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THE C=O STRETCHING VIBRATION OF CO ON Ni(100) BY INFRARED EMISSION SPECTROSCOPY

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Infrared emission spectroscopy has been used 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 suggest the presence of \( c(2x2) \) islands even at low coverage, though low energy electron diffraction shows no sign of such ordering.

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Introduction

Infrared emission spectroscopy has been shown to be a powerful tool for the vibrational spectroscopy of adsorbates on single crystal surfaces. It allows high resolution measurements to be made at monolayer and submonolayer coverages of adsorbate vibrations from 330 cm\(^{-1}\) to approximately 3000 cm\(^{-1}\). It is the only technique reported to date capable of high resolution surface vibrational spectroscopy on single crystal surfaces in the important frequency range of several hundred cm\(^{-1}\), which includes many adsorbate-substrate vibrations. Recently, the first measurement of the linewidth of the C-Ni stretch vibration of CO on Ni(100), using infrared emission spectroscopy, was reported [1].

This paper concerns the application of emission spectroscopy to the C=O stretching vibration of CO on Ni(100). Although this frequency region has been previously investigated with electron energy loss spectroscopy (EELS) [2,3], and infrared (IR) spectroscopy [4], we find interesting new results. In contrast to the previous experiments, we find no band due to bridge-bonded CO on a clean surface, at coverages up to \(\theta = 0.5\), but we find that bridging sites are occupied when a slightly contaminated surface is investigated. Consideration of the lineshape as a function of CO exposure suggests that significant short-range ordering occurs within the overlayer at exposures below those for which low energy electron diffraction (LEED) shows evidence of ordering.
Experimental

Since the infrared emission apparatus has been described previously [5], and will be discussed in detail in another publication [6], it will only be summarized here. Thermal radiation from the sample, which is near room temperature, is focused onto the entrance slit of a grating spectrometer which is cooled to 5 K to reduce background radiation. The sample is surrounded by absorbing baffles at -100 K to provide the temperature contrast necessary for emission measurements. The Si:Sb photoconductive infrared detector is sensitive to frequencies above 330 cm⁻¹.

The sample is mounted on a manipulator in a conventional ultrahigh vacuum UHV chamber with a base pressure less than 10⁻¹⁰ torr. The chamber is equipped with low energy electron diffraction and retarding field Auger spectroscopy optics. It also has a 3 keV ion gun for sample sputtering and a mass spectrometer for thermal desorption measurements. The sample was heated by passing electrical current through it; its temperature was monitored by a chromel-alumel thermocouple spot-welded to the back.
The sample was a Ni(100) single crystal, 5 x 15 mm, prepared by the Materials Research Laboratory at Cornell University. It was cleaned by Ar ion sputtering, followed by annealing at 685°C, combined with repeated oxygen exposure-heating cycles to eliminate residual carbon. Thermal desorption of CO was used during the heating cycles to determine when the surface was free of carbon, and to prevent excessive exposure to oxygen. The carbon contamination combined with oxygen to produce CO which produces a characteristic set of desorption peaks at T > 500 K. Heating to 950°C removed the oxygen from the surface, probably by dissolution into the bulk [7]. The best indicator of surface cleanliness was the ability to obtain a sharp c(2x2) LEED pattern from a saturation coverage of CO at room temperature. Amounts of carbon or oxygen too small to be detected by retarding field Auger spectroscopy were sufficient to prevent this ordering.

Once a clear c(2x2) pattern was obtained, the sample was again heated to desorb the CO. For the infrared studies, the sample temperature was actively regulated to within 0.05 K in the neighborhood of 310 K, the temperature at which the sharpest LEED patterns were seen.

A reference spectrum of the clean nickel surface was first measured by recording the detector signal as a function of the grating position under computer control with one second of integration time at each point. A number of such spectra were measured and compared to verify the stability of all parts of the
instrument. Approximately ten reference spectra were then recorded and averaged. The sample was then exposed to successive measured doses of CO. After each dose, another set of spectra was averaged. A ratio to the reference spectrum was computed to isolate the contribution due to the adsorbate. The sample was not moved until all data had been measured. The sample was then moved in front of the LEED screen, and the presence of a sharp c(2x2) pattern at saturation was verified. At the higher exposure levels, 20 min. was allowed between dosing with CO and measuring spectra to allow equilibration within the layer. Our LEED observations indicated that visible sharpening of the pattern occurred during this period. Absolute frequency calibration was achieved by comparison with a He:Ne laser observed in high orders of diffraction from the grating.

The spectrometer was designed to have a resolution of less than 10 cm\(^{-1}\) at frequencies between 330 and 2500 cm\(^{-1}\), using three different gratings. Unfortunately, excessive light scattering at low frequencies prevented us from using the least dispersive of the gratings; as a result the instrumental resolution for the spectra shown here was nearly 20 cm\(^{-1}\), and was not sufficient to resolve the narrowest lines. This problem will be remedied by the installation of a low frequency rejection filter.
Results and Discussion

Figure 1 shows a set of spectra of the C=O stretching vibration of CO on Ni(100), for exposures from 0.05 L (1 L = 10^{-6} torr-sec) to the formation of an ordered c(2×2) overlayer (coverage θ = 0.5) which occurs for exposures > 1.5 L. The C-Ni stretching vibration was also observed for this system; these results have been presented elsewhere [1].

At all exposures studied, only one band is observed, in the frequency range 2010-2050 cm\(^{-1}\). We believe that the other structures visible in the spectra indicate the noise level in the experiment. The C=O band at 2024 cm\(^{-1}\) in the 0.05 L spectrum is scarcely larger than the noise feature at -2070 cm\(^{-1}\), and can be confidently identified only because it develops smoothly into the conspicuous band at higher exposures.

Previous studies of this system have shown two vibrational bands in the spectral region displayed. Andersson [2] observed CO on Ni(100) with electron energy loss spectroscopy. At low coverage (0.3 L CO) and 293 K, he found C=O stretch bands both at 1916 cm\(^{-1}\) and at 2048 cm\(^{-1}\), with nearly equal intensities. For a c(2×2) overlayer, he observed a single strong band with a peak at 2052 cm\(^{-1}\), but with a conspicuous shoulder at 1920 cm\(^{-1}\). In another EELS study, Bertolini and Tardy [3] observed two overlapping bands at both low and high coverage: one in the range 1900-1935 cm\(^{-1}\) and the other at 2000-2015 cm\(^{-1}\). The two bands had nearly equal intensity. In an IR ellipsometry experiment, Dignam [4] also found two bands, the band near 1900 cm\(^{-1}\) being broader and less intense than the band near 2000 cm\(^{-1}\).
When we measured CO adsorbed on Ni(100) surfaces which are contaminated with small quantities of carbon, oxygen or sulfur, we measured spectra similar to those reported previously. Typical spectra for CO exposures of 0.2 and 0.5 L on a contaminated surface are shown in Figure 2. Two bands are visible; the ∼2000 cm⁻¹ band has a width of ∼30 cm⁻¹, and the band near 1900 cm⁻¹ has a width of ∼70 cm⁻¹, and an integrated intensity about half that of the higher frequency band.

Conventionally a C=O stretch band in the range 1900-1950 cm⁻¹ is assigned to CO bridge bonded to two substrate atoms. Thus the EELS and IR data discussed above indicate the presence of bridging CO at a concentration comparable to that of linear CO at all coverages, though they differ considerably in the ratio seen at high coverage. This result is surprising, since it has been shown [7] that in the c(2×2) layer all the adsorption sites are four-fold symmetric, so that bridge sites should be excluded.

In our present experiment, we reproduce the earlier results only for a somewhat contaminated surface. For a clean surface, (Fig. 1), we observe no occupation of bridging sites at any coverage up to θ = 0.5. Based on these observations, it seems that the concentration of bridging CO is highly sensitive to the state of the surface, possibly because contaminants change the binding energy of CO on neighboring sites, or impede the surface migration of the adsorbate to unoccupied linear sites.
Despite the limited instrumental resolution and signal-to-noise ratio, the data suggest interesting changes in the infrared lineshape as a function of exposure. The line first appears at low coverage at 2024 cm\(^{-1}\) and appears symmetric, with an instrumentally limited linewidth. At a full c(2x2) overlayer, the spectrum again consists of a single symmetric line, at 2055 cm\(^{-1}\), the linewidth limited by the instrumental resolution. At intermediate coverages, the band is broadened and asymmetric. It appears to be composed of two components.

For an exposure of 0.2 L, a higher frequency component, at approximately 2050 cm\(^{-1}\), appears to overlap the original low coverage band. By 0.4 L, the high frequency component becomes dominant. With more exposure the low frequency component diminishes further and the line narrows as the overlayer orders.

The observation of this exposure-dependent structure within the infrared band suggests the presence of at least two distinct types of linearly bonded CO at intermediate coverages. Since only the high frequency component remains at saturation, and it does not appear to shift in frequency as the exposure is increased, this line appears to represent CO in an environment that is at least locally c(2x2), that is, in locally ordered islands. The lower frequency component could then be attributed to disordered CO in the regions not occupied by ordered islands. As the exposure is increased, the intensity of this component at first grows, as the number of disordered molecules increases, but then
diminishes as the ordered regions dominate the surface. Because the density of the disordered phase increases continuously, dipole coupling causes an upward shift in frequency, as has been repeatedly shown in many systems [8]. At saturation, only ordered regions remain, and only the single sharp line at 2055 cm$^{-1}$ is observed.

Similar lineshape effects, due to molecules in different local environments, have been observed by Dignam [4] for CO on Ni(110), and by Pfnüer, et al. [9] for CO on Ru(001). In his study of CO on Ni(100) at 298 K, Dignam did not detect such lineshape variations; however, the observed linewidth was $\sim 34$ cm$^{-1}$, much broader than we have observed on the clean surface, but similar to that shown in Fig. 2 for a contaminated surface. For CO on Ru(001), at coverages below $\theta = 0.33$, Pfnüer, et al. accounted semiquantitatively for lineshapes similar to ours. They assumed ordered islands of various sizes, in the ($\sqrt{3} \times \sqrt{3}$) R 30° phase, and included the smaller dipole coupling for molecules at the edges, compared with those within the islands. Their model is consistent with the LEED observation of ($\sqrt{3} \times \sqrt{3}$) R 30° structure at low coverage.
In the case of CO on Ni(100), Tracy's \cite{7} LEED data showed signs of c(2\times2) ordering only very near $\theta = 0.5$, for a temperature of 300 K. There was no evidence for island formation at low coverage in his measurements (or in our lower sensitivity measurements). This observation does not agree with our qualitative explanation of the infrared lineshapes, suggesting either that the islands are too small for LEED to detect or that an alternative model is needed.

Conclusions

The application of IR emission spectroscopy to the C=O stretching vibration of CO on Ni(100) demonstrates the usefulness of using IR techniques, even on systems already studied with EELS. We have shown that for a sufficiently clean surface, only linear bond sites are occupied, at coverages up to $\theta = 0.5$. This result reconciles vibrational spectra with LEED results, which excluded bridge-bonded CO from the c(2\times2) overlayer \cite{7}.

Variations of the vibrational lineshape with coverage suggest local ordering at low coverage, and illustrate the importance of high resolution vibrational spectra in understanding overlayer ordering.

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References


Figure Captions

Figure 1. IR emission spectra of CO on a clean Ni(100) surface at 310 K. The instrumental resolution was -18 cm⁻¹.

Figure 2. IR emission spectra of CO on a slightly contaminated Ni(100) surface at -300 K. The instrumental resolution was -18 cm⁻¹.
FIGURE 1

CO ON Ni (100)

EMISSIVITY

FREQUENCY (cm⁻¹)

1800 1900 2000 2100 2200

c(2x2) 0.6 L 0.4 L 0.2 L 0.05 L

1.0%
FIGURE 2

Ni(100)/CO
300 K

Emissivity

Frequency (cm⁻¹)

0.1 %

0.5L

0.2L

1800 1900 2000 2100 2200

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