

Molecular beam and infrared spectroscopic studies of the thermodynamics of CO on clean and vinylidene-covered Pd(111)

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A differentially pumped, capillary array molecular beam source is used to study the reversible adsorption of CO on CO/Pd(111) [$\Theta(\text{CO})=0.55$] and vinylidene/Pd(111) [$\Theta(\text{vinylidene})=1.0$] at 300 K. Differentially pumping allows the beam to equilibrate rapidly (in ~ 2 s) while maintaining good beam uniformity. The isosteric heat of adsorption of reversibly held CO on a surface precovered with 0.55 monolayers of chemisorbed CO is 5.6 ± 0.2 kcal/mol at low excess coverages but decreases linearly with coverage so that an additional 2% of a monolayer of CO reduces the isosteric heat of adsorption to 3.0 ± 0.2 kcal/mol. CO adsorbs reversibly on vinylidene-saturated Pd(111) with an isosteric heat of adsorption of 1.0 ± 0.5 kcal/mol for coverages up to $\sim 1\%$ of a monolayer of CO. Infrared spectra of CO on vinylidene-covered Pd(111) at higher pressures (several Torr) reveal that CO adsorbs on the metal surface. Assuming that the heat of adsorption of CO on vinylidene-covered Pd(111) decreases with CO coverage at higher coverages shows that the low-coverage data measured using molecular beam methods are consistent with the isotherm measured using infrared spectroscopy at higher pressures. © 2001 American Institute of Physics. [DOI: 10.1063/1.1386808]

I. INTRODUCTION

The adsorption of CO has been studied extensively on transition metals surfaces including Pd(111). The most recent model proposes that, rather than adsorbing at bridge sites at intermediate coverages as conventionally assumed,¹ CO initially adsorbs at a face-centered-cubic (fcc) hollow site and, at coverages of 0.33 monolayers, both fcc and hexagonal-close-packed (hcp) sites become occupied.² For coverages between 0.5 and 0.75 monolayers obtained at low temperatures, both fcc and hcp hollow, as well as atop, sites are occupied.^{2,3} It has been demonstrated that additional CO above the saturation coverage attainable in ultrahigh vacuum can be accommodated onto the surface on Pd(111), Pt(111) and Rh(111), when it is pressurized, as evidenced by sum-frequency generation experiments⁴ and scanning-tunneling microscopy.^{5,6} In the case of CO/Pt(111), an ordered compressed layer was found under high pressures and temperatures.⁵ Molecular beam methods have been used to monitor the extra CO adsorbed onto a CO-saturated Pt(111) surface where it was found that the additional CO desorbed with an activation energy of 6 ± 1 kcal/mol.⁷ Attempts have been made to mimic high-pressure, high-temperature adsorption by adsorption at low temperatures,⁸ although Somorjai has suggested that the two regimes are not equivalent.⁵ A somewhat different approach is taken in this work to probe adsorption at high temperatures (~ 300 K) and moderate pressures using molecular beams. In this case, the amount of additional CO adsorbing onto the surface is measured as a function of sample temperature and beam pressure by mov-

ing the sample to intercept the molecular beam. Since this CO adsorbs reversibly, it desorbs when the sample is moved away from the beam, where the areas under the adsorption and desorption curves are equal for reversible adsorption. The relatively low pressures attainable in the beam (up to $\sim 10^{-5}$ Torr) ensure that only relatively low values of additional coverage above the saturated overlayer obtained in ultrahigh vacuum ($\Delta\Theta < 0.05$ monolayers) are probed. These data are then analyzed to yield isosteric heats of adsorption to provide direct measurements of this value as a function of $\Delta\Theta$.

This methodology is then applied to examining the reversible adsorption of CO on a vinylidene-covered Pd(111) surface to measure enthalpy changes for this process at low coverages. These experiments were performed since it now appears clear that many, if not all, transition-metal-catalyzed hydrocarbon conversion reactions proceed in the presence of a relatively strongly bound carbonaceous layer adsorbed on the surface of the catalyst. Such carbonaceous layers were first discovered for ethylene hydrogenation, where the platinum surface is covered by a persistent carbonaceous layer consisting of ethylidyne.⁹ We have shown previously that the ethylidyne overlayer ($\Theta_{\text{sat}}=0.25$ monolayers) is sufficiently open to allow the adsorption of CO onto the surface in the presence of an ethylidyne layer under ultrahigh vacuum conditions.¹⁰ There is also sufficient space to allow acetylene cyclotrimerization to benzene.¹¹ Subsequently, several other varieties of carbonaceous layer were discovered. In the case of palladium-catalyzed reactions involving acetylene, these are vinylidene species.¹² Thick carbonaceous layers form on molybdenum.¹³ It has been shown that a relatively large amount of CO can adsorb onto the thick

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carbonaceous layer present on molybdenum when the sample was pressurized with ~ 30 Torr of CO.¹³ Ethylene has been found to adsorb onto an ethylidyne-covered surface.¹⁴ The cyclotrimerization of acetylene on Pd(111) has been shown to proceed on the palladium surface in spite of the presence of a saturated vinylidene overlayer.¹⁵ We have investigated the adsorption of CO on a vinylidene-covered Pd(111) surface both using molecular beam strategies and by infrared spectroscopy. The structure of vinylidene has been measured on Pd(111) and it adsorbs with its C=C axis tilted with respect to the surface and forms a relatively close-packed overlayer since its saturation coverage is unity.¹²

II. EXPERIMENT

Molecular beam experiments were carried out in an 8 in. diameter, stainless-steel vacuum chamber pumped by means of a 6 in. diameter, liquid-nitrogen trapped diffusion pump (pumping speed 850 l/s). This configuration was selected to maximize the pumping speed compared to the chamber volume to minimize the background pressure when the beam is operating. A diffusion pump also provides the throughput necessary for a molecular beam apparatus where gas is continually leaked into the system. The chamber operates at a base pressure of 5×10^{-11} Torr following bakeout. The Pd(111) sample is mounted to a carousel geometry manipulator, which allows the sample to be moved in and out of the beam. The sample can be resistively heated to 1200 K, and cooled to 80 K by thermal contact to a liquid nitrogen-filled reservoir. The manipulator also allows the sample to be translated along the x, y and z directions. The chamber also houses a quadrupole mass spectrometer, which is mounted to a 6 in. nipple attached to the side of the chamber so that the mass spectrometer is not in line of sight of the sample. The quadrupole mass spectrometer is under computer control and can sequentially monitor the intensity of up to five masses. This is used for leak testing, gauging the purity of gases, temperature-programmed desorption experiments and measuring the background pressure during a molecular beam experiment. Background pressures are monitored by a nude ionization gauge located in the chamber and all pressures are uncorrected for ionization gauge sensitivity.

Molecular beam experiments are performed using a capillary array dosing source to provide a uniform beam profile at the sample. A major drawback to this arrangement is that the effusing beam flux requires some time to equilibrate so that corrections have to be made to take account of adsorption that occurs during this period.⁷ We have therefore used an alternative design displayed in Fig. 1. In this case, the source consists of a capillary (i.d.=0.5 mm) collinear with a 1.2 cm diameter multichannel array of glass microcapillaries 2 mm long and 10 μm in diameter with the space between the two being differentially pumped. This means that those molecules effusing from the first capillary that are not moving in the forward direction do not enter the second and are pumped away. Pressures are monitored by means of an ionization gauge in this section of the apparatus to allow reproducible fluxes to be obtained. As demonstrated below, the rise time for the beam to attain its equilibrium value using this arrangement is ~ 2 s.

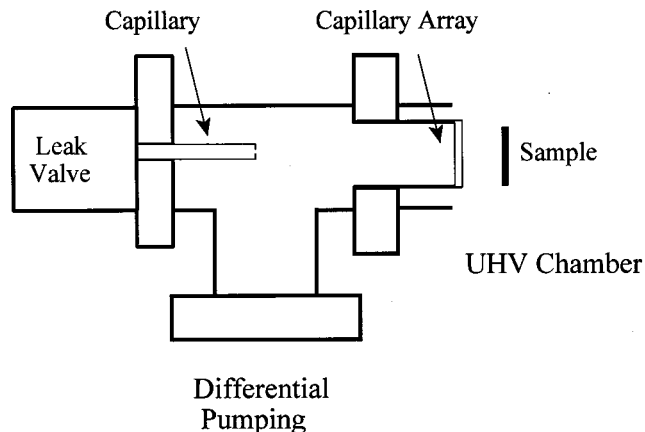


FIG. 1. Schematic diagram of the molecular beam apparatus.

The 12 mm diameter, Pd(111) sample is cleaned using a standard procedure which consists of heating at 1000 K in $\sim 4 \times 10^{-8}$ Torr of oxygen and annealing at 1200 K *in vacuo* to remove any remaining oxygen. Since the carbon KLL Auger feature is effectively obscured by a strong palladium peak, Auger spectroscopy is not particularly sensitive to the presence of small amounts of carbon on the surface. It was found that a more sensitive gauge of carbon coverage was to saturate the surface with oxygen and to perform a temperature-programmed desorption experiment. The presence of surface carbon is manifested by the desorption of CO. As the surface becomes depleted of carbon, the CO yield decreases and the yield of oxygen increases correspondingly in intensity. The complete absence of carbon is indicated by the desorption of only O₂.

Infrared experiments were carried out in a vacuum system that has been described in detail elsewhere.¹⁴ Briefly, the main 12 in. diameter stainless-steel vacuum chamber is pumped by an ion and turbo-molecular pump and operates at a base pressure of $\sim 8 \times 10^{-11}$ Torr following bakeout. The chamber is equipped with a single-pass, cylindrical-mirror analyzer for Auger analysis of the sample and a quadrupole mass analyzer for temperature-programmed desorption experiments, leak testing and gauging the purity of gases leaked into the chamber. The sample is mounted to the end of a horizontal sample manipulator, which can be retracted to move the sample into a small-volume infrared cell which is isolated from the main sample chamber by means of a gate valve. The sample can also be resistively heated and cooled to ~ 80 K by pumping liquid nitrogen down the center of the sample support. The infrared apparatus is mounted on an optical table for stability and infrared radiation from a Midac Fourier-transform spectrometer is steered and focused onto the sample. The reflected light is collected and focused onto a mercury-cadmium-telluride detector and the resulting signal collected and analyzed by a microcomputer running SpectraCalc software. The optical path is completely enclosed and purged with dry air. The infrared radiation is furnished by an air-cooled source and spectra are typically collected at a resolution of 4 cm^{-1} for 1000 scans which typically takes 4 min to accumulate.

The acetylene used for these experiments (Linde, puri-

fied grade) was transferred from the cylinder to a glass bottle and purified by several bulb-to-bulb distillations. Similarly, the CO was also transferred to a glass bottle and any less volatile impurities were condensed by liquid nitrogen in a cold finger. In both cases, the gases were stored in glass until use. A possible CO contaminant is iron carbonyl, which should be removed by this procedure. In order to ensure that this has not adsorbed onto the surface during the high-pressure experiment, an Auger spectrum was collected after the experiment and no iron was detected. Cyclohexane (EM Science, research grade) was transferred to a glass vial and further purified by repeated freeze-pump-thaw cycles and its cleanliness monitored mass spectroscopically.

III. RESULTS

A. Beam source calibration

Adsorption kinetics are measured using effusive beam sources by a method first developed by King and Wells in which molecules adsorbing onto the surface cause a decrease in background pressure proportional to the sticking coefficient.¹⁶ The time dependence of the sticking coefficient as a function of time $s(t)$ is given by

$$s(t) = \frac{1}{f} \frac{P_{\text{eq}} - P(t)}{P_{\text{eq}} - P_{\text{base}}} = \frac{1}{f} \frac{\Delta P(t)}{P_{\text{eq}} - P_{\text{base}}}, \quad (1)$$

where P_{base} is the base pressure of the vacuum chamber, P_{eq} is the background pressure with the beam source on, $P(t)$ is the time course of the background pressure after the sample has been moved to intercept the beam and f is the fraction of molecules effusing from the source which intercept the sample. This latter value has to be determined experimentally. It is also important that the beam profile be relatively uniform over the sample and both f and the beam uniformity are calibrated for a particular beam source and sample geometry. The value of f is most conveniently measured from the initial pressure drop P_0 immediately after the sample is moved to intercept the beam using an adsorbate with a known initial sticking coefficient s_0 . The value of f is then calculated from

$$f = \frac{1}{s_0} \frac{P_{\text{eq}} - P_0}{P_{\text{eq}} - P_{\text{base}}}. \quad (2)$$

This experiment is carried out using an adsorbate that condenses onto the surface⁷ where it is assumed that $s_0 = 1$. This approach had the advantage that the adsorbate is likely to be relatively immobile. An alternative method is to use an adsorbate of known sticking coefficient to carry out the same experiment. Both methods were used in this work to calibrate the dosing source where cyclohexane was condensed with the sample held at 80 K and CO adsorbed at a sample temperature of 300 K where $s_0 \approx 0.7$.¹⁷ This was done to establish that the beam profiles for two reactants with different molecular weights were identical. The resulting plot of f vs. d , the distance of the sample from the beam source, is shown in Fig. 2. As expected, the value of f decreases as the sample is moved farther from the source and the characteristics of the source are in good agreement with those mea-

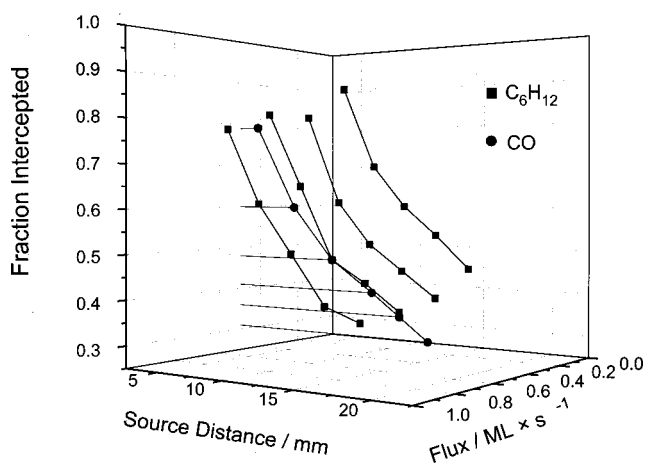


FIG. 2. Plot of the fraction of the beam intercepted (f) as a function of the distance from the sample to the source and as a function of flux using cyclohexane at a sample temperature of 80 K (■) and using CO at a sample temperature of 300 K (●).

sured elsewhere.⁷ We chose $d = 10$ mm so that $f \geq 0.5$ for the various values of flux used in these experiments.

The total flux effusing from the source can be measured in several ways. In principle, the total flux can be calculated from the pressure rise when the beam is on, ($P_{\text{eq}} - P_{\text{base}}$), using the pumping speed of the system (the diffusion pump). Unfortunately, this approach tends not to yield reliable results since pumping speeds are difficult to measure precisely. A more reliable approach is to calibrate the flux by adsorption onto a surface for which the saturation coverage is known. The calibration, in this case, was carried out using CO on Pd(111) at a sample temperature of 300 K where the saturation coverage is 0.55 (Ref. 17) [where the coverage is referenced to the number of exposed palladium atoms on the (111) face]. The results of a typical experiment are shown in Fig. 3, which plots the CO (28 amu) signal, monitored by the mass spectrometer, as a function of time, with the sample

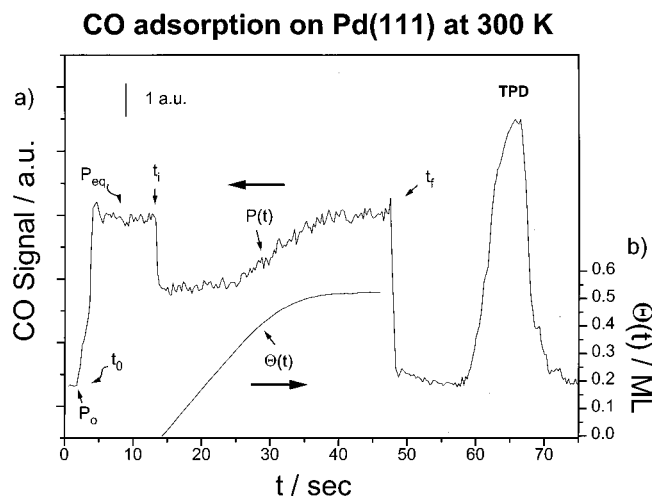


FIG. 3. A typical time course of a molecular beam experiment at a flux of 0.1 ML/s for the adsorption of CO on clean Pd(111) at a sample temperature of 300 K followed by a CO temperature-programmed desorption experiment. Shown at the bottom is the corresponding CO uptake curve.

CO / CO / Pd(111) at 300 K

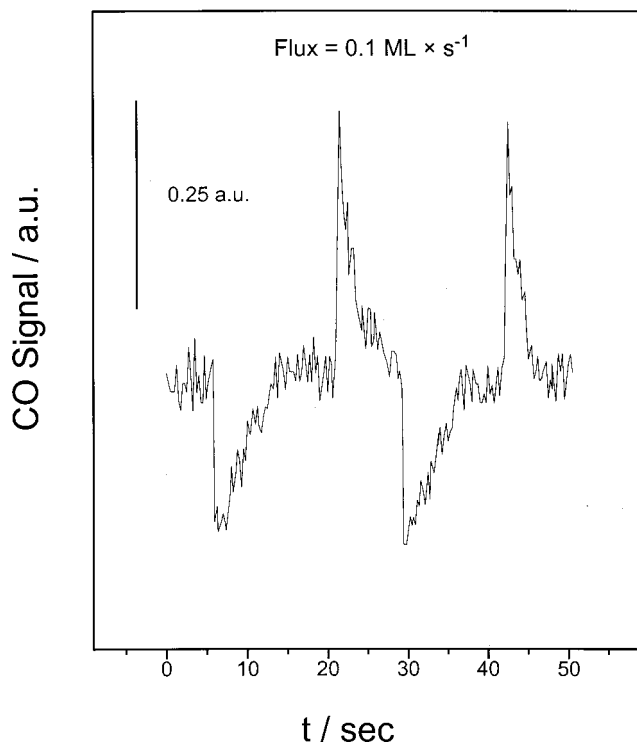


FIG. 4. The reversible adsorption of additional CO on a CO-covered Pd(111) surface [$\Theta(\text{CO})=0.55$] at 300 K. The beam flux was 0.1 monolayers and the positive excursions correspond to CO evolution when the sample is removed from the beam and the negative excursions to CO adsorption when the sample is moved to intercept the beam.

located 10 mm from the source. At $t=0$, the pressure corresponds to P_0 ($\sim 3 \times 10^{-10}$ Torr) due to some background carbon monoxide. The leak valve to the source (Fig. 1) is opened at $t=t_0$ with the sample away from the beam so that the pressure rises to P_{eq} . Note that the pressure attains its equilibrium value in ~ 2 s. The true background pressure measured using the ionization gauge at this point is $\sim 1 \times 10^{-9}$ Torr so that the CO exposure prior to moving the sample to intercept the beam is less than 0.015 L. At time t_i , the Pd(111) sample is moved to intercept the beam where the pressure drops due to adsorption onto the surface. The sticking probability versus time can be calculated from these data. Knowing the saturation coverage ($\Theta_{\text{sat}}=0.55$) and using

$$\Theta(t) = F \int_0^t s(\tau) d\tau, \quad (3)$$

the flux F can be calculated by integrating up to $t=\infty$ (experimentally up to t_f). An example of a plot of coverage Θ vs. t is shown at the bottom of Fig. 3 where the value obtained for the flux is $F=0.10 \pm 0.01$ ML/s. Similar experiments were carried out using different pressures in the differentially pumped stage, and hence incident beam fluxes, to measure F as a function of pressure. Finally, the shutter is closed at $t=t_f$ so that the pressure rapidly falls to its original value. A temperature-programmed desorption spectrum was then collected, in this case versus time, where the amount of

MB Isotherms of CO / CO / Pd(111)

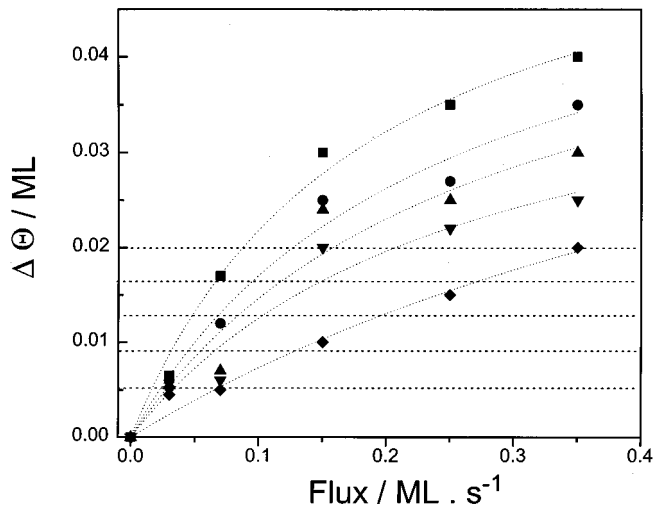


FIG. 5. Adsorption isotherms for CO adsorption on a CO-covered Pd(111) surface at various temperatures where the coverages are measured using molecular beams. ■, $T=252$ K; ●, $T=267$ K; ▲, $T=277$ K; ▼, $T=292$ K; ◆, $T=307$ K.

CO desorbing from the surface (as gauged by the area under the desorption trace) is equal, within 10%, to the area under the $\Delta(P)$ versus time curve indicating that CO adsorbs reversibly.

B. Measurement of adsorption isotherms using molecular beams

It has been noted previously on Pt(111) that, if the sample is moved from the beam after saturating the surface with the beam still on, the pressure rises due to some CO desorption.⁷ If the sample is then again moved to intercept the beam, the pressure once again drops slightly. This effect was ascribed to additional CO being reversibly adsorbed in the presence of the CO overlayer already present. This adsorption/desorption cycle could be repeated by moving the sample into and out of the beam and typical results of this experiment on CO-covered Pd(111) at 300 K are shown in Fig. 4. Positive excursions in this trace correspond to CO desorption as the sample is moved out of the beam and negative excursions to adsorption. It should be emphasized that this reversible adsorption takes place in the presence of a chemisorbed CO overlayer ($\Theta=0.55$). The areas under each of these traces are equal, confirming that this adsorption is completely reversible. Furthermore, these areas correspond to the coverage of reversible CO where the resulting coverages are calibrated as described above. The resulting adsorption isotherms for various sample temperatures measured using the molecular beams are shown in Fig. 5. The line plotted through each of these data is a Langmuir isotherm, which is primarily used as a guide to the eye. These data can be used to calculate the isosteric values of ΔH_{ads} from plots of $\ln(\text{Flux})$ vs. $1/T$ at constant coverage using the equation^{18,19}

$$\left[\frac{\partial}{\partial t} (\ln P) \right]_{\Theta} = \frac{-\Delta H_{\text{(ads)}}}{RT^2}. \quad (4)$$

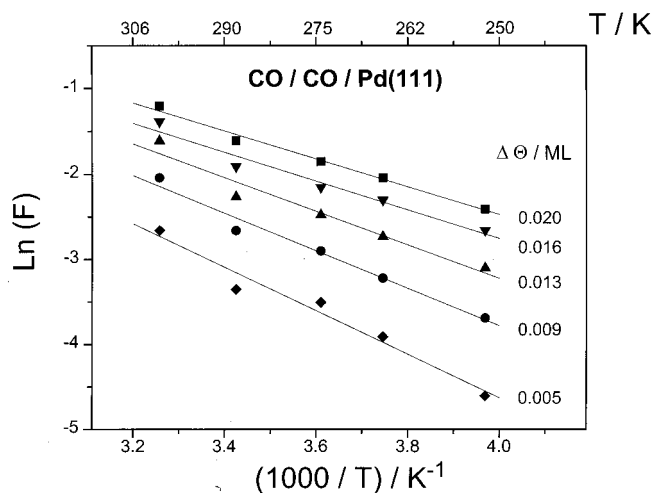


FIG. 6. Plot of $\ln(F)$ versus $1/T$ for constant excess CO coverage ($\Delta\Theta$) taken from the data in Fig. 5. ■, $\Delta\Theta=0.020$; ▼, $\Delta\Theta=0.016$; ▲, $\Delta\Theta=0.013$; ●, $\Delta\Theta=0.009$; ◆, $\Delta\Theta=0.005$ monolayers.

The resulting plots are displayed in Fig. 6 where they are all good straight lines. The slopes yield ΔH_{ads} and the isosteric heats of adsorption $q_{\text{st}} = -\Delta H_{\text{(ads)}}$ which is plotted versus $\Delta\Theta$ in Fig. 7.

This strategy was also applied to examining the reversible adsorption of CO on vinylidene-covered Pd(111) at ~ 300 K where the vinylidene layer was formed by dosing clean Pd(111) with acetylene at 300 K. The acetylene adsorption kinetics on clean Pd(111) was followed to confirm that the saturation coverage was 1.0 as found previously.¹² It was found that CO adsorbed onto the vinylidene-covered surface, although the amount adsorbing was substantially less than that found on compressed CO overlayers on clean Pd(111). The resulting adsorption isotherms are shown in Fig. 8 where the CO coverage is plotted versus pressure for various sample temperatures. The resulting values of isosteric heat of adsorption $q_{\text{isost}} = -\Delta H_{\text{(ads)}}$ remain constant within experimental error at 1.0 ± 0.5 kcal/mol over the coverage range explored.

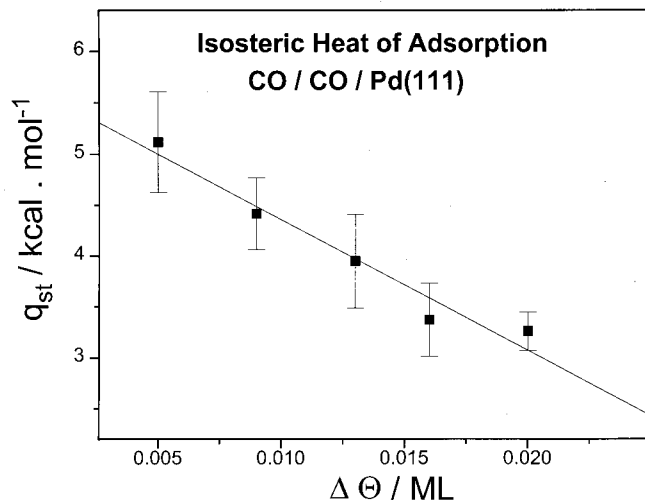


FIG. 7. Plot of isosteric heat of adsorption, q_{isost} , versus $\Delta\Theta$ for the adsorption of CO on CO-covered Pd(111).

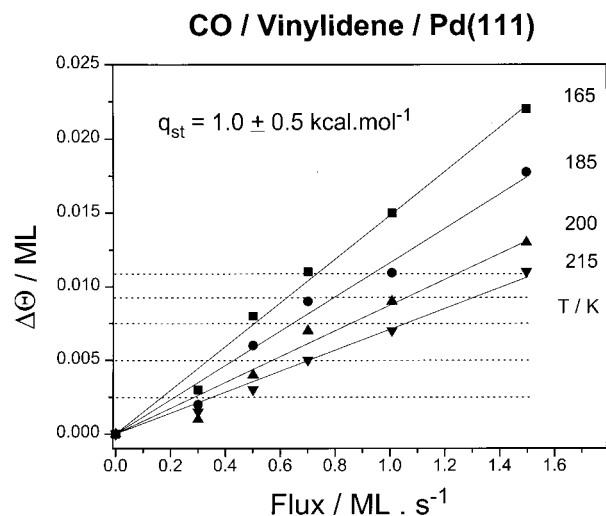


FIG. 8. Adsorption isotherms for CO adsorption on a vinylidene-covered Pd(111) surface at various temperatures where the coverages are measured using molecular beams. ■, $T=165$ K; ●, $T=185$ K; ▲, $T=200$ K; ▼, $T=251$ K.

Finally, shown in Fig. 9 is the change in intensity of the CO infrared absorption peak detected on a vinylidene-covered Pd(111) surface at 1860 cm^{-1} as a function of CO pressure. The presence of a CO peak at this frequency suggests that CO is adsorbed on the metal surface. The change in integral absorbance for CO on clean Pd(111) as a function of coverage at low coverages is used to estimate the CO coverage on vinylidene-covered Pd(111) and the resulting coverage scale plotted as the ordinate. This suggests that the saturation CO coverage is ~ 0.16 monolayers on CO on the vinylidene-covered surface.

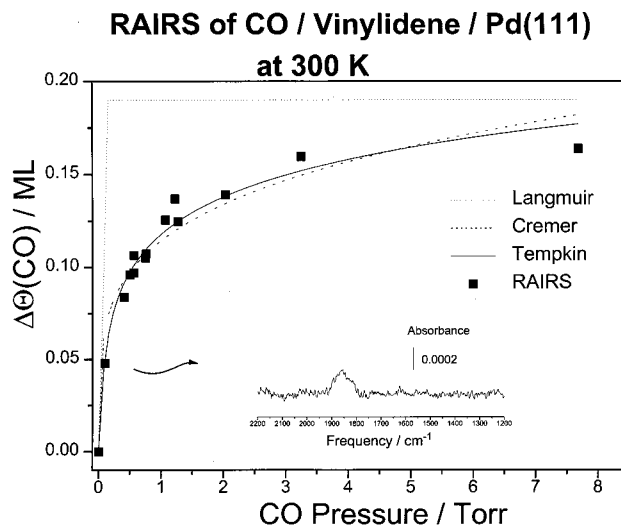


FIG. 9. An adsorption isotherm measured for CO on vinylidene-covered Pd(111) using infrared spectroscopy where coverages are measured from the integrated area of the CO feature at 1860 cm^{-1} . A typical infrared spectrum is shown as an inset. Shown plotted onto these data is a Langmuir isotherm using parameters from the molecular beam experiments (\cdots) and best fits to Tempkin (—) and Cremer ($---$) isotherms.

IV. DISCUSSION

Molecular beam methods can be used to measure isosteric heats of adsorption of CO reversibly adsorbed on Pd(111) in the presence of a saturated overlayer of CO. Similar results have been found on Pt(111).⁷ It has been shown both using molecular beams (Fig. 8) and by infrared spectroscopy (Fig. 9) that CO can adsorb on the surface in spite of the presence of a saturated vinylidene overlayer. The presence of a CO stretching mode at 1860 cm⁻¹ confirms that CO adsorbs onto the metal surface since a physisorbed layer would lead to a substantially smaller perturbation. These results also suggest that CO adsorbs on a threefold hollow site on the vinylidene-covered surface.³

Extremely compressed layers have also been found under relatively high pressures of CO on Pt(111) using second-harmonic generation and scanning-tunneling microscopy and on Pd(111) using infrared spectroscopy.²⁰ Indeed, it has been suggested that metal carbonyls form when a single crystal surface is pressurized with CO.²¹ This has led to the suggestion that the additional CO is accommodated when the surface is pressurized because the surface is proposed to be sufficiently flexible to allow the surface atoms to decrease their coordination with the substrate to accommodate additional CO.²¹

The resulting experimental plots of isosteric heat of adsorption versus coverage for CO on CO/Pd(111) at 300 K obtained using molecular beams are shown in Fig. 7 where these data are taken from the plots in Fig. 6. The plots shown in Fig. 6 are good straight lines and the error bars displayed in Fig. 7 represent measured standard deviations of the slopes. The heat of adsorption of CO has been measured on Pd(111) using lower pressures and temperatures where the isosteric heat of adsorption up to a coverage of 0.33 (where the CO forms a $\sqrt{3}\times\sqrt{3}$ R30° overlayer with the CO adsorbed in fcc hollow sites) remains constant at 34 kcal/mol.¹⁸ At coverages between 0.33 and 0.45, the heat of adsorption is ~ 2 kcal/mol lower and the CO forms a compressed structure but is still proposed to be adsorbed at a combination of fcc and hcp hollow sites. The heat of adsorption decreases drastically as the surface approaches saturation ($\Theta(\text{CO}) = 0.55$) to below 20 kcal/mol.²² This value was measured from the desorption temperature following adsorption at 200 K, arguing that adsorption at low pressures and temperatures mimics the effect of adsorption at higher temperatures and pressures. Our experiments probe the higher temperature and pressure regimes directly. The value for the isosteric heat of adsorption for $\Delta\Theta = 0$ is 5.6 ± 0.2 kcal/mol [$\Theta(\text{CO}) \approx 0.55$] which is lower than the value found for the saturated overlayer. The heat of adsorption also decreases significantly as $\Delta\Theta$ increases so that for the adsorption of an additional 2% of a monolayer, the heat of adsorption decreases to 3.0 ± 0.2 kcal/mol. These results suggest that coverage measurements made using molecular beams can be successfully used to measure isosteric heats of adsorption for low $\Delta\Theta$.

This method was applied to probing the adsorption of CO at low coverages ($\Delta\Theta$) on a vinylidene-saturated Pd(111) surface. A much lower coverage range was accessible on this surface and reveals a constant isosteric heat of adsorption of

TABLE I. Comparison of the initial slope (for a coverage $\Delta\Theta = 0.01$, normalized to $T = 200$ K, $p = 1.0 \times 10^{-6}$ Torr) for fits of various isotherms to the experimental data of Fig. 9 with the results for molecular beam experiments at $T = 200$ K. Units for the slopes are in Torr⁻¹.

Experimental molecular beam data	Data from fits to CO adsorption isotherm (Fig. 9)	
	Tempkin	Cremer
$\sim 2 \times 10^3$	$\sim 19 \times 10^3$	$\sim 1.5 \times 10^3$

1.0 ± 0.5 kcal/mol. The low-coverage adsorption isotherms are linear (Fig. 8) and can be written as

$$\Delta\Theta = \alpha \exp(-\Delta H_{(\text{ads})}/RT)p, \quad (5)$$

where $\Delta\Theta$ is the CO coverage and p is the pressure. α can be measured from the data shown in Fig. 8 and is $2.7 \pm 0.1 \times 10^4$ Torr⁻¹. Supposing that the heat of adsorption remains constant as a function of coverage leads to a Langmuir adsorption isotherm:

$$\frac{\Delta\Theta}{\Delta\Theta_{\text{sat}}} = \frac{\alpha e^{-\Delta H_{(\text{ads})}/RT} p}{1 + \alpha e^{-\Delta H_{(\text{ads})}/RT} p}, \quad (6)$$

where $\Delta\Theta_{\text{sat}}$ is the saturation CO coverage. Figure 9 displays the CO adsorption isotherm on vinylidene-covered Pd(111) for CO pressures up to 8 Torr at 300 K. It should be noted that care should be taken in measuring coverages from infrared data since dipole-dipole coupling can lead to nonlinearities in plots of coverage versus absorbance. Nevertheless, coverages are sufficiently low in this case that this approximation should be reasonable. The Langmuir isotherm shown in Eq. (6) is plotted onto these data (\cdots) and clearly predicts a much more rapid adsorption than found experimentally, suggesting that the assumption that the heat of adsorption remains constant with increasing coverage is not valid. In view of the change in heat of adsorption measured for the compressed CO overlayer with coverage (Fig. 7), this is not surprising. A linear variation of heat of adsorption q_{st} with coverage leads to the Tempkin isotherm:²³

$$\Delta\Theta = t_1 T \ln(t_2 p), \quad (7)$$

where t_1 and t_2 are constants. A logarithmic variation of q_{st} with coverage leads to the Cremer isotherm:²⁴

$$\Delta\Theta = c_1(T)p^{c_2 T}. \quad (8)$$

Fits of these isotherms are compared with the experimental data in Fig. 9, where both of these reproduce the experimental data reasonably well. The fitting parameters used for the Tempkin isotherm were $t_1 = 9.73 \times 10^{-5}$ and $t_2 = 56$ and for the Cremer isotherm, $c_1 = 0.11$ and $c_2 = 7.59 \times 10^{-4}$. The values of the *initial* slopes of the isotherms, $d\Delta\Theta/dp$, are calculated using these best-fit parameters and evaluated at $\Delta\Theta = 0.01$, $p = 1 \times 10^{-6}$ Torr and $T = 200$ K, and the results are shown in Table I for the Tempkin and Cremer isotherms. The corresponding value of $d\Delta\Theta/dp$ for the molecular beam data of Fig. 8 is also shown in Table I. In this case, the flux at the sample was converted to pressure using the equation $F = p/\sqrt{(2\pi mkT)}$ where 1 ML/s corresponds to a pressure of 4×10^{-6} Torr. Both the Cremer and Tempkin isotherms yield initial slopes that are in reasonable agreement with the mo-

lecular beam data although the fit to the Temkin isotherm²³ is somewhat better. These results indicate that the initial isosteric heat of adsorption of CO on vinylidene-covered Pd(111) is 1.0 ± 0.5 kcal/mol but that this value decreases with increasing coverage. According to the fitting parameters used for the Temkin isotherm, the change in heat of adsorption for a CO coverage of 0.01 monolayers on vinylidene-covered Pd(111) is ~ 0.2 kcal/mol. This is less than the uncertainty in the heat of adsorption (~ 0.5 kcal/mol) and so is not detected in the molecular beam measurements. However, the decrease found for CO reversibly adsorbed on CO-covered Pd(111) (Fig. 7) is in accord with this observation.

The bond strength between CO and a palladium surface at low coverages is ~ 34 kcal/mol.¹⁸ The decrease to ~ 1 kcal/mol on the vinylidene-covered surface may partially be due to electronic perturbations of the surface due to the presence of vinylidene species. The majority of the energy difference is likely to be due to the energy required to perturb the surface to allow CO to access the palladium.

V. CONCLUSIONS

A molecular beam apparatus has been designed and calibrated which provides a good beam uniformity and a rapid response. This has been used to study the adsorption of reversibly held CO on CO-saturated Pd(111) ($\Theta = 0.55$) where an isosteric heat of adsorption of 5.6 ± 0.2 kcal/mol was measured for low excess coverages. The heat of adsorption decreases linearly with excess coverage, $\Delta\Theta$, so that an additional $\sim 2\%$ of a monolayer decreases the heat of adsorption to 3.0 ± 0.2 kcal/mol. The apparatus was also used to measure the isosteric heat of adsorption of CO on vinylidene-covered Pd(111) which yields a value of 1.0 ± 0.5 kcal/mol at low coverages. Infrared spectroscopy shows that this is due to CO adsorbed on the metal surface and the variation in CO absorbance with pressure at 300 K can be used to construct an adsorption isotherm. Assuming that the heat of adsorption decreases with coverage reproduces both the heat of adsorption measurements made at low pressures using the molecu-

lar beam methods and the shape of the adsorption isotherm measured using infrared spectroscopy at higher pressures.

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