

Diffusion of CO on Pt(111) studied by an optical diffraction method

Jianwei Ma, Xudong Xiao,* N. J. DiNardo,[†] and M. M. T. Loy

Department of Physics, The Hong Kong University of Science and Technology, Hong Kong, China

(Received 23 February 1998)

We have measured the diffusion of CO on flat and stepped Pt(111) surfaces using the linear optical diffraction method from an adsorbate grating. Measurements over a wide range of temperatures (133–313 K) and CO coverages (0.1–0.67 ML) indicate Arrhenius behavior with diffusion activation energies of 3.0–4.7 kcal/mol and 7.3–7.9 kcal/mol for flat and stepped surfaces, respectively. Comparisons of our measurements on flat and stepped (defected) surfaces with previous experiments by various groups using various techniques resolves several discrepancies and illustrates the importance of defect-induced effects on variations in measured diffusion parameters. [S0163-1829(98)09631-3]

I. INTRODUCTION

Surface diffusion of CO on platinum is important for investigating the mechanisms of CO hydrogenation in the synthetic fuel industry and of CO oxidation in the automotive industry, where Pt is used as a catalyst. To map out the potential energy surface for CO/Pt(111), extensive studies using various techniques involving adsorption, desorption, and diffusion have been made. While the CO adsorption energies at the top and bridge sites are now reasonably well understood,^{1–3} the energies at the saddle points of the diffusion paths remain an open question. In past years, CO diffusion on Pt(111) has been measured by a number of techniques including field emission (FE) shadowing in the 1960's,⁴ helium scattering⁵ and time-resolved infrared absorption spectroscopy⁶ (IRAS) in the 1980's, and laser-induced thermal desorption⁷ (LITD) and high-resolution electron-energy-loss spectroscopy⁸ (HREELS) in the 1990's. Despite the work done using five different techniques over three decades, there are still no definitive values for the diffusion coefficient D , the activation energy E_d , and the prefactor D_0 . The deduced activation energies range from 4 kcal/mol to 12 kcal/mol and the extrapolated diffusion coefficients can differ by more than four orders of magnitude at some temperatures. It is therefore critical to determine the correct values of D , E_d , and D_0 and to account for these serious discrepancies.

Figure 1 summarizes the results of previous diffusion measurements (dashed lines) and compares them with our results (data points), which are to be presented in this paper. Previous measurements were obtained either at high temperatures (>300 K) or at low temperatures (<200 K). One may suspect that the *temperature difference* might be a cause of the discrepancies since it is unknown whether simple Arrhenius law would be valid over a wide temperature range.⁹ As also indicated in Fig. 1, the CO coverages used in these experiments are very different, ranging from very low ($\theta_{\text{CO}} < 0.025$ ML, where 1 ML corresponds to one CO per Pt(111) surface atom and θ_{CO} is the CO coverage) to high ($\theta_{\text{CO}} \sim 0.5$ ML). An apparent discrepancy can arise if CO diffusion is strongly *coverage dependent*.

A third possible cause for a discrepancy involves *defects* in the surface of the samples used. For example, in FE, CO

was first dosed on one side of the field emitter and then the advancing edge of CO was monitored by the electron emission pattern.⁴ The emitter consisted of many low Miller-index facets and diffusion reflects a properties of the facets rather than diffusion over a single-crystal surface. In LITD, a $\theta_{\text{CO}} \sim 0$ coverage “hole” was first created by a few laser pulses at high power on a uniformly dosed single-crystal surface and the refilling rate of the hole was subsequently measured.⁷ Other than the possible damage induced by the laser pulses, the surface was well characterized with low step density ($<0.25^\circ$ miscut). In HREELS,⁸ CO was uniformly dosed over a strip area on a single-crystal surface followed by measuring the CO coverage as a function of position on the surface by electron-energy-loss spectroscopy. Because of the low spatial resolution (~ 0.3 mm), the measurements were carried out only at high temperatures where desorption has to be taken into account. While FE, LITD, and HREELS require an initial coverage gradient, He scattering and IRAS are techniques that required no initial coverage gradient. Diffusion measurements for the latter group relied on step (and kink) sites as CO traps on which a higher relative coverage than on terraces was eventually reached due to the larger binding energies. In the He-scattering method,⁵ the decrease of CO population at terrace sites via diffusion to defect sites was measured by the intensity increase of the coherent specular helium beam. In order to obtain enough traps for CO, pits with step and kink sites at their perimeters were created by ion sputtering a well-ordered surface. In IRAS,⁶ the diffusion was measured by monitoring the population evolution of CO at terrace and step sites from an initially uniform CO dose via the intensities of the respective IR absorption modes. A stepped surface was necessary to provide the traps. How the purposely created defects—pits in He scattering and steps in IRAS—and the unintentionally introduced defects—facet boundaries in FE shadowing and laser-induced damage in LITD—contribute to the discrepancy of the diffusion data remains to be evaluated.

In view of the above conjectures, we have employed a recently developed method, optical diffraction off an adsorbate coverage grating,¹⁰ to measure the surface diffusion for the CO/Pt(111) system. Unlike some of the previous techniques, namely, He scattering, IRAS, and HREELS, which rely on modeling the detailed kinetic processes for deduction

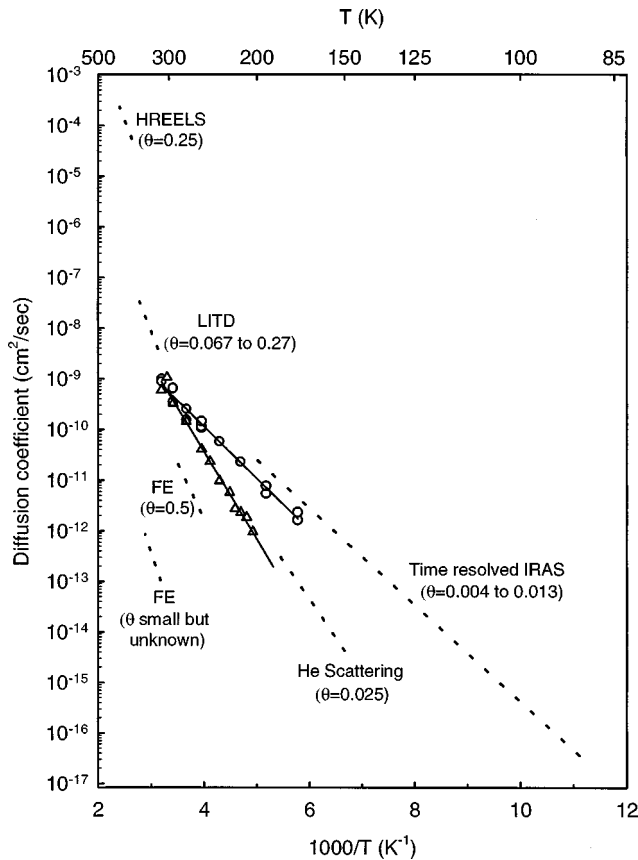


FIG. 1. Summary of previous CO diffusion results (Refs. 4–8) on Pt(111) plotted as dashed lines in the relevant temperature ranges of the measurements. Data from the present study are included as data points for comparison. The circles are the diffusion data on a $<0.1^\circ$ miscut surface at $\theta_{\text{CO}} \sim 0.1$ ML and the triangles are the data for diffusion perpendicular to steps on a 2° miscut sample at $\theta_{\text{CO}} \sim 0.3$ ML.

of the diffusion coefficient, the optical diffraction technique is model free. In this technique, an initial coverage gradient is created in the form of a periodic grating and its decay is measured by the time dependence of the first-order diffraction signal. The decay time of the first-order diffraction signal can be related to the diffusion coefficient D by solving the diffusion equation $\partial\theta/\partial t = D\partial^2\theta/\partial x^2$ even without the need to know the details of the coverage modulation as long as D remains constant in the relevant coverage range.¹⁰ This technique possesses a number of other advantages including a large dynamic range,¹¹ sensitivity at low adsorbate coverages, and capability for directional diffusion measurements.¹² It enables us to measure diffusion over a wide temperature range, in particular, to fill the temperature gap from 200 to 300 K, and over a large coverage range to examine the effects of CO-CO interactions on diffusion and the coverage dependence. Furthermore, we can study the effects of step defects on diffusion by performing measurements on well-characterized stepped surfaces. Since the period of the coverage grating is on the micron scale so it contains many steps, step effects can appear in our measurements if they are important.¹³ By aligning the one-dimensional adsorbate grating parallel or perpendicular to the steps, diffusion anisotropy can be measured.

In this paper, we first present our results of CO diffusion

on Pt(111) surfaces with and without a miscut over a wide temperature range from 133 to 313 K for a wide range of coverages from 0.1 to 0.67 ML. Then, we will discuss what effects temperature, coverage, and step defects can have in causing discrepancies between previous measurements. Finally, the significance of our results for understanding of the potential energy surface of CO/Pt(111) and the CO-CO interaction will be discussed.

II. EXPERIMENTS AND RESULTS

We have employed the linear optical diffraction technique to measure the surface diffusion coefficient. The technique has been described in detail elsewhere.¹⁰ Here, we summarize only the key points of the technique. First, a uniform layer with a prescribed coverage of CO is deposited on the Pt(111) surface. Then, a one-dimensional grating of adsorbates is created by LITD using the interference pattern of two laser beams split from a Nd:YAG pulsed laser ($1.06 \mu\text{m}$, 10 ns). A shallow coverage modulation, typically with $\Delta\theta_{\text{CO}} \sim 0.02$ ML, is thereby created. Within this coverage modulation range, the diffusion coefficient D , can be treated as a constant, i.e., there is a negligible coverage dependence. The modulation is obtained by properly adjusting the intensities of the two interfering laser beams such that ~ 0.02 ML CO is desorbed from the maximum laser intensity regions and no CO is desorbed from the minimum intensity regions. As determined by the laser interference pattern, the grating spacing was $s = 4.4 \mu\text{m}$ in the present experiment.

The evolution of the adsorbate grating could be detected by linear diffraction of a He-Ne laser beam with polarization modulation. As the adsorbate grating is smeared out by surface diffusion, the first-order diffraction signal exhibits an exponential decay in time by solving the diffusion equation with the given initial and boundary condition:¹⁰

$$S(t) = S(0)\exp(-t/\tau), \quad \text{with } \tau = s^2/8\pi^2D, \quad (1)$$

where D is the chemical diffusion coefficient and s is the grating period. Note that the decay time τ depends on D and s but not on the detailed shape of the grating, which only affects the absolute signal strength $S(0)$. In the present study, D was measured as a function of substrate temperature and adsorbate coverage.

The experiment was performed with the sample situated in an ultrahigh vacuum (UHV) chamber with a base pressure of 2.0×10^{-10} torr. Two mechanically polished Pt(111) single crystals were used. One was cut to within 0.1° of the (111) plane; the other was cut 2° off the (111) plane, which provides steps along the $[11\bar{2}]$ direction, the same as used in the previous IRAS experiment.⁶ Sample cleaning was performed by extensive cycles of Ar^+ sputtering, oxygen treatment at 1000 K, and high-temperature annealing at 1200 K. Routine cleaning procedure of the Pt surface was Ar^+ sputtering the surface at room temperature for 30 min followed by annealing at 1200 K for 2–5 min. Auger spectra showed no detectable impurities. Observation of a sharp (1×1) low-energy electron diffraction (LEED) pattern from a clean Pt(111) surface and a $c(4 \times 2)$ pattern from 0.50 ML CO on Pt(111) ensured that the surface was well ordered.¹ The sample temperature was controlled by electron beam heating

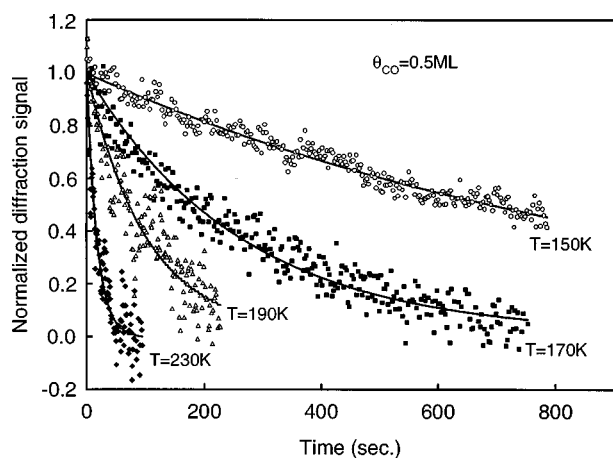


FIG. 2. Representative data of the first-order diffraction signal versus time for CO diffusion on a $<0.1^\circ$ miscut surface at $\theta_{CO} \sim 0.5 \text{ ML}$ for temperatures of 150, 170, 190, and 230 K. The solid lines are single exponential fits by Eq. (1).

and liquid-nitrogen cooling to within $\pm 1 \text{ K}$, and monitored by a K -type thermocouple spot welded at the side of the samples.

For diffusion measurement, the Pt(111) surface was first dosed with CO at 190 K to the desired coverage by backfilling the chamber through a leak valve. Coverages were controlled by exposure whose corresponding θ_{CO} was evaluated from the thermal desorption spectra (TDS), with the absolute calibration performed at 0.5 ML for the $c(4 \times 2)$ CO superstructure (exposure $\sim 2 \text{ L}$, $1 \text{ L} = 10^{-6} \text{ torr sec}$). The 0.67 ML coverage was achieved only by a large CO exposure ($\sim 200 \text{ L}$). The sample temperature was subsequently raised or lowered to the diffusion temperature before creating the CO grating by laser desorption. Once the grating was formed, the first-order diffraction signal from the grating was measured as a function of time as discussed earlier. Diffusion measurements were obtained between 133 and 313 K, with the lower temperature limited by the longest diffusion time of $\sim 2000 \text{ sec}$ and the higher temperature limited by the shortest diffusion time, $\sim 1 \text{ sec}$, or by thermal desorption. We kept it $\sim 30 \text{ K}$ below the desorption take-up temperature to avoid the influence of thermal desorption on our measurements.

Representative data of the first-order diffraction signal versus time are shown in Fig. 2. The signal-to-noise ratio for the chosen coverage modulation is 3–5, which is sufficient to deduce a reliable decay time τ . The repeatability of the measurements of D is over a range on the order of a factor of 2, which is larger than the standard deviation of τ from fitting a single set of diffraction signal data. The diffusion coefficient D can be calculated from τ by Eq. (1). In Fig. 3, the diffusion coefficients for various coverages on the $<0.1^\circ$ miscut Pt(111) surface are depicted as a function of reciprocal temperature $1/T$ in an Arrhenius plot. Over a dynamic range of about two to three orders of magnitude, the measured diffusion coefficients fit by an Arrhenius relation, $D = D_0 \exp(-E_d/kT)$, very well within the experimental uncertainty. The deduced diffusion activation energies and prefactors for all the measured coverages are given in Table I. It is clear that the coverage dependence below 0.5 ML is weak, with the activation energy decreasing slightly from 4.7 kcal/mol to 3.9 kcal/mol and the prefactor basically constant as

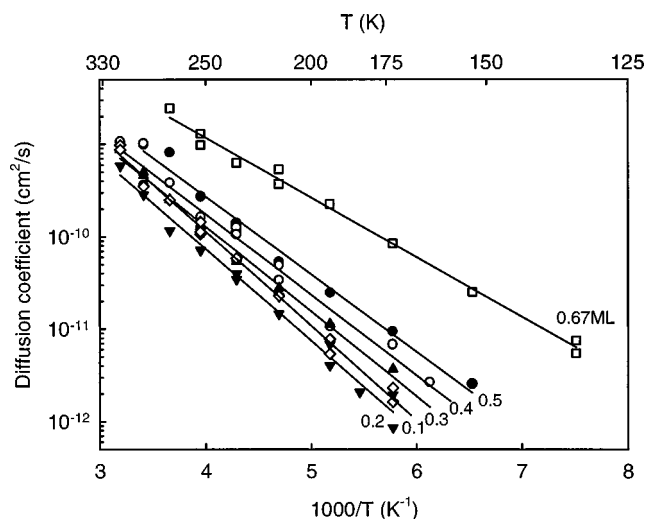


FIG. 3. Arrhenius plots of the diffusion coefficient D for CO on Pt(111) for CO coverages from 0.1 to 0.67 ML as indicated.

the coverage increases from 0.1 to 0.5 ML. The diffusion coefficient at a given temperature is observed to increase as the coverage increases except for $\theta_{CO} = 0.1 \text{ ML}$. When the coverage is increased to 0.67 ML, a significant decrease of the activation energy to 3.0 kcal/mol is obtained with significant increase in the diffusion coefficient.

CO diffusion on the 2° miscut Pt(111) surface in the direction perpendicular to the steps was measured for $\theta_{CO} \sim 0.3$ and 0.5 ML by aligning the grating parallel to the steps. The deduced diffusion activation energies and prefactors for these cases are also listed in Table I. For the purpose of comparison with the results obtained by previous measurements (as discussed below), we have plotted the present results as data points for diffusion on a stepped surface at $\theta_{CO} \sim 0.3 \text{ ML}$ and on a terrace ($<0.1^\circ$ miscut surface) at $\theta_{CO} \sim 0.1 \text{ ML}$ in Fig. 1. It is clear that diffusion perpendicular to the steps is significantly slower than that on a terrace, particularly at low temperatures. The diffusion activation energy is then substantially larger, with a value of 7.9 kcal/mol.¹⁴

III. DISCUSSION

As seen in Fig. 3, CO diffusion on Pt(111) follows a simple Arrhenius law over the wide temperature range from 133 to 313 K for all the coverages measured. The diffusion coefficient in this temperature range varies about three orders of magnitude with no indication of conversion from a *low* barrier behavior at low temperatures to a *high* barrier behavior at high temperatures. Therefore, it is unlikely that the discrepancies in the previous measurements are caused by a temperature effect. The coverages used in this study (0.1–0.67 ML) overlaps those in FE shadowing, LITD, and HREELS, but not those in He scattering and IRAS.^{4–8} However, the deduced activation energies ranging from 3.9 to 4.7 kcal/mol for diffusion on the $<0.1^\circ$ miscut surface from the present measurement are significantly lower than those obtained from FE shadowing, LITD, and HREELS (~ 10 – 12 kcal/mol) despite the similar coverages. Furthermore, the coverage dependence is rather weak, qualitatively consistent

TABLE I. Deduced diffusion activation energies and prefactors for CO diffusion on both $<0.1^\circ$ miscut surface and 2° miscut surface (diffusion perpendicular to steps) for various coverages.

θ_{CO}	$<0.1^\circ$ miscut Pt(111)		2° miscut Pt(111)	
	E_d (kcal/mol)	D_0 (cm^2/s)	E_d (kcal/mol)	D_0 (cm^2/s)
0.1	4.7 ± 0.1	$(1.4 \pm 0.4) \times 10^{-6}$		
0.2	4.6 ± 0.2	$(6.9 \pm 3.0) \times 10^{-7}$		
0.3	4.2 ± 0.1	$(6.0 \pm 1.7) \times 10^{-7}$	7.9 ± 0.3	$(2.8 \pm 1.5) \times 10^{-4}$
0.4	4.0 ± 0.2	$(5.3 \pm 2.6) \times 10^{-7}$		
0.5	3.9 ± 0.2	$(6.1 \pm 2.7) \times 10^{-7}$	7.3 ± 0.3	$(2.1 \pm 1.4) \times 10^{-4}$
0.67	3.0 ± 0.1	$(4.5 \pm 1.0) \times 10^{-7}$		

with the findings of LITD. With a repulsive CO-CO interaction, the diffusion activation energy is expected to decrease as coverage increases, in agreement with our observations. Thus, smaller values of diffusion activation energies found at lower coverages by the He scattering (0.025 ML) and IRAS (0.004 to 0.013 ML) measurements than those found in FE shadowing, LITD, and HREELS measurements at higher coverages are inconsistent with repulsive CO-CO interactions. Therefore, we conclude that coverage dependent effects are not the cause of the discrepancies.

It appears, then, that the cause for the large discrepancies in the previous experiments might come from the presence of defects. As shown in Fig. 1, our results for CO diffusion on the $<0.1^\circ$ miscut surface at $\theta_{\text{CO}} \sim 0.1$ ML agree very well with the results obtained by IRAS in both diffusion activation energy and prefactor. Our results for CO diffusion perpendicular to the steps on the 2° miscut surface at $\theta_{\text{CO}} \sim 0.3$ ML, on the other hand, show a larger activation energy (7.9 kcal/mol) close to the value obtained by He scattering. It is surprising that the extrapolation of this set of data according to Arrhenius law can almost match the data from He scattering on the lower-temperature side and the data from LITD on the higher-temperature side, although significant differences in the diffusion activation energies still exist. The values of diffusion activation energies from FE shadowing and HREELS are also close to that of diffusion on a stepped surface, but the diffusion coefficients are far off of the extrapolated lines. Therefore, our measurements on both ‘‘flat’’ and stepped Pt(111) surfaces strongly suggest that the discrepancies in the previous experiments might be caused by step defects. It is then worthwhile to devote a section to examine the possible reasons that previous experiments were affected by defects.

A. Comments on previous experiments

In this section, we will proceed in chronological order, i.e., from FE shadowing,⁴ to helium scattering,⁵ to time-resolved IRAS,⁶ to LITD,⁷ and to HREELS (Ref. 8) to evaluate of the possible causes of the defect-induced effects in the diffusion measurement.

The first diffusion measurements of CO on Pt were reported by Lewis and Gomer⁴ using the field emission shadowing method. With CO dosed initially at one side of the emitter, the diffusion was measured by following the motion of the CO advancing edge using the electron emission patterns. They reported an activation energy of 10.1 kcal/mol

for boundary diffusion at $\theta_{\text{CO}} \sim 0.5$ ML and 14.5 kcal/mol for boundary-free diffusion at low (unknown) coverage. Since the latter was known to be controlled by defects (possibly point defects), we will consider $\theta_{\text{CO}} \sim 0.5$ ML case only. From our point of view, the former case was not free of defect-induced effect either. Since the experiment measured the advancing edge of the CO layer from the $(\bar{1}\bar{1}1)$ facet on one side of the emitter to the (111) facet on other side of the emitter via the (101) facet, diffusion over the facet boundary must play a role. In this sense, this measurement was only qualitative since it was not measuring diffusion over a single crystallographic plane. The fact that they obtained a similar value of the activation energy to our step-controlled diffusion indicates that the diffusion on the emitter is step dominated. The fact that their data does not lie close to our curve was perhaps due to their inability to measure D_0 exactly by FE shadowing because of the ill-defined front edge (what is the exact CO coverage?) and possible systematic error in the magnification value of the microscope.

Making use of the fact that CO at defect sites contributed negligibly to the helium intensity of the coherent specular beam as compared to CO on terrace sites, the He-scattering method⁵ measured the population evolution of terrace CO and thus CO diffusion from the more weakly bound terrace sites to the more strongly bound defect sites via the change of the intensity of the specular beam. In order to create enough traps for CO molecules, an ion sputtered surface with a density of 10^{11} – 10^{12} pits/ cm^2 of perimeters of 10–100 step- or kink sites/pit (corresponding to an interior area of ~ 7 –800 atoms/pit) were used. At the coverage of 0.025 ML that was used, there were only ~ 20 CO molecules inside the ~ 800 -atoms-large pit, far less than the number to fill all the 100 step/kink sites at its perimeter. For smaller pits, the ratio of the number of CO molecules deposited in the interior of the pit to the number of the perimeter sites became even smaller. Therefore, significant numbers of CO molecules would have to diffuse over step edges from the upper terrace to fill these step/kink sites at the perimeters of the pits. Without separating the overstep diffusion process in the model, a reliable terrace diffusion coefficient would be difficult to obtain. The overall diffusion parameters that were deduced should only reflect the dominant process. That the reported activation energy of 7 kcal/mol and prefactor of 1.9×10^{-5} – 1.9×10^{-4} cm^2/sec were close to our result of CO diffusion perpendicular to steps on the 2° miscut Pt(111) surface with an activation energy of 7.9 kcal/mol and pref-

actor of 2.8×10^{-4} cm²/sec at $\theta_{\text{CO}} \sim 0.3$ ML (Fig. 1) indicates that the dominant process in the He-scattering measurement is diffusion over step edges. The deviation between their and our measurements could arise from the fact that (i) the step effect did not completely dominate CO diffusion in the helium scattering experiment, and (ii) with only one temperature ramp from 150 to 190 K in the helium-scattering experiment, significant error could exist in the deduced diffusion parameters.

Using a similar principle as the helium-scattering experiments, IRAS used miscut surfaces to provide steps as CO traps.⁶ By monitoring the population evolution of CO *both* at terrace and step sites from an initial spatially uniform dose of CO via the intensities of the respective IR absorption modes, the diffusion coefficient could then be deduced through detailed modeling of the kinetic process assuming CO diffuses to step sites only from the lower terrace via terrace diffusion. With samples miscut along $[\bar{1}10]$ (steps parallel to $[11\bar{2}]$) by 1.75° and 4° (12 and 28-atom-width/terrace, respectively) from Pt(111), the population change occurred in a time scale from 1 msec to 4 sec over a temperature range from 200 to 90 K, correspondingly. It is possible that the observed population change in this time scale was mainly due to terrace diffusion since diffusion of CO across steps would occur more slowly as inferred from our results. In contrast, the helium-scattering measurements were performed over a much slower time scale (>200 sec), most likely missing the fast terrace diffusion process. This is perhaps why the results from helium scattering and IRAS in the overlapping temperature range were so different. This discrepancy can now be resolved with our *independent measurements of diffusion on the terraces and over the steps*. The IRAS results, with $E_d \sim 4.4$ kcal/mol and $D_0 \sim 1.5 \times 10^{-6}$ cm²/sec, are in fair agreement with our results of terrace diffusion, $E_d \sim 4.7$ kcal/mol and $D_0 \sim 1.4 \times 10^{-6}$ cm²/sec. Note that the IRAS measurements were done at very low coverage, from 0.004 to 0.013 ML, in contrast to our measurement at 0.1 ML. The agreement between the two measurements indicates that the CO-CO interaction is indeed negligible in this range.

The LITD method,⁷ as opposed to the other studies, measured diffusion of CO on a well-prepared, $<0.25^\circ$ miscut surface. For diffusion measurement, LITD first applied a few pulses of high-energy laser light to completely desorb CO from a spot on the surface (hole burning) and subsequently measured the refilling rate of the hole by detecting the mass yield of the laser-induced desorption at the same spot. In helium scattering and IRAS, the achievable CO coverage was limited to very low values because of the number of traps. In LITD, no such limit existed. For initial coverages of 0.067, 0.17, and 0.27 ML, no significant coverage-dependence for the diffusion activation energy was found although an increase in the CO diffusion rate was observed for increasing coverages, a trend consistent with our observation. However, the value of 12.5 kcal/mol obtained for the diffusion activation energy was significantly higher than our results for terrace diffusion. As shown in Fig. 1, the LITD results lie in a region along the extrapolation of our Arrhenius curve for step-controlled diffusion. Thus, we suspect that the LITD results were also affected by defects that might have been created by the multiple laser shots of high power (higher than used in the present study since we do not desorb

all the CO). The nature of the defects induced by laser heating has been studied by scanning tunneling microscopy. They were identified as monatomic height steps along all three equivalent $\langle 110 \rangle$ directions, resulting from slip along $\{111\}$ planes of the bulk (e.g., creation of dislocations in the near surface region) in order to relieve the strain caused by the laser-induced thermal expansion.¹⁵ Furthermore, knowing that the typical repeatability of the LITD measurement of D was about a factor of two,¹⁶ deducing a diffusion activation energy from a set of data with a dynamic range less than 5 over a limited temperature range (320–360 K) could cause significant error. This might be another factor contributing to the large discrepancies among the previous results. Additional factors such as measurement method dependence could also result in discrepancies among the diffusion parameters as proposed previously by Tringides.¹⁷ In contrast to the shallow gratings with $\Delta\theta_{\text{CO}} \sim 0.02$ ML used in our experiment, the LITD method employed a large initial coverage gradient, with $\theta_{\text{CO}} \sim 0.067$, 0.17, and 0.27 ML respectively outside the hole and $\theta_{\text{CO}} \sim 0$ inside the hole. As simulated by Tringides,¹⁷ a significant deviation from the true values of the diffusion parameters can result from the LITD method when the adsorbate-adsorbate interaction is strong and attractive. The deviation becomes much moderate if the adsorbate-adsorbate interaction is repulsive. In the present case, the CO-CO interaction is repulsive and relatively weak as inferred by the coverage dependence of the diffusion results (see Fig. 3, and also next section), therefore we believe that the measurement method dependence is only a secondary cause of the discrepancy.

In the HREELS (Ref. 8) measurement, CO was dosed at a given strip area to provide a coverage gradient and the spatially resolved electron energy-loss spectroscopy (EELS) signal was used to measure the CO distribution. Unfortunately, due to the low spatial resolution, ~ 0.3 mm (electron beam size), only very fast diffusion occurring in a temperature range at which desorption could not be neglected could be measured. This led to the need of a complex analysis including adsorption, desorption and diffusion. The deduced diffusion activation energy of 12.5 kcal/mol was close to that from LITD, but the prefactor of 7.5×10^2 cm²/sec was about 100 times larger than that from LITD. This was accounted for by introducing new mechanisms such as a long jump length. With a dynamic range of ~ 3 for temperatures from 380 to 420 K, again, we believe that the reported diffusion parameters only have qualitative value.

B. Coverage dependence

Having resolved several discrepancies in the previous results, we can now concentrate on the terrace diffusion data, in particular on their significance for understanding the potential energy surface for CO/Pt(111).

Adsorption and desorption of CO/Pt(111) has been studied extensively.^{18–20} From EELS (Refs. 18 and 19) and infrared absorption spectroscopy IRAS (Refs. 6 and 20) studies, it was found that CO adsorbs on top sites first and then on the twofold bridge sites for coverages higher than 0.33 ML at relatively high temperatures although bridge site occupation sets in earlier at ~ 0.20 ML for lower adsorption temperatures.¹⁸ The adsorption energies of the top and bridge

sites have also been studied. An IRAS study concluded that the CO binding energy at a top site is stronger than that at a bridge site by 1.5 kcal/mol at $\theta_{\text{CO}} \sim 0$ but weaker by 0.5 kcal/mol at $\theta_{\text{CO}} \sim 0.5$ ML.²⁰ From an EELS study, a smaller difference in binding energies between top and bridge sites, namely, 0.8 kcal/mol at $\theta_{\text{CO}} \sim 0.1$ ML monotonically decreasing to -0.14 kcal/mol at $\theta_{\text{CO}} \sim 0.44$ ML and back to 0 at $\theta_{\text{CO}} \sim 0.5$ ML was found,¹⁹ although a larger binding energy difference of ~ 7.2 kcal/mol independent of coverage was found from a high temperature EELS study by a different group.³ If the potential energy at the diffusion saddle point is higher than both at top and bridge sites as it is inferred, our finding of a barrier energy of ~ 4.7 kcal/mol at $\theta_{\text{CO}} \sim 0.1$ ML between the saddle points and the adsorption sites would favor the first two results that found small binding-energy difference between top and bridge sites.

A repulsive CO-CO interaction exists for CO/Pt(111) as indicated by the series of ordered CO superstructures on Pt(111) identified by LEED.^{1,18,21} Up to 0.33 ML, a $(\sqrt{3} \times \sqrt{3})R30^\circ$ superstructure is formed with CO occupying top sites. At 0.5 ML, CO forms a $c(4 \times 2)$ structure containing 0.25 ML top- and 0.25 ML bridge-bonded CO. At higher CO coverages, the $c(4 \times 2)$ structure is compressed along the $[1\bar{1}0]$ direction and CO may occupy nearest-neighbor bridge sites. The desorption energy of the system as a function of CO coverage has been measured by laser-induced thermal desorption² and a combination of methods including LEED, work function, and thermal desorption.¹ It is agreed that the desorption energy decreases slowly from 32 kcal/mol to ~ 25 or 20 kcal/mol as the CO coverage increases to 0.5 ML then quickly drops to ~ 10 kcal/mol at 0.67 ML, with some variance in the coverage dependence. This is a further confirmation of a repulsive CO-CO interaction. From a recent theoretical study,²² it was found by *ab initio* calculation that an attractive CO-CO interaction exists when two top-site CO molecules are separated by a distance of about 5–8 Å at the zero coverage limit. However, the effective CO-CO interaction in the relevant coverage range of our experiment after including the many-body effect by local-density approximation (LDA) calculation was found to be always repulsive, although nonmonotonic as a function of separation.²² As is listed in Table I, the diffusion activation energy measured in the present experiment decreases from 4.7 kcal/mol at 0.1 ML to 3.9 kcal/mol at 0.5 ML slowly and then quickly drops to 3.0 kcal/mol at 0.67 ML, following the trend of the desorption energy. This is again consistent with a repulsive CO-CO interaction. In our case, the decrease of the diffusion activation energy is only $\sim 1/10$ of the decrease of the desorption energy, possibly due to the significant CO-CO interaction contribution to the saddle point for diffusion but not to the saddle point for desorption. This is supported by the relatively long range lateral CO-CO interaction found by fitting the adsorption isotherms with a lattice gas model for $\theta_{\text{CO}} < 0.33$ ML.²³ The strength of the CO-CO interaction was found to be ~ 0.24 kcal/mol for the second-nearest neighbors, ~ 0.8 kcal/mol for the third-nearest neighbors, and ~ 0.5 kcal/mol for the fourth-nearest neighbors. The first-nearest-neighbor sites are occupied by CO molecules only at high coverages. With a CO diameter of 2.8 Å and Pt-Pt separation of 2.772 Å, the molecular orbital overlap between the first-nearest-neighbor CO molecules in the high coverage

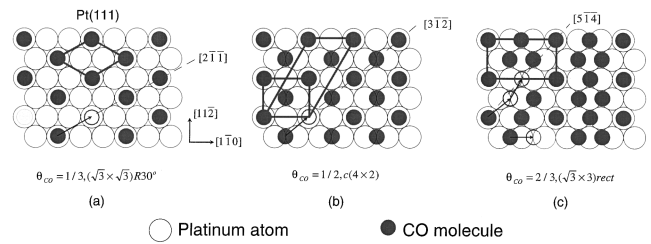


FIG. 4. Structures of CO adlayers on Pt(111) for coverages of 0.33, 0.50, and 0.67 ML. Plausible elementary diffusion paths on the surface for these coverages are indicated.

range (>0.5 ML) could be significant. This steric CO-CO interaction could be responsible for the sudden decrease in diffusion activation energy at 0.67 ML.

Considering CO diffusion pathways is also interesting. In the zero-coverage limit, one might expect CO to diffuse along the $[110]$ direction from top site to top site. At finite coverages, the situation must become more complicated. For example, near $\theta_{\text{CO}} \sim 0.33$ ML, only top sites are occupied, the bridge sites at most are local minima in the potential energy surface. If one insists on diffusion along $[110]$, a long jump length mechanism must be introduced in order to preserve the overall $(\sqrt{3} \times \sqrt{3})R30^\circ$ superstructure without a collective motion [see Fig. 4(a)]. Assuming that the hopping is via the shortest distance, then the CO must diffuse from top site to top site along the $[2\bar{1}\bar{1}]$ direction. However, the position of the saddle point remains unknown. When the coverage is above 0.33 ML, from which the bridge sites can be occupied and the maximum number of top sites are reduced back to 0.25 ML, the diffusion may proceed via top site to bridge site along the $[3\bar{1}\bar{2}]$ direction if the shortest jump length mechanism is considered [Fig. 4(b)]. At 0.67 ML coverage, the diffusion may go along the $[5\bar{1}\bar{4}]$ direction via a zigzag path [Fig. 4(c)], although diffusion along the $[110]$ direction may also occur for bridge site to bridge site hopping or top site to bridge site hopping. From the above discussion, it is clear that the diffusion paths remain an open question and need to be investigated theoretically. A construction of the potential energy surface also relies on theoretical studies.

IV. SUMMARY

In conclusion, we have measured the diffusion of CO on Pt(111) over a wide temperature range from 133 to 313 K over a wide range of coverages from 0.1 to 0.67 ML by using the optical diffraction method. Within experimental error, the data follow an Arrhenius law very well. The coverage dependence of the diffusion parameters is relatively weak. The activation energy varies slightly from 4.7 to 3.9 kcal/mol for $\theta_{\text{CO}} = 0.1$ to 0.5 ML and drops to 3.0 kcal/mol for $\theta_{\text{CO}} = 0.67$ ML, consistent with a repulsive CO-CO interaction. For a 2° miscut Pt(111) with steps along $[11\bar{2}]$, CO diffusion perpendicular to steps at 0.3 ML has an activation energy of 7.9 kcal/mol, significantly larger than that on terrace. The observed simple Arrhenius behavior over a wide temperature range from this study that fills the gap left by previous experiments and the weak coverage dependence of CO diffusion over a wide coverage range rule out both the

temperature and coverage as sources for the discrepancies among the previous results. Aided by our diffusion measurements on a 2° miscut surface in a direction perpendicular to the steps, we concluded that the discrepancies among the previous measurements were caused by the influence of defects, in particular steps. Analysis of FE shadowing, He scattering, and IRAS experiments support this conclusion. While the CO diffusion pathway remains an open question, we

have finally formulated a consistent picture for the important prototype system of CO diffusion on Pt.

ACKNOWLEDGMENT

We wish to acknowledge financial support from the Research Grant Council of Hong Kong through Grant No. RGC96/97-HKUST684/96P.

*Author to whom correspondence should be sent. Electronic address: phxudong@usthk.ust.hk

[†]Permanent address: Department of Physics, Drexel University, Philadelphia, PA 19104

¹G. Ertl, M. Neumann, and K. M. Streit, *Surf. Sci.* **64**, 393 (1977).

²E. G. Seebauer, A. C. F. Kong, and L. D. Schmidt, *Surf. Sci.* **176**, 134 (1986).

³H. Froitzheim and M. Schulze, *Surf. Sci.* **211**, 837 (1989); A. Cudok, H. Froitzheim, and M. Schulze, *Phys. Rev. B* **47**, 13 682 (1993).

⁴R. Lewis and R. Gomer, *Nuovo Cimento Suppl.* **5**, 506 (1967).

⁵B. Poelsema, L. K. Verheij, and G. Comsa, *Phys. Rev. Lett.* **49**, 1731 (1982).

⁶J. E. Reutt-Robey, D. J. Doven, Y. J. Chabal, and S. B. Christman, *Phys. Rev. Lett.* **61**, 2778 (1988); *J. Chem. Phys.* **93**, 9113 (1990).

⁷V. J. Kwasniewski and L. D. Schmidt, *Surf. Sci.* **274**, 329 (1992).

⁸H. Froitzheim and M. Schulze, *Surf. Sci.* **320**, 85 (1994).

⁹R. Gomer, *Rep. Prog. Phys.* **53**, 917 (1990).

¹⁰Xu-dong Xiao, X. D. Zhu, W. Daum, and Y. R. Shen, *Phys. Rev. B* **46**, 9732 (1992); Xu-dong Xiao, Yuanlin Xie, and Y. R. Shen, *Surf. Sci.* **271**, 295 (1992).

¹¹Eight orders of magnitude dynamic range has been recently achieved with this method by G. X. Cao, E. Nabighian, and X. D. Zhu, *Phys. Rev. Lett.* **79**, 3696 (1997).

¹²Xudong Xiao, Yuanlin Xie, and Y. R. Shen, *Phys. Rev. B* **48**, 17 452 (1993).

¹³Xudong Xiao, Yuanlin Xie, Christian Jakobsen, Heather Galloway, Miquel Salmeron, and Y. R. Shen, *Phys. Rev. Lett.* **74**, 3860 (1995).

¹⁴The true value of the barrier height at the steps is higher than 7.9 kcal/mol. Using a model proposed by Merikoski and Ying [*Phys. Rev. B* **56**, 2166 (1997)] for diffusion on stepped surfaces to subtract out the contribution of diffusion over terraces, we deduce $E_{\text{step}} = E_s + E_t + E_B = 9.4$ kcal/mol, with E_t, E_s, E_B being the terrace barrier, Schwoebel barrier, and the additional binding energy at the lower step edges, respectively. If we take $E_B = 7$ kcal/mol from Ref. 6, and $E_t = 4.2$ kcal/mol from our measurement, we deduce a negative $E_s = -1.8$ kcal/mol.

¹⁵J. Frohn, J. Reynolds, and T. Engel, *Surf. Sci.* **320**, 93 (1994).

¹⁶J. L. Brand, A. A. Deckert, and S. M. George, *Surf. Sci.* **194**, 457 (1988).

¹⁷M. C. Tringides, *J. Chem. Phys.* **92**, 2077 (1990).

¹⁸H. Steininger, S. Lehwald, and H. Ibach, *Surf. Sci.* **123**, 264 (1982).

¹⁹W. D. Miehler, L. J. Whitman, and W. Ho, *J. Chem. Phys.* **91**, 3228 (1989).

²⁰E. Schweizer, B. N. J. Persson, M. Tushaus, D. Hoge, and A. M. Bradshaw, *Surf. Sci.* **213**, 49 (1989).

²¹J. P. Biberian, M. A. Van Hove, *Surf. Sci.* **138**, 361 (1984).

²²D. R. Jennison, P. A. Schultz, and M. P. Sears, *Phys. Rev. Lett.* **77**, 4828 (1996).

²³D. C. Skelton, D. H. Wei, and S. D. Kevan, *Surf. Sci.* **320**, 77 (1994).