

Reply to "Comment on 'Surface resistivity and vibrational damping in adsorbed layers'"

B. N. J. Persson

Institut für Festkörperforschung, Forschungszentrum Jülich, D-52425 Jülich, Germany

(Received 20 September 1993)

The criticism raised by Tobin is refuted.

I completely disagree with the criticism raised by Tobin; I believe that his comments result from a misunderstanding of Refs. 1 and 2. The major objection of Tobin is his claim that only inelastic interactions between the adsorbates and the metal conduction electrons have been taken into account, i.e., that elastic-scattering processes have been neglected. This conclusion is wrong, as is perhaps most easily seen from the semiclassical equations of motion given in Ref. 2:

$$\ddot{Q} + \Omega^2 Q + \eta(\dot{Q} - \dot{x}) = 0, \quad (1)$$

$$\ddot{x} + \frac{1}{\tau_B} \dot{x} + \frac{Mn_a \eta}{mnd} (\dot{x} - \dot{Q}) = \frac{e}{m} E. \quad (2)$$

Here Q is the parallel adsorbate vibrational coordinate and $J = ne\dot{x}$ is the electronic current density in the metal film (thickness d). Now, assume first that the electric field E in the metal oscillates harmonically with a frequency well away from the resonance frequency Ω of the parallel adsorbate vibrations. In this case the adsorbates will not participate in the motion, i.e., $\dot{Q} \approx 0$. Hence the electron-adsorbate interaction is purely elastic and from (2) one gets

$$\ddot{x} + \left[\frac{1}{\tau_B} + \frac{Mn_a \eta}{mnd} \right] \dot{x} = \frac{e}{m} E. \quad (3)$$

Hence we may define an effective electron relaxation time τ_{eff}

$$\frac{1}{\tau_{\text{eff}}} = \frac{1}{\tau_B} + \frac{Mn_a \eta}{mnd}. \quad (4)$$

This relaxation rate has a contribution ($1/\tau_B$) from bulk scattering and another from *elastic* scattering from the randomly distributed adsorbates [the second term in (4)] proportional to η . Now the important point is that $\tau = 1/\eta$ is also the energy relaxation time, via coupling to electron-hole pairs in the metal, of an adsorbate vibration. This follows immediately from (1) if we set $\dot{x} = 0$ in which case one finds $Q \sim e^{-\eta t} \cos \Omega t$, i.e., $\eta = 1/\tau$ is the damping of the adsorbate vibration. Since the resistivity $\rho = m/ne^2 \tau_{\text{eff}}$ it follows from (4) that $\rho = \rho_B + Mn_a \eta/n^2 e^2 d$, i.e.,

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

The discussion above assumes implicitly that η can be considered as frequency independent as ω increases from zero to Ω —otherwise the dc resistivity and the vibrational damping would probe different $\eta = 1/\tau$. But the electronic friction η is expected to depend on frequency ω only when the variation of $\hbar\omega$ is of order of the width Γ of the adsorbate-induced electronic resonance states close to the Fermi energy (see Ref. 1). But since typically Γ is of order 1 eV or more and since $\hbar\Omega < 0.1$ eV the condition $\hbar\Omega \ll \Gamma$ is satisfied.

Another objection of Tobin is the use of the jellium model. However, in the present context (at low frequencies) this is an excellent approximation for copper. Furthermore, in a recent paper (Ref. 3) the original theory has been extended to include a finite bulk electron mean free path and also to be valid in the anomalous skin effect frequency region.

Finally, Tobin has suggested that the fact that the amplitude of the antiabsorption peak associated with the frustrated rotation for CO on copper is less than the broadband reflectance change for $\omega \approx \Omega$ is in variance with the theory presented in Refs. 1–3. But this is not true: the theory developed in Refs. 1–3 is strictly valid only for "pure" parallel adsorbate vibrations and not for frustrated rotations although the *physical* reason for the occurrence of antiabsorption resonances for the frustrated rotations is the same as for parallel adsorbate vibrations. In fact, for a frustrated rotation it is very easy to understand why, at resonance $\omega = \Omega$, the optical absorption does not return to the value of the clean surface. First note that the reason why no adsorbate-induced power absorption occurs at resonance for a pure parallel adsorbate vibration is related to the fact that when $\omega = \Omega$, according to (1), $\dot{Q} = \dot{x}$, i.e., no relative motion occurs between the adsorbates and the collective motion of the electron fluid in the metal. But for a frustrated rotation some relative motion always occurs since different parts of the adsorbate now have different parallel velocities. Hence for a frustrated rotation it is impossible to eliminate the frictional force between the adsorbates and the collective motion of the electrons. This discussion is "classical" but the same effect occurs in a quantum-mechanical treatment and, in fact, for a frustrated rotation only such a treatment can predict the *magnitude* of the antiabsorption peak.

¹B. N. J. Persson, Phys. Rev. B **44**, 3277 (1991).

²B. N. J. Persson and A. I. Volokitin, Chem. Phys. Lett. **185**,

292 (1991).

³B. N. J. Persson and A. I. Volokitin (unpublished).