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AN INFRARED SPECTROSCOPIC INVESTIGATION USING A THERMAL DETECTION TECHNIQUE

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### Authors

Dumas, P.  
Tobin, R.G.  
Richards, P.L.

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P. Dumas, R.G. Tobin, and  
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INTERACTION OF CO MOLECULES WITH EVAPORATED SILVER, GOLD, AND COPPER FILMS: AN INFRARED SPECTROSCOPIC INVESTIGATION USING A THERMAL DETECTION TECHNIQUE

P. DUMAS,<sup>1</sup> R. G. TOBIN,<sup>2</sup> and P. L. RICHARDS<sup>2</sup>

<sup>1</sup>Laboratoire de Spectrochimie Infrarouge et Raman, CNRS, 2 rue Henri Dunant, 94320-Thiais, (France)

<sup>2</sup>Department of Physics, University of California, and Center for Advanced Materials, Lawrence Berkeley Laboratory, Berkeley, California 94720 (U.S.A.)

ABSTRACT

We have used infrared absorption spectroscopy to study the adsorption of CO at low temperatures on evaporated films of silver, gold, and copper as a function of the coverage of CO and the deposition temperature of the metal. For all three metals we observe two distinct adsorption regimes when the cold metal is exposed to CO gas. These regimes arise depending on whether the deposition temperature of the metal (or the highest temperature at which the metal has been annealed) is above or below a threshold temperature. For all three metals, the shift of the vibrational frequency with CO coverage has been analyzed, and the static and dynamic contributions separated. An analysis of infrared intensities and vibrational polarizabilities shows no evidence for any special infrared enhancement analogous to the large enhancement in Raman cross section peculiar to adsorption on rough noble metal films deposited at low temperatures.

EXPERIMENTAL

A full discussion of the experimental apparatus and procedures is given elsewhere (ref.1). We used a thermal detection technique developed by Bailey et al. (ref.2) to measure directly the infrared absorption of CO on evaporated noble metal films at 2 K. A fresh film was deposited before each experiment, with the substrate held at a temperature  $T_D$ , between 4 and 330 K. The sample was exposed to CO from a calibrated effusive beam doser.

RESULTS

We have used infrared absorption spectroscopy to elucidate the low temperature adsorption behavior of CO on evaporated silver, gold, and copper films deposited at various temperatures. A full description of this work will appear elsewhere (refs.1,3). In the present paper we summarize the most important results. We show here data for gold and copper films only. The results for silver films were qualitatively the same as those for gold films.

The structural and electronic properties of evaporated films depend strongly on  $T_D$ , the temperature of the substrate during the deposition of the film or, equivalently, the highest temperature at which a film deposited at low temperature is annealed. These properties are reflected in the adsorption behavior of CO. We find that for  $T_D < 290$  K, gold films contain large numbers of chemically active sites at which CO chemisorbs. Films deposited at higher temperatures do not support chemisorption. Silver films show almost exactly the same behavior, with a threshold temperature of 150 K for the presence of chemisorption sites. Copper behaves somewhat differently, supporting CO chemisorption for all values of  $T_D$ . Nevertheless, changes in film structure as a function of  $T_D$  are reflected as significant changes in the vibrational spectrum of adsorbed CO. Infrared spectra for these adsorption states are shown in Figs. 1 and 2.

The shift in the frequency of a vibrational band with coverage is of interest because it provides a measure of the interadsorbate interactions. The shift is found to have two components: a static shift caused by chemical changes induced in an adsorbate by neighboring molecules, and a dynamic shift due to direct electromagnetic interactions between the adsorbates.

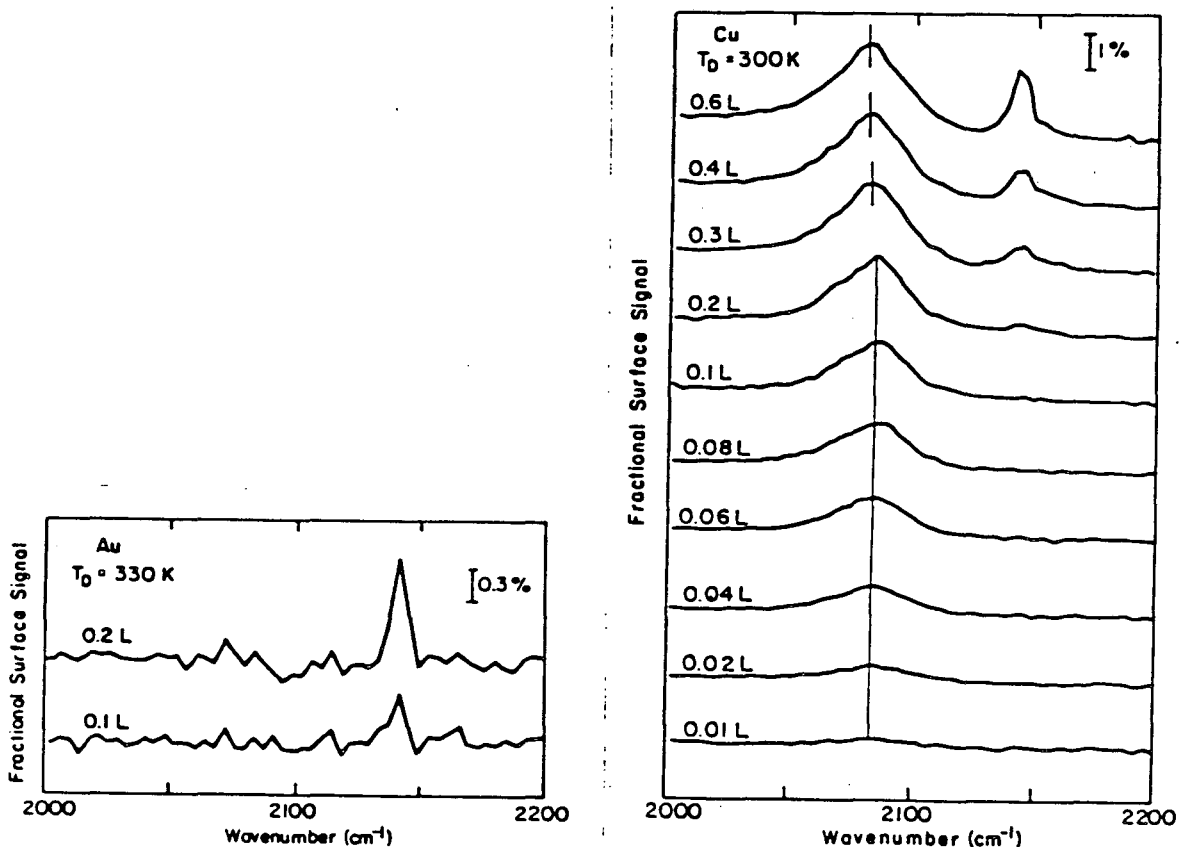


Fig. 1. Infrared spectra of CO adsorbed at 2 K on a gold film with  $T_D = 330$  K, and a copper film with  $T_D = 300$  K, well above the threshold in each case. A single band due to physisorbed CO is seen for gold. The copper film shows a broadband due to chemisorbed CO.

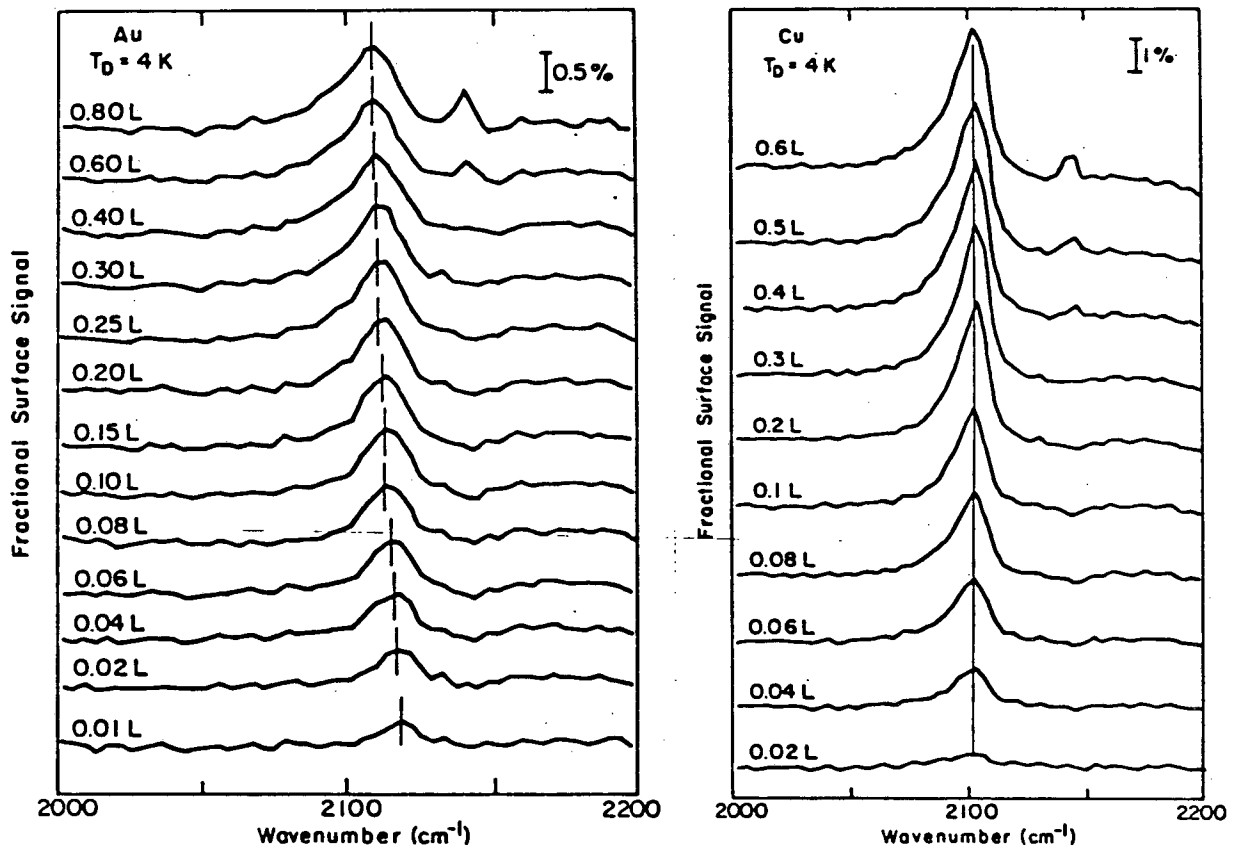


Fig. 2. Infrared spectra of CO on gold and copper films deposited at  $T_D = 4^\circ\text{K}$ , which is well below the threshold for both metals. Bands typical of chemisorbed CO are seen in each case. The relatively narrow band seen for Cu suggests a rather small range of chemisorption sites, compared to the high  $T_D$  film (ref.3). At high coverage a higher frequency band due to physisorbed CO is also seen.

We have analyzed the frequency shift with coverage for all three metals, using the isotopic substitution technique. We have fitted the dynamic contribution using the dipole coupling model of Persson and Ryberg (ref.4).

Figure 3 shows a sequence of infrared spectra for 0.02 L  $^{12}\text{CO}$  chemisorbed at 2 K on films deposited at  $T_D = 4$  K, with increasing quantities of coadsorbed  $^{13}\text{CO}$ . The higher frequency  $^{12}\text{CO}$  band shifts to lower frequency due to the chemical effect of the coadsorbed  $^{13}\text{CO}$ . The frequency of the  $^{12}\text{CO}$  band as a function of exposure is plotted in Fig. 4, together with the total shift (from Fig. 3) observed for the same exposure of  $^{13}\text{CO}$  alone.

We attribute the difference between the total shift and the chemical shift to the effect of vibrational coupling. This shift is plotted, along with the integrated intensity, in Fig. 5. The lines represent our fit to the data using the Persson-Ryberg dipole coupling model (ref.4) with the adjustable parameters listed in Table I. The dipole coupling model gives an excellent fit to the frequency shift and intensity variation.

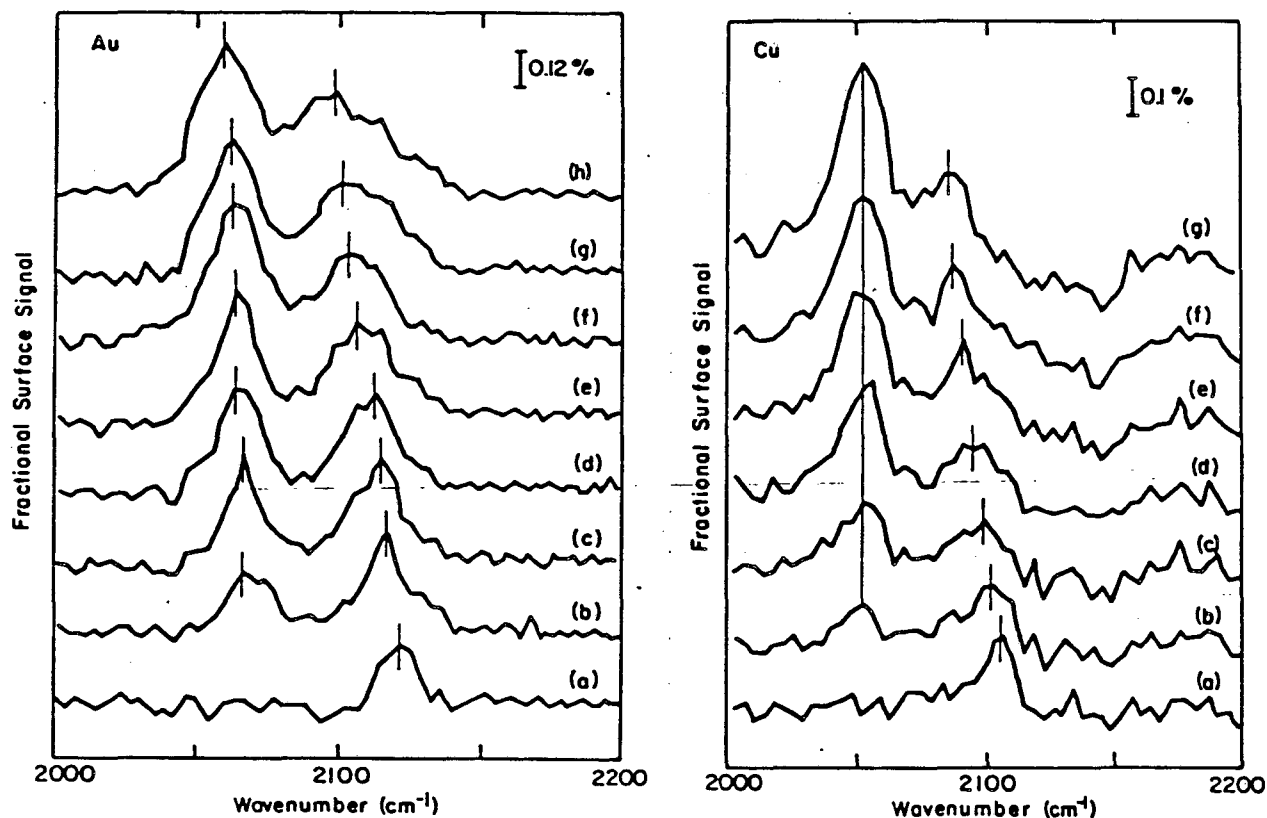


Fig. 3. Infrared spectra of 0.02L  $^{12}\text{CO}$ , coadsorbed with varying amounts of  $^{13}\text{CO}$ , on gold and copper films with  $T_D = 4^\circ\text{K}$ . The higher frequency band is due to  $^{12}\text{CO}$ . Its shift to lower frequency is due to the chemical interaction. Quantities of coadsorbed  $^{13}\text{CO}$ :  
 Au: (a) Zero. (b) 0.02 L. (c) 0.04 L. (d) 0.06 L. (e) 0.08 L. (f) 0.10 L. (g) 0.12 L. (h) 0.18 L.  
 Cu: (a) Zero. (b) 0.02 L. (c) 0.04 L. (d) 0.06 L. (e) 0.08 L. (f) 0.10 L. (g) 0.15 L.

We find that a chemical shift occurs even when additional molecules physisorb on the surface. This effect may be due to the influence of the local work function on chemisorbed CO (ref.1).

Adsorbates on noble metal films deposited at low temperatures exhibit large enhancements in Raman cross section over the values observed either in the gas phase, or for adsorption on smooth single crystals (ref.5). This phenomenon is known as surface-enhanced Raman scattering (SERS). The dynamic charge transfer associated with chemisorption on smooth single crystal surfaces or annealed polycrystalline films, which causes the infrared vibrational polarizability of chemisorbed CO to be slightly greater than that of gas phase CO should not depend strongly on the structure of the film, and cannot explain the very large ( $10^4$ - $10^6$ ) enhancements of the Raman cross section observed for molecules adsorbed on rough metal surfaces, as compared with single crystals.

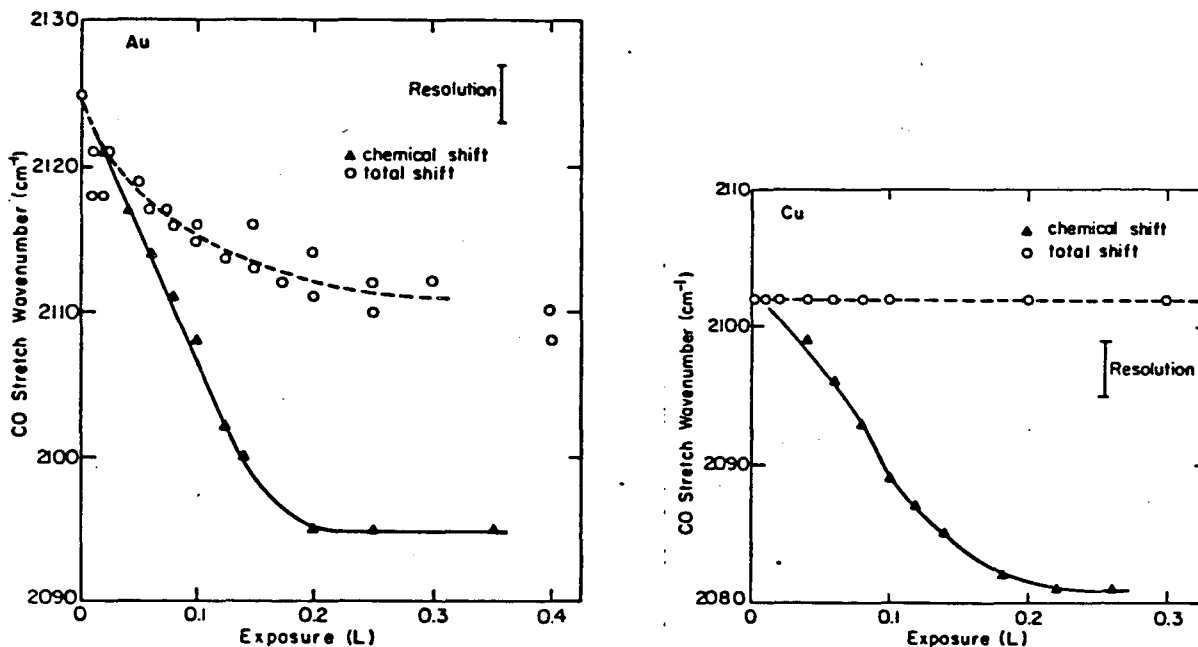


Fig. 4. Observed total and chemical shifts obtained from isotopic substitution experiments shown in Fig. 3.

A large part of the Raman enhancement observed on rough films has been attributed to electromagnetic resonances in the films at visible frequencies (ref.5), but it has also been suggested that special Raman-active sites are present in the films (ref.5). At these sites, if they exist, dynamic charge transfer processes much stronger than those at typical sites on a single crystal surface would make large contributions to the Raman cross section. Infrared spectroscopy offers a means of separating these two effects, since the charge transfer process at special sites would also be expected to enhance the infrared vibrational polarizability of the adsorbate, while the electromagnetic resonances are not excited at infrared frequencies.

The values of the vibrational polarizability,  $\alpha_v$ , given in Table I are slightly larger than the gas phase value, but they are quite close to values observed for chemisorbed CO on single crystals (ref.4). There is thus no evidence for a special infrared enhancement associated with low deposition temperatures, and no support for the special-site-model for SERS.



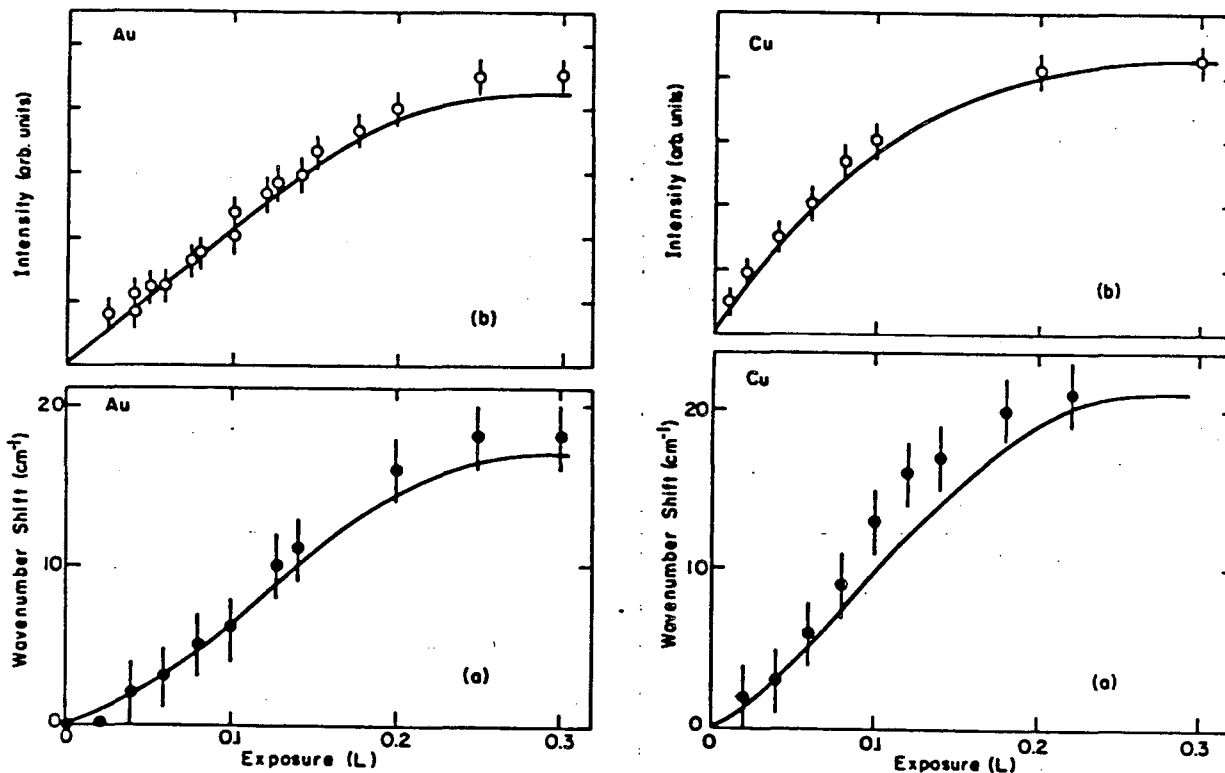


Fig. 5. (a) Dynamic contribution to the frequency shift, derived from the data in Fig. 4, for chemisorbed CO on gold, and copper films deposited at  $T_D = 4^\circ\text{K}$ . (b) Integrated band intensity, from Fig. 2. The lines are theoretical fits to the data, using the Persson-Ryberg dipole coupling model with the parameters shown in Table I.

TABLE I.

Singleton frequency, vibrational polarizability, electronic polarizability and interaction potential for CO adsorbed on the three metals

	$\omega_a$ ( $\text{cm}^{-1}$ )	$\alpha_v$ ( $\text{A}^3$ )	$\alpha_e$ ( $\text{A}^3$ )	$U(0)$ ( $\text{A}^{-3}$ )
Ag	2148	$0.27 \pm 0.0015$	3	$0.04 \pm 0.002$
Au	2125	$0.40 \pm 0.02$	3	$0.04 \pm 0.002$
Cu	2102	$0.27 \pm 0.015$	3	$0.095 \pm 0.005$
gas phase	2143	0.05	2.7	

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## REFERENCES

- 1 P. Dumas, R. G. Tobin, and P. L. Richards, to be published.
- 2 R. B. Bailey, T. Iri, and P. L. Richards, Surf. Sci., 180 (1980) 626-646.
- 3 P. Dumas, R. G. Tobin, and P. L. Richards, to be published.
- 4 B. N. J. Persson and R. Ryberg, Phys. Rev., B24 (1981) 6954-6970.
- 5 A. Otto, in M. Cardona and G. Guntherolt (Eds.) Light Scattering in Solids, Springer, Berlin, 1984, pp. 289-418, and references therein.

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