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# Surface resistivity: theory and applications

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I discuss the concept of surface resistivity and present a number of applications. The origin of the recent observations of anti-absorption peaks in infrared reflection absorption spectroscopy (IRAS) of atoms and molecules adsorbed on metal surfaces is discussed and it is shown that parallel frustrated translations of adsorbates *always* give rise to relative strong anti-absorption peaks in IRAS, even though modes are dipole forbidden with respect to a normal electric field The excitation mechanism is indirect, involving the metal electrons, and is related to the surface resistivity I discuss 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 (life time $\tau_{e-h}$) of the parallel frustrated translations of the adsorbates. From the measured $\Delta\rho$ for several different adsorbate systems we deduce the corresponding $\tau_{e-h}$ which ranges from $\sim 10^{-12}$ s for chemisorption systems to $\sim 10^{-8}$ s for physisorption systems. The experimental data are discussed in the light of a simple model calculation for the damping of parallel frustrated translations. Finally I present a number of applications related to surface resistivity, including surface diffusion and atomic scale friction

## 1. Introduction

The concept of surface resistivity has resently been shown to be very useful for the understanding of several important and interesting phenomena. It is the aim of this article to briefly review some of these developments. I focus mainly on how adsorbates influence the frequency dependent resistivity of thin metallic films and the infrared light reflectivity of semi-infinite metals. This paper is based on refs. [1–3] to which the readers are referred for more details.

## 2. On the origin of anti-absorption resonances

In the context of IRAS it has been generally believed that only vibrational modes with a non-zero dynamical dipole moment normal to the surface can be detected This conclusion was based on the very strong screening of the parallel electric field at the surface (see below). But very recently, parallel frustrated translations (H on W(100) and on Mo(100)) and frustrated rotations (CO on Cu(100)) have been observed with IRAS. In fig 1 I reproduce the reflectance spectrum from CO on Cu(100), in the vicinity of the resonance frequency $\Omega \approx 285$ cm$^{-1}$ of the frustrated rotation. Note the peculiar anti-absorption structure associated with this vibrational model. This result should be contrasted with those of vibrational modes with finite dynamical dipole moments normal to the surface, for which reflection

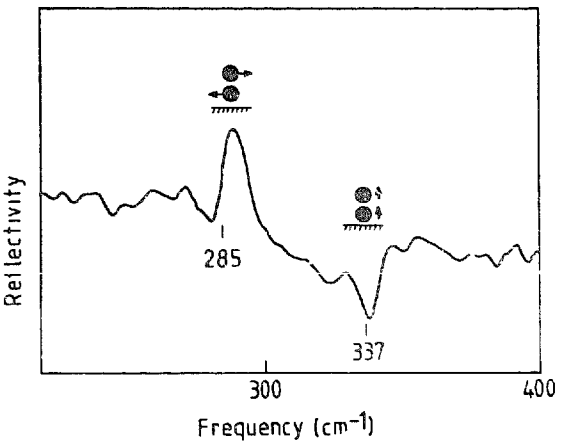


Fig 1 IRAS spectra in the frequency region of the frustrated rotation for CO on Cu(100) From ref [5]

"dips" occur, as for the Cu–CO stretch vibration in fig. 1.

Consider an electromagnetic wave incident on a metal surface. It is well known that at IR frequencies (say $\hbar\omega \sim 0.1$ eV) the electric field on the vacuum side is almost orthogonal to the surface. This follows from the continuity of $E_\parallel$ at the surface and from the strong screening of the electric field in the metal. It was therefore a surprise as Chabal [4,5] and coworkers observed formally dipole forbidden (with respect to the surface normal) low-frequency frustrated translations (H on W(100) and Mo(100)) 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 Cu–CO 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. 2), 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 $E_\parallel$ 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. 2). 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 [4,6,7].

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 broad band IR reflectivity. This was observed both for CO on Cu(100) [5] and for H on W(100) and Mo(100) [4,8]. Before presenting a quantitative study of this topic let us give a qualitative discussion about the origin of the background absorption and also about how dipole forbidden adsorbate vibrations can be excited in IRAS. We focus on the two processes shown in fig. 3.

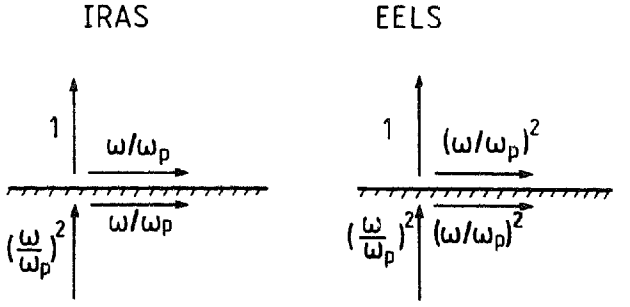


Fig 2 The relative strength of the normal and parallel electric field vector components at a metal surface investigated by IRAS and EELS The electric field ratios for IRAS follow directly from the Fresnel formulas for the electric field In EELS (dipole scattering) the momentum transfer $q_\parallel$ is so large that retardation effects can be neglected, i.e., $cq_\parallel \gg \omega$, and the electric field ratios indicated in the figure follow from the Fresnel formulas by taking the limit $c \to \infty$

Fig 3a describes a process where a photon excites an electron from a level $|\alpha\rangle$ below the Fermi surface to a level $|\beta\rangle$ above the Fermi surface. The momentum necessary for this excitation is supplied by the adsorbates and the process results in the IR background discussed above.

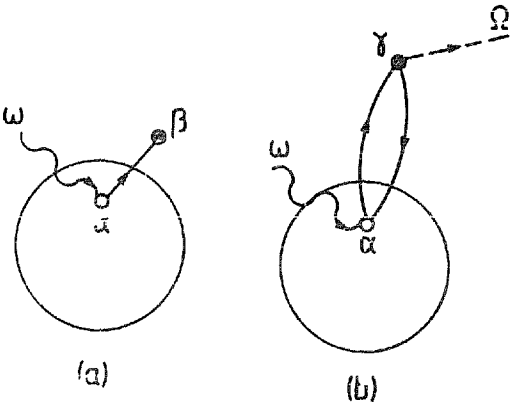


Fig 3 Elementary processes which contribute to the surface absorptivity

For a metal film in the limit $\omega \to 0$, where $\omega$ is the frequency of the oscillating electric field, this process gives the adsorbate induced contribution to the DC resistivity of the film.

We will show that process 3b does give rise to a sharp structure at $\omega = \Omega$ and furthermore that the intensity of this structure can be large. In this process, an electron is excited from a state $|\alpha\rangle$ ($\epsilon_\alpha < \epsilon_F$) to an intermediate and in general virtual state $|\gamma\rangle$ ($\epsilon_\gamma > \epsilon_F$) and $\epsilon_\gamma - \epsilon_\alpha \neq \omega$. 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 $\Omega$. 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 delta function but will be broadened due to coupling between the vibrational excited state and the electron–hole (e–h) pair excitations of the metal.

Processes 3a and 3b can be treated in a coherent but semi-classical manner as follows. Consider first a thin metallic film (thickness $d$) with a layer of adsorbed molecules. Assume that an oscillating electric field $E \sim \exp(-i\omega t)$ acts on the electrons in the film. This induces a collective (drift) motion of the electrons, corresponding to an oscillating current $J = ne\dot{x}$, where $x$ is the electron displacement and $n$ the number of conduction electrons per unit volume; see fig. 4. In addition, the adsorbates can perform oscillations parallel to the surface (normal mode coordinate $q$). In a semi-classical treatment, the equation of motion for $q$ and $x$ takes the form

$$\ddot{q} + \Omega^2 q + \frac{1}{\tau_{e-h}}(\dot{q} - \dot{x}) = 0, \tag{1}$$

$$\ddot{x} + \frac{1}{\tau_B}\dot{x} + \frac{Mn_a}{mnd\tau_{e-h}}(\dot{x} - \dot{q}) = \frac{e}{m}E, \tag{2}$$

where $n_a$ is the number of adsorbates per unit area and $m$ and $M$ the electron and adsorbate mass, respectively. Note that the friction force on the adsorbate involves the relative velocity $\dot{q} - \dot{x}$ between the vibrating adsorbate and the collective motion of the conduction electrons. The origin of this term is similar to the friction force which acts on a body moving in streaming water which, of course, is proportional to the relative velocity and, in particular, vanishes if there is no relative motion between the water and the body. The last term on the LHS of eq. (2) is the reaction force on the electrons from the friction force acting on the adsorbate. The friction coefficient $1/\tau_{e-h}$ is the damping rate, due to excitation of e–h pairs, of the frustrated translation $q$. Substituting $E = E(\omega)\exp(-i\omega t)$ in eqs. (1) and (2) gives

$$\left(-\omega^2 + \Omega^2 - i\frac{\omega}{\tau_{e-h}}\right)q(\omega) = -i\frac{\omega}{\tau_{e-h}}x(\omega), \tag{3}$$

$$\left(-\omega^2 - i\frac{\omega}{\tau_B}\right)x(\omega) - i\omega\frac{Mn_a}{mnd\tau_{e-h}}(x(\omega) - q(\omega)) = \frac{e}{m}E(\omega) \tag{4}$$

If we define the conductivity $\sigma(\omega)$ by

$$-i\omega nex(\omega) = \sigma(\omega)E(\omega)$$

then it follows from eqs. (3) and (4) that

$$\sigma(\omega) = \frac{ne^2}{m}\left[-i\omega + \frac{1}{\tau_B} + \frac{Mn_a}{mnd\tau_{e-h}}\frac{\Omega^2 - \omega^2}{\Omega^2 - \omega^2 - i\omega/\tau_{e-h}}\right]^{-1} \tag{5}$$

Hence, if we define an effective surface relaxation time $\tau_s$ by

$$\frac{1}{\tau_s} = \frac{Mn_a}{mnd\tau_{e-h}}\frac{\Omega^2 - \omega^2}{\Omega^2 - \omega^2 - i\omega/\tau_{e-h}} \tag{6}$$

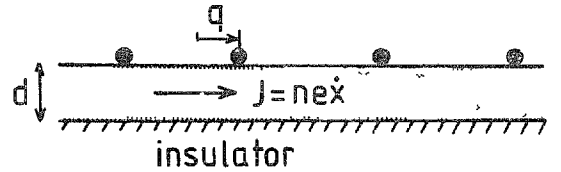


Fig. 4. A thin metallic film on an insulating substrate. An external AC potential drives a current $J = nex$ through the film.

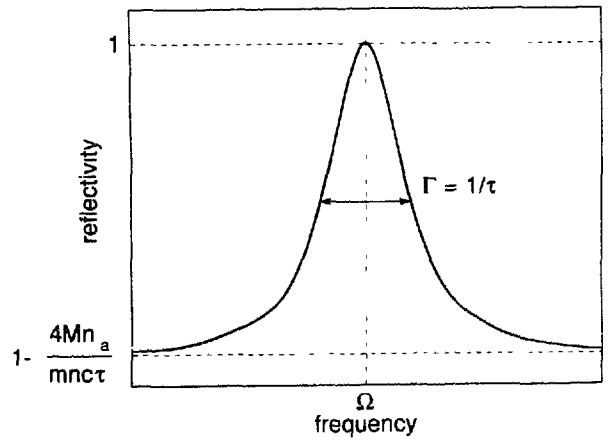


Fig 5. Theoretical IR reflectance spectra from a surface with adsorbed molecules, having frustrated translations with resonance frequency $\Omega$ and with damping $\Gamma = 1/\tau$ The inequality $\omega/\omega_p \gg v_F/c$ is assumed to hold

then the conductivity $\sigma(\omega)$ takes the usual form

$$\sigma(\omega) = \frac{ne^2}{m} \frac{1}{-i\omega + 1/\tau_{tot}}, \tag{7}$$

where

$$\frac{1}{\tau_{tot}} = \frac{1}{\tau_B} + \frac{1}{\tau_s}. \tag{8}$$

Based on these equations one can derive an expression for the change in the IR reflectance, $\Delta R$, induced by adsorbates on a semi-infinite metallic substrate It has been shown in ref. [1] that for $\omega \gg 1/\tau_B$ and $\omega/\omega_p \gg v_F/c$ the adsorbate induced change in the reflectivity is given by

$$\Delta R = -\frac{4Mn_a}{mnc\tau_{e-h}} \frac{(\Omega^2 - \omega^2)^2}{(\Omega^2 - \omega^2)^2 + (\omega/\tau_{e-h})^2}. \tag{9}$$

The reflectance predicted from this formula is shown in fig 5. For $|\Omega - \omega| \gg 1/\tau_{e-h}$ a uniform back-ground absorption occurs due to excitation of e–h pairs – this effect corresponds to process (a) in fig. 3. Centered at $\omega = \Omega$ is an anti-absorption peak, i.e , the reflectance is higher (in fact unity) at resonance $\omega \sim \Omega$ than away from resonance This has a very simple physical meaning According to eq. (1), $q - \dot{x} = 0$ for $\omega = \Omega$, i.e., no relative motion occurs between the vibrating adsorbate and the collective motion of the electron gas, resulting in no energy absorption and unity reflectivity. The anti-absorption structure, eq. (9), is similar to that observed for CO on Cu(100) (see fig. 1). For more details, see refs. [1,3].

## 3. Surface resistivity

Let us now discuss the relation between the increase in the resistivity $\Delta\rho$ of a thin metal film upon adsorption of molecules on the film surface and the e–h pair contribution $\tau_{e-h}$ to the lifetime of the parallel vibrational motion of the adsorbates. Using eqs. (6)–(8) in the limit $\omega \to 0$ gives the adsorbate induced change in the film resistivity:

$$\Delta\rho = \frac{Mn_a}{n^2e^2d\tau_{e-h}}. \tag{10}$$

Fig. 6a shows the change in resistivity [9] $\Delta\rho$ 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 eq. (10), $\partial\rho/\partial n_a \sim 1/d$ if we assume

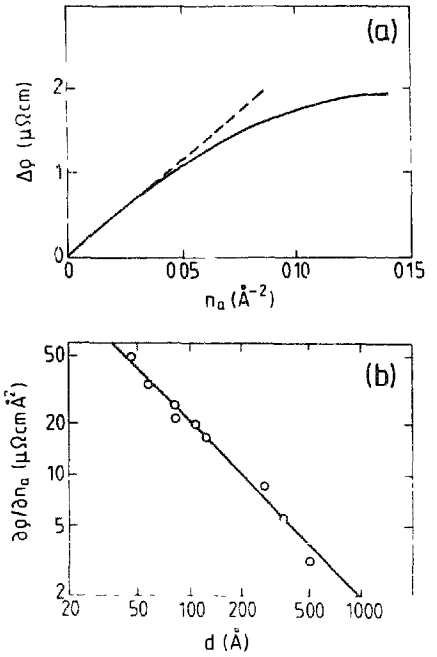


Fig 6 (a) The change in film resistivity $\Delta\rho$ as a function of CO coverage for the CO/Ni(111) chemisorption system (b) The variation of $\partial\rho/\partial n_a$ ($n_a \to 0$) with the film thickness $d$ The straight line has the slope – 1 From ref [32]

Table 1
The lifetime $\tau$ (due to excitation of electron–hole pairs) of the parallel frustrated translation for several adsorption systems (the cross section $\Sigma$ is defined in the text)

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

[a] From ref. [32]
[b] From ref [33].
[c] From ref. [34].
[d] From ref. [35]
[e] From ref [36]

that $\tau_{e-h}$ is independent of $d$ as expected if the film is thick enough. This relation is well satisfied for the CO–Ni chemisorption system [9] as shown in fig. 6b 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. 6b we get

$$d\frac{\partial\rho}{\partial n_a}\bigg|_{n_a=0} \approx 2000\mu\Omega\ cm\ \mathring{A}^3;$$

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

In table 1, we 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 we have assumed that the free electron density $n$ corresponds to one electron per substrate metal atom and that the effective electron mass $m$ is identical to the free-electron mass. These assumptions are reasonable for Ag and Cu but not so accurate for Ni. In the same table, we also give the effective ... section $\Sigma$ for diffusive scattering against an a... bate, defined by [10]

$$\Sigma = \frac{\pi e^2 d}{m v_F}\frac{\partial\rho}{\partial n_a}\bigg|_{n_a=0}. \qquad (11)$$

As expected, for physisorbed atoms and molecules, the damping rates $1/\tau_{e-h}$ are smaller by a factor of $\sim 10^{-1}$–$10^{-3}$ than for chemisorbed adsorbates.

The $\tau_{e-h}$ values given in table 1 are the energy relaxation times, of the frustrated translations, 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 [11] or inelastic helium scattering [12,13] since other, competing energy relaxation processes occur, such as decay via emission of one or several bulk phonons.

Above I have derive an equation relating the lifetime $\tau_{e-h}$ to the adsorbate induced increase in film resistivity $\Delta\rho$. I now present the results of a theoretical study of the e–h pair damping $1/\tau_{e-h}$ of frustrated translations.

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 $|k\rangle$ forming a resonance state $\rho_a(\epsilon)$ centered at $\tilde{\epsilon}_a$ and with the width (FWHM) $\Gamma$. For this model one obtains the following damping rate of the parallel frustrated translation:

$$\frac{1}{\tau_{e-h}} = 2\frac{m}{M}\omega_F \Gamma \rho_a(\epsilon_F)\langle \sin^2\theta\rangle, \qquad (12)$$

where $\hbar\omega_F = \epsilon_F$ is the Fermi energy and $\langle \sin^2\theta\rangle$ is a weighted average of $k_\parallel^2/k_F^2$ where $k_\parallel = k_F \sin\theta$ is the parallel component of the wave vector of a metal electron on the Fermi surface I have evaluated $\langle \sin^2\theta\rangle$ for adorbitals of s and $p_z$ (or $p_x$) symmetry and typically found $\langle \sin^2\theta\rangle \approx 0.20$ in the former case and $\approx 0.33$ in the latter case

Let us discuss the data in table 1 in the light of eq (12)

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

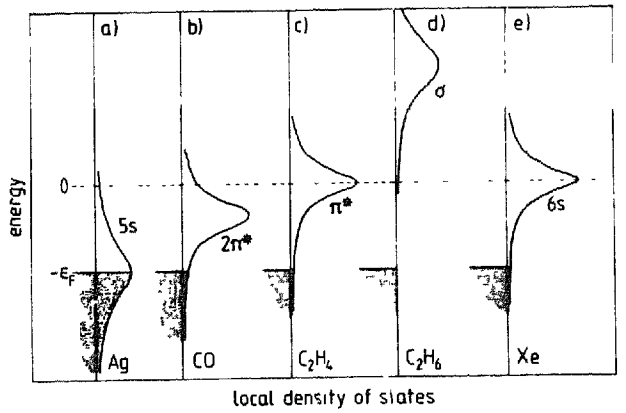


Fig 7 Local (or projected) density of states induced by (a) an Ag atom on a Ag(111) surface, (b) CO on Cu(111), (c)–(e) $C_2H_4$, $C_2H_6$ and Xe adsorbed on Ag(111) (schematic)

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 $\epsilon_F$. From measurements of the work function change when Ag atoms are adsorbed on an Ag(111) surface at low temperature, one can estimate the Ag adatom → metal charge transfer to be at most $0.04e$. Hence the Ag atom is essentially neutral, as 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, $\epsilon_F$; see fig 7a (We assume a non-magnetic 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 1. Let us focus on the cross section $\Sigma$ for diffuse scattering of a conduction electron from an adsorbed Ag atom. Using eqs (10) and (11) we can write

$$\Sigma = \frac{16}{3}\frac{M}{mn_i\tau_{e-h}},$$

and combining this with eq. (12) gives

$$\Sigma = \frac{32}{3}\frac{\omega_i\langle\sin^2\theta\rangle}{v_i n}\Gamma\rho_a(\epsilon_F)$$

But in the present case $\tilde{\epsilon}_a \approx \epsilon_F$ so that

$$\rho_a(\epsilon_F) \approx \frac{1}{\pi}\frac{\Gamma/2}{(\tilde{\epsilon}_a-\epsilon_F)^2+(\Gamma/2)^2} \approx \frac{2}{\pi\Gamma}$$

Hence $\Gamma\rho_a(\epsilon_F) \approx 2/\pi$ and

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

For Ag, $\hbar\omega_F = 5.53$ eV, $v_F = 1.4\times10^6$ m/s, $n = 0.0586$ Å$^{-3}$ and $\langle\sin^2\theta\rangle = 0.2$ (see ref. [14]) so that $\Sigma \approx 14.6$ Å$^2$, in very good agreement with the experimental cross section (13.4 Å$^2$) quoted in table 1.

Next, let us consider CO adsorbed on Cu(111) where the $2\pi^*$ resonance has been studied using inverse photo emission. The $2\pi^*$ resonance is centered at $\tilde{\epsilon}_a - \epsilon_F = 2.5$ eV and has the width (FWHM) $\Gamma = 1.5$ eV; see fig. 7b. Hence ($a \equiv 2\pi^*$)

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

Using $\langle\sin^2\theta\rangle = 0.33$ (see ref. [14]) and accounting for both $2\pi_i^*$ and $2\pi_j^*$, we get from eq (12) $\tau_{e-h} \approx 7\times10^{-11}$ s, in relatively good agreement with the lifetime deduced from the resistivity data for CO on Cu films, $\tau_{e-h} \approx 4\times10^{-11}$ s (see table 1)

Next, consider $C_2H_6$ and $C_2H_4$ on silver. These molecules are both physisorbed with very similar binding energies. This is indicated by the similar desorption temperatures, 96 K for $C_2H_6$ [15] and 90 K for $C_2H_4$ [16,17]. Nevertheless, as shown in table 1, the vibrational damping and the adsorbate induced change in the surface resistivity differ by a factor ~ 5. This remarkable result is simple to explain by noting that the lowest unoccupated molecular resonance state is much closer to the fermi energy for $C_2H_4$ than for $C_2H_6$. According to inverse photoemission results by Koch and coworkers a $\pi^*$ resonance of $C_2H_4$ adsorbed on Ag(111) is centered around the vacuum level; see fig 7c. Such a $\pi^*$ resonance does not exist for $C_2H_6$ which has only higher-lying $\sigma$ resonances, see fig. 7d This results in a much smaller adsorbate induced density of states at the fermi energy for $C_2H_6$ as com-

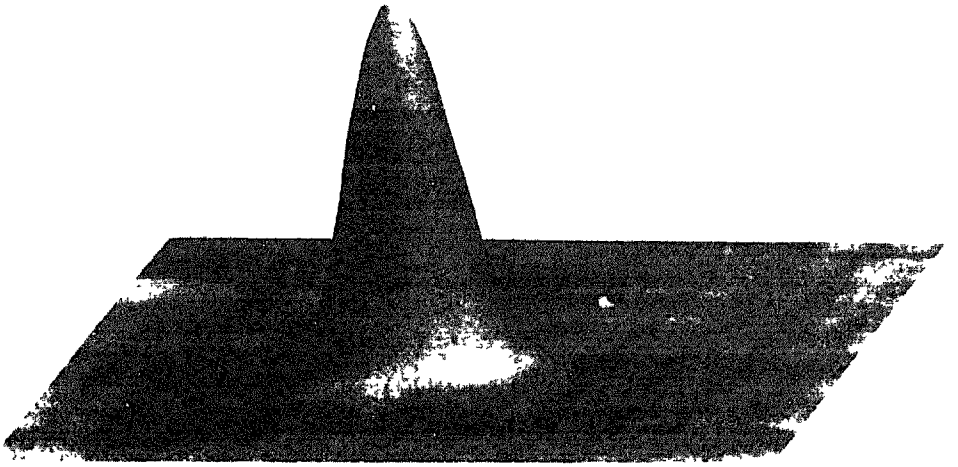

Fig. 8. A constant current STM image of Xe adsorbed on Ni(110) taken with the tip biased +0.020 V relative to the sample. Xe appears as a 1.5 Å high protrusion. From ref. [19].

pared with $C_2H_4$ which according to eq. (12) explains the observed difference in vibrational damping.

It is known from inverse photoemission measurements [18] that the 6s level in Xe on Pt(111) forms a resonance located around the vacuum level and with a width of $\Gamma \approx 1$ eV. The tail of the resonance extends down to the Fermi energy and gives rise to a low density of states at $\epsilon_F$; see fig. 7e, and fig. 4 in ref. [19]. It has been pointed out by Eigler et al. [19,20] that this is in fact the origin of why Xe shows up as a big bump in STM (where electron tunneling to adsorbate induced states in the vicinity of $\epsilon_F$ occurs); see fig. 8. Assuming a Lorentzian 6s resonance, with $\tilde{\epsilon}_a - \epsilon_F = 4$ eV and $\Gamma = 1$ eV gives $\rho_a(\epsilon_F) \approx 0.01$ eV$^{-1}$, and from eq. (12) $\tau_{e-h} \approx 7 \times 10^{-9}$ s which is 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 e–h pair damping of the corresponding parallel frustrated translations.

## 4. Applications

### 4.1 Atomic scale friction

The study presented above has shown that the e-h pair contribution, $1/\tau_{e-h}$, to the damping of parallel frustrated translations, can be directly obtained from either the adsorbate induced change in the DC resistivity of thin metallic films or from the IR spectroscopy. One can define a friction coefficient

$$\eta = \frac{1}{\tau_{e-h}} + \frac{1}{\tau_{phonon}}.$$

Here $1/\tau_{phonon}$ is the contribution to $\eta$ from phonon emission. The friction coefficient $\eta$ enters in many dynamical processes at surfaces e.g. in surface diffusion or in atomic scale friction. Atomic scale friction was recently studied by Krim et al. [21]. They evaporated thin smooth (and rough) silver and gold films on a quartz-crystal microbalance; see fig. 9. If one monolayer or less of molecules are adsorbed on the surface of the metal film this gives rise to a small shift in the resonance frequency of the crystal, which is proportional to the adsorbed mass. In addition, for

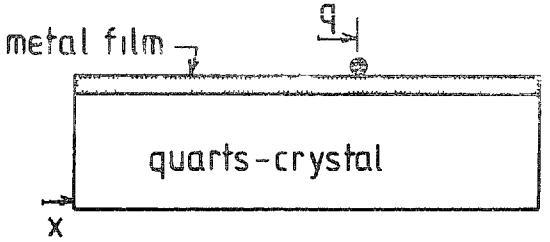


Fig. 9. Quartz-crystal microbalance with a thin metallic film containing an adsorbed layer of atoms (schematic).

very weakly adsorbed molecules such as noble gas atoms, some slippage occurs which gives a contribution to the damping of the vibrational motion and which can be measured experimentally. In particular, at high coverages incommensurate adsorbate structures are formed and the pinning of these structures by the corrugated substrate potential is often very small resulting in large slippage. If the pinning potential is neglected, the equation of motion for the adsorbates (displacement coordinate $q$) and the substrate (displacement coordinate $x$) takes the form (see fig. 9)

$$\ddot{q} + \eta(\dot{q} - \dot{x}) = 0,$$

$$x + \gamma\dot{x} + \omega_0^2 x + N\frac{m}{M}\eta(\dot{x} - \dot{q}) = F,$$

where $F$ is a driving force. In these equations, $M$ is the mass of the vibrating crystal (without adsorbates), $Nm$ is the mass of the adsorbates ($N$ is the number of adsorbates) and $\gamma$ is the damping of the vibrational motion in the absence of the adsorbates. Note the similarity between these equations and those studied earlier in the context of electric conductivity (eqs. (1) and (2)). Assuming $F = F_0 \exp(-i\omega t)$ gives

$$x(\omega) = \frac{F}{\omega_0^2 - \omega^2 - i\omega\gamma_{tot}},$$

where

$$\gamma_{tot} = \gamma + N\frac{m}{M}\frac{\omega\eta}{\omega + i\eta}.$$

Hence the adsorbates will induce a frequency shift $\Delta\omega$ and a change in the damping $\Delta\gamma$ given by

$$2\,\Delta\omega = \mathrm{Im}\ \gamma_{tot} = -N\frac{m}{M}\frac{\omega\eta^2}{\omega^2 + \eta^2},$$

$$\Delta\gamma = \mathrm{Re}\ \gamma_{tot} - \gamma = N\frac{m}{M}\frac{\omega^2\eta}{\omega^2 + \eta^2},$$

so that

$$\Delta\gamma/\Delta\omega = -2\omega/\eta$$

Using these equations, the quantities $Nm$ and $\eta$ can be immediately obtained from the adsorbate induced frequency shift $\Delta\omega$ and damping $\Delta\gamma$

The analysis presented above was carried out by Krim et al. for incommensurate layers of Kr on gold and silver films. The observed friction $\eta \approx 10^8\ s^{-1}$ corresponds to a lifetime $\tau \approx 10^{-8}$ s. This lifetime cannot be explained by excitation of bulk phonons. In fact in the absence of pinning, $\tau_{phonon} = \infty$ as shown by Aubry [22]. Similarly, the model study of Sokoloff [23] gives $\tau_{phonon} \approx 10^{-3}$ s which is completly negligible. Hence the observed damping is likely to be due to excitation of e–h pairs and, in fact, the observed lifetime is similar to that deduced from resistivity data for Xe on Ag(111) (see table 1), $\tau_{e-h} \approx 0.3 \times 10^{-8}$ s. Converted into cross sections for diffusive electron scattering one gets $\Sigma(\mathrm{Ar}) \approx 0.1$ Å$^2$ and $\Sigma(\mathrm{Xe}) \approx 0.6$ Å$^2$. The longer lifetime and smaller cross section for adsorbed Kr is consistent with the more inert nature of this atom. It is also consistent with the experimental data of Eigler and Schultz [24], who measured the cross sections $\sigma$ for spin-flip scattering of conduction electrons from Xe and Kr adsorbed on lithium. They found $\sigma(\mathrm{Kr}) = 2 \times 10^{-4}$ Å$^2$ and $\sigma(\mathrm{Xe}) = 35 \times 10^{-4}$ Å$^2$ so that $\sigma(\mathrm{Xe})/\sigma(\mathrm{Kr}) \approx 18$. (Note that $\sigma$ depends on a product of two local density-of-states factors while $\Sigma$ is proportional to one such factor, e.g. $\sigma \sim \rho_{6s}(\epsilon_F)\rho_{6p}(\epsilon_F)$ and $\Sigma \sim \rho_{6s}(\epsilon_F)$ for Xe. Hence, one expects a stronger change of $\sigma$ than of $\Sigma$ when going from Kr to Xe ) It would be interesting to extend the resistivity and quartz-crystal microbalance studies by performing these measurements on the same adsorbate system.

### 4.2. Surface diffusion

Diffusion of adsorbates is of central importance in many surface reactions. Surface resistivity studies can contribute in two ways to surface diffusion. First, it has been shown that the adsorbate diffusion coefficient $D = D_0 \exp(-E/k_BT)$ can be measured directly by monitoring the time dependence of the surface resistivity as a given dose of adsorbate is adsorbed on the surface Adsorbates bind stronger to surface defects than on the perfect surface areas, and as time increases, the adsorbates will diffuse to surface imperfections (we assume a low concentration of adsorbates) where they may stick more or less

permanently, and this diffusion process can be followed by studying the time dependence of the film resistivity. The point is that an isolated adsorbate on a flat surface area usually has a different cross section $\Sigma$ for diffusive electron scattering as compared to the case where it is bound to a step or to an other surface imperfection. Secondly, the friction coefficient $\eta$ enters directly in $D_0$. Since the e–h part of $\eta$ can be obtained from the adsorbate induced contribution to the film resistivity, this constitutes an important connection. It is not surprising that $D_0$ depends on $\eta$ since, according to the fluctuation–dissipation theorem, the fluctuations in the system, which can "kick" an adsorbate over the barrier $E$, depend on $\eta$. Indeed if we write $D_0 = w\langle l^2\rangle/4$ where $w$ is the jump rate over the barrier and $\langle l^2\rangle$ the average of the square of the jump distance, then, as Kramers [25] has shown, $w \sim 1/\eta$ as $\eta \to \infty$ and $w \sim \eta$ as $\eta \to 0$ while $w$ is roughly independent of $\eta$ for a wide range of intermediate $\eta$ values. The quantity $\langle l^2\rangle$ depends also on $\eta$: for large $\eta$ the motion of the adsorbates is strongly damped and they will only perform jumps between nearest neighbour binding sites, but for small $\eta$ the motion is weakly damped and once the adsorbate is thermally excited over the barrier $E$ it will propagate for several lattice spacings before falling down in a well; see fig. 10. For a detailed discussion of the role of $\eta$ in surface diffusion, see e.g. ref. [26].

### 4.3. Other applications

There are several other applications of surface or thin film resistivity, some of which are reviewed in the beautiful work of Schumacher [27]:

(a) The growth of thin metallic films can be studied by monitoring the variation in the film resistivity as a function of the coverage $\Theta$. In a certain temperature range the change in resistivity $\Delta\rho$ is typically found to exhibit a damped oscillatory behaviour, where the period of oscillation corresponds to $\Delta\Theta = 1$. This growth mode corresponds to a uniform layer-by-layer growth and in order to obtain a surface with a minimum of defects, it is necessary to stop the evaporation process just when a monolayer is completed where $\Delta\rho$ is at a local minima.


Fig. 10. Adsorbate diffusion on a corrugated one dimensional potential energy surface. For large friction $\eta$ the adsorbate motion is strongly damped and only jumps between nearest potential wells occur. For small friction, once excited over the barrier, the adsorbate propagates for many lattice spacings before finally falling down in a well.

(b) The damping of surface plasmon excitations in small Ag-particle systems embedded in various gas matrices was studied in ref. [28]. It was found that both the width and the peak position of the optical absorption resonances have a surface contribution proportional to $1/R$ where $R$ is the radius of the particle. This surface contribution to the linewidth $\Gamma$ is much larger (by at least a factor of $\sim 2$) for CO and $C_2H_4$ matrices as compared with more inert matrices such as Ar or $N_2$. This is similar to the influence these molecules have on the DC resistivity of thin metallic films (see table 1). However, the damping which occurs in the present case is associated with a relatively high frequency electric field ($\hbar\omega \sim 3$ eV) and it seems as if the dominant contribution to $\Gamma$ is derived from excitations caused by the electric field component normal to the surface of the particles, rather than associated with the surface resistivity. Nevertheless, the difference in $\Gamma$ between "reactive" and "inert" matrices can again be related to the occurrence or absence of low-lying nearly empty adsorbate induced resonance states.

(c) Other interesting applications of surface resistivity are to surface enhanced Raman scattering [29,30], adsorption and desorption, and interdiffusion [27,31].

## 5. Summary and outlook

In this work I have discussed the concept of surface resistivity and have presented a number of important applications. Concerning the theoretical status of this field, a relatively good overall understanding has been reached, but the theory has a number of "weak links" which deserve

further attention. For example, the derivation of the adsorbate induced change in IR reflectivity $\Delta R$ (see eq. (9)) is strictly valid only if $\omega/\omega_p \gg v_F/c$. However the experimental data are for $\omega/\omega_p < v_F/c$ and theory needs to be extended to treat this case. Also, in the derivation of the thin-film resistivity $\Delta\rho$ (see eq. (10)) it is implicitly assumed that the current $J$ is uniform throughout the film thickness $d$ and that the reaction force from the adsorbates on the conduction electrons is uniformly distributed. These assumptions hold strictly only when $\tau_B = \infty$.

The measurements of adsorbate induced changes in the thin-film resistivity are simple and cheap experiments which in most cases are easy to interpret theoretically, and deserve much more attention The measurements of the IR reflectivity spectra of low-frequency parallel adsorbate vibrations should be extended to simpler systems (e.g. H on Cu(100)) than those studied up to date in order to test the theories which have been developed to explain the origin of the intensity and the lineshape of these dipole forbidden (with respect to the surface normal) vibrational modes.

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