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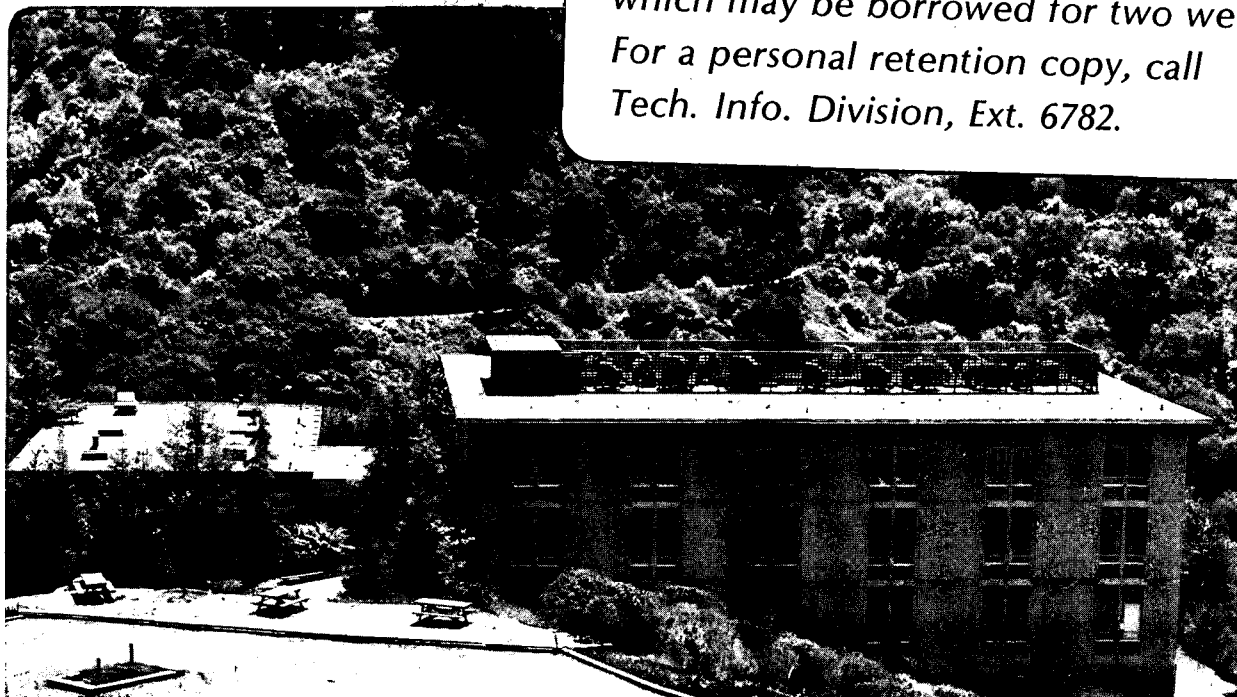
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THE MOLECULE-SUBSTRATE VIBRATION OF CO ON Ni(100)
STUDIED BY INFRARED EMISSION SPECTROSCOPY

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Abstract

We have used a novel infrared emission technique to make the first measurement of the linewidth of a molecule-substrate vibrational mode on a well characterized single crystal surface. At saturation coverage, the observed linewidth of the C-Ni mode of CO on Ni(100) is 15 cm^{-1} . This result is in agreement with predictions for broadening due to de-excitation by two-phonon emission.

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The usefulness of vibrational spectroscopy in the identification of surface species, the determination of adsorbate structures, and the study of dynamical processes has been thoroughly demonstrated.¹ Although electron energy loss spectroscopy (EELS) has been a popular technique because of its inherently high surface sensitivity and large spectral range, its relatively poor resolution of 30 to 100 cm^{-1} makes the measurement of linewidths and lineshapes extremely difficult.² Infrared spectroscopists find it easy to obtain resolution less than 5 cm^{-1} , but have had to struggle for adequate sensitivity. They have generally been unable to observe modes at frequencies less than 1000 cm^{-1} .³ Other techniques, such as inelastic tunneling spectroscopy,⁴ surface Raman spectroscopy,⁵ and surface non-linear optical techniques,⁶ all have specific advantages and particular limitations due to sample configuration, sample temperature, or sensitivity.

We show that infrared emission spectroscopy can resolve adsorbate-substrate modes on single crystal surfaces both in the frequency range of a few hundred cm^{-1} , which contains important adsorbate-substrate modes, and in the higher frequency range characteristic of intramolecular modes. The technique 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. Our apparatus was designed for the study of metal surfaces in vacuum; other

types of system would require somewhat different experimental equipment and procedures. Using the infrared emission technique,, we have made the first measurement of the linewidth of a molecule-substrate vibrational mode on a well characterized single crystal surface.

The infrared emission technique which we have developed uses a liquid helium temperature grating spectrometer to measure the radiation from a sample in thermal equilibrium near room temperature. Since a detailed description of the apparatus is to be published elsewhere,⁷ we give only a brief summary of the technique here. Figure 1 shows a diagram of the apparatus. The Ni(100) sample, from the Materials Research Laboratory of Cornell University, was mounted on a manipulator in an ultrahigh vacuum chamber, with a base pressure of 10^{-10} torr, which was equipped with conventional surface preparation and characterization facilities. It was cleaned by argon ion sputtering to remove sulfur, heating to 800° C for annealing, and oxygen treatments to remove residual carbon. During infrared measurements, the sample temperature was held constant within ± 0.05 K at approximately 310 K.

Thermal radiation emitted by the sample is focused by a lens onto the entrance slit of the spectrometer. The light is collimated, diffracted from a grating and refocused onto a Rockwell Si:Sb photoconductive detector. Liquid nitrogen temperature baffles around the sample provide contrast to observe the sample emission, and the spectrometer is maintained at 5 K

to minimize infrared background radiation. The present experiments are made in the dc mode and are limited by slow drifts. Significant improvements may be achieved by implementing an appropriate modulation. The detector noise is negligible compared to the statistical fluctuations in the photon stream of 10^{10} photons/sec reaching the detector from the sample.

A reference spectrum of the clean nickel surface is first measured by recording the detector signal as a function of the grating position, which is under computer control. After the sample has been dosed with CO, its emission spectrum is measured again. The ratio of the spectrum of Ni with CO to the reference spectrum is computed to obtain the adsorbate spectrum. Wavelengths are measured relative to the 24th order diffraction of light from a He:Ne laser.

The infrared emission spectrum of a saturation coverage of CO on Ni(100), in the frequency range of the molecule-substrate mode, is shown in Figure 2. The data represent the average of 30 spectra from 5 separate experimental runs. The total integration time at each point was 30 seconds. The peak frequency of $472 \pm 5 \text{ cm}^{-1}$, and the intensity of the observed mode are consistent with previous EELS results.⁸ The line is well resolved; the observed linewidth (full width at half maximum) is $15 \pm 1 \text{ cm}^{-1}$, while the instrumental resolution is approximately 2.5 cm^{-1} . From this spectrum, we compute an effective charge for

the C-M stretch of $\epsilon^* = 0.11$, which agrees well with Ibach's⁹ published value of 0.15. Since ordered low energy electron diffraction (LEED) patterns were not obtained in this experiment, there is a possibility of broadening due to disorder. However, a preliminary experiment with a clear, well-developed $c(2 \times 2)$ overlayer shows a similar linewidth of $16 \pm 2 \text{ cm}^{-1}$.

This spectrum represents the first measurement of the linewidth of the low frequency adsorbate-substrate mode of a molecular adsorbate on a well characterized single crystal metal surface. It strikingly demonstrates the ability of our infrared emission technique to bring high resolution and monolayer or sub-monolayer sensitivity to a wide range of vibrational frequencies. Previous measurements of such modes for molecular adsorbates have been made only with high surface area polycrystalline samples.¹⁰⁻¹² The only infrared measurements of adsorbate-substrate modes on single crystal surfaces have used atomic hydrogen, which has a high vibrational frequency, and have relied on special properties of the experimental system in order to obtain adequate sensitivity. The vibration of hydrogen on tungsten(100) was measured with a technique that exploited the coincidence of the vibrational frequency with a CO_2 laser band.¹³ An internal reflection geometry, useful for transparent substrates, has been used to resolve the vibration of hydrogen on single crystal silicon.^{14,15}

Our instrument has also been used to obtain spectra with excellent signal-to-noise ratio in the higher frequency range of the carbon-oxygen stretching vibration of CO, at $\sim 2000 \text{ cm}^{-1}$. It easily measures signals from as little as 0.05 monolayer of CO in one minute.^{16,17}

For relatively high frequency intramolecular modes, such as the carbon-oxygen vibration of adsorbed CO, the most plausible explanation for the observed linewidths seems to be the coupling of the vibration to the electrons in the metal, via an adsorbate-induced resonance in the density of states at the Fermi level.¹⁸ Because the volume of momentum space accessible to the electron-hole pairs is proportional to the vibrational energy, and because the absorption strength is believed to be related to the degree of vibrational coupling to the electron gas, it is expected from this model that the carbon-metal stretching vibration, with its lower frequency and intensity, would be much narrower than the C=O stretching mode. In fact, however, the modes have comparable widths, which suggests that other mechanisms dominate the width of the carbon-metal vibration.

Three other line-broadening processes must be considered. Inhomogeneous broadening cannot be absolutely excluded. Since our preliminary data on an ordered overlayer show a line of similar width to that seen for a disordered layer, however, it seems unlikely that inhomogeneity could entirely account for the breadth of the C-Ni line.

A second possibility is that the linewidth is dominated by the dephasing process, in which variations in the phase of vibration of an excited molecule, due to elastic collisions with phonons, broaden the line without shifting its frequency.¹⁹ Persson has estimated that the broadening due to dephasing should be forty times smaller than that due to de-excitation by phonon emission, for the C-Ni mode in question.²⁰

Vibrational decay by the excitation of substrate phonons is not important for the C=O stretching vibration,²¹ but it is expected to be more important at lower frequencies. Since the maximum phonon frequency of bulk nickel is $\sim 300 \text{ cm}^{-1}$,²² the $\sim 2000 \text{ cm}^{-1}$ intramolecular mode must decay via at least a seven-phonon process. The 472 cm^{-1} molecule-substrate mode, however, can decay by the emission of only two phonons. Ariyasu, *et al.*,²³ have calculated the linewidth due to the two-phonon process, for the C-Ni mode of CO on Ni(100) at 300 K, and found a value of 13.9 cm^{-1} , in excellent agreement with our experimental value. Their calculation also predicts a linear temperature dependence for the linewidth above 300 K. We will test this prediction in future experiments.

In summary, we have developed the technique of infrared emission spectroscopy for the observation of vibrational modes of adsorbates on metal substrates . We have made the first measurement of the linewidth of the molecule-substrate vibrational mode of CO on Ni(100). The observed linewidth appears to be explained by a process of vibrational damping by two-phonon emission, in contrast to the electronic mechanism that seems to dominate at higher frequencies. We anticipate that these data and future measurements of adsorbate-substrate modes will stimulate further discussion of the important broadening mechanisms involved.

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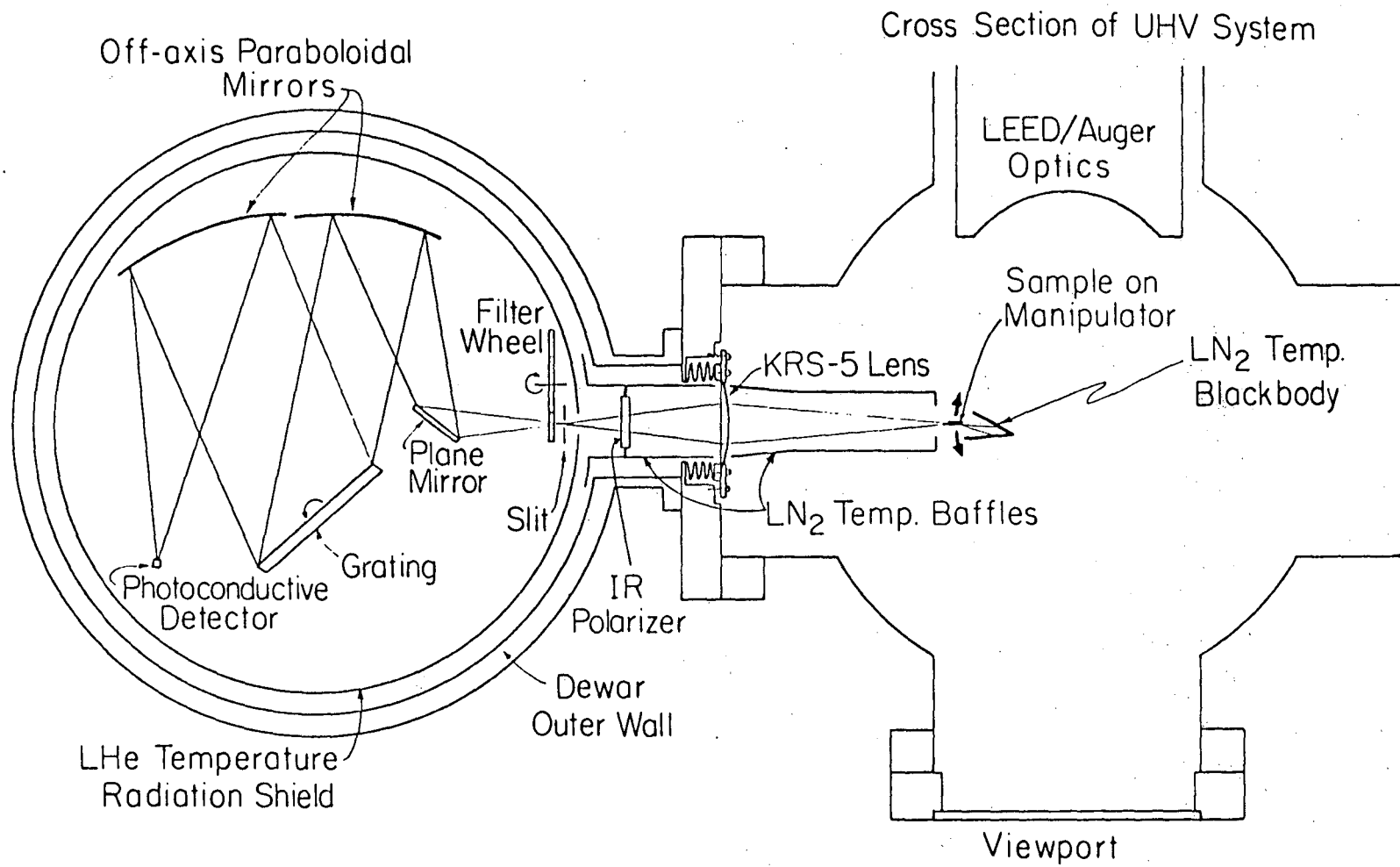
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Figure captions

1. Optical layout of the infrared emission apparatus, with LHe-cooled spectrometer on the left and ultrahigh vacuum system on the right.
2. Infrared emission spectrum of the C-Ni stretch mode of saturation coverage of CO on Ni(100). The instrumental resolution was 2.5 cm^{-1} .



Optical Layout of Infrared Emission Spectrometer

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Fig. 1.

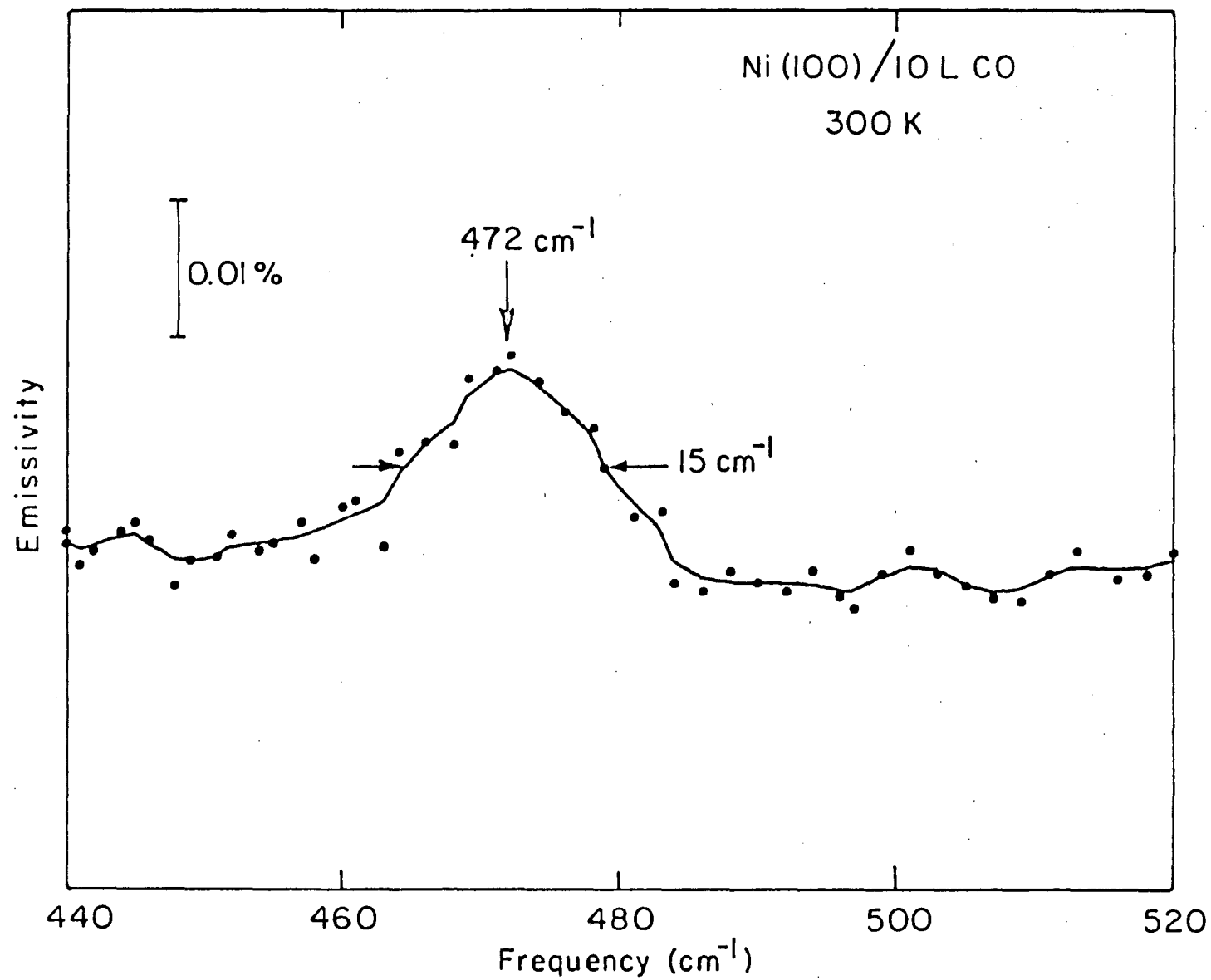


Fig. 2.

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