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VIBRATIONAL SPECTRA OF CO ON Ni (100) STUDIED BY INFRARED EMISSION SPECTROSCOPY

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Publication Date

1984-02-01



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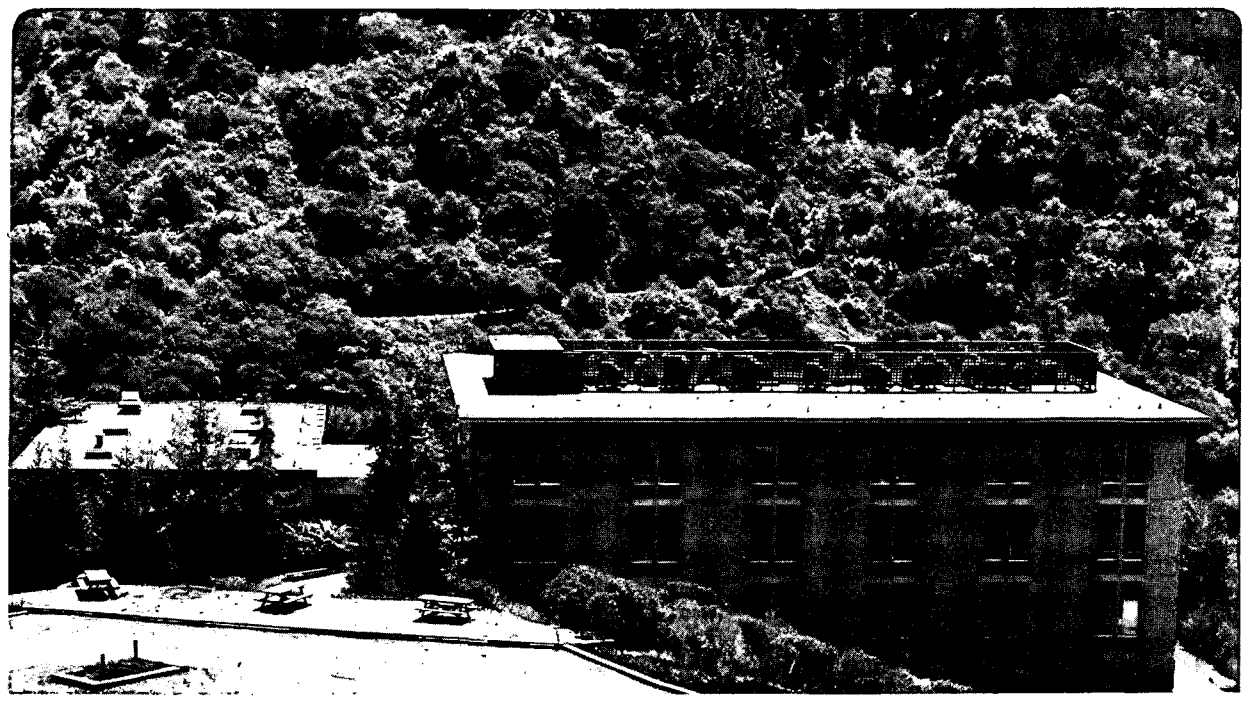
To be presented at the Third International Conference
of Infrared Physics (CIRP 3), Zurich, Switzerland,
July 23-27, 1984

VIBRATIONAL SPECTRA OF CO ON Ni(100) STUDIED
BY INFRARED EMISSION SPECTROSCOPY

S. Chiang, R.G. Tobin, P.L. Richards,
and P.A. Thiel

February 1984

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VIBRATIONAL SPECTRA OF CO ON Ni(100) STUDIED BY INFRARED EMISSION SPECTROSCOPY

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We have developed the technique of infrared emission spectroscopy in order to observe vibrational modes of molecules adsorbed on clean, single crystal metal surfaces. A novel apparatus has been constructed which measures the emission from a single crystal sample in thermal equilibrium at room temperature [1]. The apparatus consists of a liquid helium cooled infrared grating spectrometer coupled to an ultrahigh vacuum system equipped with surface preparation and characterization facilities. A schematic diagram of the apparatus is shown as Fig. 1. The system is capable of measuring over the frequency range from 330 to 3000 cm^{-1} with a resolution of 1 to 15 cm^{-1} .

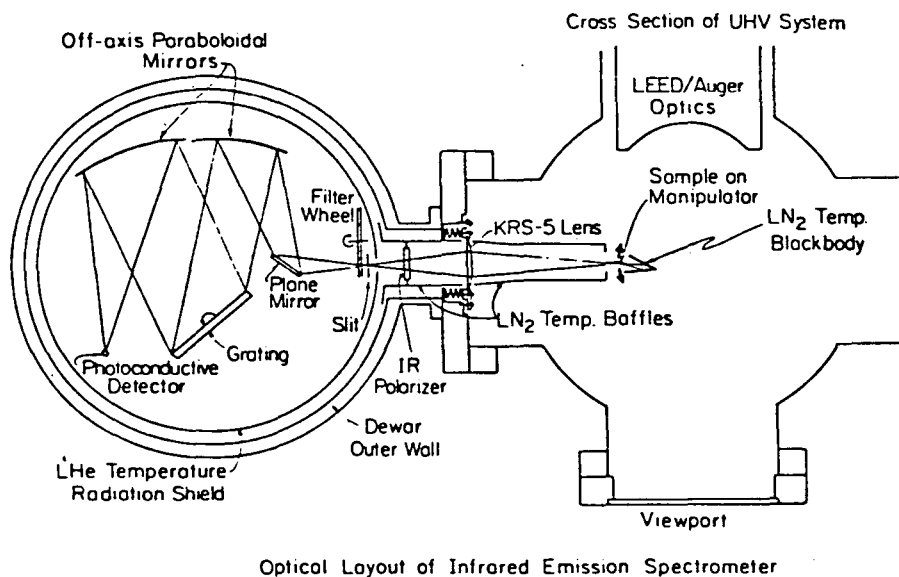


Figure 1. Optical layout of infrared emission apparatus, with LHe-cooled spectrometer on the left and ultrahigh vacuum system on the right.

Most infrared experiments on adsorbates on single crystal metal samples have used the reflection-absorption technique, which suffers from the difficulty that the high reflectivity of the metal results in a background signal which is much larger than the surface molecular signal.

By measuring the infrared emission from the sample, we can observe the same small surface signal superimposed on the smaller background arising from the emissivity of the metal. Because of this

background reduction, the dynamic range requirements on the detector are reduced by at least one order-of-magnitude. The dependence of the total detected signal on the stability of the source is also reduced by about the same factor. In addition, the emission experiment has high surface sensitivity over a broader angular range than a reflection-absorption experiment. The technique of infrared emission is equally applicable to smooth or rough surfaces, can be used with transparent substrates as well as metals, and can be used with high pressures and elevated sample temperatures. It has previously been used by several groups to observe adsorbed monolayers. Our approach is distinguished by particular attention to the reduction of the flux of background photons reaching the detector and to the detector performance.

We have used our infrared emission technique to make the first measurement of the linewidth of a molecule-substrate vibrational mode on a well characterized single crystal surface [2]. At saturation coverage, the observed linewidth of the C-Ni mode of CO on Ni(100) shown in Fig. 2 is 15 cm^{-1} . This width is much greater than expected from electron-hole relaxation mechanisms, but is in good agreement with predictions for broadening due to de-excitation by two-phonon emission.

We have also used infrared emission spectroscopy to study the C=O stretching vibration of CO on Ni(100) at 310 K. In contrast to previous electron energy loss and infrared measurements, no bridge-bonded CO is observed at any coverage below $\theta = 0.5$. Variations in the lineshape with exposure shown in Fig. 3 suggest the

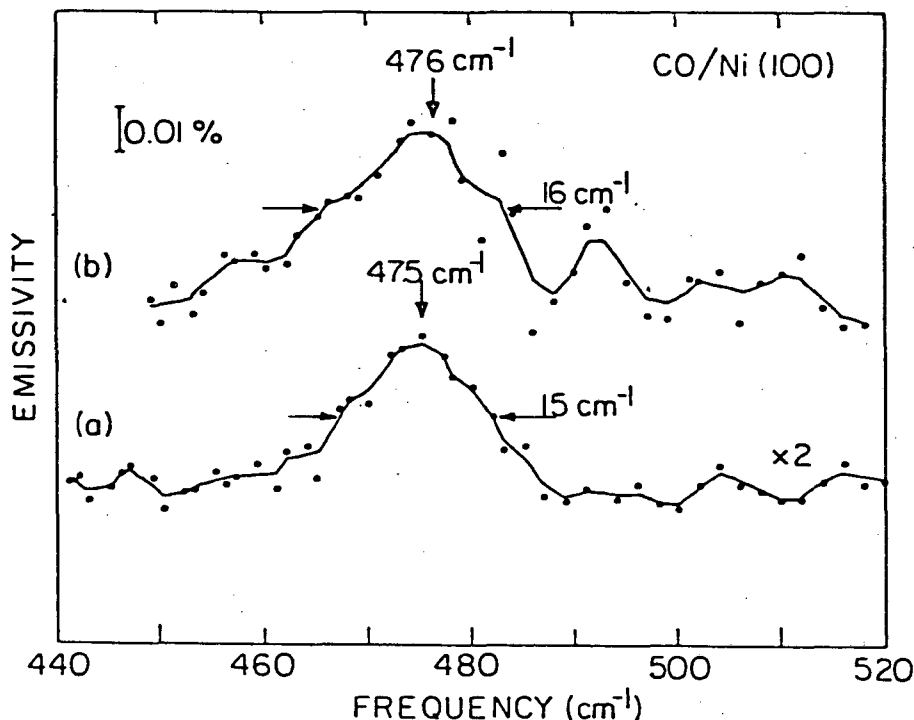


Figure 2. Infrared emission spectra from a saturation coverage of CO on Ni(100) at 310 K. The instrumental resolution was 2.5 cm^{-1} , and a linear baseline has been subtracted from the curves. The solid lines are obtained by computer smoothing of the data. (a) Spectrum of a disordered CO layer on a partially contaminated surface. (b) Spectrum of an ordered $c(2 \times 2)$ CO overlayer on a clean surface.

presence of $c(2 \times 2)$ islands even at low coverage, though low energy electron diffraction shows no sign of such ordering [3].

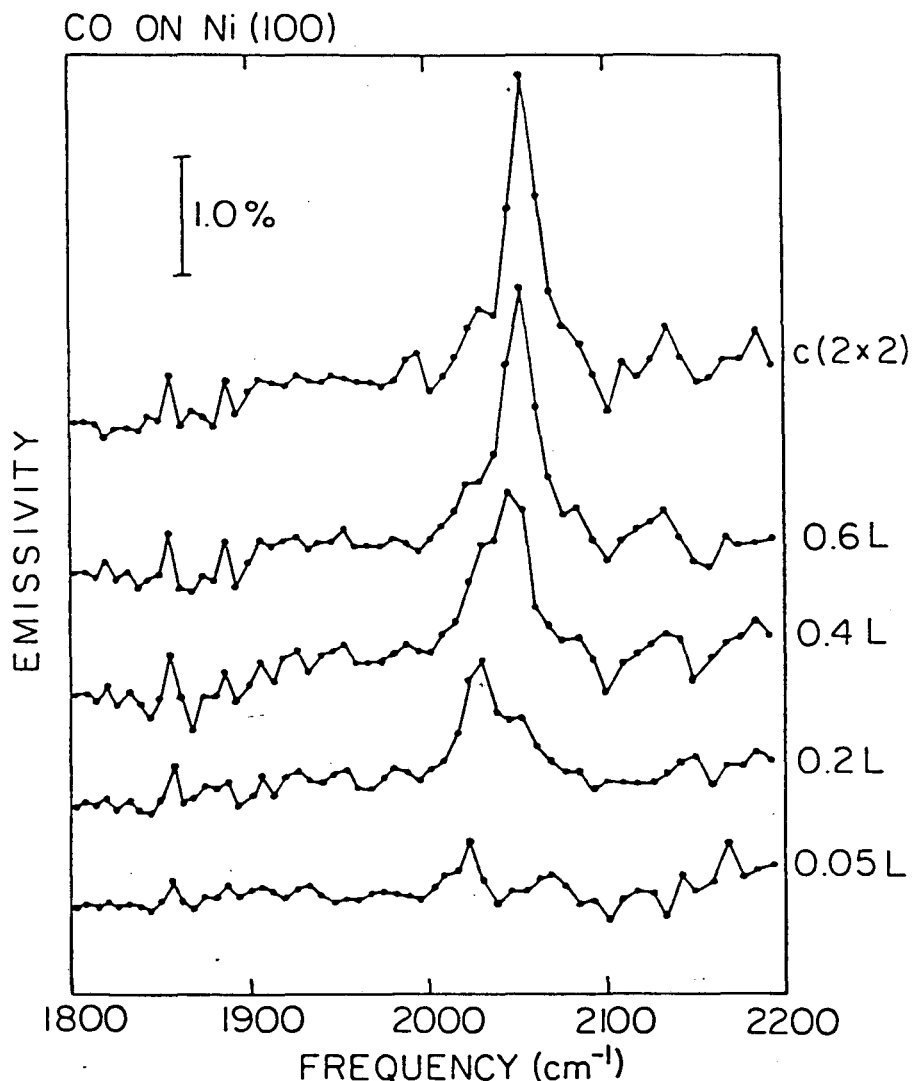


Figure 3. IR emission spectra of CO on a clean Ni(100) surface at 310 K. The instrumental resolution was ~ 18 cm⁻¹. The exposure varies from 0.05 Langmuir to saturation where a well ordered $c(2 \times 2)$ structure is seen.

This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Sciences Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

References

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This report was done with support from the Department of Energy. Any conclusions or opinions expressed in this report represent solely those of the author(s) and not necessarily those of The Regents of the University of California, the Lawrence Berkeley Laboratory or the Department of Energy.

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