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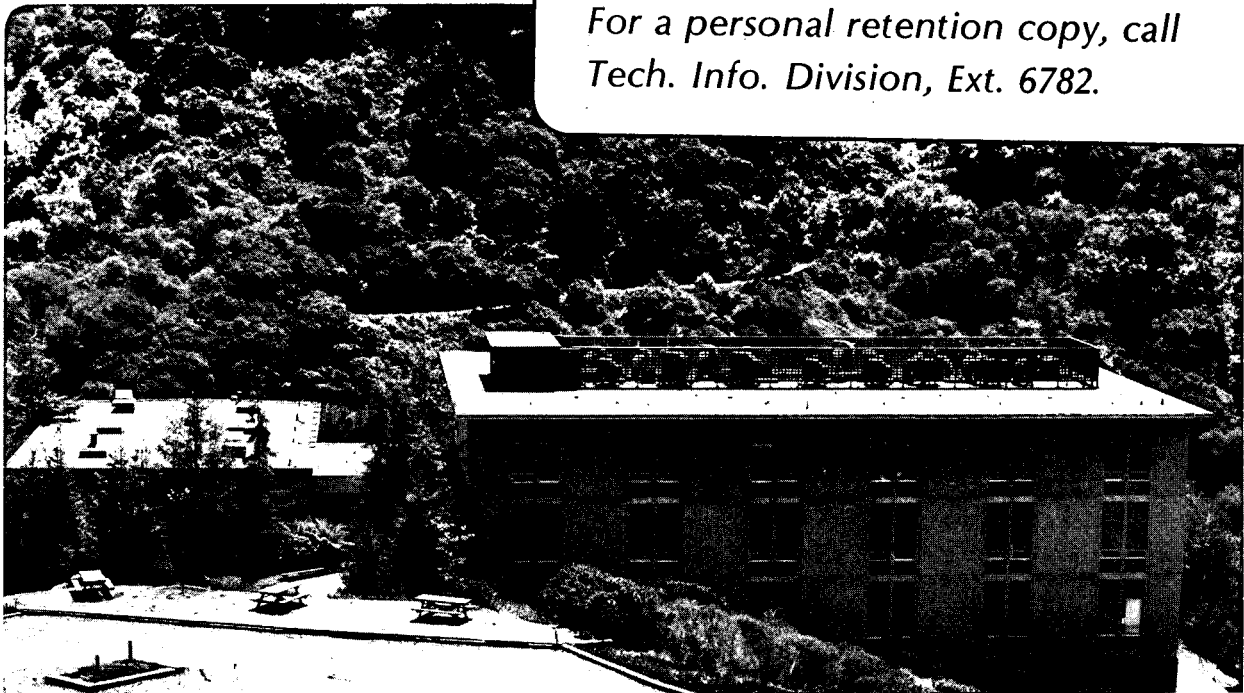## Materials & Molecular Research Division

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DISCLAIMER

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.

Infrared emission spectroscopy offers certain advantages over other types of infrared surface spectroscopy in sensitivity and versatility. For substrates that are not strongly absorbing, such as metals, it provides a reduction in background, compared to reflection-absorption spectroscopy. The method 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. Several groups

have previously used infrared emission to study adsorbed monolayers,[7] but our experiment is the first to apply the technique to sub-monolayer coverages of adsorbates on well characterized single crystal metal surfaces in ultrahigh vacuum. Our apparatus is also the first to extend the infrared spectroscopy of single crystal surfaces into the frequency range of a few hundred cm^{-1}, which contains important adsorbate-substrate modes. Sample configurations different from ours would be required or preferred in order to use emission spectroscopy to study systems other than metal surfaces in vacuum.

The infrared emission apparatus that 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,[8] 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, by heating to 800° C for annealing, and by oxygen treatments to remove residual carbon. The best indicator of sample cleanliness was the observation of a sharp c(2×2) low

energy electron diffraction (LEED) pattern when the surface was saturated with CO. 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 in signal-to-noise ratio, potentially by a factor of 10-100, 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.

Figure 2 shows infrared emission spectra from a Ni(100) surface saturated with CO at room temperature, in the frequency range of the molecule-substrate mode. The two curves were measured with different sample preparation procedures. In both cases a sharp 1×1 LEED pattern was observed before the sample was dosed with CO. Curve (a) was obtained from a disordered CO layer on a surface with significant residual contamination. The c(2×2) LEED pattern expected for CO on clean Ni(100) was not seen. Infrared emission spectra measured in the C=O stretch frequency range showed that for this surface the CO was in bridge-bonded as well as linearly bonded sites.[9] The data in curve (a) represent the average of 30 spectra from 5 separate experimental runs, with a total integration time per point of 30 seconds. The peak frequency of 475 ± 5 cm^{-1} is in good agreement with EELS results.[10] The line is well resolved; the observed linewidth (full width at half maximum) is 15 ± 1 cm^{-1}, while the instrumental resolution is approximately 2.5 cm^{-1}. The greater uncertainty in the peak frequency is due to errors in the absolute calibration of the grating angle.

Curve (b) was measured after refined cleaning procedures had improved the state of the surface. Although our available Auger system could not distinguish between the two surfaces, thermal desorption spectroscopy showed that the surface used for curve (b) had significantly less surface carbon. A sharp c(2×2) LEED pattern was observed when a saturation dose of CO was added.

Spectra from the C=O stretch range showed only linearly bonded CO as is expected for the ideal c(2×2) structure. The absence of the bridge-bonded CO suggests that this surface was significantly cleaner than those previously used for vibrational studies of the CO/Ni(100) system.[10,11] The spectrum shown in curve (b) represents a single experimental run, and a total of 10 seconds of integration per point. The signal-to-noise ratio for curve (b) is significantly less good than for curve (a). The feature at 490 cm^{-1} in curve (b), for example, is likely to be noise.

The peak frequencies and the linewidths of the two spectra are the same, within experimental error. For the ordered c(2×2) overlayer, [curve (b)], the peak frequency is 476±5 cm^{-1}, and the linewidth is 16±2 cm^{-1}. The intensity of the line is about a factor of two greater in curve (b) than that observed in curve (a). The difference could arise from incomplete surface coverage in the disordered case, or from better sample positioning for the spectrum of the ordered overlayer. Using the theory described by Ibach,[12] suitably adapted for our experiment, and assuming a rigid surface, we calculate a screened effective charge for the c(2×2) layer of e* = 0.17, in reasonable agreement with Ibach's[12,13] published value of e* = 0.21.

The spectra in figure 2 represent the first measurements of the linewidth of the low frequency adsorbate-substrate mode of a molecular adsorbate on a well characterized single crystal metal surface. They strikingly demonstrate 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.[14-16] 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.[17] An internal reflection geometry, useful for transparent substrates, has been used to resolve the vibration of hydrogen on single crystal silicon.[18,19]

Our instrument has also been used[9,20] to obtain spectra with excellent signal-to-noise ratio in the higher frequency range of the carbon-oxygen stretching vibration of CO, at ~2000 cm^{-1}. It easily measures signals from as little as 0.05 monolayer of CO in one minute, with a resolution of 15 cm^{-1}. Improved resolution would result in some loss in sensitivity.

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.[21]   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. The
measurement of the same linewidth for a well ordered c(2×2)
overlayer as for a disordered layer minimizes the likelihood of
disorder-induced broadening, but a more direct demonstration that
the linewidth is intrinsic--for example by measuring the
temperature dependence of the linewidth--is certainly important,
and will be attempted.

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.[22] Persson has estimated that the broadening due to dephasing should be thirty times smaller than that due to de-excitation by phonon emission, for the C-Ni mode in question.[23]

Vibrational decay by the excitation of substrate phonons is not important for the C=O stretching vibration,[24] but it is expected to be more important at lower frequencies. Since the maximum phonon frequency of bulk nickel[25] is -300 cm^{-1}, the -2000 cm^{-1} intramolecular mode must decay via at least a seven-phonon process. The 475 cm^{-1} molecule-substrate mode, however, can decay by the emission of only two phonons. Ariyasu, et al.,[26] 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 advanced the technique of infrared emission spectroscopy for surface vibrational studies by applying it to adsorbates on well characterized single crystal metal surfaces, and by extending it into the important frequency range of a few hundred cm^{-1}. We have made the first measurement of the

linewidth of the molecule-substrate vibrational mode of c(2×2) 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. Experiments to verify the decay mechanism are in progress. We anticipate that the data presented here, and future measurements of adsorbate-substrate modes, will stimulate further discussion and understanding of the important broadening mechanisms involved.

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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 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(2×2) CO
   overlayer on a clean surface.
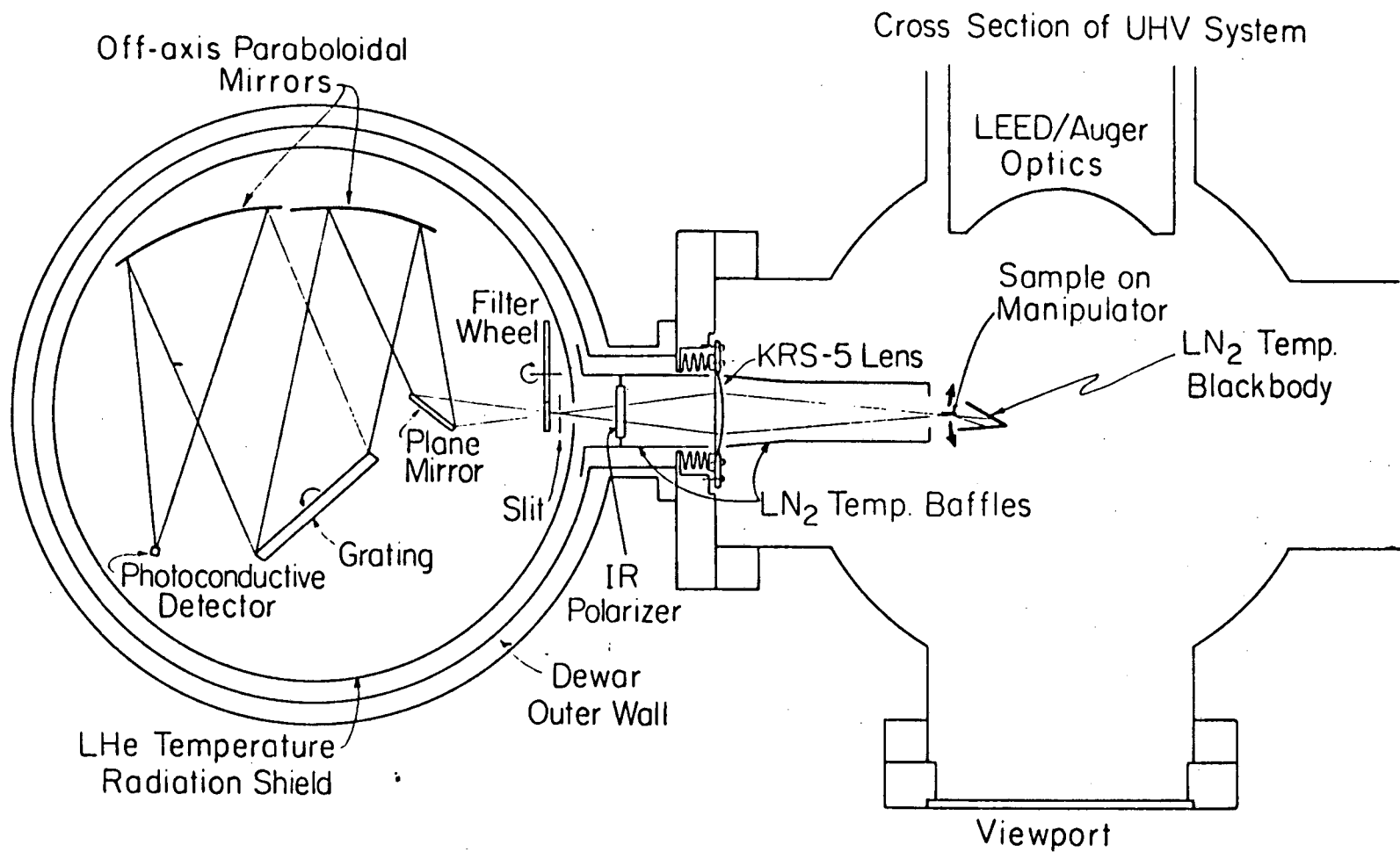
Optical Layout of Infrared' Emission Spectrometer

XBL 8012-13382A

Figure 1

Figure 2