# IR reflection spectroscopy for dipole-inactive vibrations of adsorbed molecules. Effects of nonadiabaticity and nonlocality

A. I. Volokitin

*Samara State Technical University, 443010 Samara, Russia*

B. N. J. Persson

*Institute of Solid State, Jülich, Germany*

(Submitted 9 March 1994)
Zh. Eksp. Teor. Fiz. **106**, 522–534 (August 1994)

We have computed the IR spectrum of molecules adsorbed on a surface that execute dipole-inactive vibrations (vibrations that cannot be excited by an electric field component normal to the surface) of the hindered-rotation or hindered-translation type. We discuss an indirect mechanism for exciting such molecular vibrations, connected with dragging by an electron wind. We show that this mechanism leads to broadband background absorption and an asymmetric lineshape, which is determined by the combined effects of nonadiabaticity and nonlocality. Our results are used to discuss the vibrational spectra of the systems CO/Cu(100) and H/W(100).

## 1. INTRODUCTION

The study of vibrations of adsorbed molecules is a powerful method for investigating the dynamics of surface processes such as vibrational relaxation, surface chemical reactions, surface diffusion, adhesion, desorption, etc. One way to obtain information about vibrations is to use a method involving vibrational spectroscopy of adsorbates.[1–6] Such methods include reflection and absorption IR spectroscopy (IRAS), electron energy-loss spectroscopy (EELS), and inelastic scattering of helium atoms (IHS).

Because of its high resolution, IRAS is the most suitable method for studying the lineshapes of vibrations. With regard to IRAS, it is widely believed[1–6] that it can only be used to study vibrations of molecules with nonzero dynamic dipole moment perpendicular to the surface. However, recently vibrations of hindered-translation type[7–10] were observed in IRAS for H on W(100) and Mo(100), as well as hindered-rotation vibrations[11] of CO on Cu(100) (in hindered translation, the center of gravity of the molecules translates parallel to the surface without a change of orientation of the molecular axis; in hindered rotation, both the position of the center of gravity and the orientation of the molecular axis change). Hindered rotations and translations are dipole-inactive vibrations with regard to the electric field normal to the surface. However, in the experiment these vibrations were observed to have the same spectral intensity as the dipole-active vibrations perpendicular to the surface.

In order to explain these experimental data for the vibrational spectra of dipole-inactive vibrations, we have proposed a theory based on the concept of surface conductivity.[12,13] According to this theory, scattering of electrons by the potential of adsorbed molecules leads to a change in the surface conductivity and to wideband absorption of IR radiation. For hindered translations, when the frequency of the IR radiation coincides with the resonance vibration frequency $\omega_0$ the molecules move in resonance with the collective drift motion of the conduction electrons in the electric field. Consequently, the additional surface impedance disappears at this frequency, and the IR reflectivity attains its value for a clean surface. The theory explains the intensity of the spectral peaks, their anti-absorptive nature, and the reason why dipole-inactive vibrations could not be seen by using EELS.

The theory we developed in Refs. 12,13, which was based on the semiclassical Drude model, is correct only for vibrations of the hindered-translation type, and for metals for which the "jellium" model applies. For this reason, it cannot be used for metals with complicated band structures, for example, vibrations of H on W(100).

Furthermore, the region of validity of the theory coincides with the region of validity of local optics, which is specified by the condition $v_F/\omega \ll \delta$, where $\delta = c/\omega_p$ is the skin depth, $v_F$ and $c$ are the Fermi velocity and velocity of light, respectively, and $\omega_p$ is the plasma frequency. As a consequence of the approximations used, the theory predicts a symmetric lineshape and a frequency-independent background absorption. At the same time, the experimental observations for hindered translation of H/W(100) and hindered rotations of CO/Cu(100) suggest that the lineshapes are strongly asymmetric and that the wideband background absorption is frequency dependent.

In this paper, we present a complete quantum-mechanical calculation of the vibrational spectrum of dipole-inactive vibrations based on the Kubo formalism under conditions where local optics is valid. This general approach allows us to compute the lineshape while including nonadiabaticity of the vibrations for an arbitrary type of vibration and arbitrary metallic band structure. For low-frequency vibrations, the conditions for validity of local optics may be violated. In order to investigate nonlocality, in this paper we have generalized an approach first used to study the anomalous skin effect, which is based on use of the kinetic Boltzmann equation.[14]

1063-7761/94/080286-07$10.00

## 2. REFLECTIVITY OF A SURFACE IN THE PRESENCE OF ADSORBED MOLECULES

When a beam of infrared light is incident on a metal surface covered by adsorbed molecules, with a frequency corresponding to the frequency of molecular vibrations, peaks or troughs are observed in the reflection spectra. The change in the reflectivity due to adsorbed molecules is determined by the expression

$$\Delta=\frac{\Delta R}{R_0}=\frac{R-R_0}{R_0}, \tag{1}$$

where $R$ and $R_0$ are reflection coefficients in the presence and absence of adsorbed molecules on the surface, respectively. Because the wavelength of the incident photons is many times larger than the size of a molecule, it is usually assumed that the interaction between the radiation field and the adsorbed molecule is dipolar in form:

$$H_{\text{int}}=-\hat{\mu}\mathbf{E}, \tag{2}$$

where $\hat{\mu}$ is the dipole operator of the molecule and $\mathbf{E}$ is the electric field vector at the position of the molecule. For $p$-polarized electromagnetic waves in the IR frequency range, the normal component of the electric field near the surface of the metal is approximately equal to twice the normal component of the incident wave.[15] On the other hand, the parallel component of the electric field is several orders of magnitude smaller than the normal component. This difference between the normal and parallel components of the electric field leads to an approximate selection rule, according to which only vibrational modes that have a dynamic dipole moment normal to the surface can be observed by using IRAS. Therefore, the observation of formally forbidden vibrations (with respect to the normal component of the electric field) of the hindered-translation[7–10] type for H on W(100) and CO on Mo(100), and hindered-rotation[11] type for CO on Cu(100), was unexpected. In fact, the vibrational spectra for these vibrations had the same intensity as the dipole-active modes, despite the fact that the parallel component of the electric field at the surface was smaller by a factor $E_\parallel/E_\perp\sim\omega/\omega_p\sim10^{-2}$ than the normal component of the electric field, and the corresponding dipole intensity was smaller by a factor of $|E_\parallel/E_\perp|^2\sim10^{-4}$. However, these arguments do not take into account the fact that even a small parallel component of the electric field can induce a sizable current density in the metal because of the high metallic polarizability. The interaction between the vibrations of the adsorbed molecules and this current density can lead to an appreciable change in the surface reflectivity, due to the change in the surface conductivity.

When the coupling between the current density and the bulk electric field is determined by a local relation, the change in reflectivity due to adsorbed molecules for $p$-polarized electromagnetic waves is given by the expression[16,17]

$$\Delta=-\frac{16\pi\omega}{c\cos\theta}\,\mathrm{Im}(\alpha_\perp\sin\theta-\alpha_\parallel/\varepsilon), \tag{3}$$

where $\theta$ is the angle of incidence, $\alpha_\perp$ and $\alpha_\parallel$ are the surface polarizabilities per unit area in the directions normal and parallel to the surface, and $\varepsilon$ is the dielectric constant of the metal. The polarizability $\alpha_\parallel$ is related to the change in surface conductivity in the presence of adsorbates $\sigma_S$ by the equation

$$\sigma_s=i\omega\alpha_\parallel. \tag{4}$$

For metals, the condition $|\varepsilon(\omega)|\gg1$ is usually satisfied in the infrared region of the spectrum; therefore, when $\alpha_\perp\sim\alpha_\parallel$, the first term should dominate in Eq. (3), which leads to a selection rule for the dipole-active modes. However, at the metal surface, due to the high polarizability of the metal parallel to the surface, the condition $\alpha_\parallel\gg\alpha_\perp$ may be satisfied. In this case, the second term will dominate in Eq. (3).

The normal component of the electric field does not interact directly with the hindered rotations and translations, and can only excite overtones of these vibrations with weak intensity.[18] Therefore, the reflectivity near the resonant frequency for these vibrations is determined primarily by the second term, which, taking into account Eq. (4), can be written in the form

$$\Delta=\frac{16\pi}{c\cos\theta}\,\mathrm{Re}\,\frac{\sigma_s}{\varepsilon(\omega)}. \tag{5}$$

According to the Kubo formula, for a metal with isotropic conductivity in the plane $(x,y)$ parallel to the metal surface, the conductivity $\sigma_S$ is determined by the expression[19]

$$\sigma_s=\sigma_{xx}=\sigma_{yy}=i\langle\hat{j}_x;\hat{j}_x\rangle/\omega=i\pi(\omega)/\omega, \tag{6}$$

$$\langle\langle\hat{j}_x;\hat{j}_x\rangle\rangle=-i\int_0^\infty e^{i\omega t}\langle[\hat{j}_x(t)\hat{j}_x(0)]\rangle dt. \tag{7}$$

At $T=0$ K, the average in Eq. (7) is taken over the ground state of the system, while for finite temperatures it is taken over a canonical ensemble; $\hat{j}_x(t)$ is the $x$-component of the current density in the Heisenberg picture.

For small concentrations $n_a$ of adsorbed particles, the reflectivity depends linearly on $n_a$. In order to obtain this linear contribution, it is convenient to express the conductivity in terms of the force–force response function. For this we make use of the equation of motion for the Green's function,[20] according to which

$$\omega\langle\langle\hat{j}_x;\hat{j}_x\rangle\rangle=\langle\langle[j_xH]\hat{j}_x\rangle\rangle, \tag{8}$$

$$\omega\langle\langle[\hat{j}_xH];\hat{j}_x\rangle\rangle=\langle[[\hat{j}_xH]\hat{j}_x]\rangle+\langle\langle[j_xH;Hj_x]\rangle\rangle, \tag{9}$$

where $H$ is the system Hamiltonian. Taking into account that

$$\hat{j}_x=-\frac{e}{m}\hat{P}_x, \tag{10}$$

where $\hat{P}_x$ is the $x$-component of the system momentum operator, and the force operator $\hat{F}_x$ is determined by the expression

$$\frac{d\hat{P}_x}{dt}=i[H\hat{P}_x]=\hat{F}_x, \tag{11}$$

we obtain from Eqs. (8), (9)

$$\pi(\omega)=\frac{1}{\omega^2}\left(\frac{e}{m}\right)^2[i\langle[\hat{F}_x\hat{P}_x]\rangle+\langle\langle\hat{F}_x;\hat{F}_x\rangle\rangle]. \tag{12}$$

The first term in Eq. (12) is purely real; therefore it does not give a contribution to the real part of the conductivity, and in what follows it will be omitted. In the presence of adsorbed atoms at the surface, the force operator can be written in the form

$$\hat{F}_x=\sum_a \hat{F}_a+\hat{F}_b, \tag{13}$$

where $\hat{F}_a$ and $\hat{F}_b$ are force operators associated with the interaction of electrons with the potential of the adsorbed molecules and the crystal potential, respectively. The operator $\hat{F}_b$ contributes to the change in surface conductivity due to adsorbates only when multiple scattering of electrons by the crystal potential and the potential of the adsorbed molecules is taken into account. In this paper we will neglect multiple scattering; therefore, the operator $\hat{F}_b$ will be omitted.

In order to obtain a contribution to $\Delta$ that is linear in the concentration of adsorbates $n_a$, it is sufficient to calculate the response function while neglecting the interaction between different adsorbed molecules. In this case, we have

$$\langle\langle\hat{F}_x;\hat{F}_x\rangle\rangle=n_a\langle\langle\hat{F}_a;\hat{F}_a\rangle\rangle. \tag{14}$$

For further calculations it is necessary to make the model more concrete and to choose a model Hamiltonian of the system, which we will do in the next section.

When the conditions for applicability of local optics are violated, it is necessary to use an expression for the reflectivity that is more general than (3). According to impedance theory, for $p$-polarized waves and angles of incidence that are not too close to $\pi/2$, the reflection coefficient can be determined from the expression[15]

$$R=1+\frac{4}{\cos\theta}\frac{\omega}{c}\,\mathrm{Im}\,\frac{E_x(0)}{E_x'(0)}, \tag{15}$$

where $E_x(0)$ and $E_x'(0)$ are the values of the $x$-component of the electric field and its derivative along the $z$-axis at the surface $z=0$.

In order to find $E_x(0)$ and $E_x'(0)$, it is necessary to use the Maxwell equations for the electromagnetic field within the metal, supplemented by the constitutive equations, which express how the induced current and charge couple to the electric field.

In order to obtain this coupling, which in general is nonlocal in character, in Sec. 4 of this paper we will use an approach based on the kinetic Boltzmann equation. Previously this approach was used in the theory of the anomalous skin effect.[14]

## 3. REFLECTIVITY FOR THE CASE OF LOCAL OPTICS

Let us write the Hamiltonian of the system in the form

$$H=H_0+H_{\mathrm{int}}, \tag{16}$$

$$H_0=\sum_a c_a^+c_a+\sum_k \varepsilon_k c_k^+c_k+\sum_{a,k}(V_{ak}c_a^+c_k+\mathrm{H.c.})+\sum_a \omega_0 b_a^+b_a, \tag{17}$$

$$H_{\mathrm{int}}=\sum_{a,k}(V_{ak}^Q c_a^+c_k+\mathrm{H.c.})\hat{Q}_a=\sum_a \hat{F}_a^{(3)}\hat{Q}_a. \tag{18}$$

The Hamiltonian $H_0$ describes the electronic part of the metal plus adsorbed layer system and the vibration of the adsorbed molecules, without including the electron–phonon interaction. $c_a^+$ and $c_k^+$ are creation operators for an electron in the states of the adsorbed molecule and the metal, with energies $\varepsilon_a$ and $\varepsilon_k$ respectively. $V_{ak}$ is the matrix element for hybridization between states of the adsorbate and the metal. The Hamiltonian $H_{\mathrm{int}}$ describes the electron–phonon interaction:

$$V_{ak}^Q=\left.\frac{\partial V_{ak}(x_a,Q_a)}{\partial Q_a}\right|_{\substack{x_a=0\\ Q_a=0}}, \tag{19}$$

where $\hat{Q}_a=Q_0(b_a^++b_a)$ is the normal coordinate of the vibration, $Q_0$ is the amplitude of the zero-point oscillation, $b_a^+$ is the phonon creation operator, and $x$ is the displacement of the center of gravity of the molecule along the $x$-axis. For the model (16)–(18), the force operator can be written in the form

$$\hat{F}_a=\hat{F}_a^{(1)}+\hat{F}_a^{(2)}, \tag{20}$$

$$\hat{F}_a^{(1)}=\sum_k (V_{ak}c_a^+c_k+\mathrm{H.c.}), \tag{21}$$

$$\hat{F}_a^{(2)}=\sum_k (V_{ak}^{xQ}c_a^+c_k+\mathrm{H.c.})\hat{Q}_a=\hat{F}_a^{(20)}\hat{Q}_a, \tag{22}$$

$$V_{ak}^x=\left.\frac{\partial V_{ak}(x_a,Q_a)}{\partial x_a}\right|_{\substack{x_a=0\\ Q_a=0}},$$

$$V_{ak}^{xQ}=\left.\frac{\partial^2 V_{ak}(x_a,Q_a)}{\partial x_a\partial Q_a}\right|_{\substack{x_a=0\\ Q_a=0}}. \tag{23}$$

The force–force response function in Eq. (14) can be written as follows:

$$\langle\langle\hat{F}_a;\hat{F}_a\rangle\rangle=\langle\langle\hat{F}_a^{(1)};\hat{F}_a^{(1)}\rangle\rangle+\langle\langle\hat{F}_a^{(1)};\hat{F}_a^{(2)}\rangle\rangle+\langle\langle\hat{F}_a^{(2)};\hat{F}_a^{(1)}\rangle\rangle+\langle\langle\hat{F}_a^{(2)};\hat{F}_a^{(2)}\rangle\rangle. \tag{24}$$

In order to compute the causal Green's functions that enter into Eq. (24), at $T=0$ K we can use the diagram technique for time-ordered Green's functions, which for $\omega>0$ coincide with the causal Green's functions on the real axis; for finite temperatures we use the diagram technique for the temperature Green's functions, whose analytic continuation from a discrete series of points on the imaginary axis to the real axis determines the causal Green's functions.[21] When electron–hole mechanisms generate the vibrational spectrum, as we assume in this paper, the temperature dependence of the spectrum is found to be weak;[18] therefore, in what follows, all the Green's functions will be computed at $T=0$ K.

Using the diagram technique, we can obtain

$$\langle\langle \hat{F}_a^{(1)};\hat{F}_a^{(1)}\rangle\rangle=\langle\langle \hat{F}_a^{(1)};\hat{F}_a^{(1)}\rangle\rangle_0 + Q_0^2\langle\langle \hat{F}_a^{(1)};\hat{F}_a^{(3)}\rangle\rangle_0^2 D(\omega), \tag{25}$$

$$\langle\langle \hat{F}_a^{(2)};\hat{F}_a^{(2)}\rangle\rangle=Q_0^2\langle F_a^{(20)}\rangle_0^2 D(\omega), \tag{26}$$

$$\langle\langle \hat{F}_a^{(1)};\hat{F}_a^{(2)}\rangle\rangle=\langle\langle \hat{F}_a^{(2)};\hat{F}_a^{(1)}\rangle\rangle=Q_0^2\langle\langle \hat{F}_a^{(1)};\hat{F}_a^{(3)}\rangle\rangle_0 =\langle \hat{F}_a^{(20)}\rangle_0 D(\omega), \tag{27}$$

$$D(\omega)=\frac{2\omega_0}{\omega^2-\omega_0^2-2\omega_0\langle\langle \hat{F}_a^{(3)};\hat{F}_a^{(3)}\rangle\rangle_0}. \tag{28}$$

In Eqs. (25–28), the label "0" attached to a Green's function indicates that this Green's function is calculated for a system with Hamiltonian $H_0$. Taking Eqs. (25)–(28) into account, we can write

$$\langle\langle \hat{F}_a;\hat{F}_a\rangle\rangle=\frac{1}{Q_0^2}\left\{\sum_1(\omega)+\frac{2\omega_0\Sigma_2^2(\omega)}{\omega^2-\omega_0^2-2\omega_0^2\Sigma_3(\omega)}\right\}, \tag{29}$$

where

$$\sum_1(\omega)=Q_0^2\langle\langle \hat{F}_a^{(1)};\hat{F}_a^{(1)}\rangle\rangle_0, \tag{30}$$

$$\sum_2(\omega)=Q_0^2\langle\langle \hat{F}_a^{(1)};\hat{F}_a^{(3)}\rangle\rangle_0+Q_0^2\langle F_a^{(20)}\rangle_0, \tag{31}$$

$$\sum_3(\omega)=Q_0^2\langle\langle \hat{F}_a^{(3)};\hat{F}_a^{(3)}\rangle\rangle_0. \tag{32}$$

For small values of $\omega$ we can write

$$\sum_i(\omega)=\Lambda_i-i\,\frac{\omega}{2\omega_0}\,\Gamma_i, \tag{33}$$

where $i=1,2,3$. The quantity $\Lambda_3$ leads only to a renormalization of the frequency $\omega_0$; therefore, in what follows we will assume that $\omega_0$ equals its observed value, so that we can set $\Lambda_3=0$. The quantity $\Lambda_1$ does not contribute to the reflectivity, while $\Lambda_2$ is determined by the expression

$$\Lambda_2=Q_0^2\sum_k\left[\left(V_{ak}^{x}\,\frac{V_{ak}^{*Q}}{V_{ak}^{*}}+V_{ak}^{xQ}\right)\langle c_a^{+}c_k\rangle_0+\text{c.c.}\right]. \tag{34}$$

The quantities $\Gamma_i$ are determined by the expressions

$$\Gamma_i=\frac{4\omega_0Q_0^2\rho_a(\varepsilon_F)\Gamma(\varepsilon_F)}{\langle|V_{ak}|^2\rangle\varepsilon_F}\times\begin{cases}\langle|V_{ak}^{x}|^2\rangle_{\varepsilon_F}, & i=1\\ \frac{1}{2}\langle V_{ak}^{x}V_{ak}^{*Q}+\text{c.c.}\rangle_{\varepsilon_F}, & i=2\\ \langle|V_{ak}^{Q}|^2\rangle_{\varepsilon_F}, & i=3\end{cases} \tag{35}$$

$$\rho_a(\varepsilon)=\frac{1}{\pi}\frac{\Gamma}{(\varepsilon-\varepsilon_a)^2+\Gamma^2}, \tag{36}$$

$$\Gamma(\varepsilon)=\pi\sum_k|V_{ak}|^2\delta(\varepsilon-\varepsilon_k). \tag{37}$$

In Eq. (35), $\langle ...\rangle_{\varepsilon F}$ denotes an average over the constant-energy surface with $\varepsilon=\varepsilon_F$, where $\varepsilon_F$ is the Fermi energy. In deriving Eq. (35) we have assumed that $\Gamma^Q=0$ for symmetric vibrations, for which $\Gamma(-Q)=\Gamma(Q)$. From Eqs. (5), (6), (12), (14), (29), and (35), we obtain

$$\Delta=\frac{8\pi n_a}{\cos\theta}\frac{1}{c\omega}\left(\frac{e}{m\omega}\right)^2\frac{1}{Q_0^2}\frac{1}{\varepsilon(\omega)}\left[\Gamma_1-\frac{\Gamma_2^2}{\Gamma_3}+\left(\frac{2\omega_0\Lambda_2}{\omega}\right)^2\frac{1}{\Gamma_3}\frac{(1+\lambda\gamma)^2}{1+\lambda^2}\right], \tag{38}$$

where $\lambda=\omega^2-\omega_0^2/\omega\Gamma_3$, $\gamma=\omega/2\omega_0\Gamma_2/\Lambda_2$.

Equation (38) determines the well-known expression for the Fano lineprofile,[22–23] which has a characteristic asymmetry, the magnitude and sign of which are determined by the parameter $\gamma(\omega_0)$. The asymmetry of the lineprofile is related to the imaginary part of the function $\Sigma_2(\omega)$, which in turn is due to the nonadiabaticity of the vibrations. As was shown for the first time by Langreth,[22] for an electron–hole attenuation mechanism dipole-active vibrations are also characterized by a Fano lineprofile. However, the mechanisms that lead to this profile are fundamentally different, and give different expressions for the parameters that characterize it. For example, for dipole-active vibrations the asymmetry parameter $|\gamma(\omega_0)|<1$, while for dipole-inactive vibrations this parameter can be arbitrarily large. As a special case, let us discuss vibrations of the hindered-translation type at a metal surface in the "jellium" model. In this case, we find that $Q_0=(2M\omega_0)^{-1/2}$ (atomic units are used, with $\hbar=1$); here $M$ is the mass of the adsorbate and

$$V_{ak}(x,Q)=\exp[ik_x(x+Q)]V_{ak}(0,0),$$

$$V_{ak}^{x}=V_{ak}^{Q}=ik_xV_{ak},\quad V_{ak}^{xQ}=-k_x^2V_{ak}.$$

From (35), we then obtain $\Gamma_1=\Gamma_2=\Gamma_3=\eta$, where $\eta$ is a coefficient of friction corresponding to motion along the surface. It follows from Eq. (34) that $\Lambda_2=0$. Taking into account that in the "jellium" model

$$\varepsilon(\omega)=1-\omega_p^2/\omega^2,\quad \omega_p^2=4\pi ne^2/m,$$

where $n$ is the electron density in the metal, the following expression is obtained for the reflectivity:

$$\Delta=\frac{4}{\cos\theta}\frac{n_a}{n}\frac{M}{m}\frac{1}{c\tau}\frac{(\omega^2-\omega_0^2)^2}{(\omega^2-\omega_0^2)^2+(\omega\eta)^2}, \tag{39}$$

where $\tau=\eta^{-1}$ is the lifetime of the vibration. Expression (39) has a characteristic "anti-absorptive" structure, i.e., at the resonant frequency $\omega=\omega_0$ the absorptivity turns out to be smaller than in the region outside resonance. The qualitative explanation for this result is that at the resonant frequency the molecules move synchronously with the drift motion of the conduction electrons in the electric field, i.e., there is no relative motion between them. In the "jellium" model the frictional force that acts on the molecules depends only on the relative velocity; at $\omega=\omega_0$ this motion tends to zero, implying that no energy is absorbed at resonance. The expression (39) was first obtained by us in the Drude model.[12]

## 4. REFLECTIVITY FOR THE CASE OF NONLOCAL OPTICS

In the previous section, the calculation of the reflectivity was based on the assumption that the relation between the electric field and the induced current density was local, which is admissible only when $v_F/\omega \ll \delta$ (it is assumed that the mean free path $l \gg \delta$). When $v_F/\omega \gtrsim \delta$, it is necessary to replace the local relation

$$\mathbf{j} = \sigma(\omega)\mathbf{E}(\mathbf{x},\omega) \tag{40}$$

between the current density $\mathbf{j}$ and electric field $\mathbf{E}(\mathbf{x},\omega)$ by a more general nonlocal relation

$$\mathbf{j}(\mathbf{x},\omega) = \int d^3x\,\sigma(\mathbf{x},\mathbf{x}',\omega)\mathbf{E}(\mathbf{x}',\omega). \tag{41}$$

In order to obtain this nonlocal relation, we make use of an approach based on the kinetic Boltzmann equation. Previously, this approach was used to study the anomalous skin effect without including vibrations of adsorbed molecules.[14]

Let us consider a semi-infinite metal in the "jellium" model, with a surface in the $xy$ plane and the positive $z$-axis directed into the metal. The surface is assumed to be covered with adsorbed molecules that can execute vibrations of hindered-translation type in the $x$-direction. As we showed in the previous section, local optics then predicts a completely symmetric lineshape. Within the metal, for $z > a$, where $a$ is the size of the surface region, the parallel component of the electric field greatly exceeds the perpendicular component. Neglecting the perpendicular component and assuming that the parallel component is directed along the $x$-axis, we can write the Boltzmann equation for the electron distribution $f(z,v_x,v_y,v_z)$ in the form

$$\frac{\partial f}{\partial t} + \frac{eE_x}{m}\frac{\partial f}{\partial v_x} + v_z\frac{\partial f}{\partial z} = -\frac{f-f_0}{\tau_b}, \tag{42}$$

where $\tau_b$ is the bulk relaxation time and $f_0$ is the Fermi distribution function. For a $p$-polarized wave and angles of incidence $\theta \neq 0$, in the surface region, i.e., $|z| < a$, it is necessary to include the rapid change of electron density and normal component of electric field. This purely surface effect can be included by using the theory of $d$-functions proposed in Ref. 16. However, since the normal component of the electric field does not interact with the dipole-inactive vibrations when $v_F/\omega \gg a$, these surface effects will be small, and will not be included in what follows. Following Ref. 14, we will assume that a fraction $p$ of conduction electrons is specularly reflected at the surface, while the remaining electrons are diffusely reflected with a drift velocity $V$ equal to the velocity of the vibrating adsorbed molecules along the $x$-axis. Consequently, $f(z,v_x,v_y,v_z)$ should satisfy the boundary condition

$$f(0,v_x,v_y,v_z) = pf(0,v_x,v_y,-v_z) + (1-p)f_0(0,v_x-V,v_y,v_z), \tag{43}$$

where $v_z > 0$. In order to obtain the equation of motion for the adsorbed molecules, we must incorporate the fact that the relative motion between the adsorbed molecule and the drift motion of the electrons in the metal leads to a frictional force which acts on the adsorbed molecules via momentum transfer between the conduction electrons and the adsorbed molecules when the former scatter off the latter at the surface. The momentum flux transferred by the electrons to the adsorbed molecules in the $x$-direction can be written in the form

$$\Pi_{xy} = m\int d^3v\,v_xv_zf(0,v_x,v_y,v_z)\,. \tag{44}$$

(The normalizing constant is included in the definition of the function $f(z,v_x,v_y,v_z)$). The frictional force acting on the adsorbed molecules equals the momentum flux divided by the number of adsorbed molecules per unit area $n_a$. Thus, the equation of motion for the vibration of the adsorbed molecules has the form

$$M\ddot{x} + M\omega_0^2x + \Pi_{xz}/n_a = 0. \tag{45}$$

In the linear approximation with respect to the electric field $E_x(z)$ we can find the solution to Eq. (42) with the boundary condition (43) in the same way as was done in Ref. 14 for the case of motionless adsorbed molecules, i.e., $V=0$. Using this solution, we can compute the current density induced by the external electric field,

$$j_x(z) = -e\int d^3v\,v_xf(z,v_x,v_y,v_z). \tag{46}$$

Neglecting the displacement current and normal component of the electric field in the metal, we obtain the equation for the parallel component of the electric field from the Maxwell equations:

$$\frac{d^2E_x}{dz^2} = \frac{4\pi i\omega}{c^2}\,j_x(z). \tag{47}$$

Computing $j_x(z)$ from Eq. (46) using the function $f(z,v_x,v_y,v_z)$ obtained from the solution of Eq. (42) with the boundary condition (43), after a change of variables $E(z) = g(\xi)$, $z = \xi\delta$, from (47) we obtain the following equation for the function $g(\xi)$:

$$g''(\xi) = -\int_0^\infty d\xi' g(\xi')\Bigg[k(\xi-\xi') + k(\xi+\xi') + \alpha(1-p)\Bigg[\int_0^\infty d\xi' g(\xi')k(\xi+\xi') + \frac{4i\omega\eta L(\xi)}{\omega_0^2-\omega^2-i\omega\eta}\int_0^\infty d\xi' g(\xi')L(\xi')\Bigg], \tag{48}$$

where we have used the relation[24]

$$1-p = \frac{16}{3}\frac{n_a}{n}\frac{M}{m}\frac{\eta}{v_F}, \tag{49}$$

$$L(\xi) = \int_1^\infty dy\left(\frac{1}{y^2} - \frac{1}{y^4}\right)e^{-\beta y|\xi|}, \tag{50}$$

$$k(\xi) = \int_1^\infty dy\left(\frac{1}{y} - \frac{1}{y^3}\right)e^{-\beta y|\xi|}. \tag{51}$$

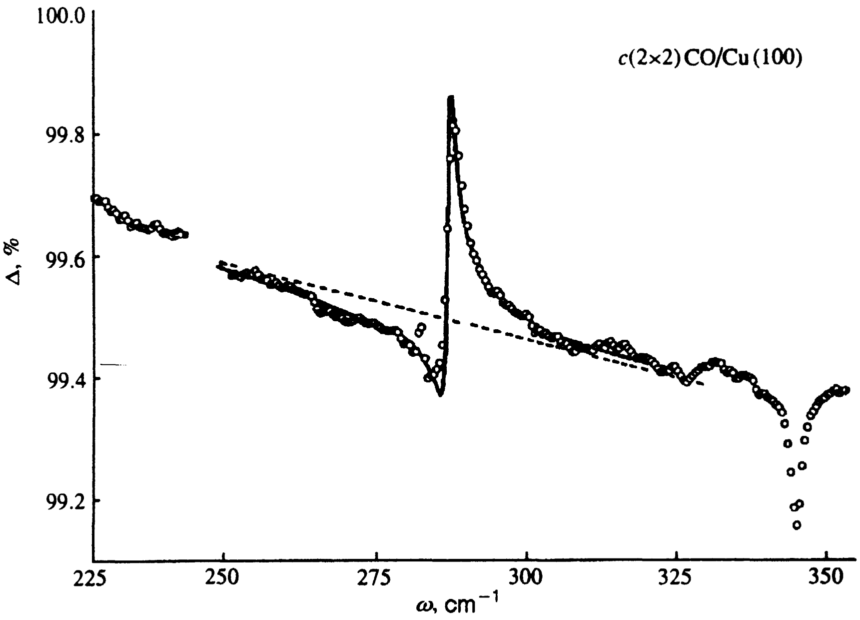

FIG. 1. Infrared spectrum for vibrations of hindered-rotation type in CO on the surface of Cu(100). The solid curve is the result from theory; see the text.

Here $\beta=\delta/l-i\omega/\omega_1$, $\omega_1=v_F/\delta$, $\alpha=3i\omega/4\omega_1$. Assuming that the quantity $1-p$ is small, the solution to Eq. (48) can be obtained by iteration in powers of $(1-p)$. To zeroth approximation, the solution to Eq. (48) was found in Ref. 14, using the Fourier method. In the first approximation, the solution is given in the form $g(\xi)=g_0(\xi)+g_1(\xi)$. After substituting this solution into Eq. (48), to linear approximation in $(1-p)$ we obtain for the function $g_1(\xi)$ an equation which can also be solved by the Fourier method. Using the solution so obtained and Eq. (15), to linear approximation in $(1-p)$ the reflection coefficient can be written in the form

$$R=R_0+\Delta R, \tag{52}$$

$$R=1-\frac{4}{\pi}\frac{\omega}{\cos\theta\omega_p}\operatorname{Im}\int_{-\infty}^{\infty}dq\,\frac{1}{S(q)}, \tag{53}$$

$$\Delta R=-\frac{3(1-p)\omega^2}{\pi^2\omega_1\omega_p\cos\theta}\operatorname{Re}G, \tag{54}$$

$$G=\int_1^{\infty}dy\left(\frac{1}{y}-\frac{1}{y^3}\right)f^2(y)+\frac{4i\eta\omega}{\omega_0^2-\omega^2-i\omega\eta}\times\left[\int_1^{\infty}dy\left(\frac{1}{y^2}-\frac{1}{y^4}\right)f(y)\right]^2, \tag{55}$$

$$f(y)=\int_{-\infty}^{\infty}dq\,\frac{1}{S(q)}\frac{1}{q+i\beta y}, \tag{56}$$

$$S(q)=q^2-\alpha\int_{-\infty}^{\infty}d\xi k(\xi)e^{-iq\xi}=q^2-\frac{\alpha}{\beta}\frac{1}{u^3}\times\left[2u+(u^2-1)\ln\frac{1+u}{1-u}\right], \tag{57}$$

where $u=iq/\beta$. In particular, when $\omega_1/\omega\ll 1$, we obtain from Eqs. (54)–(57)

$$\Delta R=-\frac{3}{4}\frac{(1-p)}{\cos\theta}\left[1-\frac{6}{5}\left(\frac{\omega_1}{\omega}\right)^2\right]\times\frac{(\omega_0^2-\omega^2)(\omega_0^2-\omega^2+16\eta\omega_1/15)}{(\omega_0^2-\omega^2)^2+\omega^2\eta^2}. \tag{58}$$

This expression agrees with (39) if we take into account Eq. (49).

## 5. DISCUSSION

The results we present in this paper imply that when an electron–hole attenuation mechanism enters into the formation of the vibrational spectra of dipole-inactive vibrations, the line profile is characterized by an asymmetry determined by the combined action of nonadiabaticity and nonlocality. Among the experimentally studied systems to which our theory applies are asymmetric vibrations[7–10] of H on W(100) and Mo(100) and hindered rotation[11] of CO on Cu(100). For asymmetric vibrations of H on W(100) we have $\omega_0=1270$ cm$^{-1}$, while the "jellium" model for tungsten yields an estimate $\omega_1\sim 300$ cm$^{-1}$. Thus, the asymmetry due to nonlocality is characterized by the small parameter $\omega_1/\omega_0\sim 0.2$, so that the observed asymmetry of the line profile is primarily due to nonadiabaticity. The experimental data can be described by a Fano line profile with parameters $\Gamma_3=22$ cm$^{-1}$, $\gamma(\omega_0)=+0.5$. The fact that nonadiabaticity of the vibrations inevitably leads to a Fano line profile was first pointed out by Langreth.[22] However, Langreth's theory applies only to dipole-active vibrations, and does not explain the strong spectral line intensity for dipole-inactive vibrations. On the other hand, for hindered rotation of CO on Cu(100) we have $\omega_0=285$ cm$^{-1}$ and $\omega_1\approx 444$ cm$^{-1}$; therefore, the asymmetry parameter due to nonlocality $\omega_1/\omega_0\sim 1$, and the effect of nonlocality for this system must be significant. Figure 1 shows a comparison of the experimental reflectivity data with theory. The reflectivity was calculated using Eqs. (54)–(57), with a coefficient of friction $\eta$ chosen so as to reproduce the asymptotic variation in the reflectivity for large $\omega$; this leads to a decrease in the reflectivity by 1.23±0.10%. The coefficient of friction $\eta=1/\tau$ obtained in this way corresponds to a lifetime for hindered translation of CO $\tau=(4.6\pm1.0)\cdot10^{-11}$ s, which is in good agreement with the value obtained by measuring the resistivity of thin Cu films, i.e., $\tau=3.9\cdot10^{-11}$ s.[24] For the parameter we used the value $\omega_1=500$ cm$^{-1}$, which is close to the value predicted for "jellium": $\omega_1=\omega_p v_F/c=444$ cm$^{-1}$.

For the frequency dependence of the background absorption and line profile, agreement between theory and experiment is satisfactory when we take into account the difference between hindered translations and hindered rotations, and the fact that Cu is different from "jellium." On the other hand, the hindered rotation of CO on Cu(100) can be described by a Fano line profile with parameters $\omega_0=285$ cm$^{-1}$, $\gamma(\omega_0)=-1.6$, $\Gamma_3=4.2$ cm$^{-1}$, which corresponds to $\tau=1.26\cdot10^{-12}$ s.[11] The larger value of the asymmetry parameter $\gamma(\omega)$ in this case can be explained by the closeness of copper to the "jellium" model, for which $|\gamma(\omega_0)|=\infty$. However, the local theory, which leads to the Fano line profile, cannot explain the frequency dependence of the broadband background absorption. From this we may conclude that for hindered rotation of CO on Cu(100), nonlocality effects play a more important role than nonadiabaticity.

In order to draw more definite conclusions, more careful measurements are required of the line profiles, in particular of those connected with the isotopic dependence of the spectral lines. For a more detailed confirmation of the theoretical predictions, it would be desirable to set up experiments for simpler systems involving hindered translation of H on Cu(100).

This work was done with partial support from the Russian Fund For Fundamental Research (project code N 93-02-14318). One of the authors (A.I.V.) is grateful to the Institute of Solid State in Jülich for their hospitality during the initial stages of the work.

[1] Y. J. Chabal, Surf. Sci. Rep. **8**, 211 (1988).
[2] R. Ryberg, in *Advances in Chemical Physics—Molecule Surface Interactions*, K. P. Lawley (ed.), Wiley, London (1989).
[3] O. M. Braun, A. I. Volokitin, and V. P. Zhdanov, Usp. Fiz. Nauk **158**, 421 (1989) [Sov. Phys. Usp. **32**, 605 (1989)].
[4] H. Ueba, Prog. Surf. Sci. **22**, 181 (1986).
[5] R. G. Tobin, Surf. Sci. **183**, 226 (1987).
[6] A. M. Bradshaw and E. Schweitzer, in *Advances in Spectroscopy*, R. E. Helster (ed.), Wiley, N. Y. (1988).
[7] Y. J. Chabal, Phys. Rev. Lett. **55**, 845 (1985).
[8] J. E. Reutt, Y. J. Chabal, and S. B. Christman, Phys. Rev. B **38**, 3112 (1988).
[9] D. M. Riffer and A. J. Sievers, Surf. Sci. **210**, 215 (1989).
[10] D. M. Riffer and A. J. Sievers, Phys. Rev. B **41**, 3406 (1990).
[11] C. J. Hizschmugl, G. P. Williams, F. M. Hoffmann, and Y. J. Chabal, Phys. Rev. Lett., **65**, 480 (1990).
[12] B. N. J. Persson and A. I. Volokitin, Chem. Phys. Lett. **185**, 292 (1991).
[13] B. N. J. Persson, Chem. Phys. Lett. **197**, 7 (1992).
[14] G. E. H. Reuter and E. H. Sondheimer, Proc. Roy. Soc. (London) A **195**, 336 (1948).
[15] L. D. Landau and E. M. Lifshitz, *Electrodynamics of Continuous Media*, Nauka, Moscow (1970). (Pergamon Press, 2nd ed., 1984).
[16] P. J. Feibelman, Prog. Surf. Sci. **12**, 287 (1982).
[17] D. C. Langreth, Phys. Rev. B **39**, 10020 (1989).
[18] A. I. Volokitin, Surf. Sci. **242**, 359 (1989).
[19] G. D. Mahan, *Many-Particle Physics*, Plenum, New York (1981).
[20] D. N. Zubarev, Usp. Fiz. Nauk **71**, 71 (1960) [Sov. Phys. Usp. **3**, 320 (1960)].
[21] A. A. Abrikosov, L. P. Gor'kov, and I. E. Dzyaloshinskii, *Methods of Quantum Field Theory in Statistical Physics* [in Russian]. Fizmatgiz, Moscow (1962) [Pergamon Press, Oxford (1965)].
[22] D. C. Langreth, Phys. Rev. Lett. **54**, 126 (1985).
[23] H. U. Fano, Phys. Rev. **124**, 1866 (1961).
[24] B. N. J. Persson, Phys. Rev. B **44**, 3277 (1991).

Translated by Frank J. Crowne