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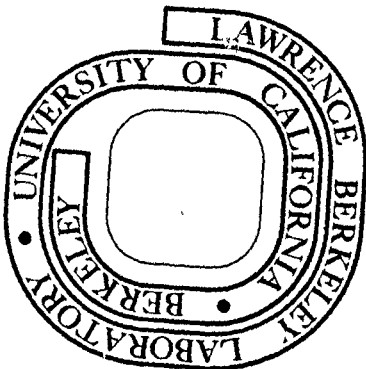
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## Infrared Measurements of Molecules Adsorbed on Metal Surfaces, A Low Temperature Thermal Detection Technique

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A low temperature thermal detection scheme has been developed and combined with the techniques of Fourier transform infrared spectroscopy to measure vibrational spectra of molecules adsorbed on metal surfaces. A small doped germanium thermometer is attached directly to the sample to detect the temperature increase which occurs when infrared radiation is absorbed. To achieve the necessary sensitivity, the sample is cooled to 1.6 K. Between infrared measurements the sample can be cleaned, heated, and exposed to gas molecules to produce a variety of chemically different surface states. Initial experiments on polycrystalline nickel films show that adsorbed carbon monoxide molecules undergo transitions between three distinct bonding configurations as the sample temperature increases from 77 K to 350 K.

The largest signal detected in the infrared absorption spectrum of a metal surface is from the conduction electrons. Vibrational modes of adsorbed molecules contribute absorption peaks which are a small fraction of this smooth background absorption. The advantage of the absorption technique described here is that the background signal is smaller than the signal detected in conventional reflection spectroscopy, making the experiment less sensitive to noise sources which modulate the total signal.

The measurements reported here have been made on thin nickel films evaporated on single crystal  $\text{Al}_2\text{O}_3$  substrates. The sample is mounted in an ultrahigh vacuum chamber with a base pressure of  $10^{-10}$  torr and is cooled to 1.6 K by a liquid helium filled cold finger. Resistive heating can be used to raise the sample temperature during evaporation and gas exposure. When the heater is turned off, the low heat capacity sample cools rapidly so that the high temperature chemical state is preserved during the low temperature spectral measurements. Argon ion bombardment is used to clean the sample surface. A reference spectrum of the clean metal is subtracted from the other spectra to isolate the absorption signals from adsorbed molecules.

Fig. 1 shows the infrared spectrum of carbon monoxide molecules chemisorbed on a polycrystalline nickel film. The metal film was evaporated at a sample temperature of 77 K, exposed to CO gas at the pressure  $2 \times 10^{-5}$  torr for several minutes, and then cooled to 1.6 K for the infrared measurements. The initial spectrum ( $T = 77$  K) shows a strong CO stretching vibration at  $2108 \text{ cm}^{-1}$ , a weaker one at  $1970 \text{ cm}^{-1}$ ,

and many sharp lines from atmospheric water vapor present in the spectrometer. Subsequent spectra of the same sample were measured after heating the crystal to successively higher temperatures for one minute intervals. The CO absorptions shift to lower frequencies as the temperature is increased. They also decrease in intensity as molecules desorb from the surface. At intermediate temperatures the low frequency vibration grows in strength at the expense of the high frequency line. At  $T = 350$  K a third vibrational mode appears at  $1820 \text{ cm}^{-1}$ .

Each of the three absorption lines is associated with a distinct bonding configuration between the carbon monoxide molecule and the nickel surface. Thermally induced changes in the absorption spectrum provide a measure of the activation energy for desorption and for transitions to different bonding states. Future experiments on single crystals will determine the effects of lattice order on the surface chemical bond.

These first reported measurements using the absorption technique are sensitive to absorptions of one part in  $10^4$  of the incident radiation in a spectrum covering the frequency range from  $1000$  to  $3000 \text{ cm}^{-1}$  with a resolution of  $2 \text{ cm}^{-1}$ . Published infrared reflection measurements<sup>1</sup> have achieved this sensitivity level only at lower resolution and over much narrower spectral ranges. With anticipated improvements the absorption technique should approach the sensitivity of electron energy loss spectroscopy<sup>2</sup> which can now detect  $10^{-3}$  monolayer of carbon monoxide, but with a spectral resolution of only  $80 \text{ cm}^{-1}$ . Broadband infrared spectra with both high resolution and high sensitivity can be used to identify many different molecules and to study their interactions on metal surfaces.

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2. H. Ibach, H. Hopster, and B. Sexton, Appl. Surf. Sci. 1, (1977).

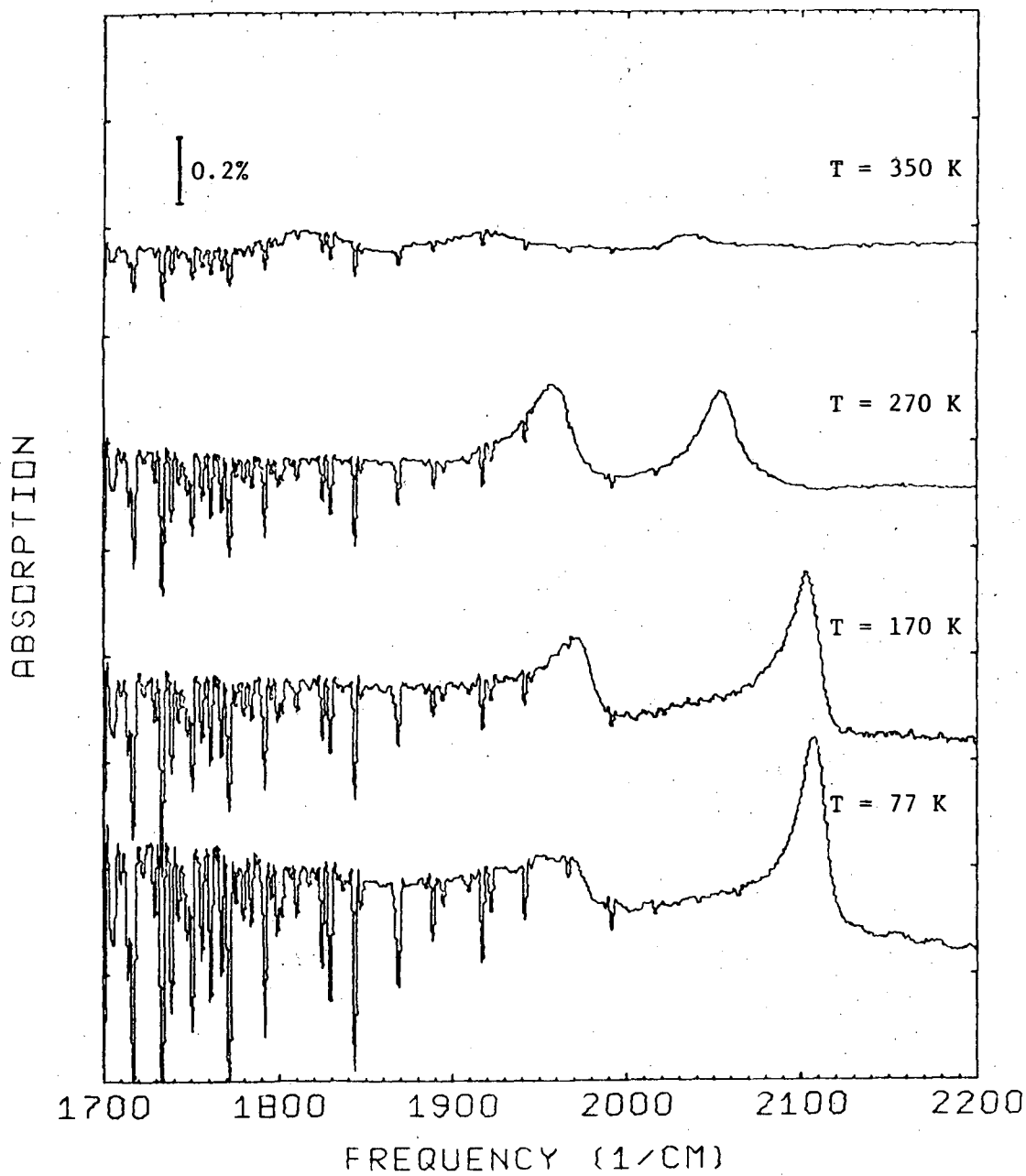


Fig. 1. Infrared absorption spectrum of CO on nickel film.

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