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Surface resistivity and vibrational damping in adsorbed layers

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I derive a simple relation between the change in dc resistivity $\Delta\rho$ of a thin metallic film due to adsorption of molecules on the film surface and the electron-hole pair damping (lifetime τ) of the frustrated translations of the adsorbates. From the measured $\Delta\rho$ for several different adsorbate systems, I deduce the corresponding τ, which ranges from $\sim 10^{-12}$ s for chemisorption systems to $\sim 10^{-9}$ s for physisorption systems. Theories for the damping of parallel frustrated translations are developed for three limiting cases of the adsorbate-substrate bond; namely, for covalent, ionic, and van der Waals bonds. I study the change in the broadband infrared (ir) light reflectivity caused by the adsorption of molecules on a semi-infinite metal and I discuss the recent ir study by Hirschmugl *et al.* for the CO-Cu(100) system. Finally, the observation by ir-spectroscopy by Chabal *et al.* of dipole-forbidden frustrated translations and rotations for H and CO chemisorbed on metals is discussed and the contribution from the excitation of the parallel frustrated translations to the surface resistivity is calculated.

I. INTRODUCTION

In this work I derive a relationship between two important quantities, namely, the increase in the resistivity $\Delta\rho$ of a thin metal film upon adsorption of molecules on the film surface and the lifetime τ of the parallel vibrational motion of the adsorbates (the so-called parallel frustrated translation) due to the excitation of electron-hole pairs. The fundamental relation is

$$\frac{1}{\tau}=\frac{n^2e^2}{M}d\left.\frac{\partial\rho}{\partial n_a}\right|_{n_a=0} . \tag{1}$$

Here M is the adsorbate mass, n is the conduction electron density in the metal, d is the film thickness, and $\partial\rho/\partial n_a$ is the initial (i.e., as $n_a \to 0$) slope of the increase of the film resistivity ρ with increasing adsorbate concentration n_a.

The electric conductivity of thin metallic films as a function of the film thickness and preparation procedure (e.g., annealing temperature) has been extensively studied for many years[1,2] and many interesting physical effects such as weak localization[3] and size quantization have been discovered. In the present work, I focus on the *change* in film resistivity upon adsorption of atoms or molecules on the film surface. A rather limited number of such studies has been reported as a function of adsorbate converge for smooth metal films of known thickness and resistivity. I note that the influence of adsorbates on the film resistance can be quite large, e.g., an increase of the resistance by a factor of ~ 2 as the coverage increases from zero to ~ 1 monolayer. Since thin metal films are of great importance in many technological applications, e.g., in microelectronic devices or as gas detectors, a thorough understanding of the role of adsorbate-induced resistivity changes is of considerable practical importance.

The damping of vibrations in adsorbed molecules has been studied intensively during the past few years.[4] It constitutes one of the simplest dynamical processes at a surface, and the damping rate enters as an important parameter in Kramers formulation[5] of activated processes at surfaces such as desorption or diffusion. It is also of considerable importance in many other nonthermal surface processes such as laser stimulated desorption.[6] The damping of many adsorbate vibrational modes at surfaces (e.g., the C-O stretch mode) can be studied directly using high-resolution ir-spectroscopy. However, this is not the case for the low-frequency parallel frustrated translations which usually are dipole forbidden (see Sec. V, however). The relation (1) represents therefore an important method of obtaining the *e-h* pair damping of frustrated translations. I note that another general method would be high-resolution inelastic helium scattering, as has recently been demonstrated for the CO-Pt(111) and CO-Ni(100) chemisorption systems.[7,8]

Using infrared-reflection absorption spectroscopy (IRAS), in a series of recent work Chabal *et al.*[4-10] have observed dipole-forbidden frustrated translations and rotations for H on W(111) and Mo(111), and for CO on Cu(100). These vibrational modes seem to be excited indirectly via the screened electric field *in the metal* which first excites *e-h* pairs which scatter inelastically from the adsorbates while exciting the frustrated translation or rotation. The momentum necessary for the *e-h* pair excitations is supplied by the adsorbates or by surface imperfections, e.g., steps, which breaks the translational symmetry parallel to the surface. Since it is the same source of momentum which determines the adsorbate-induced changes in the dc resistivity of thin metallic films, it should not be a surprise that the treatment of the dc resistivity has implications for the ir excitations of dipole-forbidden adsorbate vibrational modes. This topic will be treated in Sec. V.

The paper is organized as follows. In Sec. II, I derive (1) and use this equation to obtain the lifetime τ, caused by excitation of *e-h* pairs, for several different adsorption systems including both physisorbed and chemisorbed molecules. In Sec. III, I present a theoretical study of the damping of parallel frustrated translations using three limiting adsorption models, namely covalent, ionic, and van der Waals bonding. In Sec. IV, the change ΔR in broadband ir reflectivity upon adsorption of molecules on a metal surface is studied. The reflectivity change ΔR is caused by diffusive scattering of conduction electrons from the adsorbates and I show that in some cases ΔR can be expressed directly in terms of the *e-h* pair damping $1/\tau$ of the parallel frustrated translations. As an illustration, I analyze the ir data by Hirschmugl *et al.* from the CO-Cu(100) system, and show that the ir absorption can be explained using the same lifetime τ for the CO frustration translation as deduced earlier from dc resistivity data for CO-covered Cu films. In Sec. V, I present a discussion relating to the ir observation by Chabal *et al.* of dipole-forbidden frustrated translations and rotations as well as some comments on surface-enhanced Raman scattering (SERS). Section VI contains the summary and conclusions.

II. SURFACE RESISTIVITY AND VIBRATIONAL DAMPING

Consider a thin metallic film deposited on an insulating substrate. We assume that the film is uniform with a thickness $d \sim 100-1000$ Å. Ideally, the film is grown epitaxially on the substrate, but the films considered below were prepared by evaporating under UHV conditions and annealing to ~ 400 K. These films have uniform thickness but a relatively high concentration of imperfections (e.g., grain boundaries), and the dc resistivity is higher than for single crystals. For example, the Ag films discussed below[10] ($d \approx 100$ Å) have the dc resistivity $\rho_0 = 3$ $\mu\Omega$ cm at $T = 40$ K and $\rho_0 = 4.4$ $\mu\Omega$ cm at $T = 293$ K, corresponding to an electron mean free path of about $l = 280$ and 191 Å, respectively.

For a perfectly smooth and unreconstructed metal film, the conduction electrons will be specularly reflected by the film surfaces, i.e., the parallel momentum of the electrons will be conserved and the surfaces will not contribute to the film resistivity. Assume now that a low concentration of molecules is adsorbed on the surface at low temperature, so that the molecules are randomly distributed on the film surface. The conduction electrons in the metal scatter diffusively from the adsorbates resulting in an increase $\Delta\rho$ in the film resistivity. We now prove (1), relating $\Delta\rho$ to the lifetime τ of the parallel frustrated translation of the adsorbates due to excitation of *e-h* pairs. For simplicity, assume first that the parallel frustrated translation is double degenerate, i.e., the resonance frequency Ω and damping $1/\tau$ are independent of the direction of motion parallel to the surface. This is the case, for example, for CO bonding in the on-top or threefold symmetry sites on a (111) surface of a fcc crystal. Assume that the frustrated translation is excited along the $\hat{\mathbf{x}}$ direction. For the present purposes we can treat the vibration as a classical oscillation

$$\delta x = \delta x_0 \cos\Omega t \ ,$$

where

$$\delta x_0 = 2Q_0 = 2\left[\frac{\hbar}{2M\Omega}\right]^{1/2} . \tag{2}$$

This equation can be derived as follows. The quantized vibrational motion is characterized by the normal-mode coordinate

$$Q = Q_0(b + b^\dagger) \ ,$$

where b and $b^\dagger$ are the annihilation and creation operators of the vibration. If $\langle \cdots \rangle$ stands for averaging over time, then $\langle \delta x^2 \rangle = \delta x_0^2/2$. But quantum mechanically we must interpret $\langle \delta x^2 \rangle = \langle n=1|Q^2|n=1\rangle - \langle n=0|Q^2|n=0\rangle = 2Q_0^2$, from which (2) follows.

Let τ denote the lifetime of the frustrated translation due to excitation of *e-h* pairs. The energy transfer per unit time from the vibrational excited adsorbates to the *e-h* pair excitations in the metal is given by

$$P = n_a A \hbar\Omega/\tau \ , \tag{3}$$

where A is the surface area. Let us now change the reference frame to a new frame which is oscillating with the same amplitude and frequency as the adsorbates, i.e., $x' = x - \delta x_0 \cos\Omega t$, $y' = y$, $z' = z$ (see Fig. 1). In the new frame, the conduction electron sea is oscillating collectively with the frequency Ω and amplitude δx_0, while the adsorbates are stationary. The conduction-electron fluctuations give rise to a uniform current in the x direction

$$J = nev \ ,$$

where n is the density of conduction electrons and

$$v = \delta x_0 \Omega \sin\Omega t \ .$$

The conduction electrons will scatter against the adsorbates giving rise to Ohmic heating. The energy transfer per unit time is given by the standard formula

$$P = \langle \mathbf{J}\cdot\mathbf{E} \rangle Ad = \langle \mathbf{J}^2 \rangle Ad/\sigma = (ne\,\delta x_0\,\Omega)^2 Ad/2\sigma \ , \tag{4}$$

where σ is the conductivity at the frequency Ω which, however, is essentially identical to the dc conductivity owing to the low frequency Ω of frustrated translations (typically $\hbar\Omega \sim 5$ meV). From (3) and (4) we get

$$n_a \hbar\Omega/\tau = d(ne\,\delta x_0\,\Omega)^2/2\sigma \ ,$$

or using (2)

$$\frac{1}{\tau} = \frac{n^2 e^2 d}{M n_a \sigma} \ .$$

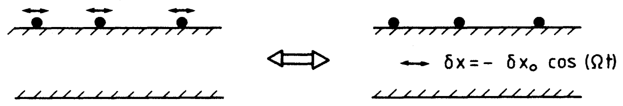

FIG. 1. The damping of the parallel frustrated translations in the adsorbates (left) can be related to the adsorbate-induced increase in film resistivity by a change of reference frame (right).

For low adsorbate coverage n_a the resistivity $\rho=1/\sigma$ is found[2] to vary linearly with n_a so that

$$\frac{1}{n_a\sigma}=\frac{\rho}{n_a}=\frac{\partial\rho}{\partial n_a}\bigg|_{n_a=0} .$$

Hence

$$\frac{1}{\tau}=\frac{n^2e^2}{M}d\frac{\partial\rho}{\partial n_a}\bigg|_{n_a=0} , \tag{5}$$

which is our fundamental result relating the vibrational lifetime τ to the slope of the initial increase in resistivity, $\partial\rho/\partial n_a$ ($n_a=0$). The derivation of (5) is based on three implicit assumptions.

(a) There is no physical principle that ensures that the physics in an accelerated (i.e., oscillating) reference frame is the same as in a nonaccelerating frame. However, in the present context such an equivalence seems to hold, presumably because ω is small and acceleration effects can be neglected. I note that frequency-dependent resistivities have been calculated earlier using this method and found to agree with calculations based on other methods.[11] In any case the result for the resistivity given by (5) can also be derived from a different approach which involves calculating the friction force on a uniformly (i.e., with constant velocity) moving adsorbate and then change the reference frame to a system where the adsorbate is fixed. This involves a Galilean transformation that leaves the (nonrelativistic) equations of motion invariant.

(b) The electric current **J** has been assumed to be uniform (i.e., **x** independent), which is necessary in order to eliminate it in the transformed reference frame. This condition is never strictly satisfied, but it has been shown by Cottley[12] that in the limit of a low concentration of surface scattering centers (i.e., $n_a\rightarrow 0$) this is a very accurate assumption (the surface-induced changes in the film resistivity is in error by a few percent or less).

(c) Equation (5) is valid only for a "pure" frustrated translation where the absorbate is assumed to vibrate as a rigid object parallel to a rigid substrate without changing its height above the surface or its angular orientation relative to the surface. This condition is never strictly satisfied for any adsorbate system, although it should be a very accurate assumption in many cases, e.g., for light atomic adsorbates such as H. In other cases, e.g., for adsorbed CO, it is not a good approximation,[13] but if the displacement pattern for the frustrated translation is known, it may be possible to estimate the actual electron-hole pair damping rate from the τ value deduced from the resistivity according to (5).

Let us now discuss how (5) can be generalized to the case of two nondegenerate frustrated translations. This occurs, for example, for CO in bridge binding sites on Ni(111). Since the (111) surface of fcc crystals is the most closely packed and energetically stable, it is expected (and found experimentally) that the surface of an annealed Ni film is (111). On this surface, at low CO coverage, the CO molecules can occupy three nonequivalent bridge sites as indicated in Fig. 2, and all these sites will be occupied with equal probability.[14] Hence the resistivity tensor can be written as

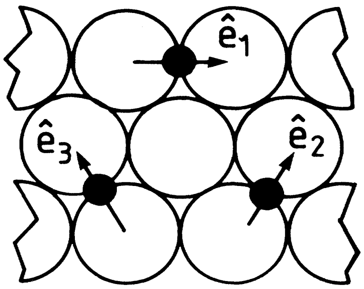

FIG. 2. Three nonequivalent bridge binding sites on a (111) surface of a fcc crystal.

$$\hat{\rho}=\hat{\rho}_1+\hat{\rho}_2+\hat{\rho}_3 ,$$

where the contributions to the resistivity from the molecules occupying sites 1 is

$$\hat{\rho}_1=\begin{bmatrix}\rho_x & 0\\ 0 & \rho_y\end{bmatrix} ,$$

where we have introduced a coordinate system (x,y) in which $\hat{\rho}_1$ is diagonal. The resistivity tensors $\hat{\rho}_2$ and $\hat{\rho}_3$ associated with binding sites 2 and 3 can be obtained from $\hat{\rho}_1$ by unitary transformations corresponding to 60° and 120° rotations, respectively, giving

$$\hat{\rho}_2=U^{\dagger}(60^\circ)\hat{\rho}_1U(60^\circ)$$
$$=\begin{bmatrix}\frac{1}{4}(\rho_x+3\rho_y) & \frac{\sqrt{3}}{4}(\rho_x-\rho_y)\\ \frac{\sqrt{3}}{4}(\rho_x-\rho_y) & \frac{1}{4}(\rho_x+3\rho_y)\end{bmatrix}$$

and

$$\hat{\rho}_3=\begin{bmatrix}\frac{1}{4}(\rho_x+3\rho_y) & -\frac{\sqrt{3}}{4}(\rho_x-\rho_y)\\ -\frac{\sqrt{3}}{4}(\rho_x-\rho_y) & \frac{1}{4}(\rho_x+3\rho_y)\end{bmatrix} .$$

Hence

$$\hat{\rho}=\frac{3}{2}\begin{bmatrix}\rho_x+\rho_y & 0\\ 0 & \rho_x+\rho_y\end{bmatrix} ,$$

i.e., $\hat{\rho}$ is isotropic with the diagonal components

$$\rho=\frac{M}{n^2e^2}\frac{n_a}{d}\frac{1}{2}\left[\frac{1}{\tau_x}+\frac{1}{\tau_y}\right] , \tag{6}$$

where $1/\tau_x$ and $1/\tau_y$ are the *e-h* pair damping rates of the two nondegenerate frustrated translations. In a similar way, the relation between resistivity and damping rates can be worked out for any other case of interest. In general, we write

$$\rho=\frac{M}{n^2e^2}\frac{n_a}{d\tau} ,$$

where $1/\tau$ is the appropriate average of the damping rates, e.g., $2/\tau = 1/\tau_x + 1/\tau_y$ for CO occupying bridge sites on a (111) surface of a fcc crystal. For CO adsorption at on-top sites, or at threefold (hollow) symmetry sites, a double degenerate vibrational level occurs characterized by a single resonance frequency Ω and damping $1/\tau$.

Let us now use (5) to deduce τ for some different adsorbate-substrate systems. Figure 3(a) shows the change in resistivity[15] $\Delta\rho$ as a function of CO coverage for the CO/Ni chemisorption system. For low CO coverage ($n_a \lesssim 0.04$ Å^{-2}), $\Delta\rho$ increases linearly with n_a. According to (5), $\partial\rho/\partial n_a \sim 1/d$ if we assume that τ is independent of d as expected if the film is thick enough. This relation is well satisfied for the CO-Ni chemisorption system[15] as shown in Fig. 3(b) where the straight line has the slope -1 as expected for a logarithmic plot, $\ln\partial\rho/\partial n_a \sim -\ln d$. From Fig. 3(b) we get

$$d\frac{\partial\rho}{\partial n_a}\bigg|_{n_a=0} \approx 2000\ \mu\Omega\,\mathrm{cm}\,\text{Å}^3\ ,$$

and using $M = 28u$ (the CO mass) and $n = 8.47\times10^{-2}$ Å^{-3} gives $\tau = 1.4\times10^{-11}$ s.

In Table I, I have summarized the results of the *e-h* pair lifetimes for the parallel frustrated translations for several different chemisorption and physisorption systems. In all cases, I have assumed that the free-electron density n corresponds to one electron per substrate metal atom and that the effective mass m is identical to the free-electron mass. These assumptions are reasonable for Ag and Cu, but are not so accurate for Ni. In Table I, I also give the effective cross section Σ for diffusive electron scattering against an adsorbate, defined by

$$\Sigma = \frac{16}{3}\frac{ne^2d}{mv_F}\frac{\partial\rho}{\partial n_a}\bigg|_{n_a=0}\ . \tag{7}$$

TABLE I. The lifetime τ (due to excitation of electron-hole pairs) of the parallel frustrated translation for several adsorption systems. The cross section Σ is defined in the text.

System	$d\frac{\partial Q}{\partial n_a}$ ($\mu\Omega$ cm Å^3)	τ (s)	Σ (Å^2)
	Chemisorption		
H/Ni[a]	1000	9.9×10^{-13}	8.2
CO/Ni[a]	2000	1.4×10^{-11}	16.0
N_2/Ni[a]	600	4.6×10^{-11}	4.8
CO/Cu[a]	700	3.9×10^{-11}	5.8
O/Cu[b]	2300	6.9×10^{-12}	18.8
Ag/Ag[c]	2170	1.0×10^{-10}	13.4
	Physisorption		
CO/Ag[d]	160	3.6×10^{-10}	1.0
C_2H_4/Ag[d]	80	7.2×10^{-10}	0.5
Xe/Ag[e]	~100	$\sim3\times10^{-9}$	~0.6
C_6H_6/Ag[e]	110	1.4×10^{-9}	0.6
C_6H_{12}/Ag[e]	100	1.7×10^{-9}	0.6
C_2H_6/Ag[e]	20	3.6×10^{-9}	0.1

[a] Data taken from Ref. 2.
[b] Data taken from Ref. 1.
[c] Data taken from Ref. 43.
[d] Data taken from Ref. 44.
[e] Data taken from Ref. 10.

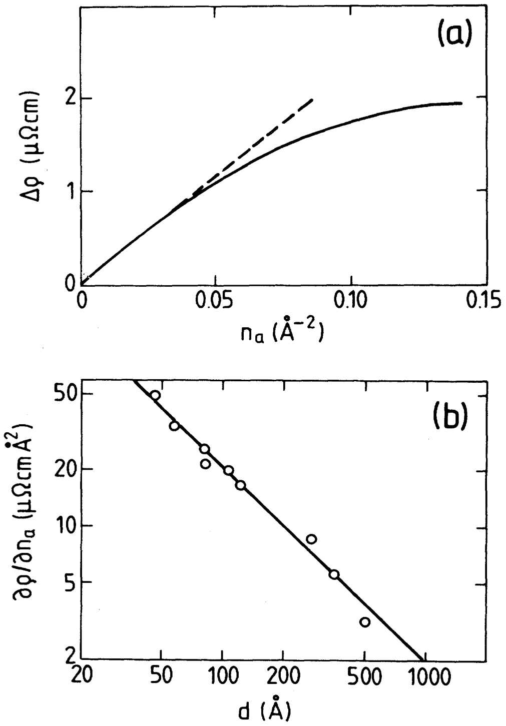

FIG. 3. (a) The change in film resistivity $\Delta\rho$ as a function of CO coverage for the CO/Ni(111) chemisorption system. (b) The variation of $\partial\rho/\partial n_a$ ($n_a \rightarrow 0$) with the film thickness d. The straight line has the slope -1. From Ref. 2.

(Owing to uncertainty in the Ag film thickness, the experimental data quoted in Table I for Xe on Ag are uncertain to within a factor of ~3.) As expected, for physisorbed atoms and molecules, the damping rates $1/\tau$ are smaller by a factor of $\sim 10^{-2}-10^{-3}$ than for chemisorbed adsorbates. Note that physisorbed molecules have almost identical internal vibrational frequencies as the corresponding gas-phase molecules, while for chemisorbed molecules large frequency shift usually occur. As an example, CO on Ag has[16] a C-O stretch frequency (2143 cm^{-1}) which agrees to within ~1 cm^{-1} with the gas-phase value (2144 cm^{-1}), while for CO on Ni(111) the resonance frequency is shifted by[14] ~300 cm^{-1} to lower frequencies.

The τ values given in Table I are the energy relaxation times due to excitation of *e-h* pairs. However, these lifetimes do not necessarily agree with the energy relaxation times *observed* directly using, e.g., ir-spectroscopy[4] or inelastic helium scattering[7,8] since other, competing energy relaxation processes occur, such as decay via emission of one or several bulk phonons. However, I expect the *e-h* pair channel to dominate in two limiting cases, namely the following.

(a) *For high-frequency modes*: If the resonance frequency $\Omega > \omega_c$, where $\omega_c \sim 200-300\ \mathrm{cm}^{-1}$ is the highest bulk phonon frequency, then decay via phonon emission requires a miltiphonon process in order to conserve the energy. But the damping rate via multiphonon emission decreases very quickly as Ω/ω_c increases and is probably negligible for $\Omega \gtrsim 2\omega_c$. High-frequency frustrated translations are observed for adsorbed H owing to its small mass. For example, for H on W(100), $\Omega = 1272\ \mathrm{cm}^{-1}$, and decay via multiphonon emission should be negligible compared with decay via excitation of *e-h* pairs. Indeed, from the observed ir linewidth one can deduce[17] $\hbar/\tau = 13\ \mathrm{cm}^{-1}$ for H on W(100) and $\hbar/\tau = 6\ \mathrm{cm}^{-1}$ for H on Mo(100), which compare favorably with the damping rates deduced from the dc resistivity change $\Delta\rho$ for Ni(100) (see Table I), $\hbar/\tau \approx 5\ \mathrm{cm}^{-1}$.

(b) *For low-frequency modes*: For $\Omega < \omega_c$, the frustrated translation can decay via emission of a single phonon, but this process is very ineffective for $\Omega \ll \omega_c$ since the damping rate[18]

$$\frac{1}{\tau} \approx \frac{3}{8\pi} \frac{M}{\rho} \left[\frac{\Omega}{c_T} \right]^3 \Omega \ , \tag{8}$$

where ρ now stands for the density and c_T is the transverse sound velocity. Hence $1/\tau \sim \Omega^4$, while decay via excitation of *e-h* pairs gives a damping rate $1/\tau \sim Q_0^2 \Omega$ and since $Q_0^2 \sim 1/\Omega$, $1/\tau$ is independent of Ω in this case. Hence, for small enough Ω, *e-h* pair damping will always dominate. For example, for CO in the on-top positions on Ni(100), the parallel frustrated translation has been studied using inelastic helium scattering[8] and $\Omega = 24\ \mathrm{cm}^{-1}$. Using (8) gives in this case $\hbar/\tau(\text{phonon}) \approx 0.05\ \mathrm{cm}^{-1}$, which should be compared with damping via excitation of *e-h* pairs as deduced from the change in dc resistivity (see Table I) $\hbar/\tau(e\text{-}h\ \text{pair}) = 0.36\ \mathrm{cm}^{-1}$. Obviously, in this case the *e-h* pair damping mechanism is much more effective than phonon emission. I expect this to hold also for most "physisorption" systems since such systems are expected to have extremely low-frequency parallel frustrated translations.

III. SIMPLE THEORIES FOR THE DAMPING OF PARALLEL FRUSTRATED TRANSLATIONS

In Sec. II, I derived an equation relating the lifetime τ to the adsorbate-induced increase in film resistivity $\Delta\rho$. In this section, I present a theoretical study of the *e-h* pair damping $1/\tau$ of frustrated translations. I consider three limiting models for the adsorbate bond, namely (A) covalent bond, (B) ionic bond, and (C) van der Waals bond.

A. Covalent bond

We consider a Newns-Anderson type of model of chemisorption. In the simplest case, the adsorbate is characterized by a single orbital $|a\rangle$, which hybridize with the metal orbitals $|k\rangle$:

$$H = \varepsilon_a c_a^\dagger c_a + \sum_k \varepsilon_k c_k^\dagger c_k + \sum_k (V_{ak} c_a^\dagger c_k + \mathrm{H.c.}) + \Omega b^\dagger b \ .$$

Here b and $b^\dagger$ are the annihilation and creation operators of the frustrated translation treated as a harmonic oscillator. The matrix element V_{ak} depends on the normal-model coordinate $\mathbf{Q}$ of the frustrated translation:

$$V_{ak} = V_{ak}(\mathbf{Q}) = \int d^3x\ \psi_a^*(\mathbf{x}-\mathbf{Q}) V(\mathbf{x}-\mathbf{Q}) \psi_k(\mathbf{x}) \ ,$$

$$V_{ak} = \int d^3x\ \psi_a^*(\mathbf{x}) V(\mathbf{x}) \psi_k(\mathbf{x}+\mathbf{Q}) \ .$$

We will estimate this matrix element using the jellium model where

$$\psi_k(\mathbf{x}) = A_k(z) e^{i\mathbf{k}_\parallel \cdot \mathbf{x}_\parallel} \ ,$$

so that

$$V_{ak}(\mathbf{Q}) = V_{ak}(0) e^{i\mathbf{k}_\parallel \cdot \mathbf{Q}} \approx V_{ak}(0)(1 + i\mathbf{k}_\parallel \cdot \mathbf{Q}) \ ,$$

where I have used that $k_\parallel Q \ll 1$ since (see below) $k_\parallel \leq k_F \sim 1\ \text{Å}^{-1}$ while $Q \sim 0.1\ \text{Å}$. We write

$$H = H_0 + H' \ ,$$

where

$$H' = \sum_k V_{ak}(0) i \mathbf{k}_\parallel \cdot \mathbf{Q} c_a^\dagger c_k + \mathrm{H.c.}$$

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

$$H_0 = \sum_\alpha \varepsilon_\alpha c_\alpha^\dagger c_\alpha + \Omega b^\dagger b \ .$$

In the new basis

$$H' = \sum_{k,\alpha,\beta} V_{ak} i \mathbf{k}_\parallel \cdot \mathbf{Q} \langle \beta | a \rangle \langle k | \alpha \rangle c_\beta^\dagger c_\alpha + \mathrm{H.c.}$$

Let us take $\mathbf{Q}$ to be along the x axis, i.e.,

$$\mathbf{Q} = Q_0 \hat{\mathbf{x}} (b + b^\dagger) \ .$$

Hence we can write

$$H' = \sum_{\alpha,\beta} V_{\alpha\beta} (b + b^\dagger) c_\beta^\dagger c_\alpha \ , \tag{9}$$

where

$$V_{\alpha\beta} = \sum_k i k_x Q_0 (V_{ak} \langle \beta | a \rangle \langle k | \alpha \rangle - V_{ak}^* \langle \beta | k \rangle \langle a | \alpha \rangle) \ . \tag{10}$$

Using Fermi's golden rule formula with H' as the perturbation, we can now calculate the rate $1/\tau$ for the vibrational excited molecule $(n = 1)$ to decay to its vibrational ground state $(n = 0)$ while exciting an electron from an orbital $|\alpha\rangle$ below the Fermi energy $(\varepsilon_\alpha < \varepsilon_F)$ to an orbital $|\beta\rangle$ above the Fermi energy:

$$\frac{1}{\tau}=\frac{2\pi}{\hbar}2\sum_{\alpha,\beta}f(\varepsilon_\alpha)[1-f(\varepsilon_\beta)]\delta(\varepsilon_\beta-\varepsilon_\alpha-\Omega)|\langle\beta,n=0|H'|\alpha,n=1\rangle|^2$$
$$=\frac{4\pi}{\hbar}\int_{\varepsilon_F-\Omega}^{\varepsilon_F}d\varepsilon\sum_{\alpha,\beta}\delta(\varepsilon-\varepsilon_\alpha)\delta(\varepsilon+\Omega-\varepsilon_\beta)|\langle\beta,n=0|H'|\alpha,n=1\rangle|^2$$
$$\approx 4\pi\Omega\sum_{\alpha,\beta}\delta(\varepsilon_F-\varepsilon_\alpha)\delta(\varepsilon_F-\varepsilon_\beta)|\langle\beta,n=0|H'|\alpha,n=1\rangle|^2 \ . \tag{11}$$

The extra factor of 2 in these equations arises from sum over spin. In the second equality, we have assumed zero temperature so that the Fermi-Dirac distribution function $f(\varepsilon)$ reduces to the step function $\Theta(\varepsilon_F-\varepsilon)$. Substituting (9) into (11) gives

$$w=4\pi\Omega Q_0^2\sum_{\alpha,\beta}\delta(\varepsilon_F-\varepsilon_\alpha)\delta(\varepsilon_F-\varepsilon_\beta)\times\left|\sum_k k_x(V_{ak}\langle\beta|a\rangle\langle k|\alpha\rangle-V_{ak}^*\langle\beta|k\rangle\langle a|\alpha\rangle)\right|^2 . \tag{12}$$

Substituting

$$Q_0^2=\frac{\hbar}{2M\Omega}$$

and expanding the absolute square in (12) gives

$$w=\frac{4\pi\hbar}{M}\sum_{k,k'}k_xk_x'[V_{ak}V_{ak'}^*\langle a|\delta(\varepsilon_F-H_0)|a\rangle\times\langle k|\delta(\varepsilon_F-H_0)|k'\rangle-\mathrm{Re}V_{ak}V_{ak'}\langle k|\delta(\varepsilon_F-H_0)|a\rangle\times\langle k'|\delta(\varepsilon_F-H_0)|a\rangle] . \tag{13}$$

To simplify this formula we use[19] that for $\mathbf{k}\neq\mathbf{k}'$,

$$\langle k|\delta(\varepsilon_F-H_0)|k'\rangle=V_{ka}V_{ak'}F$$

and

$$\langle k|\delta(\varepsilon_F-H_0)|a\rangle=V_{ka}G \ ,$$

where F and G are unchanged as $\mathbf{k}_\parallel\to-\mathbf{k}_\parallel$. Since $|V_{ak}|^2$ is unchanged as $\mathbf{k}_\parallel\to-\mathbf{k}_\parallel$, it follows that the $\mathbf{k}\neq\mathbf{k}'$ term in (13) vanishes. Hence we can put $\mathbf{k}=\mathbf{k}'$ in the sum over $\mathbf{k}$ and $\underline{\mathbf{k}}'$ in (13). But since $V_{ak}\sim1/\sqrt{\mathcal{V}}$ and $\langle a|k\rangle\sim1/\sqrt{\mathcal{V}}$, where $\mathcal{V}$ is the volume of the crystal, we can drop the second term in [ ] in (13) since this is of order $(1/\mathcal{V})^2$ and vanishes as $\mathcal{V}\to\infty$. Similarly, one has

$$\langle k|\delta(\varepsilon_F-H_0)|k\rangle=\delta(\varepsilon_F-\varepsilon_k)+O(1/\sqrt{\mathcal{V}})$$

so that in the limit $\mathcal{V}\to\infty$, (13) reduces to

$$w=\frac{4\pi\hbar}{M}\sum_k k_x^2|V_{ak}|^2\langle a|\delta(\varepsilon_F-H_0)|a\rangle\delta(\varepsilon_F-\varepsilon_k) . \tag{14}$$

But

$$\langle a|\delta(\varepsilon_F-H_0)|a\rangle=\rho_a(\varepsilon_F)=\frac{1}{\pi}\frac{\Gamma/2}{(\bar{\varepsilon}_a-\varepsilon_F)^2+(\Gamma/2)^2} ,$$

where $\rho_a(\varepsilon)$ is the adsorbate induced density of states taken as a Lorentzian centered at $\bar{\varepsilon}_a$ and with the width

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

Hence (14) takes the form

$$w=\frac{\hbar}{M}\langle k_\parallel^2\rangle\Gamma(\varepsilon_F)\rho_a(\varepsilon_F) , \tag{15}$$

where

$$\langle k_\parallel^2\rangle=\frac{\sum_k k_\parallel^2|V_{ak}|^2\delta(\varepsilon_F-\varepsilon_k)}{\sum_k|V_{ak}|^2\delta(\varepsilon_F-\varepsilon_k)} .$$

We introduce polar coordinates in $\mathbf{k}$ space and write $k_\parallel=k_F\sin\theta$ so that $\langle k_\parallel^2\rangle=k_F^2\langle\sin^2\theta\rangle$. Equation (15) can now be written as

$$w=2\frac{m}{M}\omega_F\Gamma(\varepsilon_F)\rho_a(\varepsilon_F)\langle\sin^2\theta\rangle , \tag{16}$$

where $\hbar\omega_F=\varepsilon_F$ is the Fermi energy. I have evaluated $\langle\sin^2\theta\rangle$ assuming that $V_{ak}\sim\langle a|k\rangle$ where the metal wave function $\langle\mathbf{x}|k\rangle$ has been taken from the finite barrier model and where the orbital $\langle\mathbf{x}|a\rangle$ has been taken as an s orbital of the form $\sim\exp(-\alpha r)$ or as a p_x (or p_y) orbital of the form $\sim x\exp(-\alpha r)$ where the radial decay constant α is determined by the work function ϕ of the metal substrate via $\hbar^2\alpha^2/2m=\phi$ (note: we are primarily interested in resonance states located close to E_F, which have a radial decay constant roughly determined by the work function). Note that in polar $\mathbf{k}$ coordinates, we can write

$$\langle\sin^2\theta\rangle=\frac{\int_0^{\pi/2}d\theta\sin^3\theta G(\theta)}{\int_0^{\pi/2}d\theta\sin\theta G(\theta)} ,$$

where

$$G(\theta)=\int_0^{2\pi}d\varphi|V_{ak}|^2\delta(\varepsilon_F-\varepsilon_k) .$$

In Fig. 4 I show the result for $\langle\sin^2\theta\rangle$, as a function of the separation z_0 between the center of the adatom orbital (s, p_x, or p_y) and the step edge of the finite barrier. Results are presented for $\phi/E_F=0.64$, 0.81, and 1.0. Note that $\langle\sin^2\theta\rangle$ is roughly a factor 1.6 larger for an adatom orbital of p_x (or p_y) symmetry, as compared with an s orbital. This has a simple explanation: An s orbital interacts most strongly with metal electrons that propagate normally or almost normally to the metal surface, since these electrons penetrate deepest into the vacuum and

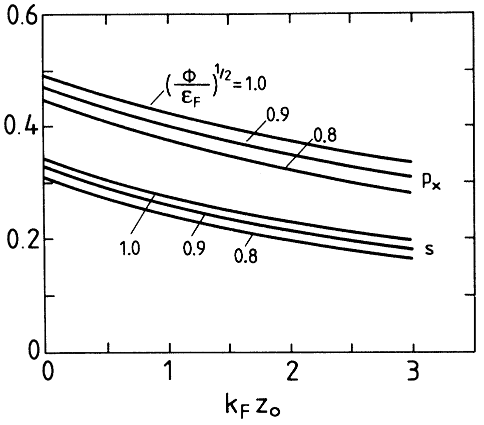

FIG. 4. The quantity $\langle \sin^2\theta \rangle$ as a function of the separation z_0 between the step edge and the center of the adatomic orbital $|a\rangle$ for orbitals of s and p_x symmetry. ϕ is the work function and E_F the Fermi energy.

have therefore a large overlap with the s orbital of the adatom, and also because an s orbital and a metal wave function at normal evidence are both even, i.e., unchanged as $x \rightarrow -x$. Metal electrons with a finite parallel momentum extend less into the vacuum and change sign parallel to the surface both of which reduce the overlap integral $\langle s|k\rangle$. This is illustrated in Fig. 5, which shows $G(\theta)$ as a function of the angle θ between the electron momentum vector and the surface normal. As expected, for an s orbital $G(\theta)$ is maximal for $\theta=0$ but decreases monotonically towards zero as $\theta \rightarrow \pi/2$. In the same figure I show $G(\theta)$ for a p_x (or p_y) orbital. In this case $G(\theta)$ is maximal at a nonzero angle $\theta \approx 30°$, while it vanishes at normal incidence. The reason that $G \rightarrow 0$ as $\theta \rightarrow 0$ is due to the fact that a p_x orbital is odd, i.e., changes sign as $x \rightarrow -x$, while the wave function of a metal electron at normal incidence is invariant under this transformation. From the general structure of $G(\theta)$ (see Fig. 5) it follows at once that $\langle \sin^2\theta \rangle$ is larger for a p_x orbital than for an s orbital.

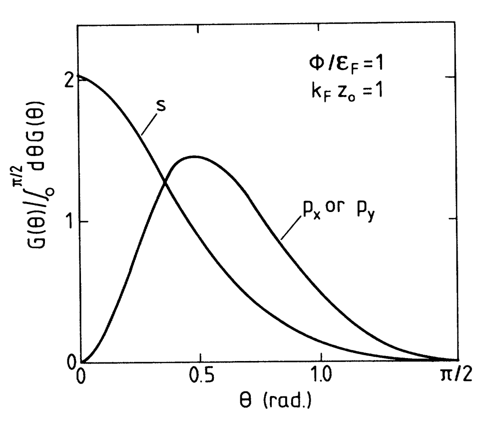

FIG. 5. The quantity $G(\theta) \sim |\langle a|k\rangle|^2$ as a function of the angle θ between the momentum vector **k** and the surface normal. Results are presented for both s and p_x orbitals with $k_F z_0 = 1.0$ and $\phi = E_F$.

Let us now illustrate (16) with a few applications.

Consider first an Ag atom on an Ag(111) surface. The highest occupied levels in atomic Ag are the $4d$ and $5s$ levels. The $4d$ levels are deep (at -19.2 eV according to Hartree-Fock calculations for atomic Ag) and will give rise to a sharp structure close to the bottom of the Ag conduction band or a split-off state below the conduction band. In any case, negligible density of states is induced in the vicinity of E_F. Using the measured change of the work function change when Ag atoms are adsorbed on an Ag(111) surface at low temperature, one can estimate the Ag-adatom–to–metal-charge transfer to be at most $0.04e$. Hence the Ag atom is essentially neutral, as is indeed expected from simple physical arguments. But this implies that the Ag $5s$ level must form a nearly half-filled resonance state centered at, or close to, E_F. (We assume a nonmagnetic state.) Accounting for both spin directions, a half-filled resonance contains one electron so that no net charge transfer has occurred. Now, let us estimate the change in resistivity expected in this case and compare it with the data presented in Table I. Let us focus on the cross section Σ for diffuse scattering of a conduction electron from an adsorbed Ag atom. Using (1) and (7) we can write

$$\Sigma = \frac{16}{3}\frac{M}{mnv_F\tau} ,$$

and combining this with (16) gives

$$\Sigma = \frac{32}{3}\frac{\omega_F}{v_F}\frac{\langle \sin^2\theta \rangle}{n}\Gamma\rho_a(\varepsilon_F) .$$

But in the present case $\tilde{\varepsilon}_a \approx \varepsilon_F$, so that $\Gamma\rho_a(\varepsilon_F) \approx 2/\pi$ and hence

$$\Sigma \approx \frac{64}{3\pi}\frac{\omega_F}{v_F}\frac{\langle \sin^2\theta \rangle}{n} .$$

For Ag, $\hbar\omega_F = 5.53$ eV, $v_F = 1.4 \times 10^6$ m/s, $n = 0.0586$ Å^{-3}, and $\langle \sin^2\theta \rangle = 0.2$ (from Fig. 4 with $k_F z_0 = 2.7$) so that $\Sigma \approx 14.6$ Å^2, in very good agreement with the experimental cross section (13.4 Å^2) quoted in Table I.

Next, let us consider CO adsorbed on Cu(111) where the $2\pi^*$ resonance has been studied using inverse photoemission. The $2\pi^*$ resonance is centered at $\tilde{\varepsilon}_a - \varepsilon_F = 2.5$ eV and has the width full width at half maximum $\Gamma = 1.5$ eV. Hence ($a = 2\pi^*$)

$$\rho_a(\varepsilon_F) \approx \frac{1}{\pi}\frac{\Gamma/2}{(\tilde{\varepsilon}_a - \varepsilon_F)^2 + (\Gamma/2)^2} \approx 0.035 \text{ eV}^{-1} .$$

Using $\langle \sin^2\theta \rangle = 0.33$ from Fig. 4, and accounting for both $2\pi_x^*$ and $2\pi_y^*$, we get from (16) $\tau \approx 7 \times 10^{-11}$ s in relatively good agreement with the lifetime deduced from the resistivity data for CO on Cu films $\tau \approx 4 \times 10^{-11}$ s (see Table I).

It is also interesting to compare C_2H_4 and C_2H_6, which both physisorb on Ag(111) with almost identical binding energy. Nevertheless, the e-h pair damping rate and the cross section Σ is about a factor of 5 larger for C_2H_4 than for C_2H_6, which can be related to the existence of a low-lying electronic state in the former molecule (centered at about 4 eV above the Fermi energy but with a tail extending to E_F) and the absence of such a state in the latter molecule.

The adsorbate-induced resonance level model predicts that if several partly filled resonance states of different symmetry occur, e.g., derived from atomic p_x, p_y, and p_z orbitals, they contribute independently and hence *additively* to the adsorbate-induced change in the resistivity. This rule seems to be obeyed for the sequence of atoms Tl, Pb, and Bi on Au(111) as will be discussed elsewhere. Furthermore, comparison of the experimental resistivity data for the same sequence of atoms dissolved in Au with those of adsorbed atoms indicates a profound difference between these two cases, reflecting the difference in the electronic structure between adsorbed metal atoms and the corresponding dissolved atoms. This will be discussed in detail in a forthcoming publication.

B. Ionic bond

In some chemisorption systems at low adsorbate coverage, the adatoms become strongly charged. For example, alkali-metal atoms on transition or noble metals give a strong reduction in the work function indicating a large charge transfer from the alkali-metal atom to the noble metal. If e^* denotes the net adatom charge, then typically $e^* \approx (0.5-0.8)|e|$ (where e is the electron charge) for alkali-metal atoms. Similarly, metal atoms on the *same* metal substrate are partly ionized. For example, from the work function change when a low concentration of Ni atoms are adsorbed on a Ni(100) surface, one can deduce the dipole moment[20] $p \approx 0.1e$ Å associated with an isolated adsorbed Ni atom. Since the separation between the image plane and the nuclei of the Ni adatoms is very small, this dipole moment implies a large charge transfer or a strongly polar adsorption bond.

We now estimate the damping of the parallel frustrated translation for a charged adatom using the jellium model for the metal. We treat the adatom as a point charge of magnitude e^* oscillating parallel to the metal surface with the frequency Ω. The Hamiltonian for the system is taken to be[21]

$$\begin{aligned} H &= H_0 + H' , \\ H_0 &= \Omega b^\dagger b + \sum_{q,\alpha} \varepsilon_{q\alpha} b_{q\alpha}^\dagger b_{q\alpha} , \\ H' &= \sum_{q,\alpha} C_{q,\alpha} e^{-qz_0} (b_{q\alpha} e^{i\mathbf{q}\cdot\mathbf{Q}} + \text{H.c.}) . \end{aligned} \tag{17}$$

Here b and $b^\dagger$ are the annihilation and creation operators for the adsorbate frustrated translation, and $b_{q\alpha}$ and $b_{q\alpha}^\dagger$ the annihilation and creation operators for the substrate *e-h* pair excitations, treated as bosons. The coordinate z_0 denotes the height of the point charge above the metal surface, and $\mathbf{Q} = Q_0 \hat{\mathbf{x}} (b + b^\dagger)$ denotes the normal-model coordinate of the frustrated translation. In (17), $\mathbf{q}$ is a two-dimensional wave vector and α is an additional quantum number necessary for a complete specification of the *e-h* pair excitations. The energy parameters $C_{q\alpha}$ can be related to the surface response function $g(q,\omega)$ via[21]

$$\sum_{\alpha} |C_{q\alpha}|^2 \delta(\omega - \omega_{q\alpha}) = \frac{2e^{*2}\hbar}{Aq} \operatorname{Im} g(q,\omega) . \tag{18}$$

Since $k_F Q \ll 1$, we can expand

$$e^{i\mathbf{q}\cdot\mathbf{Q}} \approx 1 + i\mathbf{q}\cdot\mathbf{Q} .$$

Substituting this into (17) gives

$$\begin{aligned} H' &= \sum_{q,\alpha} C_{q\alpha} e^{-qz_0} (b_{q\alpha} + b_{q\alpha}^\dagger) + V , \\ V &= \sum_{q,\alpha} C_{q\alpha} e^{-qz_0} i q_x Q_0 (b_{q\alpha} - b_{q\alpha}^\dagger)(b + b^\dagger) . \end{aligned} \tag{19}$$

The first term in (19) gives rise to a static polarization of the metal and corresponds to the image charge.[21] The second term in H' allows for the excited oscillator $(n=1)$ to decay to its vibrational ground state $(n=0)$ by exciting an *e-h* pair. The decay rate is obtained using Fermi's golden rule:

$$\frac{1}{\tau} = \frac{2\pi}{\hbar^2} \sum_{q,\alpha} |C_{q\alpha}|^2 e^{-2qz_0} Q_0^2 q_x^2 \delta(\omega_{q\alpha} - \Omega) .$$

Using (18), this gives

$$\begin{aligned} \frac{1}{\tau} &= \frac{2\pi}{\hbar} (e^* Q_0)^2 \frac{1}{A} \sum_{q} q e^{-2qz_0} \operatorname{Im} g(q,\Omega) \\ &\rightarrow (e^* Q_0)^2 \frac{1}{2\pi\hbar} \int d^2q \, q e^{-2qz_0} \operatorname{Im} g(q,\Omega) \\ &= \frac{e^{*2}}{2M\Omega} \int dq \, q^2 e^{-2qz_0} \operatorname{Im} g(q,\Omega) , \end{aligned} \tag{20}$$

where we have substituted $Q_0^2 = \hbar / 2M\Omega$. Next, for small Ω (i.e., $\Omega \ll \omega_p$),[22]

$$\operatorname{Im} g = 2\Omega q \xi(q) / k_F \omega_p .$$

Substituting this into (20) gives

$$\frac{1}{\tau} = \frac{e^{*2}}{M k_F \omega_p} \int dq \, q^3 \xi(q) e^{-2qz_0} .$$

The function $\xi(q)$ has been calculated using the time-dependent local-density approximation[23] as a function of q and for several electron-gas densities ($r_s = 2$, 3, and 4). Let us introduce

$$C(z_0) = \frac{\int dq \, q^3 \xi(q) e^{-2qz_0}}{\int dq \, q^3 \xi(0) e^{-2qz_0}}$$

so that

$$\begin{aligned} \frac{1}{\tau} &= \frac{3}{8} \frac{e^{*2}}{M k_F \omega_p} \frac{\xi(0)}{(z_0 - z_{\text{im}})^4} C(z_0 - z_{\text{im}}) \\ &\approx (4.7 \times 10^{15} \text{ s}^{-1}) \times \frac{m}{M} \left[\frac{e^*}{e} \right]^2 \left[\frac{r_s}{a_0} \right]^{5/2} \\ &\quad \times \frac{\xi(0) a_0^4}{(z_0 - z_{\text{im}})^4} C(z_0 - z_{\text{im}}) , \end{aligned} \tag{21}$$

where $\xi(0)$ and $C(z_0-z_{\text{im}})$ are tabulated in Ref. 23.

As an application of (21), consider potassium at low coverage on Cu(100). The distance $d=z_0-z_{\text{im}}$ between the K nucleus and the image plane can be deduced[24] from electronic-structure calculations to be $d\approx 1.9$ Å. From the measured change in work function[25] the dipole moment $p\approx e^*d$ and hence e^* can be deduced; one finds $e^*\approx 0.88|e|$. Since for Cu $r_s\approx 2.67a_0$, $\xi(0)\approx 0.5$, and $C(d)\approx 0.23$, we get

$$\tau\approx 2.7\times 10^{-9}\ \text{s}\ .$$

This is a rather long energy relation time which indicates that the ion model may not give the dominant contribution to the *e-h* pair damping of the frustrated translation. Indeed, I will now show that the "covalent" bond model gives a much stronger damping. When K is absorbed on Cu(100), the K 4*s* level broadens into a resonance. The study presented in Ref. 25 indicates that at low K coverage, this resonance is located about $\bar{\varepsilon}_a-\varepsilon_F\approx 2.4$ eV above the Fermi energy with a width $\Gamma\approx 1$ eV so that

$$\rho_a(\varepsilon_F)=\frac{1}{\pi}\frac{\Gamma/2}{(\bar{\varepsilon}_a-\varepsilon_F)^2+(\Gamma/2)^2}\approx 0.03\ \text{eV}^{-1}\ .$$

Hence using (16) with $M=39u$, $\varepsilon_F=7$ eV, and $\langle\sin^2\theta\rangle=0.17$ gives

$$\tau=7\times 10^{-10}\ \text{s}\ ,$$

which is a factor of $\sim\frac{1}{4}$ shorter lifetime than the prediction of the ion-bond model.

C. van der Waals bond

Some "inert" (closed-shell) atoms and molecules adsorb mainly via the weak van der Waals force. Typical examples are noble-gas atoms on *all* metal surfaces and many molecules, e.g., CH_4 and C_2H_6, on silver. The van der Waals bond results from an attraction due to the interaction between fluctuating charge distributions (virtual transitions) in the adsorbate and the resulting screening charges induced in the metal, and a short-ranged repulsion (Pauli repulsion).[26] Here, we will assume that the damping of the frustrated translation is due mainly to the short-ranged repulsive interaction. We will treat the adsorbate as a "hard" sphere of radius R, i.e., we assume that the metal electrons are excluded from the volume of the sphere. The wave functions ψ of the metal electrons must therefore satisfy $\psi=0$ on the surface of the sphere. The hard-core radius R for the noble-gas atoms has been chosen as half the nearest-neighbor distance in the fcc crystal structures observed at low temperature. As an example, for Xe this gives $R=2.19$ Å. That this radius gives a good estimate of the hard-sphere radius for Xe, in its interaction with metal electrons, is shown in Fig. 6, which illustrates the results of an electronic-structure calculation of Lang[27] for Xe on a semi-infinite jellium ($r_s=2$) at distances of 2.12 and 2.65 Å from the jellium edge. The dotted area denotes the hard-sphere region with radius $R=2.19$ Å.

The Hamiltonian for the adsorbate-substrate system is taken to be

$$H=\sum_k \varepsilon_k c_k^\dagger c_k+\Omega b^\dagger b+\sum_{k,k'} V_{kk'}(\mathbf{Q})c_k^\dagger c_{k'}\ , \tag{22}$$

where $\mathbf{Q}$ is the vibrational normal mode coordinate, c_k and $c_k^\dagger$ are the annihilation and creation operators for the metal states $|k\rangle$. The matrix element $V_{kk'}$ describes the (repulsive) adsorbate-substrate interaction

$$\begin{aligned}V_{kk'}&=\int d^3x\ \psi_k^*(\mathbf{x})V(\mathbf{x}-\mathbf{Q})\psi_{k'}(x)\\&=\int d^3x\ \psi_k^*(\mathbf{x}+\mathbf{Q})V(\mathbf{x})\psi_{k'}(\mathbf{x}+\mathbf{Q})\\&=e^{i(\mathbf{k}'_\parallel-\mathbf{k}_\parallel)\cdot\mathbf{Q}}V_{kk'}(0)\\&\approx[1+i(\mathbf{k}'_\parallel-\mathbf{k}_\parallel)\cdot\mathbf{Q}]V_{kk'}(0)\ ,\end{aligned}$$

where we have used that $k_\parallel Q\le k_F Q\ll 1$ in the expansion in the last step. We now write (22) as

$$H=H_0+H'\ ,$$

$$H_0=\sum_k \varepsilon_k c_k^\dagger c_k+\Omega b^\dagger b+\sum_{k,k'} V_{kk'}(0)c_k^\dagger c_{k'}\ , \tag{23}$$

$$H'=\sum_{k,k'} V_{kk'}(0)c_k^\dagger c_{k'}i(\mathbf{k}'_\parallel-\mathbf{k}_\parallel)\cdot\hat{\mathbf{x}}Q_0(b+b^\dagger)\ . \tag{24}$$

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

$$H_0=\sum_\alpha \varepsilon_\alpha c_\alpha^\dagger c_\alpha+\Omega b^\dagger b\ .$$

We now use perturbation theory (Fermi's golden rule) with H' as the perturbation. At first, this might seem impossible because $V_{kk'}$ is not small but almost infinite because of the strong repulsive potential inside the adsorbate ($r\le R$). But the eigenstates to H_0 practically vanish inside the adsorbate so that in the $\{|\alpha\rangle\}$ basis the perturbation H' is small. Hence, using Fermi's golden rule, we calculate the rate $1/\tau$ for the vibrational excited adsorbate ($n=1$) to decay to its vibrational ground state ($n=0$) while an electron is excited from an orbital $|\alpha\rangle$ below the Fermi surface to an orbital $|\beta\rangle$ above the Fermi surface:

$$\begin{aligned}\frac{1}{\tau}&=\frac{2\pi}{\hbar}2\sum_{\alpha,\beta}f(\varepsilon_\alpha)[1-f(\varepsilon_\beta)]\delta(\varepsilon_\beta-\varepsilon_\alpha-\Omega)|\langle\beta,n=0|H'|\alpha,n=1\rangle|^2\\&=\frac{4\pi}{\hbar}\int_{\varepsilon_F-\Omega}^{\varepsilon_F}d\varepsilon'\sum_{\alpha,\beta}\delta(\varepsilon'-\varepsilon_\alpha)\delta(\varepsilon'+\Omega-\varepsilon_\beta)Q_0^2\left|\left\langle\beta\left|\sum_{k,k'}V_{kk'}(0)c_k^\dagger c_{k'}(\mathbf{k}_\parallel-\mathbf{k}'_\parallel)\cdot\hat{\mathbf{x}}\right|\alpha\right\rangle\right|^2\ ,\end{aligned} \tag{25}$$

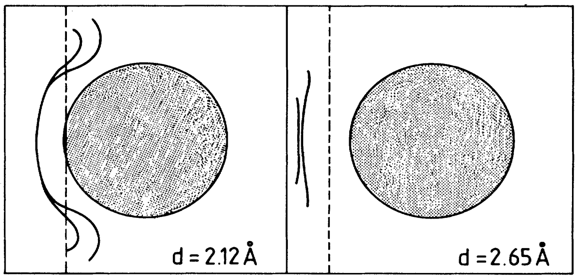

FIG. 6. The constant electron-density contours of a Xe atom at a $r_s=2$ jellium surface. The dashed lines denote the positive background edge and the separation between this edge and the nuclei of the Xe atom amounts to $d=2.12$ Å (left) and 2.65 Å (right).

where the extra factor of 2 comes from sum over spin. But

$$\sum_{k,k'} V_{kk'}(0)c_k^\dagger c_{k'}(\mathbf{k}_\parallel-\mathbf{k}'_\parallel)\cdot\hat{\mathbf{x}}=\left[\sum_{k,k'} V_{kk'}(0)c_k^\dagger c_{k'},p_x\right]$$
$$=[H_0,p_x] \tag{26}$$

where

$$\mathbf{p}=\sum_k \mathbf{k}c_k^\dagger c_k$$

is the momentum operator, and where the last equality in (26) follows directly from the definition (23) of H_0. Since

$$\langle\beta|[H_0,p_x]|\alpha\rangle=(\varepsilon_\beta-\varepsilon_\alpha)\langle\beta|p_x|\alpha\rangle=\Omega\langle\beta|p_x|\alpha\rangle\ ,$$

we get from (25) and (26)

$$\frac{1}{\tau}=\frac{4\pi}{\hbar}Q_0^2\int_{\varepsilon_F-\Omega}^{\varepsilon_F}d\varepsilon'\sum_{\alpha,\beta}\delta(\varepsilon'-\varepsilon_\alpha)\delta(\varepsilon'+\Omega-\varepsilon_\beta)$$
$$\times|\langle\beta|p_x|\alpha\rangle\Omega|^2\ . \tag{27}$$

We use the jellium model and write the one-particle eigenstates $\{|\alpha\rangle\}$ of H_0 as

$$\psi_k=\frac{1}{(2\pi)^{3/2}}(e^{ik_zz}+e^{-ik_zz+i\phi_k})e^{i\mathbf{k}_\parallel\cdot\mathbf{x}_\parallel}$$
$$+\frac{1}{2\pi}\int d^2q\ A(\mathbf{k}_\parallel,\mathbf{q}_\parallel,\varepsilon_k)e^{i\mathbf{q}_\parallel\cdot\mathbf{x}_\parallel-iq_zz}\ , \tag{28}$$

where

$$\varepsilon_k=\frac{\hbar^2k^2}{2m}=\frac{\hbar^2}{2m}(k_\parallel^2+k_z^2)=\frac{\hbar^2}{2m}(q_\parallel^2+q_z^2)\ .$$

We have taken the energy zero at the bottom of the potential well inside the metal. We write (28) as $\psi_k=\psi_k^0+\psi_k^s$, where ψ_k^0 is a metal eigenstate in the absence of the adsorbate and ψ_k^s is the "scattered" field from the adsorbate. In principle, the first term in (28) is not identical to ψ_k^0 since the wave function in the surface region is modified from the "bulk" form, i.e., not simply a sum of an incident and reflected plane wave as the first term in (28). However, in deriving (30) below the detailed form of the wave function in the surface region is irrelevant (as $\Omega\to0$); see Ref. 28. Hence with $\langle x|\alpha\rangle=\psi_k$ and $\langle x|\beta\rangle=\psi_{k'}$ we get ($\mathbf{k}\neq\mathbf{k}'$)

$$\langle\beta|p_x|\alpha\rangle=\int d^3x(\psi_{k'}^0+\psi_{k'}^s)^*p_x(\psi_k^0+\psi_k^s)$$
$$=\int d^3x(\psi_{k'}^{0*}p_x\psi_k^s+\psi_{k'}^{s*}p_x\psi_k^0) \tag{29}$$

plus a term $\sim\psi_{k'}^{s*}\psi_k^s$, which can be neglected. Substituting (28) into (29) gives, as $\Omega\to0$,

$$\Omega\langle\beta|p_x|\alpha\rangle\to\frac{1}{\sqrt{2\pi}}\frac{\hbar^2}{mi}[k'_xk'_ze^{-i\phi_{k'}}A(\mathbf{k}_\parallel,\mathbf{k}'_\parallel,\varepsilon_k)$$
$$+k_xk_ze^{i\phi_k}A^*(\mathbf{k}'_\parallel,\mathbf{k}_\parallel,\varepsilon_{k'})]\ .$$

Substituting this result into (27) gives

$$\frac{1}{\tau}=\frac{2\hbar^4}{Mm^2}\sum_{k,k'}\delta(\varepsilon_F-\varepsilon_k)\delta(\varepsilon_F-\varepsilon_{k'})\{k_x^2k_z^2|A(\mathbf{k}'_\parallel,\mathbf{k}_\parallel,\varepsilon_F)|^2+k_xk'_xk_zk'_z\mathrm{Re}[e^{-i(\phi_k+\phi'_k)}A(\mathbf{k}_\parallel,\mathbf{k}'_\parallel,\varepsilon_F)A(\mathbf{k}'_\parallel,\mathbf{k}_\parallel,\varepsilon_F)]\}\ . \tag{30}$$

Let us now calculate the scattering amplitude $A(\mathbf{k}_\parallel,\mathbf{k}'_\parallel,\varepsilon_F)$. We will do this approximately by using Kirchoff's integral representation. Let us first calculate the eigenfunctions of the metal in the absence of the adsorbate, i.e.,

$$\left[-\frac{\hbar^2}{2m}\nabla^2+U(z)\right]\psi=\varepsilon_F\psi\ ,$$

where the effective potential $U(z)$ is taken to be a step function, i.e., $U=0$ for $z<0$ and $U(z)=\varepsilon_F+\phi$ for $z>0$ where ϕ is the work function. Hence we get

$$\psi_k^0=\frac{1}{(2\pi)^{3/2}}e^{i\mathbf{k}_\parallel\cdot\mathbf{x}_\parallel}B_k(z)\ ,$$

where

$$B_k(z)=\begin{cases}e^{ik_zz}+r_ke^{-ik_zz}, & z<0\\ (1+r_k)e^{-\alpha_kz}, & z>0\end{cases}$$

where

$$r_k=e^{i\phi_k}=\frac{ik_z+\alpha_k}{ik_z-\alpha_k}\ .$$

In these equations

$$\frac{\hbar^2}{2m}(k_\parallel^2+k_z^2)=\varepsilon_F,\quad \frac{\hbar^2}{2m}(k_\parallel^2-\alpha_k^2)=-\phi\ ,$$

i.e.,

$$k_z=(k_F^2-k_\parallel^2)^{1/2},\quad \alpha_k=\left[\frac{2m\phi}{\hbar^2}+k_\parallel^2\right]^{1/2}.$$

Next, let us define a Green's function

$$[\nabla^2+k^2(z)]G(\mathbf{x},\mathbf{x}')=-\delta(\mathbf{x}-\mathbf{x}')\ , \tag{31}$$

where $k^2(z)=2m[\varepsilon_F-U(z)]/\hbar^2$. Hence

$$\int_V d^3x(\psi\nabla^2G-G\nabla^2\psi)=-\psi(\mathbf{x}')$$

or

$$\psi(\mathbf{x}')=-\int_S d^2x\ \mathbf{n}\cdot(\psi\nabla G-G\nabla\psi)\ , \tag{32}$$

where V and S are the volume and surface of the "hard-sphere" adsorbate. The unit vector $\mathbf{n}$ is normal to the surface S pointing away from the volume V. Let us decompose $\psi=\psi^0+\psi^s$ and substitute this into (32)

$$\psi^s(\mathbf{x}')=\int_S d^2x\ \mathbf{n}\cdot(\psi^s\nabla G-G\nabla\psi^s)\ .$$

But on S we have assumed that $\psi=0$, i.e., $\psi^s=-\psi^0$. Furthermore, if the radius of the adsorbate is large, then we can approximate $\partial\psi^s/\partial n=\partial\psi^0/\partial n$, which is satisfied for a flat surface S. Hence

$$\psi^s(\mathbf{x}')\approx-\int_S d^2x\left[\psi^0\frac{\partial G}{\partial n}+G\frac{\partial\psi^0}{\partial n}\right]. \tag{33}$$

For $z'<0$ and $z>0$, it is easy to show from (31) that

$$G=\frac{1}{(2\pi)^2}\int d^2q\ e^{i\mathbf{q}_\parallel\cdot(\mathbf{x}_\parallel-\mathbf{x}_\parallel')}a_q e^{-\alpha_q z}\ , \tag{34}$$

where

$$a_q=\frac{i}{2q_z}(1+r_q)e^{-iq_z z'}\ ,$$

$$q_z=(k_F^2-q_\parallel^2)^{1/2}\ .$$

On the surface S, $z=z_0-(R^2-x_\parallel^2)^{1/2}(z<z_0)$ and for $R\gg|\mathbf{x}_\parallel|$, $z\approx z_0-R(1-x_\parallel^2/2R^2)$, so that

$$e^{-\alpha_q z}\approx e^{-\alpha_q(z_0-R)-\alpha_q x_\parallel^2/2R}\ . \tag{35}$$

Substituting (30) and (34) into (33), and using (35) gives, after some simplifications,

$$\begin{aligned}\psi^s(\mathbf{x}')=\frac{iR}{2(2\pi)^{5/2}}\int d^2q_\parallel(1+r_k)(1+r_q)\frac{1}{q_z}\\ \times e^{-(\alpha_k+\alpha_q)(z_0-R)}\\ \times\exp\left[-\frac{R}{2}\frac{(\mathbf{k}_\parallel+\mathbf{q}_\parallel)^2}{\alpha_k+\alpha_q}\right]\\ \times e^{-iq_z z'-i\mathbf{q}_\parallel\cdot\mathbf{x}_\parallel'}\ .\end{aligned}$$

Comparing this with (28) gives

$$\begin{aligned}A(\mathbf{k}_\parallel,\mathbf{k}_\parallel',\varepsilon_F)=\frac{iR}{2(2\pi)^{3/2}}(1+r_k)(1+r_{k'})\frac{1}{k_z'}\\ \times e^{-(\alpha_k+\alpha_{k'})(z_0-R)}\\ \times\exp\left[-\frac{R}{2}\frac{(\mathbf{k}_\parallel-\mathbf{k}_\parallel')^2}{\alpha_k+\alpha_{k'}}\right].\end{aligned}$$

Substituting this result into (30) gives, after some simplifications,

$$\begin{aligned}\frac{1}{\tau}=\frac{R^2}{(4\pi)^3M}\int d^2k_\parallel d^2k_\parallel'|1+r_k|^2|1+r_{k'}|^2(\mathbf{k}_\parallel-\mathbf{k}_\parallel')^2\\ \times\frac{1}{k_zk_z'}e^{-2(\alpha_k+\alpha_{k'})(z_0-R)}\\ \times\exp\left[-R\frac{(\mathbf{k}_\parallel-\mathbf{k}_\parallel')^2}{\alpha_k+\alpha_{k'}}\right].\end{aligned}$$

Since

$$|1+r_k|^2=\frac{4k_z^2}{k_z^2+\alpha_z^2}\ ,$$

and writing $\mathbf{k}_\parallel=k_F\mathbf{x}$ and $\mathbf{k}_\parallel'=k_F\mathbf{x}'$, we get, after some simplifications,

$$\begin{aligned}\frac{1}{\tau}=C(k_FR)^2\int_0^1 dx\ dx'x(1-x^2)^{1/2}x'(1-x'^2)^{1/2}\\ \times\int_0^{2\pi}d\varphi(x^2+x'^2-2xx'\cos\varphi)e^{-2\alpha k_F(z_0-R)}e^{-k_FR/\alpha(x^2+x'^2-2xx'\cos\varphi)}\equiv CJ\ ,\end{aligned} \tag{36}$$

where

$$\alpha=(\phi/\varepsilon_F+x^2)^{1/2}+(\phi/\varepsilon_F+x'^2)^{1/2}$$

and

$$C=\frac{1}{2\pi^2M}\frac{k_F^2}{(\phi/\varepsilon_F+1)^2}=\frac{Ry}{\hbar}\frac{m}{M}\left[\frac{k_Fa_0}{\phi/\varepsilon_F+1}\right]^2\frac{1}{\pi^2}\ .$$

I have calculated the integral J, for several values of k_FR, as a function $k_F(z_0-R)$ and the result is shown in Fig. 7. Note that z_0 is the distance between the center of the adsorbate and the edge of the potential step $U(z)$. This step edge can be related to the edge of the positive background in the jellium model via the condition of charge neutrality which places the jellium edge on the vacuum side of the potential step by the amount

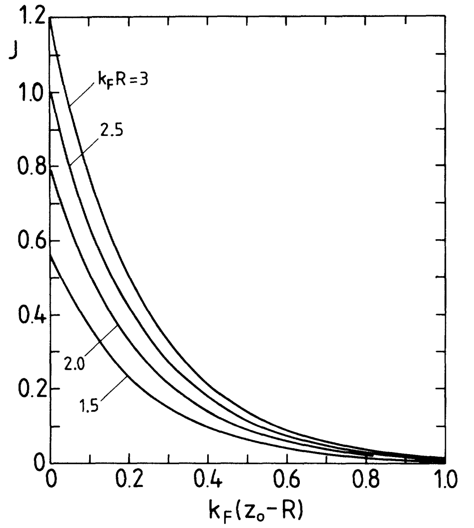

FIG. 7. The function J as a function of $k_F(z_0-R)$ for several k_FR values.

$$\Delta=\frac{3}{2k_F}\int_0^1 dr\, r^2\int_{-1}^{1} dx \left[\frac{\phi}{\varepsilon_F}+r^2(1-x^2)\right]^{-1/2} .$$

For Ag, this equation gives $\Delta=0.79$ Å.

Let us now compare theory with experiment for Xe on Ag(111). From low-energy electron diffraction studies, it is known that the separation between the Xe nucleus and the first layer of Ag atoms is 3.55 ± 0.1 Å. Hence the separation between nuclei of the Xe atom and the jellium edge amounts to 2.37 ± 0.1 Å. Using $\Delta=0.79$ Å, we get $z_0-R=0.97\pm0.1$ Å. This value for z_0-R needs one correction: The electron density profile at the surface in the finite step model is steeper than using the more realistic jellium model; we can roughly account for this effect by reducing z_0-R by ~0.1 Å, giving $z_0-R\approx0.87\pm0.1$ Å. Hence $k_F(z_0-R)\approx1.0\pm0.1$. From Fig. 7 with $k_FR=2.6$ we get $J\approx0.015$. For Xe on Ag, we get $C=4.3\times10^9$ s^{-1} and using (36) we estimate the vibrational lifetime $\tau\approx16\times10^{-9}$ s (corresponding to a cross section $\Sigma=0.11$ Å^2). This lifetime is longer, by a factor of ~5, than that deduced from the change in dc resistivity, $\tau\sim3\times10^{-9}$ s (see Table I).

It is known from inverse photoemission measurements[29] that the 6s level in Xe form a resonance located about 4 eV above ε_F and with a width of $\Gamma\approx1$ eV. The tail of the resonance extends down to the Fermi energy and gives rise to a low density of states at ε_F. It has been pointed out by Eigler and Schweizer[30] that this is in fact the origin of why Xe shows up as a big bump in a scanning tunnel microscope (where electron tunneling to adsorbate-induced states in the vicinity of ε_F occurs). Assuming a Lorentzian 6s resonance with $\tilde{\varepsilon}_a-\varepsilon_F=4$ eV and $\Gamma=1$ eV, Eq. (16) gives $\tau\approx7\times10^{-9}$, which is quite close to the lifetime deduced from the resistivity data. This indicates that even for a "physisorption" system such as Xe/Ag(111) "chemical" effects may give the dominating adsorbate-induced contribution to thin-film resistivities and the electron-hole pair damping of the corresponding parallel frustrated translations.

One problem with the analysis above is that Xe on Ag(111) does not adsorb randomly on the surface, but forms islands. But since the Xe atoms form incommensurate structures and since the Xe-Xe lattice constant is very large, it is not unreasonable to use the random-adsorption assumption even in this case.

As pointed out earlier, C_2H_6 has *no* low-lying empty electronic level, i.e., it is more "inert" than Xe. Furthermore, since C_2H_6 binds to Ag(111) with almost the same binding energy as Xe, and since the effective Lennard-Jones radius of C_2H_6 is practically identical to that of Xe, the cross section $\Sigma=0.11$ Å^2 derived above for Xe, due to the hard-sphere repulsion, should also be valid for C_2H_6 on Ag(111). It is therefore very satisfactory to note that this cross section agrees exactly with that deduced from thin film resistivity and quoted in Table I.

IV. ANOMALOUS SKIN EFFECT AND SURFACE RESISTIVITY

In Sec. II, I discussed the influence of adsorbates on the dc resistivity of thin metallic films. But adsorbates also influence the reflectivity of light from surfaces. Here, we are interested in light frequencies ω in the infrared region. For $\omega\gg1/\tau_B$ and $\delta\gg v_F/\omega$ (where τ_B is the bulk Drude relaxation time and δ is the so-called skin depth defined below) the influence of the adsorbates on the reflectivity can be described by a simple formula which depends on the *e-h* pair damping $1/\tau$ of the parallel frustrated translation of the adsorbates. As an application, we consider the recent ir measurements by Hirschmugl *et al.* for the CO-Cu(100) chemisorption system and deduce from the change in ir reflectivity an *e-h* pair damping rate $1/\tau$ in good agreement with that deduced earlier from dc resistivity data of thin Cu film (see Table I). This result differs from the suggestion by Hirschmugl *et al.*, who attributed the observed adsorbate-induced changes in reflectivity to inter- or intraband transitions involving *adsorbate-induced* surface states.

The optical reflectivity of metal surfaces is often well described using the standard Fresnel formulas. For example, for *s*-polarized light (i.e., the electric-field vector parallel to the surface) at normal incidence, the reflectivity is given by

$$r_s=\frac{1-\sqrt{\varepsilon}}{1+\sqrt{\varepsilon}} ,$$

where ε is the bulk dielectric function which at infrared frequencies often is well approximated by the Drude formula

$$\varepsilon=1-\frac{\omega_p^2}{\omega(\omega+i/\tau_B)} .$$

The electric field in the metal ($z>0$) is given by

$$E=E_0(1+r_s)e^{-z/\delta}\cos(\omega t+\alpha) , \qquad (37)$$

where the penetration depth δ satisfies

$$\frac{1}{\delta^2}=-\varepsilon\left[\frac{\omega}{c}\right]^2 .$$

In the limit $\tau_B\to\infty$, this gives

$$\frac{1}{\delta^2}=-\left[1-\frac{\omega_p^2}{\omega^2}\right]\left[\frac{\omega}{c}\right]^2\approx\left[\frac{\omega_p}{c}\right]^2 ,$$

i.e., $\delta\approx c/\omega_p$. In a typical case, $\delta\approx 200$ Å, i.e., the electric field is localized to a very thin layer at the metal surface. For noble metals, at liquid-nitrogen temperatures, $\hbar/\tau_B\approx 25\ \mathrm{cm}^{-1}$ so that the condition $\omega\gg 1/\tau_B$ is satisfied for $\omega\gtrsim 100\ \mathrm{cm}^{-1}$. Note also that the electron mean free path in the bulk $l_B=v_F\tau_B\approx 3000$ Å is much larger than δ.

In the limit $\tau_B\to\infty$, $\sqrt{\varepsilon}$ is purely imaginary and $|r_s|=1$, i.e., no ir absorption would occur. However, this result is incorrect for the following reason. An electron that propagates in the surface region $\delta>z>0$, where the electric field is nonvanishing, will experience a force for a time period $\Delta t\sim\delta/v_F$. Hence as the electron leaves the surface region, it will in general have acquired some extra kinetic energy and will propagate ballistically as a "hot" electron towards $z=\infty$. As a result, even in the strict $\tau_B\to\infty$ limit, the external electromagnetic radiation will transfer energy to the substrate and the reflectance $|r_s|^2<1$. The treatment of this so-called anomalous skin effect is in general (i.e., when $l_B\sim\delta$) quite complicated and an accurate theory for p-polarized radiation is still not available. Note, in particular, that for $l_B\sim\delta$ the expansion of r_s and r_p to leading order in $q_\parallel$ (the Feibelman[31] $d_\parallel$ and $d_\perp$ formalism) is not possible and r_s and r_p have to be evaluated using the full nonlocal (τ_B-dependent) dielectric response function $\varepsilon(\mathbf{x},\mathbf{x}',\omega)$. However, *if* in addition to $\omega\gg 1/\tau_B$ the condition $\delta\ll l_B$ (and $\delta\gg v_F/\omega$) is satisfied, the problem simplifies and, as shown by Holstein,[10] the absorptance (i.e., the change in reflectance) can be evaluated using the picture presented above where the electron is accelerated by the screened external electric field when entering the surface region $0<z<\delta$ without, in general, changing its momentum by scattering against bulk imperfections or phonons (i.e., $\delta\ll l_B$). The energy transfer can then be calculated by simply evaluating the change in the electron momentum during the transition through the surface region. Holstein studied the general case where, due to surface imperfections (e.g., adsorbates), a fraction $1-p$ ($0\le p\le 1$) of the electrons scatter diffusively from the film surface and the remaining fraction p specularly, and he obtained the following result for the reflectance:

$$|r_s|^2=1-\frac{1}{2}\frac{\omega_p^2}{\omega^2}\left[\frac{v_F}{c}\right]^3 -(1-p)\left[\frac{3}{4}\frac{v_F}{c}-\frac{1}{2}\frac{\omega_p^2}{\omega^2}\left[\frac{v_F}{c}\right]^3\right] .$$

The change in reflectance due to the influence of the surface is

$$\Delta R=1-|r_s|^2=(1-p)\left[\frac{3}{4}\frac{v_F}{c}-\frac{1}{2}\frac{\omega_p^2}{\omega^2}\left[\frac{v_F}{c}\right]^3\right] .$$

We assume that ω is so large that the second term in $[\cdots]$ can be neglected compared with the first term so that

$$\Delta R=(1-p)\frac{3}{4}\frac{v_F}{c} . \tag{38}$$

This formula can be related to the surface induced change in dc resistivity $\Delta\rho$ of a thin metallic film of the same metal and with the same surface conditions (e.g., distribution of adsorbates):

$$\frac{\Delta\rho}{\rho_0}=(1-p)\frac{3}{16}\frac{l_B}{d} , \tag{39}$$

where d is the film thickness. Using (38) and (39) gives

$$\Delta R=4\frac{v_F}{c}\frac{d}{l_B}\frac{\Delta\rho}{\rho_0} .$$

But

$$\rho_0=\frac{m}{ne^2\tau_B} ,$$

so that

$$\Delta R=\frac{4}{c}\frac{ne^2}{m}d\Delta\rho . \tag{40}$$

Finally, using the relation (5), which we now write

$$d\Delta\rho=\frac{Mn_a}{n^2e^2\tau} , \tag{41}$$

we get from (40)

$$\Delta R=4\frac{M}{m}\frac{n_a}{n}\frac{1}{c\tau} . \tag{42}$$

Hence, from the adsorbate-induced change in ir reflectivity ΔR (assuming $\omega\gg 1/\tau_B$ and $\delta\ll l_B$), one can immediately deduce the e-h pair damping $1/\tau$ of the parallel frustrated translation of the adsorbates.

Equation (42) can also be derived, and generalized, by the following very simple arguments: According to the Feibelman d-parameter formalism (see also Langreth, Ref. 33), for an electromagnetic wave at normal incidence

$$|r|^2=|r_0|^2\left[1-\frac{4\omega}{c}\mathrm{Im}\,d_\parallel(\omega)\right] \tag{43}$$

where $r_0=(1-\sqrt{\varepsilon})/(1+\sqrt{\varepsilon})$, i.e., $|r_0|=1$ in our case, and where

$$d_\parallel=\frac{\int dz\, z\dfrac{\partial J_\parallel}{\partial z}}{\int dz\dfrac{\partial J_\parallel}{\partial z}} , \tag{44}$$

where $J_\parallel$ is the current induced parallel to the surface due to an external uniform electric field with the electric-field vector parallel to the metal surface. (Note: we can neglect retardation[32] when calculating $d_\parallel$, and a *uniform* electric field with the time dependence $\cos\omega t$ satisfies Maxwell's equations in the limit $c\to\infty$.) The electric current deep inside the crystal must be $\mathbf{J}_B=\sigma_B\mathbf{E}$, where

$$\sigma_B=\frac{i\omega}{4\pi}(1-\varepsilon_B)=\frac{i\omega_p^2}{4\pi\omega}\ . \tag{45}$$

However, in the vicinity of the surface, the current density is reduced owing to the "surface resistivity" caused by electron scattering against the adsorbates. The current in the vicinity of the surface will heal to its bulk value $\mathbf{J}_B$ for $z\gtrsim l_B$ (for the moment l_B is taken to be large but finite) since l_B is the effective radius of nonlocality of $\sigma(\mathbf{x},\mathbf{x}',\omega)$. In the simplest approximation, we take

$$\begin{aligned}\mathbf{J}&=\mathbf{J}_B \quad \text{for } z>l_B\\ &=\mathbf{J}_S \quad \text{for } 0<z<l_B\ ,\end{aligned}$$

where $\mathbf{J}_S$ is determined as follows: We write $\mathbf{J}_S=\sigma_S\mathbf{E}$, where σ_S is taken to be the conductivity of a metal slab of thickness l_B, i.e.,

$$\sigma_S=\frac{i\omega_p^2}{4\pi(\omega+i/\tau_s)}\ , \tag{46}$$

where the "surface" relaxation time τ_s is chosen so that the dc resistivity agrees with (41) with $d=l_B$:

$$\frac{\omega_p^2\tau_s}{4\pi}=\frac{n^2e^2\tau}{Mn_a}l_B$$

or

$$\tau_s=\tau l_B\frac{n}{n_a}\frac{m}{M}\ . \tag{47}$$

Now since

$$J_\parallel=J_S\theta(z)+(J_B-J_S)\theta(z-l_B)\ ,$$

we get

$$\frac{\partial J_\parallel}{\partial z}=J_S\delta(z)+(J_B-J_S)\delta(z-l_B)\ ,$$

so that (44) reduces to

$$d_\parallel=\frac{J_B-J_S}{J_B}l_B=\frac{\sigma_B-\sigma_S}{\sigma_B}l_B\ .$$

Substituting (45) and (46) into this equation gives

$$d_\parallel=\frac{l_B}{1-i\omega\tau_s}\ . \tag{48a}$$

Substituting (47) into this equation and letting $l_B\to\infty$ gives

$$d_\parallel=i\frac{n_a}{n}\frac{M}{m}\frac{1}{\omega\tau}\ , \tag{48b}$$

which is our fundamental result. Substituting (48b) in (43) gives

$$\Delta R=4\frac{M}{m}\frac{n_a}{n}\frac{1}{c\tau}\ ,$$

which is identical to (42). However, the Feibelman d-parameter formalism allows us now to generalize this result to p-polarized light at an arbitrary angle of incidence θ:

$$\Delta R_p=-\frac{4\omega}{c}\frac{1}{\cos\theta}\mathrm{Im}d_\parallel=-4\frac{M}{m}\frac{n_a}{n}\frac{1}{c\tau}\frac{1}{\cos\theta}\ , \tag{49}$$

where we have neglected the contribution from $d_\perp$ to ΔR_p (which is very small, see Sec. V).

As an application of (49), let us consider the recent work by Hirschmugl *et al.*,[9] who studied the change in ir reflectivity of a Cu(100) surface upon adsorption of CO. The reflectance was measured as a function of ω for 200 $\mathrm{cm}^{-1}<\omega<500\ \mathrm{cm}^{-1}$ and is reproduced in Fig. 8 for a clean Cu(100) surface as well as for a surface with a $\theta=0.15$ coverage of CO. In order to analyze the experimental data, the data is filled with the curve (solid line in Fig. 8)

$$\Delta R=-a\frac{\omega^2}{\omega^2+b^2}\ ,$$

where

$$a=9.05\times10^{-3},\quad b=357\ \mathrm{cm}^{-1}\ .$$

Hence $\Delta R\to -a$ as $\omega\gg b$, which must equal (49). Note that while the condition $\omega\gg1/\tau_B\sim25\ \mathrm{cm}^{-1}$ is well satisfied in the frequency range presented in Fig. 8, the other condition $\delta\gg v_F/\omega$ necessary for the validity of (49) is not satisfied since $\delta\sim200$ Å, while $v_F/\omega\approx160$ Å for $\omega=500\ \mathrm{cm}^{-1}$. This is the reason why we must extrapolate to $\omega>500\ \mathrm{cm}^{-1}$. Using (49) with $n_a=0.023$ Å^{-2} (corresponding to $\theta=0.15$), $n=8.47\times10^{-2}$ Å^{-3} and $\Delta R=a$ gives $\tau=2.6\times10^{-11}$ s, which is in rather good agreement with the lifetime deduced from dc resistivity data in Sec. II, namely $\tau=3.9\times10^{-11}$ s. Hence we conclude that the decrease in ir reflectivity upon CO adsorption is most likely due to the increase in surface resistivity and not, as suggested by Hirschmugl *et al.*, due to

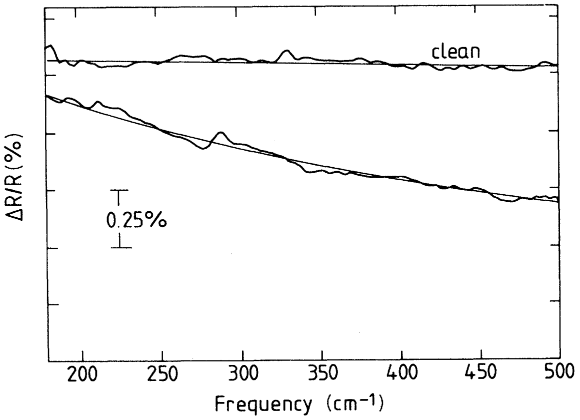

FIG. 8. The reflectance of a clean and adsorbate covered Cu(100) surface. The CO coverage $\theta=0.15$ and the temperature $T\approx90$ K. The smooth solid line is discussed in the text. From Ref. 9.

inter- or intraband transitions involving *adsorbate-induced* electronic surface states.

V. ir SPECTROSCOPY OF DIPOLE-FORBIDDEN ADSORBATE VIBRATIONAL MODES

Consider an electromagnetic wave incident on a metal surface. It is well known that at ir frequencies (say $\omega \sim 500\ \text{cm}^{-1}$) the electric field at the vacuum side is almost orthogonal to the surface. This follows from the continuity of $\mathbf{E}_{\parallel}$ at the surface and from the strong screening of the electric field in the metal. It was therefore a surprise as Chabal and co-workers[17,9] observed formally dipole-forbidden (with respect to the surface normal) low-frequency frustrated translations (H on W and Mo) and rotations [CO on Cu(100)] of adsorbates on metallic surfaces. In fact, these modes are observed as strong as the low-frequency *dipole-active* modes (e.g., the H-W, H-Mo, and CO-Cu stretching vibrations) even though the parallel electric-field vector at the surface is reduced by a factor $|E_{\parallel}/E_{\perp}| \sim \omega/\omega_p \sim 0.01$ compared with the normal electric-field component, and the corresponding ir intensity ratio is reduced by the factor $|E_{\parallel}/E_{\perp}|^2 \sim \omega^2/\omega_p^2 \sim 10^{-4}$. A clue to the explanation of these puzzling results followed from the observation that the dipole-forbidden modes observed with ir spectroscopy could not be observed by electron-energy-loss spectroscopy (EELS) (dipole scattering). In EELS, the ratio between the parallel and normal electric-field components at the vacuum side of the metal surface is even smaller than in IRAS (see Fig. 9), namely $\sim \omega^2/\omega_p^2 \sim 10^{-4}$ and the field intensity ratio $\sim \omega^4/\omega_p^4 \sim 10^{-8}$. However, *this* difference between IRAS and EELS is not likely to be of any practical relevance since already with IRAS the reduction is strong enough ($\sim 10^{-4}$) to exclude the *direct* coupling between the adsorbates and the parallel electric field. On the other hand, since $\mathbf{E}_{\parallel}$ is continuous at the surface, the same difference in electric-field strength between IRAS and EELS occurs in the surface region inside the metal (see Fig. 9). Hence *if* the excitation of the dipole-forbidden modes are *mediated by the metal electrons,* then a big difference [by a factor of $(\omega/\omega_p)^2 \sim 10^{-4}$] can be expected between IRAS and EELS. This fact has already been pointed out by Chabal and co-workers (see also Refs. 33 and 34).

A second observation, which supports the indirect, via the metal electrons, excitation of the dipole-forbidden vibrational modes, is the observation of an adsorbate-induced change in broadband ir reflectivity, as discussed in Sec. IV for CO on Cu(100) and also observed for H on W(100) and Mo(100).[35] It is the aim of this section to extend the study of Sec. IV by calculating the surface resistivity including a coupling between the metal electrons and the dipole-forbidden vibrational modes. More exactly, we will calculate the contribution from this coupling to the "thin-film" conductivity σ_S [see Eq. (46)], which is simply related to the change in ir reflectance according to the formulas given in Sec. IV (assuming that the conditions $\Omega \gg 1/\tau_B$ and $\delta \gg v_F/\Omega$ are satisfied). However, before doing this, I would like to present a general discussion about the relative importance of the $d_{\parallel}$ and $d_{\perp}$ corrections to the Fresnel formulas relevant to IRAS and EELS.

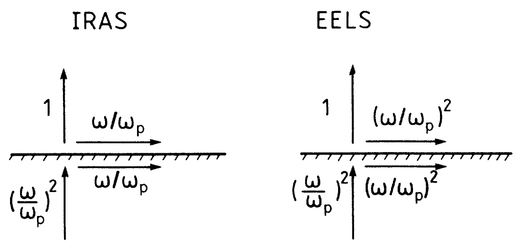

FIG. 9. The relative strength of the normal and parallel electric-field vector components at a metal surface in IRAS and EELS.

In the Feibelman d-parameter formalism, the reflectance of a metal surface to a p-polarized incident electromagnetic wave is given by

$$|r|^2 = |r_0|^2 \left[1 - \frac{4\omega}{c} \frac{\sin^2\theta}{\cos\theta} \left[\text{Im} d_{\perp} + \frac{1}{\sin^2\theta} \text{Im} d_{\parallel} \right] \right] ,$$

where $|r_0|^2$ is the standard Fresnel formula for the reflectance. Hence the adsorbate-induced change in reflectance is given by

$$\frac{\Delta R}{R_0} = - \frac{4\omega}{c} \frac{\sin^2\theta}{\cos\theta} \left[\text{Im} d_{\perp} + \frac{1}{\sin^2\theta} \text{Im} d_{\parallel} \right] . \tag{50}$$

As discussed in Sec. IV, this formula is in general not valid in the anomalous skin effect region where an expansion of r in $q_{\parallel}$ fails. In EELS, the cross section (assuming dipole scattering) for inelastic electron scattering is proportional to Img where for $q_{\parallel} \to 0$

$$g = \frac{\varepsilon - 1}{\varepsilon + 1} \left[1 + 2 q_{\parallel} \frac{d_{\parallel} + \varepsilon d_{\perp}}{\varepsilon + 1} \right] . \tag{51}$$

This formula is in general incomplete as there are additional bulk and bulk-surface interference conditions to Img, but the adsorbate-induced contributions should be correctly given by the last term in (51). If we take ε to be real (i.e., $\tau_B \to \infty$) and large (i.e., $\omega \ll \omega_p$), then (51) gives

$$\text{Im} g \approx 2 q_{\parallel} \text{Im} \frac{d_{\parallel} + \varepsilon d_{\perp}}{\varepsilon + 1} . \tag{52}$$

The response functions $d_{\parallel}(\omega)$ and $d_{\perp}(\omega)$ characterize the surface influence on the dynamical response of the metal to a spatially uniform time varying electric fields polarized parallel and perpendicularly to the metal surface, respectively. By comparing (50) and (52) we conclude the following.

(a) Since in EELS, $q_{\parallel} \sim \omega/v$, where v is the velocity of the incident electrons, EELS is more *surface sensitive* than IRAS by a factor $q_{\parallel}/(\omega/c) \sim c/v \sim 300$.

(b) While $d_{\parallel}$ and $d_{\perp}$ enter with similar weight in IRAS, the weight of $d_{\parallel}$ at ir frequencies is reduced by a factor $\sim 1/\varepsilon \sim (\omega/\omega_p)^2 \sim 10^{-4}$ in EELS. This just reflects the extra factor of $1/\sqrt{\varepsilon} \sim \omega/\omega_p$ in the reduction of $\mathbf{E}_{\parallel}$ (see

Fig. 9) when comparing IRAS and EELS.

For a flat surface without imperfections or adsorbates, $\mathrm{Im}d_{\parallel}=0$, at least in the jellium model. This follows directly from the translational invariance parallel to the surface.[32] The point is that in order to excite *e-h* pairs by $\mathbf{E}_{\parallel}$, a source of momentum is needed and a perfectly flat surface cannot supply any momentum in the parallel direction. On the contrary, $\mathrm{Im}d_{\perp}\neq 0$ (for $\omega>0$) even for a perfect surface since the translational invariance is broken in the perpendicular direction and the surface potential can supply the necessary momentum.

Assume now that a low concentration of adsorbates are randomly distributed on an otherwise perfect metal surface. The translational invariance is now broken in the parallel direction and $\mathrm{Im}d_{\parallel}\neq 0$ (for $\omega>0$). In fact, using (48), we have

$$\mathrm{Im}d_{\parallel}=\frac{n_a}{n}\frac{M}{m}\frac{1}{\omega\tau}\ . \tag{53}$$

In the jellium model, for a clean metal surface,

$$\mathrm{Im}d_{\perp}=\frac{\xi}{k_F}\frac{\omega}{\omega_p}\quad(\omega\ll\omega_p)\ , \tag{54}$$

where $\xi\sim 1$ is a parameter which only depends on the electron gas density parameter r_s, and which has been tabulated in the literature. For example, for $r_s=2.67$ (Cu), both theory[36] and experiment[22] [EELS from Cu(100)] give $\xi\approx 0.5$. Most adsorbates have only a relatively small influence on $\mathrm{Im}d_{\perp}$ at infrared frequencies, typically smaller than a factor of 2 even at relatively high adsorbate coverages. In general, the contribution from adsorbates to $\mathrm{Im}d_{\perp}$ can be written as

$$\mathrm{Im}d_{\perp}\approx 4\pi n_a \mathrm{Im}\alpha_{\perp}\ ,$$

where $\alpha_{\perp}(\omega)$ is the polarizability of an adsorbate. If we assume that the adsorbates have a partly filled resonance state (only in this case the contribution to $\mathrm{Im}d_{\perp}$ will be large), then

$$\mathrm{Im}\alpha_{\perp}(\omega)\approx 2\pi\omega(ed)^2\rho_a^2(\varepsilon_F)\ .$$

Hence the contribution from the adsorbates to $\mathrm{Im}d_{\perp}$ is

$$\mathrm{Im}d_{\perp}=8\pi^2 n_a\omega(ed)^2\rho_a^2(\varepsilon_F)\ . \tag{55}$$

As an example, consider CO on Cu(100) at $\theta=0.15$ (i.e., $n_a=0.023$ Å^{-2}) and at $\omega=500$ cm^{-1}. In this case, (53)–(55) give

$$\mathrm{Im}d_{\parallel}=5\ \text{Å}\ ,$$

$$(\mathrm{Im}d_{\perp})_{\text{clean}}=2.6\times 10^{-3}\ \text{Å}\ ,$$

$$(\mathrm{Im}d_{\perp})_{\text{ads}}=2.0\times 10^{-3}\ \text{Å}\ .$$

Hence in ir spectroscopy, where $d_{\perp}$ and $d_{\parallel}$ enter with a similar weight, $d_{\parallel}$ will always give the dominant contribution at infrared frequencies and nonzero adsorbate coverage. On the other hand, in EELS, the contribution from $d_{\parallel}$ is reduced by a factor $1/\varepsilon\sim(\omega/\omega_p)^2\sim 4\times 10^{-5}$ at $\omega=500$ cm^{-1} and the contribution from $d_{\perp}$ will dominate by more than one order of magnitude. This is why for $\omega\gtrsim 0.1$ eV, $d_{\perp}$ can be directly probed using EELS.[28]

Let us now discuss the second topic of this section, namely how dipole-forbidden adsorbate vibrations can be studied using IRAS. We focus on the three processes shown in Fig. 10.

Figure 10(a) describes the process studied in Sec. IV where a photon excites an electron from a level $|\alpha\rangle$ below the Fermi surface to a level $|\beta\rangle$ above the Fermi surface. In the limits $\delta\gg v_F/\omega$ and $\omega\gg 1/\tau_B$ this process gives rise to the change in reflectivity given by (49).

In Fig. 10(b), we indicate a process where a photon is absorbed while an electron is excited from a level $|\alpha\rangle$ $(\varepsilon_\alpha<\varepsilon_F)$ to a level $|\gamma\rangle$ $(\varepsilon_\gamma>\varepsilon_F)$. The intermediate state $|\gamma\rangle$ is in general a virtual state, i.e., $\varepsilon_\gamma-\varepsilon_\alpha\neq\omega$. Note that the momentum needed for this excitation is supplied by the adsorbate. Next, the excited electron scatters inelastically from the adsorbate resulting in a vibrational excited molecule and an electron in an orbital $|\beta\rangle$ above the Fermi energy $(\varepsilon_\beta=\varepsilon_\alpha+\omega-\Omega>\varepsilon_F)$. This process does not give rise to a sharp structure in the reflectance at $\omega=\Omega$ but to an onset at $\omega=\Omega$, i.e., $\Delta R\sim\theta(\omega-\Omega)(\omega-\Omega)$ in the vicinity of $\omega=\Omega$.

I will now show that the process in Fig. 10(c) does give rise to a sharp structure at $\omega=\Omega$ and furthermore that the intensity of this structure can be very large. In the process in Fig. 10(c), an electron is excited from a state $|\alpha\rangle$ $(\varepsilon_\alpha<\varepsilon_F)$ to an intermediate and in general virtual state $|\gamma\rangle$ $(\varepsilon_\gamma>\varepsilon_F)$ and $\varepsilon_\gamma-\varepsilon_\alpha\neq\omega$. Again the momentum needed for this excitation is supplied by the adsorbate. Next, the excited electron scatters inelastically from the adsorbate while exciting the vibration Ω. In contrast to the case in Fig. 10(b), the electron does not end up in a state $|\beta\rangle$ above the Fermi energy but recombines with its own hole. Energy conservation, therefore, requires that $\omega=\Omega$, i.e., this process gives rise to a sharp structure at $\omega=\Omega$. In general, the structure is not a Dirac δ function but will broaden due to coupling between the vibrational excited state and the *e-h* pair excitations of the metal.

Let us now study the process in Fig. 10(c) using the "energy loss" method.[11] Consider a thin (say $d\sim 1000$ Å) metallic film with adsorbed molecules. We assume that the adsorbates have resonance states in the vicinity of the Fermi energy, e.g., the $2\pi^*$ resonance for adsorbed CO. It is only in this case that one would expect a strong coupling between the adsorbate vibrations and the electron-

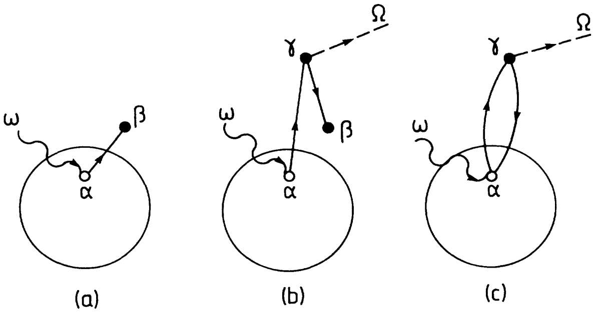

FIG. 10. Elementary processes which contribute to the surface resistivity.

hole pair excitations of the substrate. We consider the same model Hamiltonian as used before,

$$H=\varepsilon_a c_a^\dagger c_a+\sum_k (V_{ak}c_a^\dagger c_k+\text{H.c.})+\sum_k \varepsilon_k c_k^\dagger c_k+\Omega b^\dagger b \ . \tag{56}$$

To calculate the frequency-dependent resistivity, we assume an oscillating external electric field which gives rise to an oscillating electric current in the metal film (say, in the x direction)

$$J_x=-ne\delta x_0\omega\sin\omega t \ .$$

The energy transfer per unit time is given by

$$P=\langle \mathbf{J}\cdot\mathbf{E}\rangle Ad=\tfrac{1}{2}(ne\omega\delta x_0)^2 Ad\,\text{Re}\frac{1}{\sigma(\omega)} \ , \tag{57}$$

where $\sigma(\omega)$ is the frequency-dependent conductivity. Next, we change the reference frame to an oscillating frame in which $\mathbf{J}$ vanishes, but the adsorbates oscillate as $\mathbf{R}(t)=\hat{\mathbf{x}}\delta x_0\cos\omega t$. In addition, the adsorbates can perform quantized vibrations parallel to the surface (frustrated translations) described by the normal-mode coordinate $\mathbf{Q}=Q_0\hat{\mathbf{x}}(b+b^\dagger)$. Hence, in analogy with the discussion in Sec. III A, we get

$$V_{ak}=V_{ak}(\mathbf{Q}+\mathbf{R})\approx V_{ak}(0)[1+i\mathbf{k}_\parallel\cdot(\mathbf{Q}+\mathbf{R})] \ . \tag{58}$$

Substituting this into (56) gives

$$H=H_0+H' \ ,$$

where

$$\begin{aligned} H_0=&\varepsilon_a c_a^\dagger c_a+\sum_k [V_{ak}(0)c_a^\dagger c_k+\text{H.c.}]\\ &+\sum_k \varepsilon_k c_k^\dagger c_k+\Omega b^\dagger b\\ &+\sum_k [V_{ak}(0)c_a^\dagger c_k i\mathbf{k}_\parallel\cdot\mathbf{Q}+\text{H.c.}] \ ,\\ H'=&\sum_k [V_{ak}(0)c_a^\dagger c_k i\mathbf{k}_\parallel\cdot\mathbf{R}+\text{H.c.}] \ . \end{aligned}$$

We now introduce a new basis in which the part of H_0 that is quadratic in annihilation and creation operators becomes diagonal, i.e.,

$$H_0=\sum_\alpha \varepsilon_\alpha c_\alpha^\dagger c_\alpha+\Omega b^\dagger b+\sum_{\alpha,\beta} V_{\alpha\beta}c_\alpha^\dagger c_\beta Q_0(b+b^\dagger) \ , \tag{59}$$

where

$$V_{\alpha\beta}=\sum_k (V_{ak}\langle \alpha|a\rangle\langle k|\beta\rangle-V_{ak}^*\langle a|\beta\rangle\langle \alpha|k\rangle)ik_x \ . \tag{60}$$

In the new basis, H' becomes

$$H'=\sum_{\alpha,\beta} V_{\alpha\beta}c_\alpha^\dagger c_\beta\delta x_0\cos\omega t\equiv\hat{\phi}\frac{\delta x_0}{2}(e^{i\omega t}+e^{-\omega t}) \ .$$

We now use perturbation theory (Fermi's golden rule) to calculate the rate of energy absorption

$$w=\frac{2\pi}{\hbar}\sum_f |\langle f|\hat{\phi}\delta x_0/2|0\rangle|^2\delta(E_f-E_0-\omega) \ , \tag{61}$$

where $|0\rangle$ is the ground state and $|f\rangle$ an excited state of H_0 with energies E_0 and E_f, respectively. Equation (61) can be rewritten as

$$\begin{aligned} w&=\frac{\pi}{2\hbar}\delta x_0^2\sum_f \langle 0|\hat{\phi}\delta(H_0-E_0-\omega)|f\rangle\langle f|\hat{\phi}|0\rangle\\ &=\frac{1}{2\hbar}\delta x_0^2\,\text{Im}\left\langle 0\left|\hat{\phi}\frac{1}{H_0-E_0-\omega-i0}\hat{\phi}\right|0\right\rangle \ . \end{aligned} \tag{62}$$

The energy absorption per unit time is

$$P=w\hbar\omega n_a A \ . \tag{63}$$

Using (57), (62), and (63) gives

$$\text{Re}\frac{1}{\sigma}=\frac{n_a}{n^2e^2\omega d}\text{Im}\left\langle 0\left|\hat{\phi}\frac{1}{H_0-E_0-\omega-i0}\hat{\phi}\right|0\right\rangle \ . \tag{64}$$

Following Ref. 37, one can show that

$$\left\langle 0\left|\hat{\phi}\frac{1}{H_0-E_0-\omega-i0}\hat{\phi}\right|0\right\rangle =\frac{1}{Q_0^2}\left[\frac{\Sigma^2(\omega)}{\Omega-\omega-\Sigma(\omega)}+\Sigma(\omega)\right] \ , \tag{65}$$

where

$$\Sigma(\omega)=2Q_0^2\int_{-\infty}^{\varepsilon_F}d\varepsilon\int_{\varepsilon_F}^{\infty}d\varepsilon'\sum_{\alpha,\beta}|V_{\alpha\beta}|^2\delta(\varepsilon-\varepsilon_\alpha)\delta(\varepsilon'-\varepsilon_\beta) \times\frac{1}{\varepsilon'-\varepsilon-\omega-i0} \ . \tag{66}$$

Hence

$$\begin{aligned} \text{Im}\Sigma(\omega)&=2\pi Q_0^2\int_{\varepsilon_F-\omega}^{\varepsilon_F}d\varepsilon\sum_{\alpha,\beta}|V_{\alpha\beta}|^2\delta(\varepsilon-\varepsilon_\alpha)\delta(\varepsilon+\omega-\varepsilon_\beta)\\ &\approx\frac{\omega}{2\tau\Omega} \ , \end{aligned} \tag{67}$$

where, in the last equality, we have used (11) to relate $\text{Im}\Sigma$ to the e-h pair damping $1/\tau$ of the parallel frustrated translation.

According to (66), $\text{Re}\Sigma(\omega=0)\neq 0$. The correct result is that $\text{Re}\Sigma(0)=0$ as can be proved by keeping the second-order term $\sim[\mathbf{k}_\parallel\cdot(\mathbf{Q}+\mathbf{R})]^2$ in the expansion (58). The proof is straightforward but tedious and will not be presented here. However, the result can be made plausible by the following very simple argument: The quantity $\Sigma(\omega)$ is essentially the phonon self-energy and a nonvanishing $\Sigma(0)$ therefore corresponds to a shift in the phonon frequency due to coupling to the electronic degrees of freedom. But for a translational invariant substrate no such frequency shift should occur. For example, in the Newns-Anderson model studied above, the adsorbate binding energy depends only on the parameter

$$\sum_k |V_{ak}e^{i\mathbf{k}_\parallel\cdot\mathbf{Q}}|^2\delta(\varepsilon-\varepsilon_k)=\sum_k |V_{ak}|^2\delta(\varepsilon-\varepsilon_k) \ , \tag{68}$$

which is independent of $\mathbf{Q}$. However, if we were to approximate

$$e^{i\mathbf{k}_\parallel\cdot\mathbf{Q}}\approx 1+i\mathbf{k}_\parallel\cdot\mathbf{Q} \ ,$$

then the energy *would* depend on **Q** since

$$\sum_k |V_{ak}(1+i\mathbf{k}_\parallel\cdot\mathbf{Q})|^2\delta(\varepsilon-\varepsilon_k)$$
$$=\sum_k |V_{ak}|^2(1+|\mathbf{k}_\parallel\cdot\mathbf{Q}|^2)\delta(\varepsilon-\varepsilon_k)\ . \qquad (69)$$

Hence, in this approximation, the electron-phonon interaction would give a contribution to the adsorbate binding energy $\sim Q^2$, i.e., it would renormalize the resonance frequency Ω of the Einstein oscillator. But this is obviously an artifact of limiting the expansion (58) to first order in **Q** and it is easy to see that including the next term in the expansion eliminates the quadratic Q contribution to the adsorbate binding energy. Hence, for frequencies small compared with the Fermi frequency and the width Γ of the resonance ρ_a, we have

$$\Sigma(\omega)\approx\frac{i\omega}{2\tau\Omega}\ .$$

Using (64) and (65) gives

$$\mathrm{Re}\frac{1}{\sigma}=\frac{2M\Omega n_a}{n^2e^2\omega d}\mathrm{Im}\left[\frac{\Sigma^2(\omega)}{\Omega-\omega-\Sigma(\omega)}+\Sigma(\omega)\right]\ . \qquad (70)$$

The last term in large parentheses describes the "background" resistance arising from direct excitation of electron-hole pairs [process (a) in Fig. 10], which was studied in Sec. IV [see (46) and (47)].

We can relate the film resistivity (70) to the change in reflectance of a semi-infinite solid using the approach outlined in Sec. IV. Let us first define the surface conductivity

$$\sigma_S=\frac{i\omega_p^2}{4\pi(\omega+i/\tau_s)}\ ,$$

where $1/\tau_s$ now is a complex, frequency-dependent quantity which should give the film resistivity (70) for $d=l_B$. Since

$$\mathrm{Re}\frac{1}{\sigma_S}=\frac{4\pi}{\omega_p^2}\mathrm{Re}\frac{1}{\tau_s}\ ,$$

we get

$$\frac{1}{\tau_s}=-2i\frac{M}{m}\frac{\Omega}{\omega}\frac{n_a}{nl_B}\left[\frac{\Sigma^2(\omega)}{\Omega-\omega-\Sigma(\omega)}+\Sigma(\omega)\right]\ .$$

But from (48a), as $l_B\rightarrow\infty$,

$$d_\parallel=-\frac{l_B}{i\omega\tau_s}=2\frac{M}{m}\frac{\Omega}{\omega}\frac{n_a}{n}\frac{1}{\omega}\left[\frac{\Sigma^2(\omega)}{\Omega-\omega-\Sigma(\omega)}+\Sigma(\omega)\right]\ ,$$

and the change in reflectance

$$\Delta R_p=-\frac{4\omega}{c}\frac{1}{\cos\theta}\mathrm{Im}d_\parallel$$
$$=-\frac{8}{c}\frac{M}{m}\frac{\Omega}{\omega}\frac{n_a}{n}\frac{1}{\cos\theta}\mathrm{Im}\left[\frac{\Sigma^2(\omega)}{\Omega-\omega-\Sigma(\omega)}+\Sigma(\omega)\right]\ . \qquad (71)$$

For $\omega\approx\Omega$, we have $\Sigma(\omega)=i/2\tau$, and substituting this into (71) gives

$$\Delta R_p=-\frac{4}{c}\frac{M}{m}\frac{n_a}{n}\frac{1}{\cos\theta}\frac{1}{\tau}\frac{[2\tau(\omega-\Omega)]^2}{[2\tau(\Omega_0-\omega)]^2+1}\ . \qquad (72)$$

For $|\Omega-\omega|\gg 1/\tau$ this formula predicts a uniform background absorption due to excitation of electron-hole pairs—this effect corresponds to process (a) in Fig. 10 and was studied in Sec. IV. Centered at $\omega=\Omega$ is an antiabsorption peak, i.e., the reflectance is *higher* (in fact unity) at resonance $\omega\sim\Omega$ than away from resonance. Equation (72) is only valid for $\omega\gg 1/\tau_B$ and $\delta\gg v_F/\omega$. If these conditions are satisfied, (72) predicts that the absorption background should be ω independent. But this is not observed in the frequency region 200 $\mathrm{cm}^{-1}<\omega<500\ \mathrm{cm}^{-1}$ for CO on Cu(100), where the results reported by Hirschmugl *et al.* show a strongly frequency-dependent background absorption. As pointed out in Sec. IV, this is due to the fact that the second inequality given above is not obeyed in the studied frequency interval. For the same reason one cannot expect the line shape of the Fano structure at $\omega\approx\Omega$ to be in perfect agreement with experiment.

Using ir spectroscopy, Chabal and co-workers have observed Fano line shapes for the dipole-forbidden frustrated translation for H on Mo(100) and W(100) and from the frustrated rotation for CO on Cu(100). Note that the frustrated rotation has some parallel translation in addition to the rotation, and some (reduced) coupling between $\mathbf{E}_\parallel$ and the frustrated rotation should occur. In another publication we will discuss these experimental data in more detail in light of the theory presented above.

In the model discussed above, the parallel frustrated translations (and rotations) derive their ir intensity from the indirect process illustrated in Fig. 10(c). That is, an incident photon first excites an *e-h* pair, which then scatters inelastically from the adsorbate resulting in a vibrational excitation. The momentum necessary for the excitation of the *e-h* pair is, in the model calculation, assumed to be supplied by the adsorbates which break the parallel translational invariance (with respect to a bulk lattice vector) of the clean surface, but it could also be supplied by intrinsic surface imperfections, e.g., steps.

ir measurements have also been performed on coldly evaporated metal films which consist of relative small grains (diameter ~100 Å) separated by "porous" grain boundaries.[38] The rough grain boundaries can supply the momentum necessary for the excitation of *e-h* pairs and as a result a strong broadband ir absorption occurs both for *s*- and *p*-polarized light. For adsorbate-covered surfaces, the generated *e-h* pairs can scatter inelastically from the adsorbates and excite not only the parallel frustrated translations (and rotations), but also other adsorbate modes. This is probably an important excitation process even for strongly dipole-active modes such as the C-O stretch vibration. Indeed, early ir measurements by Bradshaw and Pritchard[39] (see Fig. 11) and later measurements by Chester, Erturk, and Otto[40] show intense Fano line shapes for the C-O stretch mode for CO on coldly evaporated Cu, Ag, and Au films. A fraction of the intensity of these ir structures may be due to the in-

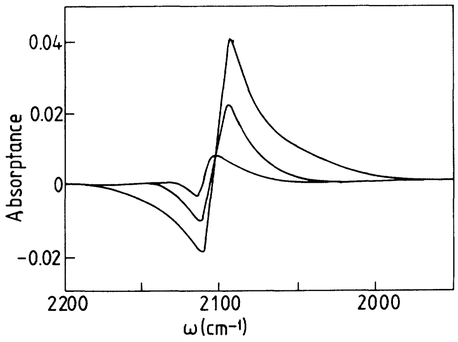

FIG. 11. ir absorption spectra of CO on a copper film deposited and maintained at 113 K at three stages during gas dosing. The ir spectra of an annealed Cu film or a single crystal show a nearly Lorentzian absorption profile. Similar spectra are obtained for CO on coldly evaporated films of Ag and Au and also on some transition metals. From Ref. 39.

direct excitation process discussed above (phonon→*e-h* pair→adsorbate vibration), but the Fano line-shape parameters now depend not only on the nature of the adsorbate-substrate bond, but also on how and where the *e-h* pairs are excited. Alternatively, the intensity of the Fano lines is due to the usual dipole interaction $-\hat{\mu}\cdot\mathbf{E}$, where **E** is the local electric field at the adsorbate under consideration. In the present case, where strong bulk absorption occurs, Mal'shukov[41] has shown that this coupling may result in strong Fano line shapes, even without any strong adsorbate-substrate interaction. The latter point is important since there is no indication of a drastically different chemisorption bond for CO adsorbed on a coldly evaporated metal film, as compared with adsorption on a flat metal surface. For example, the C-O stretch frequency shifts from $\sim 2080\ \mathrm{cm}^{-1}$ for CO on a flat Cu surface to $2105\ \mathrm{cm}^{-1}$ for CO on a coldly evaporated Cu film. The small blueshift of $\sim 25\ \mathrm{cm}^{-1}$ of the C-O resonance frequency does not indicate any major shift of the $2\pi^*$ electronic resonance towards the Fermi energy.

The first mechanism discussed above for the ir intensity of the C-O stretch vibration for CO adsorbed on coldly evaporated noble metal films is consistent with the so-called "chemical contribution" to surface-enhanced Raman scattering, as proposed by Otto *et al.*[42] Based on a very extensive and detailed set of experiments, Otto *et al.* suggest that the chemical contribution is derived from a process where an incident photon (with energy ω now in the optical region) excites an *e-h* pair with the momentum coming from surface defects. The *e-h* pair scatter inelastically from the adsorbate giving rise to a vibrational excited adsorbate and another *e-h* pair. Finally the electron recombines with its hole while emitting a photon with energy $\omega-\Omega$; see Fig. 12.

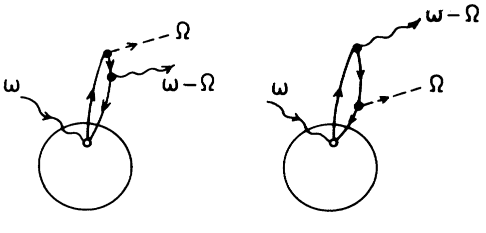

FIG. 12. Two inelastic light scattering processes which constitute the so-called "chemical contribution" of SERS according to the model of Otto *et al.* (Ref. 42). The wavy lines are photon lines and the dashed lines correspond to a vibrational excited molecule.

VI. SUMMARY AND CONCLUSIONS

This work has focused on the adsorbate-induced changes in the dc resistivity $\Delta\rho$ of thin metallic films and the damping $1/\tau$, via excitation of electron-hole pairs, of the corresponding parallel frustrated translation of the adsorbates. The main results can be summarized as follows.

(a) Using the "energy loss" method, in Sec. II I derived a very simple relation between $\Delta\rho$ and τ [Eq. (11)] and from experimental $\Delta\rho$ data I derived the damping $1/\tau$ for several adsorbate systems.

(b) In Sec. III I derived simple theoretical results for the *e-h* pair damping $1/\tau$. I considered three limiting models of the adsorbate-substrate bond, namely covalent, ionic, and van der Waals bonds. For CO chemisorbed on Cu(111), and Xe physisorbed on Ag(111), good agreement between theory and experiment is obtained.

(c) In Sec. IV, I showed that the damping rate $1/\tau$ can also be obtained from the adsorbate-induced change in ir reflectivity. I analyzed the ir data by Hirschmugl *et al.* on the CO-Cu(100) chemisorption system and found practically the same damping rate $1/\tau$ of the CO frustrated translation as deduced earlier from dc resistivity data.

(d) In Sec. V, I presented a general discussion about the relative importance of the Feibelman $d_{\parallel}$ and $d_{\perp}$ parameters in IRAS and EELS from adsorbate-covered surfaces. In short, at ir frequencies, I found that IRAS probes mainly $d_{\parallel}$ and EELS mainly $d_{\perp}$. In the same section, I also studied the change in surface resistivity caused by excitation of the parallel frustrated translations in adsorbates.

Finally, I would like to suggest that many more studies of the *change* in the dc resistivity of thin metallic films upon adsorbate exposure should be performed, in particular on *epitaxially* grown films. Such studies, performed as a function of the adsorbate coverage, could be the most direct and generally valid method of obtaining *e-h* pair damping of the dipole-forbidden parallel frustrated translations. Furthermore, since the *e-h* pair damping depends on the adsorbate configuration, e.g., on the adsorbate binding sites, it should be possible, using this method, to directly probe phase transitions and other adsorbate rearrangement processes in adsorbed layers, induced by changes in temperature and adsorbate coverage.

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