Pressure Dependence (10^{-10}–700 Torr) of the Vibrational Spectra of Adsorbed CO on Pt(111) Studied by Sum Frequency Generation

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The vibrational spectrum of CO on Pt(111) was monitored over 13 orders of magnitude in CO pressure by using infrared-visible sum frequency generation. Surprising results at high pressures indicate a pressure-induced major reorganization of CO on Pt(111). At low pressures (10^{-10}–10^{-1} Torr) CO bonds at atop and bridge sites, but above 10 Torr new features appear, and by 700 Torr they dominate the spectrum. They suggest the presence of an incommensurate CO overlayer together with some terminally bound CO at atop defect sites. [S0031-9007(96)01551-7]

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The bonding geometry of CO on Pt(111) has been shown to vary as a function of coverage and temperature under ultrahigh vacuum (UHV) conditions [1–4]. However, for heterogeneous catalysis and many other surface phenomena, it is more important to explore the location and bonding geometry of surface species on transition metals at near atmospheric pressures, but such experiments have not yet been reported because techniques were not available for surface studies in that pressure regime until recently. We can now bridge this pressure gap using infrared-visible sum frequency generation (SFG) spectroscopy [5]. In this Letter we report the adsorption of carbon monoxide on Pt(111) in the 10^{-10}–700 Torr pressure range. Dramatic changes in the vibrational spectrum of surface species were observed with increasing CO pressures. At pressures >10 Torr, the results indicate the presence of an incommensurate CO overlayer together with CO adsorbed on distorted atop sites of Pt(111) or on dislocated surface platinum atoms.

The SFG technique permits surface studies under atmospheric pressures and has been described in detail elsewhere [6–8]. Briefly, SFG is a second order nonlinear optical process in which a tunable infrared beam is mixed with a visible beam to generate a sum frequency output. This process is allowed only in the electric dipole approximation in a medium without centrosymmetry. As a result, in the present case of the gas/Pt system, the SFG signal is dominated by contribution from the Pt(111) surface, where the inversion symmetry is necessarily broken. Both the surface platinum atoms and the adsorbed molecules contribute to the SFG output. However, for the CO/Pt(111), the signal from the surface platinum atoms is much weaker than that from the CO adsorbate in the CO stretch region.

The Pt(111) single crystal was cleaned by conventional surface science procedures in an UHV chamber. The CO gas used was purified by passing through a liquid-nitrogen-cooled molecular sieve to remove traces of iron carbonyls and other contaminants. On-line mass spectroscopy, gas chromatography, and Auger electron spectroscopy were used to check the cleanliness of the gas and the surface before and after the experiments. No contaminants were found in all the experiments conducted. SFG spectra were taken at 295 K from 10^{-10} to 700 Torr of CO.

A 20-picosecond passive/active mode-locked Nd:YAG laser system was the source for our optical measurements. Part of its output was frequency doubled to 532 nm and used as the visible input for the SFG. The other part was used to pump an optical parametric system to generate an infrared beam tunable between 1100–2400 cm^{-1}. These two beams were focused and overlapped on the Pt(111) crystal with near grazing angles. Both visible and IR beams were *p* polarized. The *p*-polarized sum frequency signal reflected from the Pt surface was detected by a photomultiplier and a gated integrator.

Figure 1 shows SFG spectra of CO/Pt(111) under various CO pressures ranging from 10^{-7} to 700 Torr. When the clean Pt(111) surface was exposed to 10^{-7} Torr of CO, two peaks at 1845 and 2095 cm^{-1}, characteristic of stretch vibrations of CO adsorbed at bridge and atop sites, respectively, were observed. The spectrum is identical to that of a Pt(111) surface exposed to 10 L ($1\ \mathrm{L} = 10^{-6}$ Torr sec) of CO. Low energy electron diffraction revealed a $c(4 \times 2)$ structure, in which an equal number of carbon monoxide molecules occupies atop and bridge sites [3]. Such results are in agreement with previous high resolution electron energy loss (HREEL) and reflection-absorption infrared spectroscopy (RAIRS) studies [1–4]. The relative intensity ratio of the two peaks in the SFG spectrum (Fig. 1), however, is very different from those of HREELS and RAIRS. This is because of the different selection rules of SFG as it involves both Raman and IR transitions [9].

Raising the pressure to 1 Torr, the bridge-bonded CO was no longer observable and the frequency of atop

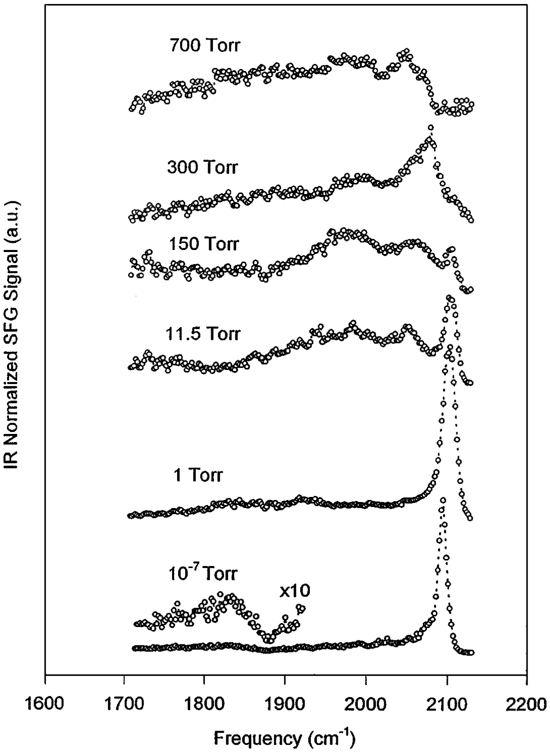

FIG. 1. Pressure dependence of the SFG spectra of carbon monoxide on Pt(111). The spectral change indicates that new surface species appeared at high pressures.

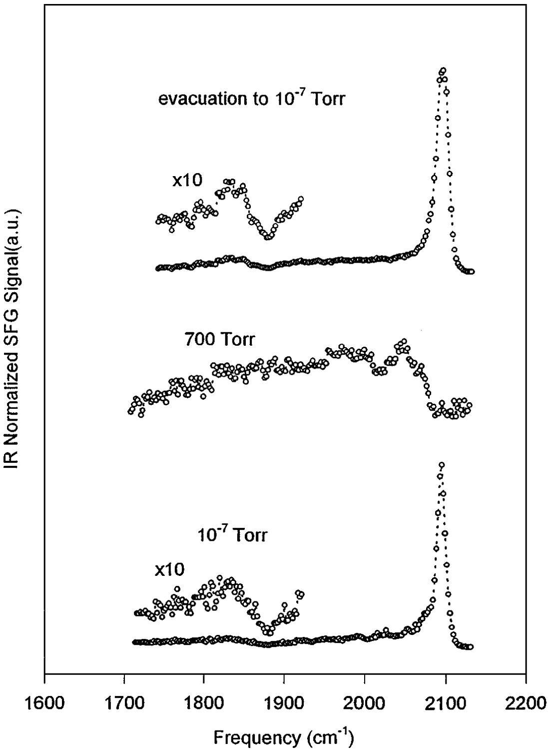

FIG. 2. Reversibility of the CO pressure-induced changes of the SFG spectrum of adsorbed CO on Pt(111). The spectrum taken with the clean Pt(111) exposed to 10^{-7} Torr is identical to that taken after evacuation of the chamber from 700 to 10^{-7} Torr.

species shifted to a higher value, 2105 cm^{-1}. This has been found on the same system with high CO exposure in UHV studies [1,10]. The frequency shift is the result of enhancement of dipole coupling between CO molecules on the surface as their packing density increases at high coverage [11], thereby weakening their bonds to the metal [12]. Further increases of the pressure decreased the intensity of the atop CO without further frequency shift or broadening. At the same time, a new peak at 2045 cm^{-1} together with a broad background became visible. By 700 Torr of CO, the spectrum was dominated by the new feature and the broad background extended to 1700 cm^{-1}. The spectra were completely reversible and reproducible with variation of the gas pressure. The reversibility was demonstrated in Fig. 2, in which the spectra taken after exposing a clean Pt(111) sample to 10^{-7} Torr of CO, then to 700 Torr, and finally back to 10^{-7} Torr, are presented.

In Fig. 3 the spectra were taken under the same conditions as that of Fig. 1 but the sample used had a larger concentration of surface defects resulting from argon ion bombardment. In UHV the atop bonded CO dominated the spectrum and appeared at a frequency of 2084 cm^{-1}, which is at least 10 cm^{-1} lower than the equivalent spectrum at the well ordered Pt(111) surface [13]. This may be due to the stronger bonding of CO to the metal surface near or at the defect sites [12]. The atop CO stretch shifted again to higher frequency [11], 2095 cm^{-1}, with increasing pressure. The high pressure spectrum was again dominated by the 2045 cm^{-1} peak superimposed on a broad background, but these features became clearly visible only beyond 150 Torr. The relative strength of the 2045 cm^{-1} peak to the overall broad background seemed higher for the ion bombarded surface than that for the annealed Pt(111) surface because the broad background extended only to ~1850 cm^{-1} at 700 Torr.

The higher carbon monoxide pressure should lead to more adsorption of CO on the Pt(111) surface and, hence, a more compressed CO monolayer. This would form an incommensurate overlayer of CO molecules on the surface as the adsorbed CO would lose registry with the platinum surface atoms. The randomly adsorbed CO distribution explains the broad background in the CO stretch spectra.

The presence of the 2045 cm^{-1} peak in the high-pressure spectra is intriguing (Fig. 1). The frequency is characteristic of terminally bonded (Pt-CO) molecules [14]. Therefore the peak that was observed only at high CO coverages could be associated with CO squeezed onto a Pt atom at defect or distorted atop site causing the frequency shift to the lower value. Higher CO coverages would increase the number of CO at such sites. Indeed, it is seen in Fig. 1 that the intensity of atop CO decreases

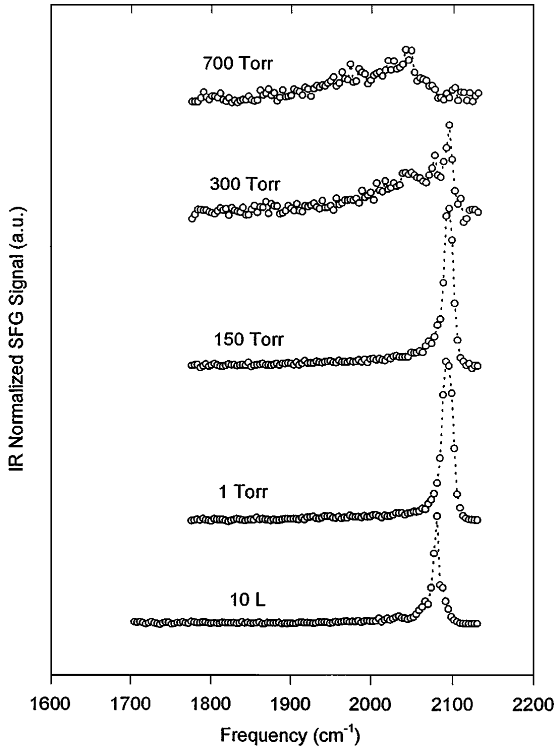

FIG. 3. SFG spectra of adsorbed CO as a function of CO pressure on Pt(111) disordered by argon ion bombardment.

with increasing pressure, while the 2045 cm^{-1} feature intensity increases.

An alternative interpretation of the 2045 cm^{-1} peak is that the higher CO surface density may induce relocation of surface Pt atoms and CO bonded to these metal atoms may have a stretch frequency comparable to the vibrational frequency of terminally bonded CO (Pt-CO) in carbonyl molecules. It may even be possible that multiply bonded platinum carbonyl binary complexes Pt-$(\text{CO})_n$ $(n = 1, 2, 3, 4)$ are present on the Pt(111) surface if some local Pt surface structures are heavily reconstructed. Ozin *et al.* have shown that Pt-$(\text{CO})_n$ $(n = 1, 2, 3, 4)$ in an argon matrix have CO stretch frequencies all near 2050 cm^{-1} [15]. It is possible that surface reconstruction or relocation of metal atoms can be more easily induced near a defect, step, or kink site.

Argon ion bombardment would introduce a higher concentration of defects on the Pt surface. CO molecules are expected to bind to the Pt surface atoms defect more strongly near defect sites [12,13,16] and hence exhibit a lower stretch frequency at lower coverage. They are more difficult to displace. Therefore, the high density of defects may deter the formation of the incommensurate CO overlayer until a much higher CO pressure is reached as compared to the case of the annealed Pt(111) surface.

We have shown in this Letter that the adsorptions of CO on Pt(111) below 10 Torr and at higher pressures are very different. At high pressures, incommensurate CO overlayers and CO adsorbed at defected or distorted atop sites resembling terminally bonded CO to Pt atoms can be stabilized. There is reversibility between the adsorbed CO species observed in the two pressure regimes. Our observation should have important consequences for catalytic surface reactions involving CO (oxidation or hydrogenation), since in practice these reactions are often carried out under high reactant pressures. Moreover, these pressure-dependent changes could be expected for many other systems. We shall report catalytic CO oxidation reaction studies in the high-pressure range using SFG spectroscopy in a separate publication.

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