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VIBRATIONAL SPECTROSCOPY OF CHEMISORBED MOLECULES
BY INFRARED EMISSION

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Abstract

The technique of infrared emission spectroscopy has been developed 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. The apparatus consists of a liquid helium cooled infrared grating spectrometer coupled to an ultrahigh vacuum system equipped with surface preparation and characterization facilities. 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} . Using this technique, we have measured the linewidths of both the carbon-metal and carbon-oxygen stretching vibrations of monolayer coverage of CO on Ni(100).

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I. INTRODUCTION

Vibrational spectroscopy is an important tool for the study of the chemical bonds at a surface. Many techniques have been used to obtain vibrational spectra. Electron energy loss spectroscopy (EELS) has high surface sensitivity over a large spectral range, but its relatively poor resolution of 30 to 100 cm^{-1} makes the observation of the resonant line shapes of adsorbed molecules very difficult.¹ Raman and infrared photon spectroscopies have the advantage that resolutions of 1 to 10 cm^{-1} are easily obtainable, but sensitivity to the surface is more difficult to obtain. Although many optical techniques have been developed, each has special limitations due to sample configuration, sample temperature, or sensitivity.²

Our goal has been the development of a high resolution spectroscopic technique with sufficient sensitivity to measure the linewidths of weak low frequency adsorbate-substrate vibrations on clean, single crystal samples. We have designed and built an apparatus to measure the infrared emission from a single crystal sample in thermal equilibrium at room temperature. The sample is located in a conventional UHV system which is coupled to an LHe temperature infrared grating spectrometer. The apparatus is capable of measuring surface vibrations over the range of infrared frequencies from 330 to 3000 cm^{-1} with an instrumental resolution of 1 to 15 cm^{-1} .

We have used this infrared emission technique to measure both the carbon-nickel stretching vibration at $\sim 470 \text{ cm}^{-1}$ and the

carbon-oxygen stretching vibration at $\sim 2000 \text{ cm}^{-1}$ of CO adsorbed on Ni(100). Our infrared emission apparatus is currently the only surface apparatus capable of studying the carbon-metal mode with sufficient sensitivity and resolution to measure its linewidth on a single crystal surface.

II. CONCEPT OF THE EMISSION EXPERIMENT

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,³ which is much larger than the surface molecular signal.

By measuring the infrared emission from a single crystal sample in thermal equilibrium at room temperature, 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.⁴ 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.⁵ Our approach is

distinguished by particular attention to the reduction of the flux of background photons reaching the detector and to the detector performance.

Figure 1 shows blackbody curves for $T = 77$ K, 300 K, and 400 K. We see that a room temperature sample emits significant radiation in the frequency range between 100 and 300 cm^{-1} , which includes most intramolecular and molecule-substrate vibrations. The 300 K blackbody curve has more intensity at frequencies between 300 and 1200 cm^{-1} than in the CO stretch frequency range around 2000 cm^{-1} . Raising the temperature of the sample to 400 K would increase the signal by a factor of 2 or 3 in the range from 300 to 1000 cm^{-1} , and a factor 10 at 1000 cm^{-1} .

In order to provide a contrast between the radiation emitted from the room temperature sample and that reflected or transmitted from its surroundings, we cool the surroundings with LN. Radiation from these parts of the apparatus is negligible for frequencies above $\sim 400\text{ cm}^{-1}$.

The noise in modern photoconductive infrared detectors is limited by the fluctuations in the stream of arriving photons. The best sensitivity is therefore obtained by minimizing the photon background. We decided to cool our entire spectrometer with LHe at 4.2 K for two reasons: (1) The emission from the optical elements inside the spectrometer is then completely negligible. (2) Doped silicon photoconductive detectors, which are capable of photon noise limited performance for $330 < \bar{\nu} < 1500\text{ cm}^{-1}$, must be cooled to less than 20 K in order to operate.

Our choice of a grating spectrometer rather than a Fourier transform infrared spectrometer (FTIR) was governed by the following considerations. If the system is limited by detector noise which is independent of the power reaching the detector, Fourier transform instruments have the well-known multiplex advantage.⁶ Since photon noise, which varies as the square root of the power, is larger than detector noise in our experiment, a grating instrument can give performance comparable to or better than that of an FTIR and is easier to cool.

III. DESIGN OF THE INFRARED SYSTEM

A horizontal cross section through the apparatus is shown in figure 2. The sample is mounted on a holder on the end of a Huntington manipulator, which is mounted in the top flange of a conventional Varian surface analysis system. The sample holder includes an L-shaped bracket which places the sample off the axis of the chamber so that it can be positioned in front of the various pieces of surface preparation and characterization

equipment, which include low energy electron diffraction (LEED) and retarding field Auger optics, a mass spectrometer for residual gas analysis and thermal desorption spectroscopy, and a 3 keV ion gun for sputter cleaning. After baking for 24 hours at 110°C, the system pressure is $<10^{-10}$ torr.

Only light with an electric field component normal to the metal surface interacts with surface molecules. Therefore the sample is observed at near grazing angles for maximum infrared surface sensitivity. For other types of surface analysis, normal incidence is required, so the sample holder includes a mechanism that transforms the coaxial linear motion of a rod within the manipulator shaft into a rotation of the sample about a vertical axis in the plane of its surface.

The sample is mounted by spot welding to tantalum foil strips, and can be heated resistively. A chromel-alumel thermocouple junction spot-welded to the back of the sample allows its temperature to be measured and regulated by a feedback temperature controller. The sample temperature is controlled within 50 mK for infrared measurements.

In order to perform the emission experiment, a limited number of optical components are needed inside the UHV system. These components are all mounted together on one 8 inch O.D. flange which is bolted into the large port on the left side of the UHV system in Fig. 2. Thus, a similar flange could be bolted into any conventional ultrahigh vacuum system with a suitable port, permitting infrared emission measurements of the sample in addition to other more conventional surface analysis techniques.

An LN cooled blackbody is placed behind the sample. To conserve space, this blackbody consists of concentric circular grooves in a copper surface which approximates the properties of a conical absorber with a 25° apex angle. The surface of the copper is coated with gold black, which consists of particles of gold evaporated in ~ 10 torr argon atmosphere in a separate evaporator.⁷ We have measured the emissivity of gold black to be ~ 0.97 in the range from 900 to 1600 cm^{-1} .

An LN cooled copper baffle coated with gold black surrounds the optical path between the sample and the infrared lens. Near the sample, an oversized slit is mounted in the baffle to limit the amount of stray radiation reaching the lens. These optical components are bolted to the outside of a heat exchanger through which LN flows continuously. To obtain high heat conduction, indium foil is pressed between each pair of cold surfaces. The temperature of these black components is $\sim 100\text{ K}$, which is just cold enough for experiments at $\sim 400\text{ cm}^{-1}$.

The thermal radiation from the sample passes through an KRS-5 infrared lens which also serves as a vacuum window for the UHV system. The lens is clamped to a stainless steel ring with a 0.1 mm thick indium gasket to make the vacuum seal. The room temperature lens is the only warm optical component in the beam. A bellows permits the adjustment of the position of the lens to focus light from the sample onto the entrance slit of the spectrometer.

The spectrometer is a compact Czerny-Turner⁸ type grating instrument which bolts directly onto the 8 inch flange on the

side of the UHV system. The entire optical path is evacuated, with ultrahigh vacuum on one side of the lens and thermal vacuum in the cryostat on the other, so that absorption by water vapor and other atmospheric gases is eliminated. The throughput of the instrument is $A\Omega = 2.5 \times 10^{-3} \text{ cm}^2 \text{ steradian}$.

After passing through an LN-cooled infrared polarizer which eliminates the component of the emitted light which has no surface signal, the radiation enters the 1 mm $\times$ 3 mm LHe-cooled entrance slit of the spectrometer. The filter wheel behind the slit contains four low pass filters, a beam block, and an open hole so that visible light from a helium-neon laser can be sent through the spectrometer to calibrate the frequency scale. The aluminum front-surface spectrometer mirrors are 10 cm diameter circles with an effective focal length of 18.4 cm and an off-axis angle of 26° .

The detector, which has dimensions of 2 mm $\times$ 1 mm $\times$ 1 mm, is mounted inside a gold-plated copper integrating cavity with a 2 mm high $\times$ 1 mm wide aperture. The detector is turned at 45° with respect to the optical axis so as to trap reflected light inside the cavity.

Because the detector impedance is typically $10^9 - 10^{11} \Omega$ under experimental conditions, the first stage of the trans-impedance amplifier circuit must have high input impedance and low noise. It must also be located near the detector to minimize pickup.⁹ The detector, the load resistor, and the low temperature JFET preamplifier package from Infrared Laboratories Inc., are mounted together on a small printed circuit board inside the cryostat.

A PDP-11/20 minicomputer is used to collect and analyze the data for this experiment. This computer is equipped with a 16 bit analog-to-digital converter and an interface to a preset indexer to drive the grating. To obtain an infrared spectrum of the sample, we measure the detector signal as a function of the grating position. For each data point, the computer averages 1000 samples of 1 msec. each. It then steps the grating and waits an additional 300 msec for mechanical vibrations to damp out. This procedure is repeated for each data point in the spectrum. After the measurement of the spectrum, the computer rewinds the grating drive and advances it a short distance to remove the backlash from the drive system.

The spectrometer is aligned at room temperature, using a visible light source, when it is open to the atmosphere. Small alignment errors in the horizontal plane are not important because the rotation of the diffraction grating will move the image onto the detector. The height of the entrance slit was chosen to produce an image that is higher than the detector aperture in order to be certain that radiation will reach the detector.

When the whole system is assembled and ready to measure data, only the sample position and the grating angle can be adjusted. The sample position which gives the maximum signal from the adsorbed molecules is determined experimentally by measuring the carbon-oxygen stretching vibration of CO on Ni. Once we have determined the optimal sample position, we can

replace the sample reproducibly in that position and obtain good infrared emission spectra of adsorbed molecules over periods of weeks.

IV. CRYOGENIC SYSTEM

An Infrared Laboratories model HD-3 liquid helium dewar is used to cool the spectrometer. It was modified to increase the volume at liquid helium temperature. The optical components of the spectrometer are screwed to a 30.5 cm diameter aluminum plate which is then screwed to the copper bottom of the liquid helium can. The optical components are surrounded by an LHe-cooled radiation shield, which is in turn surrounded by an LN-cooled radiation shield. Inside the LHe temperature shield, all parts except for the optical elements themselves are coated with 3M Velvet Black paint to reduce stray reflections. Aluminum foil is attached to the other surfaces of the radiation shields to reduce radiation loss. The entrance slit of the spectrometer is the only hole in the radiation shields. In operation, the optical components reach a temperature of ~ 5 K.

The grating rotation is driven by an Slo-Syn stepping motor under computer control and a 20:1 planetary gear speed reducer. A ferrofluidic feedthrough and a thin-walled fiberglass tube, which has very low thermal conduction and high torsional strength at low temperatures, are used to introduce the drive into the cold space. Each jog of the stepping motor corresponds to a rotation of the grating by 1.57×10^{-4} radians. Two retractable mechanical feedthroughs, each consisting of a shaft pushed through

an O-ring seal in the outer vacuum jacket, permit us to move the polarizer and the filter wheel.

Because of the large thermal mass of the optical components, about five hours are required to cool the spectrometer from 300 K to 77 K. About 8 to 10 liters of liquid helium are transferred into the cryostat over about one hour. As long as the LN tank is kept cold, the 1.2 liters of liquid helium last for 12 to 13 hours. Since subsequent liquid helium transfers take only five minutes and use only 1.5 to 2 liters of LHe, it is relatively easy to keep the spectrometer continuously at LHe temperature for several days. The conventional Perkin-Elmer polarizer, Optical Coating Laboratory filters, and Bausch and Lomb replica gratings on aluminum substrates have been successfully cooled at least 50 times.

V. PERFORMANCE OF THE INFRARED SYSTEM

We define the spectrometer efficiency E as the ratio of the measured number of photons per second at the detector to the predicted number accepted from the source by the throughput and bandpass of the spectrometer. The photon flux at the detector is inferred from the measured signal using detector characteristics measured in a separate cryostat with a calibrated infrared source.¹⁰ Considering the known transmission and reflection losses of the various optical elements, we expect $E = 0.10$. The difference between the expected value and the measured efficiency $E = 0.03$ is primarily due to misalignment and imperfection of the off-axis paraboloidal mirrors.

Our Si:Sb photoconductive detector, made by Rockwell International, is similar to those used on the Infrared Astronomy Satellite, where high responsivity and low noise in very low backgrounds are essential. The noise equivalent power in low backgrounds is limited by amplifier noise to $< 10^{-16}$ watt/HZ $^{\frac{1}{2}}$ at 2000 cm $^{-1}$. For photon rates $> 2 \times 10^8$ photon/sec, our detector is photon noise limited. Signal photon rates in this experiment are typically in the range from $10^9 - 10^{10}$ photons/sec.

With our measured spectrometer efficiency of ~3%, the photon noise limited performance would permit the measurement of emission from the C=O stretching mode at a coverage of 0.01 monolayer, with a signal to noise ratio of unity in a one Hz bandwidth. Unfortunately, since modulation has not yet been implemented, the system is limited by instabilities in the source and other parts of the apparatus. Even without further development, however, we can routinely measure emission from 0.05 L CO on Ni, with a line center signal-to-noise ratio of 4 in one second.

Sources of our observed dc signal drift include temperature drifts of the load resistor and of the LN-cooled parts of the optical system. Variations in the temperature of the sample may also contribute to dc signal drifts. Other sources of noise may be fluctuations in the sample position, non-reproducibility of

the diffraction grating angle, and changes in the small amount of room temperature radiation which leaks into the system.

In order to estimate the usefulness of our apparatus, we have calculated the photon noise limited detection threshold of our instrument for small molecular signals superimposed on the bulk emission of the metal. The solid lines in figure 3 give the minimum ratio of the surface molecular signal to background metal signal which could be measured by the instrument with a surface signal-to-noise ratio of unity, in a one hertz bandwidth, as a function of the optical frequency. This detection threshold is just the ratio of photon noise to total signal. The calculations were done using the parameters for a Pt (111) surface with emissivity $\epsilon = 0.10$ and include variations in spectrometer resolution and detector quantum efficiency as a function of frequency. The dashed lines show the present performance of the instrument, limited by low frequency drifts.

We also show in Fig. 3 the ratio of molecular signal to metallic background calculated for a variety of vibrational modes of molecules on Pt(111), estimated from EELS intensities¹¹ using an approach due to Ibach.¹² In addition, we include in Fig. 3 the ratios for CO on Ni(100) which were observed in the experiments described in Section VI. While it is easy to observe the C=O stretching vibration with the present sensitivity of the system, the size of the signal from the C-Ni mode is the smallest which can be seen with the instrument without further improvements.

VI. EXPERIMENTS ON CARBON MONOXIDE ADSORBED ON NICKEL

We have observed thermally emitted infrared radiation from CO adsorbed on Ni(100). The crystal, obtained from the Materials Research Laboratory of Cornell University, was 0.5 cm high $\times$ 1.5 cm wide $\times$ 1 mm thick, the dimensions chosen so that it fills the entrance slit of the spectrometer when turned to the optimum angle for surface sensitivity.

For each set of measurements, the nickel single crystal was cleaned by methods described previously.¹³ An infrared spectrum of the clean nickel surface was measured to serve as a reference. For measurements of the C=O stretching vibration, the sample was exposed to doses of 0.05L or 0.10L CO (1L = 10^{-6} torr sec) by letting 10^{-8} torr of CO gas, of 99.5% purity, into the UHV system through a leak valve for 5 or 10 seconds. The spectra of nickel with CO were then divided by the reference spectrum to eliminate the frequency dependence of the blackbody intensity and optical efficiency of the instrument. After subtraction of a constant background, the results from 3 or 4 independent experiments, with spectral scans of one minute each, were averaged together to yield a series of spectra. Figure 4 shows the observed spectra of the carbon-oxygen stretching vibration for 0.2L and 0.5L CO on Ni(100), which will be discussed in more detail elsewhere.¹⁴

To measure the carbon-nickel stretching vibration of CO on Ni(100), a similar procedure was followed, using a grating of higher dispersion. Since the surface signal due to this mode is about thirty times weaker than that of the carbon-oxygen

vibration, a correspondingly longer integration time was required. The spectrum shown in figure 5 is the result of five independent experiments, with a total integration time of about 30 seconds per point.

Our measurement of the carbon-nickel vibration of CO on Ni(100) gives the first measurement of the linewidth of a molecule-substrate vibration. It clearly illustrates the power of our infrared emission technique. The frequency of the observed C-Ni vibration at $472 \pm 5 \text{ cm}^{-1}$ agrees well with previous EELS results.¹⁵ With instrumental resolution of 2.5 cm^{-1} , the observed linewidth, measured full width at half maximum (FWHM), is $15 \pm 2 \text{ cm}^{-1}$. Further discussion of the linewidth of the adsorbate-substrate mode will be published elsewhere.¹⁶

VII. CONCLUSIONS

We have demonstrated that the technique of infrared emission spectroscopy can be used to measure the vibrational modes of sub-monolayer coverages of molecules adsorbed on clean, single crystal metal surfaces. An infrared emission apparatus, consisting of a liquid helium temperature grating spectrometer coupled to a conventional ultrahigh vacuum system, has been built and used to measure the vibrational modes of CO on Ni(100). This is the first apparatus which has had sufficient spectral range, resolution and sensitivity to measure the linewidths of both the intramolecular vibration and the very weak adsorbate-substrate mode for this system. Now that the linewidth of the carbon-nickel vibration has been measured, we expect that more theoretical and experi-

mental work on the linewidths of vibrational modes will follow, yielding additional insight into the processes damping the modes.

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FIGURE CAPTIONS

1. Expected photon rate at our detector as a function of frequency for source temperatures of 77, 300 and 400 K. These curves do not include the details of the frequency dependences of the efficiencies of the spectrometer and the detector.
2. Optical layout of infrared emission apparatus, with LHe-cooled spectrometer on the left and ultrahigh vacuum system on the right.
3. The solid curves show the calculated detection threshold for our emission apparatus if it were limited by photon noise. The dashed lines show our current experimental sensitivity without modulation. The x's show our measured surface signal from CO on Ni(100). The chemical symbols indicate the signal levels to be expected from monolayer coverages of various adsorbates on Pt(111).
4. Observed spectra of C=O stretch on Ni(100) for 0.2 and 0.5L exposure to CO. The mode at $\sim 1900\text{ cm}^{-1}$ is usually ascribed to bridge bonded molecules. The mode at $\sim 2030\text{ cm}^{-1}$ is from CO molecules in the linear site. The vertical bar indicates 0.1% absolute emissivity. The instrumental resolution was 20 cm^{-1} .
5. Observed spectrum of C-Ni stretch on Ni(100). The instrumental resolution was 2.5 cm^{-1} .

XBL 838-10975

Fig. 1

Optical Layout of Infrared Emission Spectrometer

XBL 8012-13382 A

Fig. 2

XBL 838-11018

Fig. 3

XBL833 - 5422

Fig. 4

XBL 833-5421

Fig. 5

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