Photoelastic modulation-reflection absorption infrared spectroscopy of CO on Pd(111)

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The photoelastic modulation-reflection absorption infrared spectrum (PEM-RAIRS) of CO on single crystal Pd(111) is measured for CO pressures up to ~150 Torr. The ac component of the signal, corresponding to the infrared signal of the surface, is measured using a synchronous demodulator circuit rather than using a lock-in amplifier as used in previous experiments to measure the infrared spectra of model catalysts surfaces. This allows the spectra to be collected at almost the same speed as RAIRS spectra performed in ultrahigh vacuum. A simplified synchronous demodulator circuit is described consisting of two sample-and-hold circuits operating at 100 kHz. Spectra are obtained that are in excellent agreement with previous results showing that a combination of hcp and fcc threefold sites are occupied by CO at 300 K. Atop sites become occupied as the CO pressure increases. Heating the Pd(111) sample to ~500 K removes all adsorbed CO. © 2002 American Vacuum Society. [DOI: 10.1116/1.1517995]

I. INTRODUCTION

The goal of fully understanding catalytic reactions relies on being able to interrogate the surface of a model catalytic system under realistic, i.e., high-pressure, conditions. For example, it has been shown, in the case of Pd(111)-mediated acetylene cyclotrimerization to benzene, that benzene is formed by completely different routes in ultrahigh vacuum in temperature-programmed desorption or catalytically at high pressures.[1,2] Thus, in ultrahigh vacuum, benzene is formed in a sequential reaction between two di-σ-adsorbed acetylene molecules to form a C_4 metallacycle,[3] which subsequently reacts with a third acetylene to form benzene.[4] In contrast, at high pressures, the model Pd(111) catalyst surface is completely covered by vinylidene species.[5] In this case, it has been shown that the initial metallacycle is formed by a reaction between adsorbed acetylene and vinylidene species at a much lower rate than in ultrahigh vacuum.[6] Thus, while a significant amount of information on the nature of the catalytic reaction pathway is available from ultrahigh vacuum studies, the high-pressure reaction pathway may well be substantially different from that found in ultrahigh vacuum. In order to probe these differences, therefore, it is necessary to be able to interrogate the nature of the surface species in the presence of high pressures of reactant gas. Achieving this relies primarily on using surface-sensitive techniques based on photons. Two methods are available for probing the vibrational spectra of surface species in the presence of high gas pressures. The first is sum-frequency generation (SFG) in which high-intensity visible and infrared radiation couple at the surface to yield a sum frequency.[7,8] The infrared frequency is scanned and resonances between the infrared radiation and surface vibrational modes lead to increases in the SFG cross section at these frequencies. Only those modes

that are both infrared and Raman allowed are allowed in sum-frequency generation. Since this only occurs for a medium that does not possess a center of inversion, the SFG spectrum of the gas phase and the sample bulk is symmetry forbidden, while vibrational modes of molecules adsorbed onto the surface may be allowed if they obey the surface selection rules. Another method, which is experimentally rather simpler, relies on the surface selection rules for reflection-absorption infrared spectroscopy (RAIRS). In this case, on a metal surface, only vibrational modes having components of their normal modes that are oriented perpendicular to the surface are excited by the incident infrared radiation while those modes which vibrate parallel to the surface are not. This means that surface infrared modes are only excited by *p*-polarized but not by *s*-polarized radiation.[9,10] The experiment, in this case, consists of changing the polarization of the incident radiation from *p* to *s* polarized and measuring the difference between the absorbances for these two polarizations $I_p - I_s$. Since the surface selection rules show that I_p and I_s are different for adsorbed species, $I_p - I_s$ is nonzero. In contrast, for gas phase species, the absorbance is independent of polarization, so that $I_p - I_s = 0$. This provides an ideal method for measuring the infrared spectrum of adsorbed species in the presence of a gas or liquid. Since the incident intensity is a function of frequency $I_p - I_s$ is normalized to the sum of both $I_p + I_s$. The polarization can be modulated in two ways. Firstly, either *s*- or *p*-polarized light can be selected by a rotatable polarizer placed in the path of the incident beam.[11] The RAIRS spectrum is then collected using *s*- or *p*-polarized light and the above ratio calculated. The problem with this method is that, in many cases, the intensities of the *s*- and *p*-polarized light emanating from the Michaelson interferometer used in Fourier-transform infrared spectrometers can be rather large making the small values of $I_p - I_s$ for surface species difficult to measure. This problem can be avoided by modulating *p*-polarized light using a pho-

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toelastic modulator (PEM).[12,13] The main disadvantage of this method is that the polarization is only modulated by 90° at a single frequency. In practice, this means that the background signal is effectively canceled out over a relatively narrow frequency range. However, the spectral range of interest is often well known from RAIRS spectra carried out in ultrahigh vacuum (UHV) so that this is not necessarily a major problem. This technique is known as PEM-RAIRS.

This has previously been used to great effect to examine surfaces in the presence of liquids.[14–16] It has, however, been less extensively applied to examining the nature of model catalyst surfaces under reaction conditions and has been used to examine cobalt-catalyzed CO–hydrogenation reactions under high pressures,[17] where the ac signal was measured using a lock-in amplifier. This is not the most ideal method for measuring the ac component of the infrared signal since lock-in amplifiers have an inherent time constant which limits the speed at which the interferogram can be collected to about 1 kHz without it being distorted due to these time constants.[15] A more effective method is to use a sampling demodulator to measure the intensity while the polarization is being modulated, resulting in the measurement of I_p or I_s directly.[12,13,15] These circuits are generally rather fast and can easily operate at the 100 kHz polarization modulation frequency. This fast response time further allows the interferometer to be operated at the same speed as used for collecting RAIRS data (40 kHz), thus decreasing the spectral detection time and also decreasing the detector signal-to-noise ratio by allowing it to operate at higher frequencies. It is shown in the following that it is possible to measure the surface infrared spectrum of CO on Pd(111) in the presence of up to 150–200 Torr of CO without undue interference from gas-phase CO.

II. EXPERIMENT

The experiments were carried out in a stainless-steel, ultrahigh vacuum (UHV) chamber operating at a base pressure of $\sim 8 \times 10^{-11}$ Torr following bakeout, and which has been described in detail elsewhere.[18] Infrared data were collected from a Pd(111) single crystal sample mounted in a modified 2 3/4 in. six-way cross equipped with infrared-transparent, KBr windows. The small cell dimensions minimized the infrared light path through the high-pressure gas. The sample could be resistively heated to 1000 K, or cooled to 80 K using liquid nitrogen. Light from a Bruker Equinox infrared spectrometer passes through a polarizer so that it is *p* polarized, and is focused on the sample at an incidence angle of $\sim 80°$, and the reflected light steered onto the detector of a liquid-nitrogen-cooled, mercury–cadmium–telluride (MCT) detector. The complete light path is enclosed and purged with dry, CO_2-free air. A PEM (PEM-90, Hinds Instruments. Willsboro, OK) is placed in the incident light path just before the entrance window to the sample cell at an angle of 45° to the incident polarization allowing the incident light to be modulated between *p* and *s* polarization at 100 kHz. The λ/2
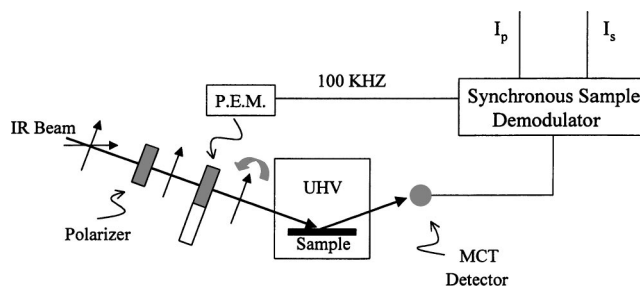

FIG. 1. Schematic diagram of the arrangement used for the PEM-RAIRS experiment.

frequency was chosen to be close to the vibrational frequency of CO on Pd(111) (~ 2100 cm^{-1}). The experimental arrangement is displayed in Fig. 1.

Green *et al.*[19] have described a synchronous sampling demodulator circuit, where the composite output of the detector is synchronously sampled to I_p and I_s and then recombined to output a derived $I_p - I_s$ signal as well as an average composite signal, before being fed to the infrared spectrometer's analog to digital (AD) convertors. This demodulator is available commercially from GWC Instruments, Madison, WI.

The synchronous sampling demodulator described here was designed to take advantage of the two AD convertors that are a feature of the Bruker Equinox spectrometer (Fig. 2). The composite signal from the MCT detector is fed to a voltage follower and the output of the follower is then applied to the inputs of two fast sample-and-hold (SH) circuits (Analog Devices AD783). The SH circuits are sampled using the timing from the $2f$ output of the photoelastic modulator control electronics. Two adjustable monostable delay circuits using 74LS123 integrated circuits provided the timing delays needed for sampling I_p and I_s signals, respectively. It was found that filtering the two outputs was not necessary. The I_p and I_s outputs are fed into each of the AD converters of the Bruker infrared spectrometer, where the data are then stored in the memory of the control computer. These are used to calculate the ratios described above. It should be emphasized that this circuit is significantly simpler than that described by Green *et al.*[12] The spectrometer was typically operated at 4 cm^{-1} resolution and data collected for 1000 scans for RAIRS experiments (~ 4 min), and 8 cm^{-1} and 3000 scans for PEM-RAIRS (~ 10 min).
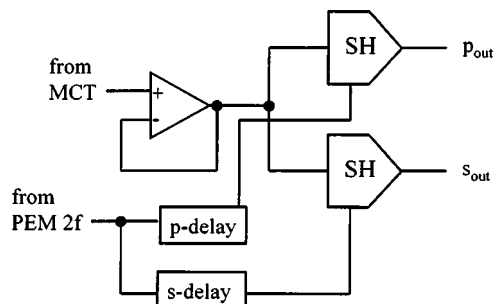

FIG. 2. Block diagram of the electronic circuit used to collect the ac component of the interferogram in the PEM-RAIRS experiment.

The carbon monoxide used for these experiments (Linde, Research Grade) was transferred from the cylinder to a glass bottle and dosed while a cold finger on the bottle was immersed in liquid nitrogen, to prevent possible less volatile contaminants (e.g., carbonyls) from entering the system.

III. RESULTS AND DISCUSSION

A. Design of photoelastic modulation experiment

Photoelastic modulation experiments were carried out using a Bruker Equinox Fourier transform infrared spectrometer using an experimental design shown in Fig. 1. The signal from the MCT detector was fed into the synchronous demodulator box. A block diagram of the box is displayed in Fig. 2 and is synchronized to the photoelastic modulator by a 100 kHz signal from the PEM interface box. This samples the input signal at locations on the modulated ac signal and these are selected to measure the intensity at the maximum (I_p) and at the minimum (I_s) of the modulated signal. These positions are selected by displaying the output signal on an oscilloscope which shows both the output from the detector and a timing pulse from the sample-and-hold circuit. The delay for each of these can be adjusted to coincide with the maximum or minimum of the modulated output. In principle, these signals can be added or subtracted electronically to yield the interferograms for $I_p - I_s$ and $I_p + I_s$ directly. In the case of the experiments carried out here, both I_p and I_s were collected independently in each channel of the AD convertor and separately Fourier transformed and the ratios calculated numerically. Since the sample was cleaned in UHV, a background PEM-RAIRS was collected of the clean Pd(111) surface and, following a previously suggested protocol,[20] was used to correct for differences in the optical response of the system for each polarization.

B. Carbon monoxide on Pd(111) as a function of pressure

The high-pressure adsorption of CO on Pd(111) has been studied as a test case since previous RAIRS[19] and sum-frequency data[21] have been collected for this surface for comparison. In the case of RAIRS data collected at high pressures, the background clean surface spectra were collected by heating the Pd(111) sample to remove all surface species.[19] This approach is limited to only those molecules that adsorb and desorb reversibly without undergoing any surface decomposition as with CO/Pd(111), but is not generally applicable. The data collected for a sample temperature of 300 K with various pressures of CO are summarized in Fig. 3. Shown at the bottom is the RAIRS spectrum for CO on Pd(111) following saturation at 300 K in UHV [$\Theta(CO) = 0.5$ ML], exhibiting a feature at 1925 cm^{-1}. Early work ascribed this mode to CO adsorbed on a bridge site on Pd(111). More recently, the 0.5 monolayer structure has been reinterpreted as being due to CO in both face-centered-cubic (fcc) and hexagonal-close-packed (hcp) sites where the resulting frequency arises from a combination of chemical and dipole–dipole coupling interactions.[22,23] This feature
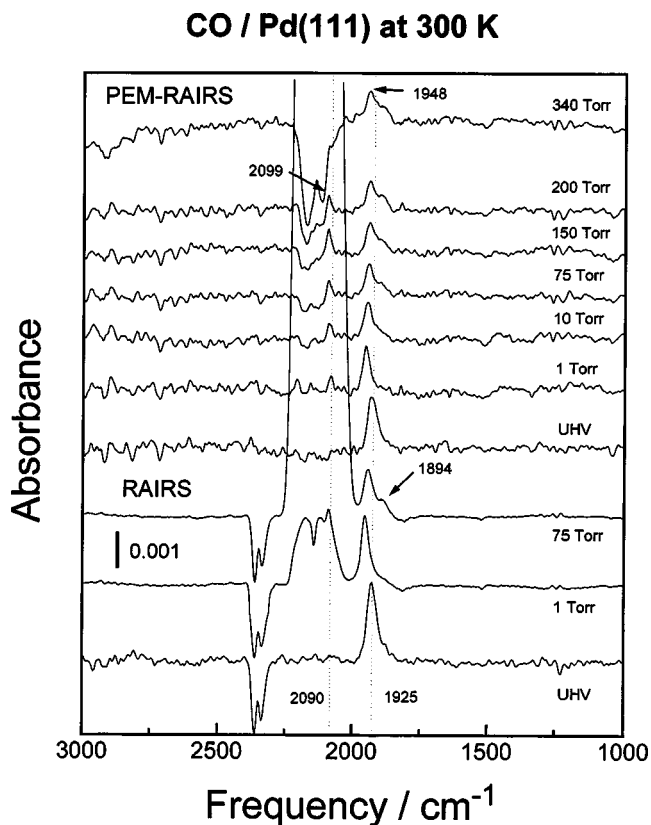

CO / Pd(111) at 300 K

FIG. 3. Reflection–absorption infrared spectra (RAIRS) of CO on Pd(111) after dosing 10 L at 80 K (marked UHV) and with CO pressures of 1 and 75 Torr. A series of PEM-RAIRS of 10 L of CO adsorbed on Pd(111) at 80 K (marked UHV) and PEM-RAIRS spectra of a Pd(111) surface pressurized to 1, 10, 75, 150, 200, and 350 Torr of CO, where pressures are marked adjacent to the corresponding spectra.

shifts to higher frequencies ($\sim$1950 cm^{-1}) as the pressure is increased to 1 Torr in accord with previous observations. The gas-phase CO signal is now evident displaying the typical *P* and *R* branches. Superimposed on this background is a small peak at 2090 cm^{-1} due to CO adsorbed on the atop site. As the pressure is further increased to 75 Torr, the intensity of the feature at $\sim$1950 cm^{-1} decreases and a feature appears at $\sim$1894 cm^{-1}. This has been assigned to CO adsorbed in a combination of fcc and hcp hollow and atop sites at $\Theta(CO) = 0.75$.[23] Now, however, the gas-phase CO signal is extremely large and completely obscures any signals that may be due to CO adsorbed in the atop site. The negative excursion at $\sim$2300 cm^{-1} in these spectra is due to a small amount of residual CO_2 in the light path that has not been subtracted from the spectrum.

Shown above these spectra are a series of spectra collected using the photoelastic modulator. The spectrum marked UHV is collected for a monolayer of CO dosed at a sample temperature of 300 K. This exactly reproduces the RAIRS spectrum below. Shown above are a series of PEM-RAIRS spectra as a function of pressure. The spectra detected here are in excellent agreement with previous RAIRS[19] and SFG results.[21] The signal due to atop CO, which is coincident with the gas-phase signal, is clearly evident at $\sim$2090 cm^{-1} at a pressure of 1 Torr, also seen in the

RAIRS spectra below. Coincidentally, the feature at 1925 cm^{-1} for the monolayer shifts to ~1950 cm^{-1}. Similar shifts have been seen previously for CO adsorbed on ethylidyne-covered Pd(111),[24] where a single feature was detected at 1946 cm^{-1} following a 2 L dose of CO on ethylidyne-covered Pd(111) ascribed to CO adsorbed in the hcp threefold site. When this surface was pressurized with 10 mTorr of CO, an additional feature appeared at 2080 cm^{-1} assigned to CO adsorbed at the atop site, close to the value of 2099 cm^{-1} measured here. In addition, the mode at 1907 cm^{-1} shifted to ~1946 cm^{-1} due to a strong dipole coupling between these two modes. Furthermore, while the atop and hcp threefold-hollow site populations were proposed to be similar, the intensity of the high-frequency mode was lower than that of the lower-frequency one, again due to dipole–dipole coupling. This suggests that the relatively low intensity of the 2099 cm^{-1} mode for the atop site does not necessarily imply that its relative coverage is substantially lower than that of CO in the hcp site.

As the CO pressure increases to 10 Torr, the atop feature shifts slightly to ~2099 cm^{-1} as seen previously in the SFG data,[21] and its intensity increases. The mode at ~1950 cm^{-1} decreases further in intensity, where both the shifts in frequency and relative intensity changes are consistent with an increase in the atop site population. In addition, a small shoulder appears at ~1890 cm^{-1}, also detected by SFG,[21] and assigned as above to the high-coverage [$\Theta(CO)$ = 0.75 ML] structure. This feature is also evident in the RAIRS spectrum collected at 75 Torr. As the pressure is further increased to 150 Torr, both the intensity of the atop features at 2099 and 1948 cm^{-1} increase in intensity.

A small amount of gas-phase signal is evident at pressures of 75 and 150 Torr, although these are sufficiently small that they do not unduly obscure the background. As the CO pressure is increased to 340 Torr, this gas-phase background becomes sufficiently large that the atop signal is completely obscured although the bridge and threefold hollow signals are still clearly evident.

C. Carbon monoxide on Pd(111) at 150 Torr as a function of temperature

The effect of temperature on a Pd(111) surface was monitored using PEM-RAIRS and the results, collected using a CO pressure of 100 Torr, are displayed in Fig. 4. Heating to 325 K initially removes the most weakly bound threefold hollow CO. Heating to 350 K causes the atop-site mode (2099 cm^{-1}) intensity to decrease and the 1950 cm^{-1} intensity to increase, mirroring the change found as the surface was pressurized at 300 K (Fig. 3), and this process is complete at 400 K. Heating to 500 K completely removes all CO from the surface in accord with previous observations by Kuhn et al. at lower pressures.[19] As exemplified by the 325 K spectrum during cooling, the adsorption of CO was found to be completely reversible on Pd(111).
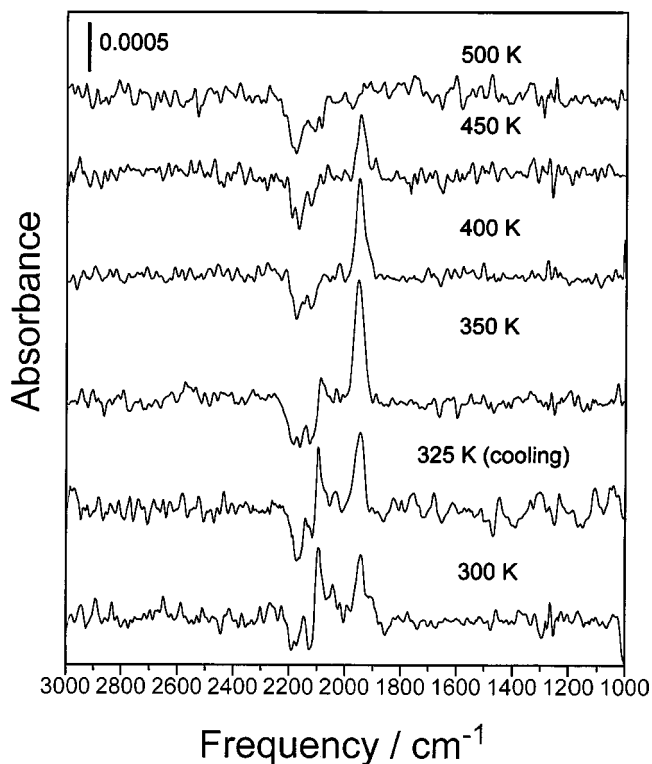

FIG. 4. PEM-RAIRS spectra of CO on Pd(111) collected at a CO pressure of 100 Torr as a function of sample temperature where sample temperatures are marked adjacent to the corresponding spectrum.

IV. CONCLUSIONS

The results shown above demonstrate that PEM-RAIRS is capable of detecting surface species in the presence of up to ~150–200 Torr of CO with results that are in excellent agreement with data found previously, demonstrating that this technique is capable of monitoring model catalytic systems under reaction conditions with collection times similar to those used for RAIRS, provided that the $I_p - I_s$ signal is measured using a synchronous demodulator rather than a lock-in amplifier. A simplified synchronous demodulation circuit for measuring this difference signal at 100 kHz is described comprising two sample-and-hold circuits. Either an hcp or a combination of hcp and fcc threefold hollow sites are occupied by CO in UHV at 300 K. Atop sites become occupied as the surface is pressurized causing the hcp frequency to increase due to dipole–dipole coupling. At pressures above 10 Torr, an additional feature is evident at 1894 cm^{-1} due to CO adsorbed in a high-coverage structure [$\Theta(CO)$ = 0.75]. Heating the surface at ~350 K initially removes the fcc threefold-hollow and atop adsorbed CO, and further heating to 500 K completely removes all remaining CO.

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