

INFRARED-EMISSION SPECTROSCOPY OF CO ON Ni*

DE83 002328

S. CHIANG, R. G. TOBIN, and P. L. RICHARDS

Department of Physics, University of California at Berkeley,
and Materials and Molecular Research Division, Lawrence Berkeley Laboratory,
Berkeley, California 94720

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Therefore, the United States Government is authorized to reproduce and distribute reprints for government purposes, not withstanding any copyright notation that may appear hereon. It does not constitute an endorsement or approval of the views or opinions expressed hereon, or the products or processes named, by the United States Government. It is understood that neither the United States Government nor any agency thereof, nor any of its employees, makes any warranty, expressed or implied, or assumes any legal liability or responsibility for the accuracy or completeness of any information provided, or for any actions taken by individuals as a result of using any information contained in this report. This report is the property of the United States Government or any agency thereof. This work and the results of any research described herein are not to be distributed outside the United States Government or any agency thereof.

ABSTRACT

We report the first observation of thermally emitted infrared radiation from vibrational modes of molecules adsorbed on clean, single crystal metal surfaces. The observation of emission from CO adsorbed on Ni demonstrates the surface sensitivity of a novel apparatus for infrared vibrational spectroscopy, with a resolution of 1 to 15 cm^{-1} over the frequency range from 330 to 3000 cm^{-1} . A liquid helium cooled grating spectrometer measures the thermal radiation from a room temperature, single crystal sample, which is mounted in an ultrahigh vacuum system. Measurements of frequencies and linewidths of CO on a single crystal Ni sample, as a function of coverage, are discussed.

INTRODUCTION

Vibrational spectroscopy can be used to identify adsorbed atoms and molecules on surfaces and to study the chemistry of their bonding to the surface. Many techniques can be used to obtain vibrational spectra, but each has its own limitations. Electron energy loss spectroscopy has the advantage of inherently high surface sensitivity over a large spectral range, but resolution better than 30 cm^{-1} is difficult to achieve, so that linewidths and small frequency shifts are often unobservable (ref.1). Inelastic tunneling spectroscopy yields both good resolution and high surface sensitivity, but because the sample must be in the form of a tunnel junction, the interpretation of the results is not always clear (ref.2).

Photon spectroscopies easily obtain resolution of 1 to 10 cm^{-1} , but they are not as surface specific as electron spectroscopies. Conventional reflection-absorption infrared spectroscopy suffers from the difficulty that the surface molecular absorption signal is very small compared to the experimental background which arises from reflection from the bulk metal (ref.3). Measuring the infrared absorption directly by placing a thermometer on the sample allows the

This manuscript was printed from originals provided by the authors.

*Work 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.

observation of the same small surface signal on top of the smaller background arising from the bulk absorption (refs. 4 and 5). Adequate sensitivity with thermal sources, however, can only be obtained at extremely low temperatures ($\sim 1.5\text{K}$) and with substrates of low thermal mass. Since emission is thermodynamically equivalent to absorption, an infrared emission experiment benefits from the same reduction of background, and conventional single crystal samples at room temperature can easily be used. Because of this background reduction, an infrared emission experiment should be less influenced by instability of the source and apparatus than a reflection experiment. In order to exploit the advantages of an emission measurement, we have designed and constructed an apparatus to measure the infrared emission from a single crystal sample in thermal equilibrium at room temperature. A room temperature source emits significantly in the range from 100 to 3000 cm^{-1} , a range which includes the frequencies of most vibrational modes and also of most adsorbate-substrate modes.

DESIGN OF THE INFRARED EMISSION APPARATUS

Historically, infrared experiments have often been limited by intrinsic noise produced by the detector. Modern photoconductors developed for low-background astronomy, however, are limited by statistical fluctuations in the photon stream, even at very low flux levels. When such detectors are used, it is desirable that no radiation from sources other than the sample reach the detector. In practice we approximate this condition by cooling the entire spectrometer to liquid helium temperatures ($\sim 5\text{K}$) and surrounding the sample with baffles at liquid nitrogen temperature (77K). Under these conditions, approximately 80% of the radiation reaching the detector comes from the sample.

Our infrared emission apparatus consists of a liquid helium temperature infrared grating spectrometer coupled to a conventional ultrahigh vacuum (UHV) system, as shown in Fig. 1. The sample is mounted on a manipulator in the UHV system, which is equipped with facilities for low energy electron diffraction (LEED), Auger spectroscopy, argon ion sputtering, and mass spectrometry. The sample can also be heated and dosed with controlled amounts of gas.

Because the parallel component of the electric field must be zero at a conducting surface, only light with an electric field component normal to the surface interacts with the molecules there. Therefore, the sample is placed at near grazing incidence for maximum surface sensitivity (ref.6). Radiation from the sample is coupled into the cooled spectrometer by a low-emissivity KRS-5 lens. To reduce background light, a cold infrared polarizer removes the component of the radiation polarized parallel to the surface. After passing through the entrance slit of the spectrometer, the light is filtered to eliminate second and higher orders of diffraction, reflected by a plane mirror, and then collimated by an off-axis paraboloidal mirror. The beam is diffracted by the

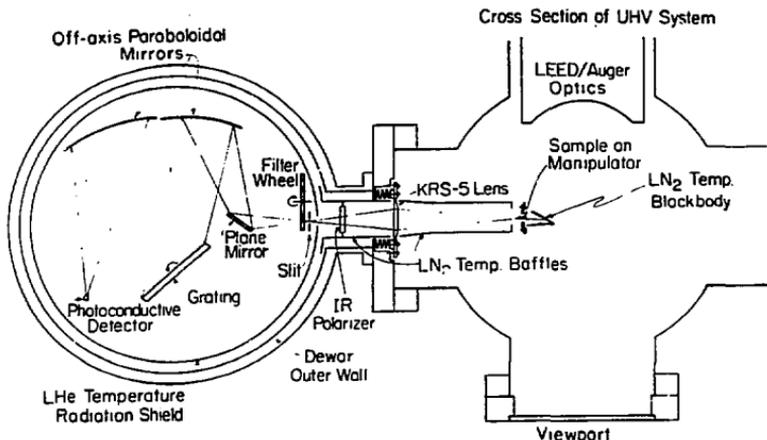


Fig. 1. Optical layout of infrared emission apparatus, with liquid helium cooled spectrometer on the left and ultrahigh vacuum system on the right. See text for details.

grating and refocused by a second off-axis paraboloid onto the detector.

Our detector is a Si:Sb photoconductor from Rockwell International, which is sensitive to radiation with frequencies higher than 330 cm^{-1} . The photocurrent is amplified by a transimpedance amplifier with a cold JFET input stage (ref.7). Our measurements indicate that, at modulation frequencies above 1 Hz, the instrument is noise limited by the fluctuations in the photon stream, most of which comes from the sample emission. Detector and amplifier noise are negligible. With our spectrometer efficiency of $\sim 7\%$, the photon-noise limited sensitivity would permit the measurement of emission from a CO coverage of 0.005 monolayer, with a signal to noise ratio of unity in a one Hz bandwidth. Because modulation has not yet been implemented, the sensitivity of the instrument is now limited by long term instabilities in the optics and electronics. Even without further development, we can routinely measure emission from 0.05L CO on Ni, with a line center signal to noise ratio of 4 in one second of integration.

Our instrument is able to measure signals from 330 cm^{-1} to 3000 cm^{-1} using three different diffraction gratings. With slit widths of 1 mm, the instrumental resolution ranges from about 1 cm^{-1} at 400 cm^{-1} to about 15 cm^{-1} at 3000 cm^{-1} , which should be sufficient to measure frequencies and linewidths of both adsorbate-substrate and molecular vibrations.

We have observed thermally emitted infrared radiation from the carbon-oxygen stretching vibration of CO on a clean single crystal of nickel. The nickel single crystal, obtained from the Materials Research Laboratory of Cornell University, was cut at about 8° from a (100) surface. The crystal was mounted in a UHV system with base pressure of 2×10^{-10} torr and cleaned by argon ion bombardment (1 μ A at 1000 eV), heating up to 650°C, and oxidation in 2×10^{-8} torr oxygen at 600°C to remove residual carbon. The surface cleanliness was monitored by LEED and Auger spectroscopy.

Infrared data were obtained by first measuring a reference spectrum of the clean Ni surface, then exposing the sample to doses of 0.05L or 0.10L CO by letting 10^{-8} torr CO gas into the UHV system through a leak valve for 5 or 10 sec. The spectra of Ni with CO were divided by the reference spectrum to eliminate variations in blackbody intensity and optical efficiency. A constant background was then subtracted. The results from 3 or 4 completely independent experiments, with spectral scans of only one minute each, were then averaged together to yield the series of spectra shown in Fig. 2. The instrumental resolution was 15 cm^{-1} .

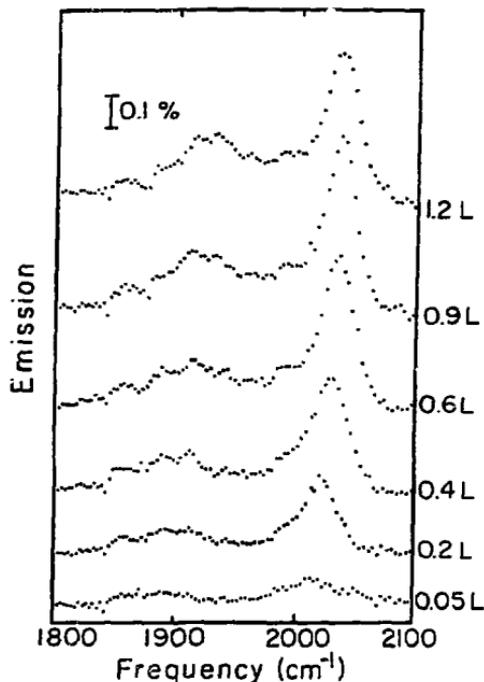


Fig. 2. Observed emission spectra from Ni(100) 8° stepped surface as a function of frequency for CO exposures from 0.05L to 1.2L.

DISCUSSION

We observe two prominent emission bands due to the C-O stretching vibration. The strongest band falls in the range $2010\text{--}2035\text{ cm}^{-1}$ and has a width of about 35 cm^{-1} . A weaker band, with a width of $60\text{--}80\text{ cm}^{-1}$, is observed in the range $1850\text{--}1930\text{ cm}^{-1}$. Peaks falling in these frequency ranges have been attributed to terminally bonded and bridge bonded molecules, respectively (ref.8).

Figures 3 and 4 show the peak positions and integrated intensities of the two bands as a function of coverage. A quadratic baseline has been subtracted from each spectrum before the calculation of areas; uncertainty in the determination of this baseline is the primary source of error in these values. The peak frequencies shift continuously upward with increasing exposure, reaching a total shift of 25 cm^{-1} for the on-top site and 35 cm^{-1} for the bridge site at saturation. These shifts are comparable to those previously observed on Ni(100) (refs. 9 and 10), but they are much smaller than those observed on Ni(111) (refs. 9, 11, and 12) and on evaporated Ni films (ref.5).

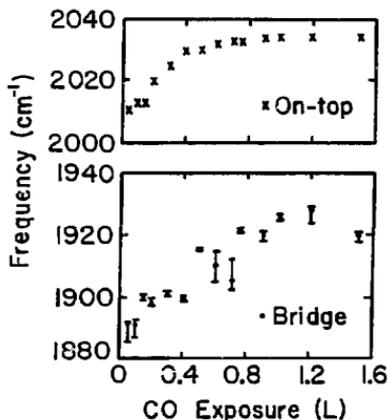


Fig. 3. Frequencies of observed infrared lines on Ni(100) 8° stepped surface as a function of CO exposure. x's mark the peak position for the on-top site. •'s mark the centroid of the line for the bridge site.

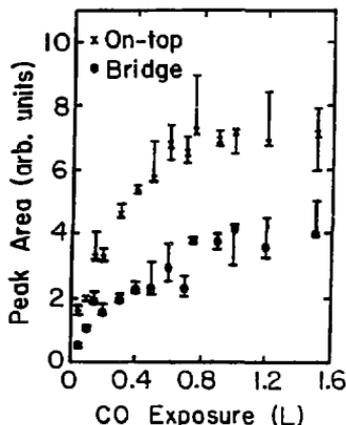


Fig. 4. Areas of the observed infrared peaks on Ni(100) 8° stepped surface as a function of CO exposure. x's mark the on-top site; •'s mark the bridge site. The large errors are due primarily to difficulty in determining the baseline.

All infrared measurements of CO on Ni, both on single crystals and on films, have observed that the bridge site band is much broader than the terminal site band. If these observations are representative of natural vibrational lifetimes, they suggest that the coupling to the metal is considerably stronger for molecules bonded to two Ni atoms than for those bonded to only one.

CONCLUSION

We have shown that infrared emission spectroscopy is a sensitive, high-resolution probe of the vibrational spectra of adsorbed molecules. Further refinements of the apparatus hold the promise of still greater sensitivity. The frequency range of our instrument includes the frequencies of many adsorbate-substrate modes, and we will soon attempt to observe such modes on a Ni(100) sample.

REFERENCES

- 1 H. Ibach, H. Hopster, and B. Sexton, *Appl. of Surf. Sci.* 1, 1 (1977).
- 2 P. K. Hansma, *Phys. Rep.* 30C, 145 (1977).
- 3 Robert G. Greenler, *J. Chem. Phys.* 44, 310 (1966).
- 4 R. B. Bailey, T. Iri, and P. L. Richards, *Surf. Sci.* 100, 626 (1980).
- 5 H. J. Levinson, R. G. Tobin, and P. L. Richards, these proceedings.
- 6 Robert G. Greenler, *Surf. Sci.* 69, 647 (1977).
- 7 E. L. Dereniak, R. R. Joyce, and R. W. Capps, *Rev. Sci. Inst.* 48, 392 (1977).
- 8 R. P. Eischens, S. A. Francis, and W. A. Pliskin, *J. Phys. Chem.* 60, 194 (1956).
- 9 J. C. Bertolini and B. Tardy, *Surf. Sci.* 102, 131 (1981).
- 10 M. J. Dignam, in *Vibrations at Surfaces: Proceeding of an International Conference at Namur, Belgium*, R. Caudano, J. M. Gilles, and A. A. Lucas (Eds.), Plenum, New York (1982).
- 11 W. Erley, H. Wagner, and H. Ibach, *Surf. Sci.* 80, 612 (1979).
- 12 J. C. Campuzano and R. G. Greenler, *Surf. Sci.* 93, 301 (1979).