

## Adsorption and desorption kinetics of CO on Cu(110) studied by optical differential reflectance

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Optical differential reflectance was shown to be a viable technique to study surface adsorption and desorption kinetics. Its application to CO on Cu(110) leads to clearly improved results and better understanding of the system in comparison with earlier thermal desorption measurements. [S0163-1829(96)06932-9]

Molecular adsorption, desorption, and diffusion are generally considered to be the three most important surface processes in modern surface science.<sup>1</sup> Many techniques have been developed for their study, but few are capable of probing all three. The linear optical differential reflectance method (which has a number of variations) is an exception. It is known to have a submonolayer sensitivity,<sup>2</sup> and, recently, has been employed to study surface diffusion with a viability that can hardly be matched by other techniques.<sup>3</sup> We now show that it can also be used to study adsorption and desorption with many advantages over existing techniques.<sup>4</sup> We take CO on Cu(110) as an example. This system has already been investigated by a number of researchers<sup>5-7</sup> because CO plays a major role in the catalytical synthesis of alcohol over Cu.<sup>8</sup> The results of our linear optical study indicate that, contrary to what has been suggested in the literature, CO adsorption on Cu(110) follows the Langmuir adsorption kinetics at low coverage ( $\theta < 0.4$ ) and the precursor mediated adsorption kinetics at higher coverage ( $\theta > 0.4$ ), and that the earlier desorption measurements of CO/Cu(110) were deficient,<sup>5,6</sup> leading to incorrect values of the desorption parameters.

The differential reflectance (DR) method we have adopted exploits the different reflectance changes for  $s$  and  $p$ -polarized beams affected by adsorbates on a substrate. It is well known that adsorbates on a metal can change the reflectance of a  $p$ -polarized light from the metal much more appreciably than that of an  $s$ -polarized light. The difference in the reflectance changes for the two polarizations is a measure of the amount of adsorbates appearing on the surface. The optical arrangement is basically the same as that described in Ref. 9. A 10-mW He-Ne laser beam, after passing through a photoelastic modulator to produce a 50-kHz  $s$ - $p$  polarization-modulated beam, was directed onto the sample with an incident angle of  $10^\circ$ . The reflected beam from the sample was detected by a photodiode with a lock-in amplifier tuned to the second harmonics of the modulated frequency. To null out the background signal in the absence of adsorbates, an analyzer was inserted in front of the photodiode and properly adjusted. The observed signal could then be described by

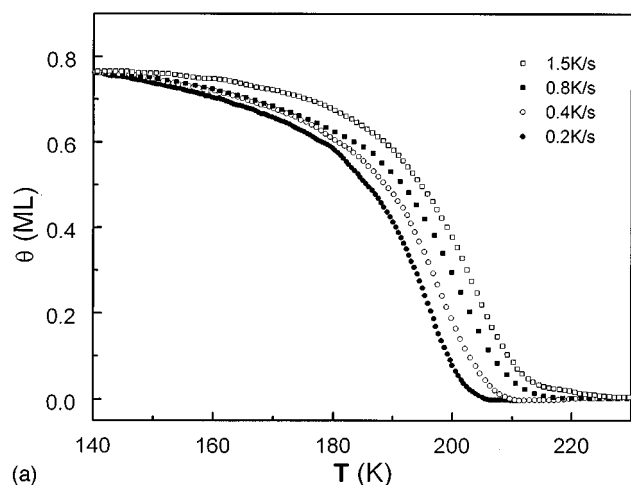
$$I(2\omega_m) = I_0(|r_p(\theta)|^2 - \gamma|r_s(\theta)|^2), \quad (1)$$

where  $\omega_m$  is the modulation frequency,  $I_0$  is a constant,  $|r_p(\theta)|^2$  and  $|r_s(\theta)|^2$  are the reflectances at coverage  $\theta$  for  $p$

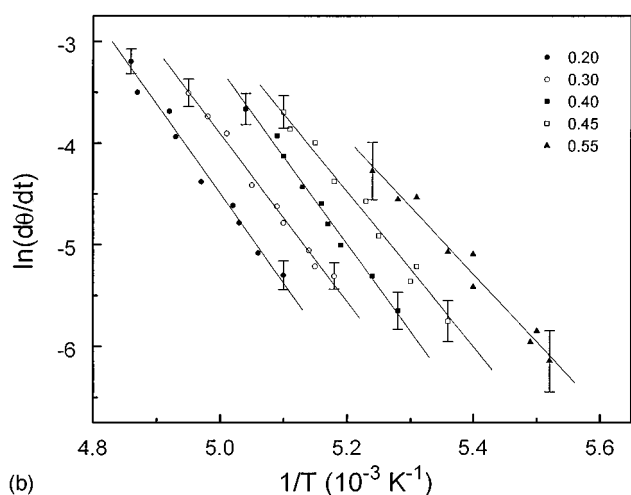
and  $s$  polarizations, respectively, and  $\gamma = |r_p(0)/r_s(0)|^2$  so that, for  $\theta=0$ , we have  $I(2\omega_m)=0$ . How the quantity  $(|r_p(\theta)|^2 - \gamma|r_s(\theta)|^2)$  varies with  $\theta$  can be experimentally calibrated using, for example, thermal desorption spectroscopy (TDS). In the case of CO/Cu(110), we found that  $(|r_p(\theta)|^2 - \gamma|r_s(\theta)|^2)$  was linearly proportional to  $\theta$  with the maximum corresponding to the saturation coverage  $\theta_s$ . This technique measures the surface coverage *in situ*. Therefore, in contrast to TDS, the measurement is free from possible complications due to unwanted background arising from various sources and has a better time resolution due to the faster response of the detection.

Our experiment was performed with a single crystal of Cu(110) situated in an ultrahigh-vacuum chamber with a base pressure of  $2.0 \times 10^{-10}$  torr. The Cu crystal was cut and polished to within  $0.2^\circ$  of the (110) plane, and was mounted with its [001] axes in the horizontal plane. An  $e$ -beam heater, controlled by a thermal controller, was located at the back side of the sample. To clean the sample surface, repeated 500-eV Ar<sup>+</sup> sputtering at room temperature was used, followed by annealing at 860 K for 10 min and a slow cooling back to room temperature. The cleaned surface showed no traces of C, O, and S as checked by Auger spectroscopy. A sharp ( $1 \times 1$ ) low-energy electron diffraction (LEED) pattern was observed, indicating that the surface was well ordered. A thermocouple attached to the surface of the sample was used to monitor the sample temperature during the measurements.

CO on Cu(110) has been studied by various techniques. The following properties are known.<sup>5,8,10</sup> CO molecules adsorb on the surface with the carbon atom facing the surface. Deposited at 110 K, they presumably appear around the top sites at low surface coverages for  $\theta < 0.4-0.5$ , leading to a somewhat diffuse ( $1 \times 1$ ) LEED pattern with additional streaks at half spacings along the [0,1] direction. Annealing at 170 K for a few minutes and cooling back to 110 K convert it to a ( $2 \times 1$ ) pattern. At higher coverages, a new pattern starts to develop as adsorbed CO molecules rearrange to form locally a more compressed structure. At the saturation coverage  $\theta_s = 0.77$ , the annealed sample gives a diffuse  $c(\frac{5}{4} \times 2)$  LEED pattern. The adsorption and desorption kinetics of CO on Cu(110) are, however, less well understood. For adsorption, the TDS work of Harendt *et al.* led to the conclusion that the adsorption is dominated by a precursor-mediated mechanism from the very beginning.<sup>5</sup> As we shall see later, this conclusion was incorrect because their experimental result had suffered from insufficient accuracy and



(a)

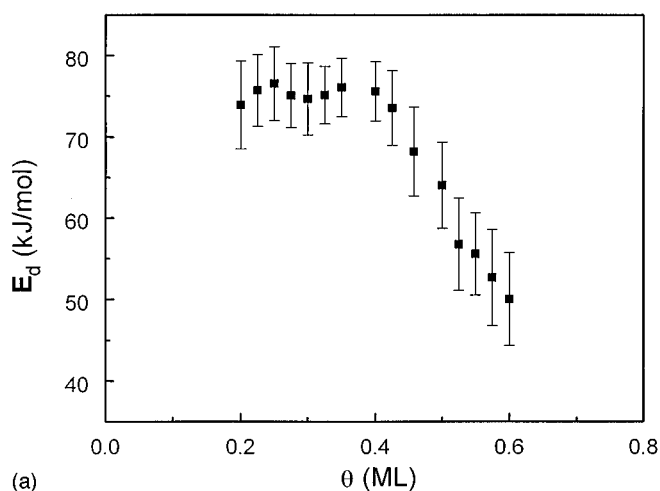


(b)

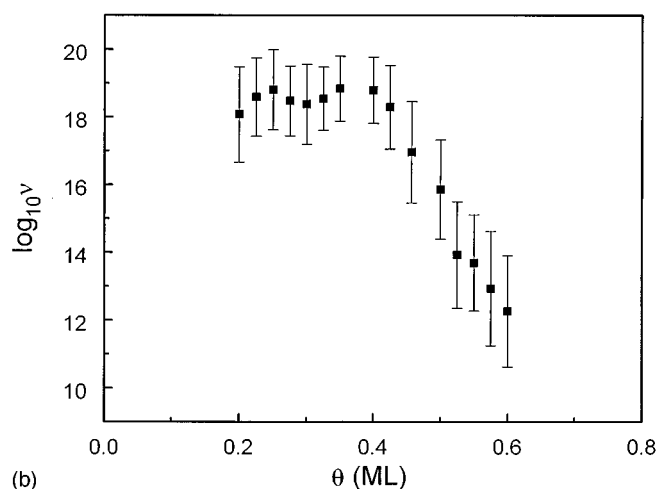
FIG. 1. (a) Surface coverage  $\theta$  of CO/Cu(110) versus temperature  $T$  for different temperature ramping rates  $\beta$  (K/sec) in thermal desorption. (b)  $\ln(d\theta/dt)$  versus  $1/T$  calculated from (a) at several fixed values of  $\theta$  as labeled. The straight lines are least-squares fits of the data points using Eq. (2), from which  $E_d$  and  $\nu$  are derived.

poor resolution. For desorption, the result of Christiansen *et al.*<sup>6</sup> seems to be not so reproducible.<sup>7</sup> Harendt *et al.* deduced the coverage-dependent desorption energy and preexponential factor from their TDS measurement,<sup>5</sup> but the temperature ramping rate used in the experiment was too high for their analysis to be valid. We shall show below that the improved experimental data obtained with our linear optical technique leads us to a better understanding of the adsorption and desorption kinetics of CO on Cu(110).

Consider first desorption of CO/Cu(110). We used the usual schemes adopted for thermal desorption spectroscopy TDS, one with the initial CO coverage  $\theta_0$  kept constant and the linear temperature ramping rate  $\beta$  varied, and the other with  $\beta$  constant and  $\theta_0$  varied. Unlike TDS, we measured the CO coverage left on Cu(110) using DR. It is known that the first scheme often provides a more accurate determination of the kinetic parameters.<sup>11</sup> We show in Fig. 1(a) a set of  $\theta$  versus  $T$  curves obtained with  $\theta_0=0.77$  and  $\beta$  varied from 0.2 to 1.5 K/sec. From these curves, we find for each  $\theta$  a set of data points of  $\ln(d\theta/dt)$  versus  $1/T$ . A few representative cases are given in Fig. 1(b). For each  $\theta$ , the data can be fit by



(a)



(b)

FIG. 2. Coverage dependence of (a) the desorption energy  $E_d$ , and (b) the preexponential factor  $\nu$ .

a straight line. A careful analysis shows that the desorption can be well described by the first-order kinetics with the equation

$$d\theta/dt = -\nu\theta \exp(-E_d/kT), \quad (2)$$

where  $E_d$  is the desorption energy and  $\nu$  the preexponential factor. The values of  $E_d$  and  $\nu$  versus  $\theta$  deduced from the fit in Fig. 1(b) are presented in Fig. 2. It is seen that  $E_d=75\pm 5$  kJ/mol and  $\log_{10}\nu=18.6\pm 1.1$  are independent of  $\theta$  for  $\theta\leq 0.4$ , but decrease with  $\theta$  for  $\theta\geq 0.4$ . This result indicates that repulsive interactions among adsorbed CO molecules must have set in around  $\theta\sim 0.4$ . Presumably, these are the CO molecules packed to form the  $c(\frac{5}{4}\times 2)$  structure; because of the close distance between neighboring CO molecules in the structure, the CO-CO repulsion becomes significant.

The above results are consistent with those obtained in the measurement of  $\theta$  versus  $T$  with  $\theta_0$  varied and  $\beta$  fixed. We found in the latter measurement that, for  $\theta_0\geq 0.4-0.5$ , the  $d\theta/dt$  versus  $T$  curve begins to broaden at the low-temperature side and eventually exhibits a clear shoulder, suggesting that a significant part of the adsorbed CO must have appeared at sites with lower desorption energies.

Harendt *et al.*<sup>5</sup> have reported a TDS study of CO/Cu(110) showing smaller values of  $E_d$  and  $\nu$  than ours,<sup>12</sup> a slight

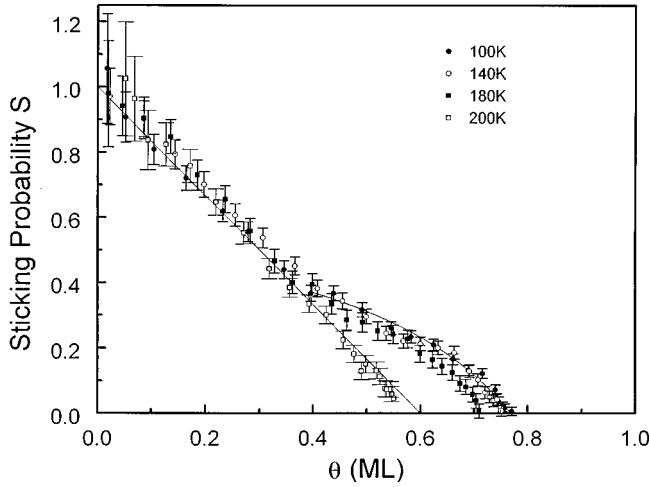


FIG. 3. Sticking probability  $S$  as a function of surface coverage of CO/Cu(110) at several different temperatures. The solid lines are theoretical fits.

increase of  $E_d$  and  $\nu$  for  $\theta > 0.3$  which has been disputed by Christiansen *et al.*,<sup>6</sup> and a rapid decrease of  $E_d$  and  $\nu$  for  $\theta > 0.3$ . In their experiment, they also found that for  $\beta \geq 2.75$  K/sec, the peak of  $d\theta/dt$  versus  $T$  shifts to lower temperature with increasing  $\beta$ , contrary to what Eq. (2) would predict. They proposed that this could be due to CO diffusion from the  $c(\frac{5}{4} \times 2)$  region to the  $(2 \times 1)$  region during desorption. Although Eq. (2) no longer properly describes the desorption process, they still used it to deduce  $E_d$  and  $\nu$ . We must therefore consider their results tentative. We have observed the same anomaly described by Harendt *et al.* at both  $\theta \leq 0.4$  and  $\theta \geq 0.4$  with hardly any  $\theta$  dependence. Since for  $\theta < 0.4$ , the adsorbed CO form a single phase, the mechanism proposed by Harendt *et al.* cannot be operative. It seems that for all  $\theta$ , CO desorption at low  $\beta$  must have gone through a precursor state that can be by-passed at high  $\beta$ , but we cannot offer any concrete suggestion.

We now consider adsorption of CO on Cu(110). The kinetic equation governing the isothermal adsorption can be written as

$$(d\theta/dt)_{\text{ads},T} = P(2\pi mkT_g)^{-1/2} N_s^{-1} S(\theta, T) - |(d\theta/dt)_{\text{des},T}|, \quad (3)$$

where  $S$  is the sticking probability,  $N_s = 1.09 \times 10^{15}/\text{cm}^2$  is the surface density of Cu(110),  $P = 2.1 \times 10^{-7}$  torr is the pressure, and  $T_g = 300$  K the temperature of the ambient CO gas,  $m$  is the mass of CO, and  $(d\theta/dt)_{\text{des},T}$  is the CO desorption rate at the substrate temperature  $T$ . Using DR, we measured  $\theta(t)$  in adsorption and desorption at constant  $T$  separately to obtain  $(d\theta/dt)_{\text{ads},T}$  and  $(d\theta/dt)_{\text{des},T}$ . The sticking probability  $S(\theta, T_g)$ , could then be deduced from Eq. (3). We note that  $(d\theta/dt)_{\text{des},T}$  is negligible for  $T < 140$  K in our case. The results of  $S$  versus  $\theta$  for a set of different temperatures are depicted in Fig. 3. We find that within experimental uncertainty,  $S$  is temperature independent for  $\theta \leq 0.4$  and can be described by

$$S = S_0(1 - \theta/\theta_c) \quad (4)$$

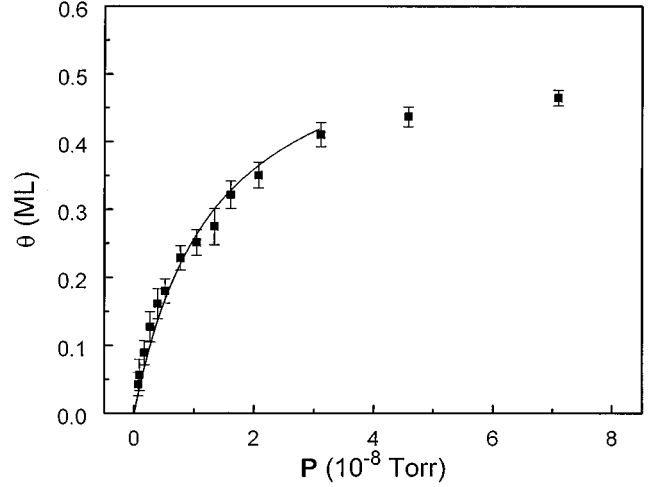


FIG. 4. Equilibrium surface coverage of CO/Cu(110) as a function of CO gas pressure. The solid curve is a prediction of the Langmuir isotherm described by Eq. (5).

with  $\theta_c = 0.6$ . Because of the usual difficulty in calibrating  $P$  accurately, we simply set  $S_0 = 1$  (with the scale of  $P$  adjusted accordingly) so that  $S = 1$  at  $\theta = 0$ . The linear dependence in  $\theta$  indicates that the isothermal adsorption follows the simple Langmuir kinetics. The parameter  $\theta_c$  has no real physical meaning here, but is determined by the relative magnitude of  $S$  at  $\theta = 0$  and  $\theta = 0.4$ . Knowing that the desorption of CO from Cu(110) for  $\theta \leq 0.4$  obeys Eq. (2) with  $E_d$  and  $\nu$  independent of  $\theta$ , we expect that for Cu(110) exposed to a CO ambient gas of  $P$  and  $T_g$ , the equilibrium CO coverage on Cu follows the Langmuir adsorption isotherm

$$\theta(T) = \frac{\theta_c}{1 + (\theta_c B/A)/P} \quad (\theta \leq 0.4), \quad (5)$$

with  $A = (2\pi mkT_g)^{-1/2} N_s^{-1}$ , and  $B = \nu \exp(-E_d/kT)$ . We have measured  $\theta$  as a function of  $P$  at  $T = 200$  K. As shown in Fig. 4, the experimental result can be fit very well by Eq. (5) using  $E_d = 75.8$  kJ/mol and  $\log_{10} \nu = 18.4$ . These values agree to within 2% of those deduced earlier from the desorption experiment. This proves unequivocally the consistency and reliability of our measurements using DR.

For  $\theta \geq 0.4$ , the sticking probability  $S$  in Fig. 3 deviates from the linear dependence with  $\theta$  except for  $T = 200$  K. The result must have reflected the fact that the adsorbed CO molecules now begin to rearrange themselves and partly form the  $c(\frac{5}{4} \times 2)$  structure. The experimental data for  $T = 100$  and  $140$  K can be fit by the equation

$$S(\theta)/S(\theta_x) = \left( 1 + \frac{K(\theta - \theta_x)}{(\theta_s - \theta)} \right)^{-1} \quad (6)$$

for  $0.4 < \theta < 0.77$ , with  $\theta_s = 0.77$ ,  $\theta_x = 0.4$ , and  $K = 0.5$ . This equation was derived by Kisliuk<sup>13</sup> assuming a precursor-mediated adsorption mechanism. In the model,  $K$  is a parameter describing the surface mobility of the adsorbed CO, with larger  $K$  corresponding to weaker mobility and  $K = 1$  in the simple Langmuir limit. The result therefore suggests that for  $\theta > 0.4$ , CO would first adsorb to the surface and then rearrange themselves and neighboring CO to form a more stable structure. At higher  $T$ , simultaneous CO desorption during

adsorption becomes more important. Fast desorption could effectively reduce the precursor movement. In the limit, desorption might occur before the adsorbed CO could move and the kinetics would become Langmuir-like. This seems to be the case at  $T=200$  K shown in Fig. 3.

Harendt *et al.*<sup>5</sup> used TDS to study adsorption of CO on Cu(110). They deduced from their data a sticking probability which was nearly independent of  $\theta$  for  $0 < \theta < 0.6$  and suggested that the adsorption process must be precursor mediated. We believe that their result is erroneous because of insufficient data points at small  $\theta$ . Our technique allows an *in situ* continuous measurement of  $\theta(t)$  and is a clear improvement over the TDS method.

In summary, we have shown that optical DR is a powerful technique for studies of adsorption and desorption kinetics. It avoids a number of difficulties inherent in the usual TDS

method, and allows much-improved experimental results. Its application to CO/Cu(110) provides us with a better understanding of the system. For  $\theta \leq 0.4$ , the adsorbed CO are noninteracting and in a single phase, and the corresponding adsorption and desorption follow simple kinetics. For  $\theta \geq 0.4$  until saturation, adsorption and desorption kinetics reflect the fact that the adsorbed CO begin to form a more compressed structure in which the CO-CO repulsive interaction becomes significant.

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<sup>1</sup>See, for example, D. A. King, *CRC Crit. Rev. Solid State Mater. Sci.* **7**, 167 (1978).

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<sup>12</sup>The TDS measurements reported in Refs. 5–7 appear to yield broader  $d\theta/dt$  versus  $t$  curves, leading to smaller values of  $E_d$  and  $v$ .

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