(100). This value is close both to the theoretical estimate ≈40–100 ps obtained for CO on Cu(100) at zero temperature[20] and to the value ≈40 ps obtained from resistance measurements for a copper thin film covered with CO (Ref. 9). Finally, to obtain the theoretical curves in the inset in Fig. 2, we used the friction coefficient $\eta_0=1.7$ cm$^{-1}$, which corresponds to a lifetime following the excitation of electron-hole pairs equal to ≈3 ps and is in good agreement with the theoretical estimate ≈1 ps (Ref. 20). We also note that in the present calculations there is no contribution to the asymmetry of the line shape from the effect of the nonadiabaticity of the modes. This contribution arises because in the general case the current density induced in a metal as a result of the adsorbate modes has imaginary and real parts: $I(q)=I_1+iI_2$. The imaginary part arises because the induced current density is not in phase with the modes of the adsorbates. The real part $I_1$ is associated with the paths around the poles in Eq. (40) and is governed by the frictional force between the modes of the adsorbate molecules and the drift of the conduction electrons, while the real part $l_2$ is associated with the adiabatic oscillations of the polarization charge. It follows from the analysis conducted in the present work that $l_2/l_1 \sim \omega/W$, where $W$ is the width of the conduction band. Hence it follows that in the case of broad-band metals $l_2$ and, accordingly, the contribution of the nonadiabaticity effects to the asymmetry of the line shape can be neglected. We note that the nonadiabaticity parameter for dipole-active modes is determined by the ration $\omega/\Gamma$ (Ref. 5). The contribution of the nonadiabaticity effects to the asymmetry of the line shape can be significant only for narrow-band metals. This situation apparently occurs for the asymmetric modes of $H$ on $W(100)$, for which there is a narrow band of surface states near the Fermi level.[1,6]

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