

Asymmetric lines and background shifts in reflection-absorption infrared spectroscopy

R. G. Tobin

*Department of Physics and Astronomy, Michigan State University, East Lansing, Michigan 48824-1116
and Center for Fundamental Materials Research, Michigan State University, East Lansing, Michigan 48824-1116*

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The approximations commonly used in interpreting infrared spectra of adsorbates on metal surfaces neglect the dielectric response of the metal. At high angles of incidence, these approximations can be inadequate, particularly on low-conductivity metals. Straightforward analytic expressions are presented that are valid at all angles. The dielectric response produces an asymmetric line shape even for a Lorentzian oscillator, reduces the intensity of the band, and slightly enhances the broadband reflectance of the surface.

Reflection-absorption infrared spectroscopy (RAIRS) is widely used in the study of adsorption on metal surfaces.¹ Radiation polarized in the plane of incidence (*p*-polarized) is reflected from the surface at near-grazing incidence ($80^\circ < \theta < 90^\circ$) and the reflected intensity is measured both for the clean surface (I_0) and after adsorption (I). The fractional change in reflectance $\Delta R/R = (I - I_0)/I_0$ is calculated. It is almost invariably assumed that the dielectric constant of the metal is so high that $\Delta R/R$ can be attributed entirely to absorption of light by the layer of adsorbates. Under realistic experimental conditions this assumption can break down and the dielectric response of the metal can significantly affect the intensity and shape of the vibrational band. As experimenters move to higher angles of incidence in pursuit of improved sensitivity,¹ and as the interpretation of spectra becomes more detailed, these effects take on increasing importance. They must certainly be considered in examining vibrational lines for the subtle asymmetry predicted by Langreth² for modes that decay by the excitation of electron-hole pairs.³⁻⁵

The basis of most RAIRS analysis is the three-layer model introduced by Greenler⁶ and refined by McIntyre and Aspnes,⁷ Dignam, Moskovits, and Stobie,⁸ and Bagchi, Barrera, and Rajagopal.⁹ The adsorbate is modeled as a macroscopic layer of thickness d and (complex) dielectric constant ϵ_2 between vacuum and a substrate of dielectric constant ϵ_3 . The assumptions of sharp interfaces and local response functions, while problematic in principle, do not create serious difficulties in practice.^{1,9} The fundamental problem is that the model seeks to represent an essentially two-dimensional layer—one with a “thickness” of atomic dimensions—by a macroscopic dielectric function. A more natural description^{10,11} is in terms of a surface susceptibility ($N_s\alpha$) where the notation, following Langreth,¹⁰ suggests a surface density N_s of oscillators with individual polarizabilities α , although such an interpretation is not necessary. The connection between ($N_s\alpha$) and the three-dimensional dielectric function ϵ_2 is made through the parameter d : $\epsilon_2 = 1 + 4\pi N_s\alpha/d$. In general there is no way to determine d . Chabal has given a lucid discussion of this issue.¹

The indeterminacy of d can be avoided if two condi-

tions are met: first, that ϵ_3 is very large and θ is not too close to grazing,

$$\tan^2\theta \ll |\epsilon_3|, \quad (1)$$

and second, that the susceptibility of the adsorbed layer is small,

$$\left| \frac{4\pi N_s\alpha}{d} \right| \ll 1. \quad (2)$$

Under these circumstances, the response in the three-layer model can be linearized,⁷ with no dependence on d :

$$\frac{\Delta R}{R} = -32\pi^2\nu \frac{\sin^2\theta}{\cos\theta} \text{Im}(N_s\alpha). \quad (3)$$

(In this work I adopt the usual convention that the time dependence of the electric field is given by $e^{-i\omega t}$; Ref. 7 assumes a time dependence of $e^{i\omega t}$.) Unfortunately, conditions (1) and (2) are often violated in practice. At the frequency of the C=O stretch vibration of adsorbed CO, $\tan^2\theta = |\epsilon_3|$ at 86° on Ni and at 87° on Pt—well within the range of many experiments. Moreover, for a saturated CO layer $4\pi N_s\alpha$ is of the order of a few angstroms, so the left side of (2) is not small for reasonable values of d . Nevertheless Eq. (3) is commonly used in the interpretation of RAIR spectra.

If the polarizability is anisotropic, as for an oriented layer, the response is dominated by the polarizability α_z perpendicular to the surface. The response to the component parallel to the surface is smaller⁸⁻¹⁰ by a factor of $\cos\theta/\sqrt{\epsilon_3}$. I consider here only the perpendicular component; Mal'shukov has recently analyzed the parallel component.¹²

An alternate approach has been developed by Persson.^{11,13} The overlayer is modeled by a surface susceptibility ($N_s\alpha$). If the local electric field at the surface is not seriously perturbed by the adsorbate, the power per unit area absorbed in the surface layer can be calculated. If it is assumed that ΔR is due entirely to this surface absorption, then

$$\frac{\Delta R}{R} = -32\pi^2\nu \left| \frac{1+r}{2r} \right|^2 \frac{\sin^2\theta}{\cos\theta} \text{Im}(N_s\alpha), \quad (4)$$

where r is the Fresnel amplitude reflection coefficient for p -polarized light.¹ Although this approach avoids introducing a bulk dielectric function for the layer, it neglects adsorbate-induced changes in the substrate absorption.

Langreth¹⁰ has developed a macroscopic theory of reflectivity that makes it possible to derive a straightforward analytical expression for $\Delta R/R$, valid in virtually all experimental situations, that includes the dielectric response of the substrate and models the overlayer through $(N_s\alpha)$. His paper, however, provides explicit results only when θ is not too large [condition (1) is satisfied]; the results below are valid at all angles. The response $\Delta R/R$ is linear in $(N_s\alpha)$, provided that

$$\left| \frac{8\pi^2\nu N_s\alpha}{\cos\theta \pm 1/\sqrt{\epsilon_3}} \right| \ll 1, \quad (5)$$

a condition much weaker than (2) that is valid at all angles for monolayers on metals; for a saturated layer of CO on a typical metal the left-hand side is at most 0.01.

The fractional change in reflectivity can be written

$$\frac{\Delta R}{R} = -32\pi^2\nu \frac{\sin^2\theta}{\cos\theta} [\beta_1 \text{Im}(N_s\alpha) + \beta_2 \text{Re}(N_s\alpha)] \quad (6)$$

with

$$\begin{aligned} \beta_1 &= \text{Re} \left[\frac{1}{(1-1/\epsilon_3)(1-\tan^2\theta/\epsilon_3)} \right] \\ &\approx \frac{|\epsilon_3|^2 - \tan^2\theta \text{Re}(\epsilon_3)}{|\epsilon_3 - \tan^2\theta|^2}, \\ \beta_2 &= \text{Im} \left[\frac{1}{(1-1/\epsilon_3)(1-\tan^2\theta/\epsilon_3)} \right] \\ &\approx -\frac{\tan^2\theta \text{Im}(\epsilon_3)}{|\epsilon_3 - \tan^2\theta|^2}, \end{aligned} \quad (7)$$

where the approximate forms in Eqs. (7) are valid for $|\epsilon_3| \gg 1$. For metals in the ir, this is an excellent approximation; also $\text{Re}(\epsilon_3) < 0$ and $\text{Im}(\epsilon_3) > 0$, so β_1 is positive and β_2 is negative. Identical coefficients can be derived from the work of Bagchi, Barrera, and Rajagopal⁹ if condition (2) is satisfied; Langreth's work shows that the weaker condition (5) is sufficient.

The complete expression (6) differs from the approximate forms (3) and (4) in two significant ways: the response to $\text{Im}(N_s\alpha)$ is weakened and there is an additional term proportional to $\text{Re}(N_s\alpha)$. As a guide to situations in which the extra term is significant, Table I presents the maximum value attained by β_2 , and the angle at which this value is reached, for several metals at 1000, 2000, and 3000 cm^{-1} . Except at extremely high angles ($\theta > 88^\circ$) β_2 is negligible below 1000 cm^{-1} for all metals, and it is negligible even at 3000 cm^{-1} for such "good" metals as copper, silver, and aluminum. For transition metals such as iron, cobalt, nickel, and platinum, β_2 is significant at 2000 cm^{-1} for angles θ above about 84° .

For surface layers with extremely strong absorption bands, condition (5) and the resulting linear expression (6) may not be valid and $\text{Re}(N_s\alpha)$ can dominate the spec-

TABLE I. For four metals and at three frequencies, $(\beta_2)_{\text{max}}$, the maximum value attained by the coefficient β_2 , and the angle θ_m at which that maximum value is reached. Values of ϵ_3 are taken from Ref. 29 for all metals except Cu; for Cu the values are from Ref. 30.

Metal	Quantity	Frequency (cm^{-1})		
		1000	2000	3000
Fe	$(\beta_2)_{\text{max}}$	-0.123	-0.166	-0.232
	θ_m	88.0°	86.2°	84.8°
Cu	$(\beta_2)_{\text{max}}$	-0.066	-0.049	-0.040
	θ_m	89.2°	88.3°	87.4°
Ni	$(\beta_2)_{\text{max}}$	-0.091	-0.120	-0.164
	θ_m	88.4°	86.8°	85.4°
Pt	$(\beta_2)_{\text{max}}$	-0.135	-0.123	-0.124
	θ_m	88.6°	87.2°	85.1°

trum even at low frequencies and on high-conductivity metals. This point was conclusively demonstrated¹⁴ by Greenler, Rahn, and Schwartz for the 609- cm^{-1} optical phonon of Cu_2O on Cu.

Figure 1 shows plots of β_1 and $-\beta_2$ as a function of angle for iron and copper at 2000 cm^{-1} . Also shown is the coefficient $|(1+r)/2r|^2$ that appears in Eq. (4) for the power absorbed in the surface layer. Even when β_2 is small Eq. (4) overestimates the signal; the substrate absorption is reduced by the presence of the adsorbate. The

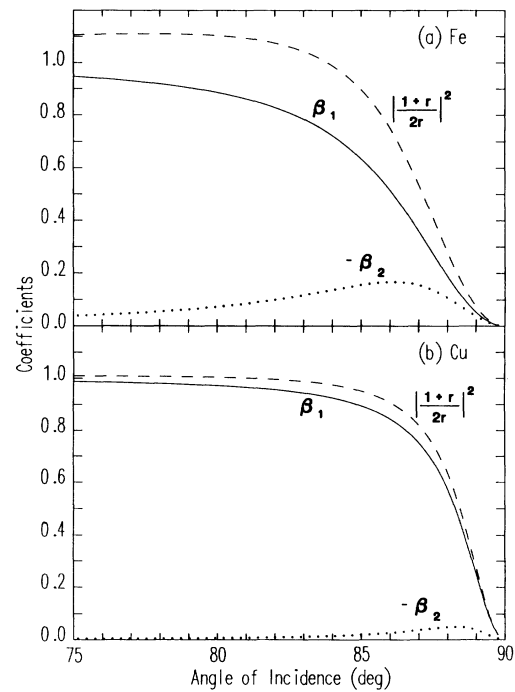


FIG. 1. Calculated values of the coefficients β_1 (solid), $-\beta_2$ (dotted), and $|(1+r)/2r|^2$ (dashed) that appear in Eqs. (4) and (6) as a function of incidence angle θ , at $\nu = 2000 \text{ cm}^{-1}$, for (a) iron and (b) copper. Values of ϵ_3 were taken from Ref. 29 for iron and from Ref. 30 for copper.

approximate expression (3) corresponds to the assumptions $\beta_1=1$, $\beta_2=0$; at large angles it seriously overestimates the absorption.

Equation (6) predicts an asymmetric line shape, even if the polarizability can be described by a Lorentzian function:

$$\alpha(\nu) = \alpha_e + \frac{\alpha_v}{1 - (\nu/\nu_0)(\nu/\nu_0 + i\gamma/\nu_0)}. \quad (8)$$

Here α_e is the frequency-independent electronic polarizability, α_v is the vibrational polarizability, ν_0 is the resonant frequency, and γ is the linewidth. The term $\beta_2 \text{Re}(N_s \alpha)$ skews the line toward the blue, with a sharp onset on the low-frequency side and a tail to higher frequencies. As an example, the solid line in Fig. 2 shows the calculated RAIR spectrum at $\theta=85^\circ$ for a Lorentzian oscillator on Fe with a vibrational frequency of 3300 cm^{-1} , e.g., the N-H stretching vibration of ammonia.¹⁵ The dashed line shows the signal calculated from Eq. (4). More subtle but still observable asymmetries are to be expected for CO on such other metals as Ni and Pt at high θ .

In a recent paper Mal'shukov has shown that vibrations *parallel* to the surface, if they are observable, will exhibit strong asymmetries even for high-conductivity metals, low frequencies, and small angles of incidence.¹² Because his analysis was confined to the low-angle case in which condition (1) is satisfied, he concluded that vibrations *normal* to the surface show negligible asymmetry.

Although Greenler in 1966 made the qualitative observation that vibrational bands polarized perpendicular to the surface would appear asymmetric at sufficiently large angles,⁶ and Lambert¹⁶ tabulated values of β_1 and β_2 for CO on Ni, the extensive literature^{2-4,17-24} on vibrational line shapes has ignored the asymmetry caused by the dielectric response of the substrate. Theoretical treatments^{2,20-24} invariably begin with the assumption that $\Delta R/R$ is caused entirely by absorption in the surface lay-

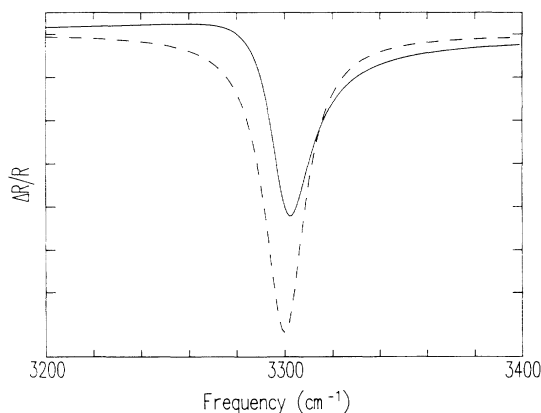


FIG. 2. Calculated RAIR spectra for a Lorentzian oscillator at 3300 cm^{-1} on iron. The solid line shows the asymmetric line predicted by Eq. (6). The dashed line shows the Lorentzian line predicted by Persson's model, Eq. (4). The value of ϵ_3 was taken from Ref. 29 and α_e was assumed to be zero. The amplitude and linewidth are arbitrary.

er and is therefore proportional to $\text{Im}(N_s \alpha)$. Experimental analyses—even those that hinge on subtle features of the line shape—have failed to consider dielectric effects.^{3,4,17-19}

Certainly in many cases dielectric effects are in fact negligible. For some systems, however, they should have observable consequences. Figure 3 shows the calculated $\Delta R/R$ for a Lorentzian oscillator representing 0.1 monolayer (ML) of CO on Pt at $\theta=87^\circ$. The frequency, amplitude, and linewidth have been chosen to fit the experimental data of Beckerle *et al.*;⁵ these data were chosen for the high angle of incidence used, which should maximize the dielectric effects. The line shape is determined entirely by θ and ϵ_3 , which are not adjustable. While the data are consistent with the predicted asymmetric line shape, a symmetric Lorentzian shape is actually somewhat superior (mean-square deviation 35% smaller). At 0.5 ML coverage the superiority of a Lorentzian shape is even more marked. The symmetric shapes may arise from a fortuitous cancellation of a polarizability function with a low-frequency tail with the asymmetry of the opposite sense caused by the substrate response. Published spectra measured at lower angles of incidence do show a tail to the low-frequency side,^{25,26} but of too large an amplitude to be canceled by the dielectric response at 87° . Other possible explanations are that the dielectric constant or incident angle was different than assumed (the intensity, however, is consistent with the assumed values). These issues could be resolved by measurements at various angles of incidence.

Adsorbate-induced changes in the broadband reflectance, far from any vibrational resonance, are a subject of current investigation.^{1,27,28} Since the term in $\text{Re}(N_s \alpha)$ produces such a change, it is of interest to estimate its magnitude. Far from a vibrational resonance,

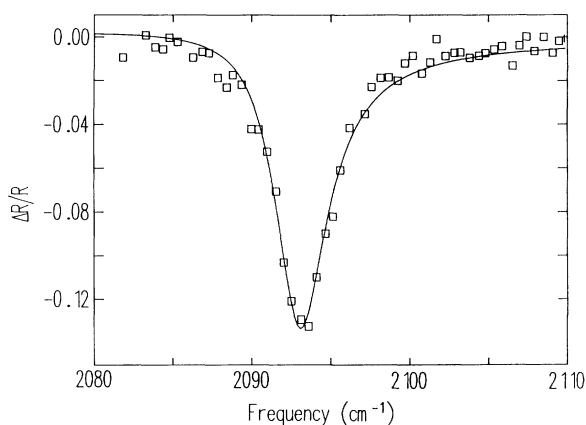


FIG. 3. Calculated (line) and experimental (points) RAIR spectra for 0.1 ML of CO on Pt(111) at $\theta=87^\circ$. The experimental data are taken from Ref. 5. The calculated spectrum assumes a Lorentzian oscillator with center frequency, width, and amplitude adjusted to fit the data; the shape is determined by θ and ϵ_3 and is not adjustable. The parameters used were $\alpha_e=0$, $\alpha_v=0.25 \text{ \AA}^3$, $N_s=1.5 \times 10^{14} \text{ cm}^{-2}$, $\nu_0=2092.9 \text{ cm}^{-1}$, $\gamma=4.16 \text{ cm}^{-1}$, $\epsilon_3=-392+205i$ (from Ref. 29).

$\Delta R/R = -32\pi^2\nu\beta_2 \operatorname{Re}(N_s\alpha_e)$. This term is far too small, and of the wrong sign, to explain the experimental results.^{1,27} For $5.0 \times 10^{14} \text{ cm}^{-2}$ of CO ($\alpha_e = 2.5 \text{ \AA}^3$) on Cu, $\Delta R/R = +1.5 \times 10^{-5}$ at 2000 cm^{-1} and 85° ; even on Fe, for the same conditions the shift is only $+1.2 \times 10^{-4}$.

I have shown that the approximate expressions commonly used in the analysis of RAIR spectra are inadequate when the dielectric constant of the metal is relatively low and the angle of incidence is high, specifically when condition (1) is not well satisfied. Under these conditions, the dielectric response of the metal causes a reduction in the signal strength, a very small increase in

the broadband reflectivity, and most importantly an asymmetry in the line shape. I have presented simple analytical expressions valid at all angles on any metal; these expressions should be used whenever precise analysis of intensities or line shapes is required.

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