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Lateral Displacement by Transient Mobility in Chemisorption of CO on Pt(997)

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We investigated adsorbed states of CO on Pt(997) at 11 K using infrared reflection absorption spectroscopy. At 11 K, thermal migration is suppressed and thus the initial chemisorption at terrace sites and step sites is controlled by the transient mobility of the adsorbing molecule. The initial occupation ratio between atop CO on the terrace and atop CO at the step is directly determined to be 3.6:1. With a simple isotropic migration model, we estimated the mean lateral displacement from the first impact point to the initial chemisorption site to be 6.8 Å. We also discuss the origin of transient mobility of CO on metal surfaces.

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When a gaseous molecule enters a chemisorption potential well and chemisorbs on the surface, the adsorption energy has to be dissipated. This energy is transferred to not only various motions of the molecule on the surface but also electron-hole pair and phonon excitations of the substrate [1–3]. A "hot precursor" species in such energy dissipation processes is transiently mobile on the surface [4,5], which plays an important role in thin film growth, surface chemical reaction, and molecular manipulation of adsorbates [6–8]. However, the lateral displacement by the transient mobility of an incoming molecule has not been accurately determined yet, although previous scanning tunneling microscopy (STM) studies reported that the mean free path of the hot precursor O_2 on Ag(110) was on the order of 100 Å [9] and a Xe atom transiently traveled hundreds of angstroms on Pt(111) upon adsorption [10]. This Letter reports the first experimental estimation of lateral displacement of the hot precursor CO on transition metal surfaces.

We investigated the adsorbed states of CO on Pt(997) at 11 K using infrared reflection absorption spectroscopy (IRAS), where thermal migration is suppressed and the initial chemisorption at terrace and step sites is controlled by the transient mobility on the surface. When an incoming gaseous CO collides with the surface, the internal stretching vibration, rotations, and lateral translations are excited and they are dissipated into the substrate via electron-hole pair and phonon excitations [1–3], and finally the molecule is chemisorbed at a potential minimum. At sufficiently low temperature, CO molecules cannot thermally migrate on the surface. By heating the substrate, CO molecules thermally migrate on the Pt(111) terrace and all the molecules are adsorbed at the steps, since the step sites are thermodynamically more stable than the terrace sites on stepped Pt surfaces [11–16]. At very low coverage, we can accurately estimate how many molecules are initially adsorbed at terrace and step sites from the peak intensities in the IRAS spectra. We estimated the mean lateral displacement from the first impact point to the initial chemisorption site using an isotropic migration model.

Experiments were carried out in an ultrahigh vacuum chamber for a low-temperature IRAS measurement. The Pt(997) clean surface was carefully prepared by Ne ion sputtering, annealing, oxidation, and flashing cycles and checked with a 4-grid retarding field analyzer in the preparation chamber. The sample was transferred to the low-temperature chamber in which the sample holder was connected to a liquid He reservoir and surrounded by triple thermal shields. When all the windows were closed, the lowest sample temperature was 6 K, but the temperature was increased at 11 K when the shutter was open for IRAS measurements. Note that the liquid or solid N_2 cooling was not sufficient for the present purpose (thermal migration may occur). Gaseous CO at 300 K was introduced to the sample surface about 45° from the surface normal through an effusive doser. With a constant pressure in the gas line and a constant duration time of opening the pulse valve, the exposure was accurately controlled by the number of shots. IRAS measurements were performed using a modified Fourier-transform infrared spectrometer (Jasco FTIR620V) with a polarizer. A liquid N_2 cooled Mercury Cadmium Telluride detector was used. The background pressure of the chamber was less than 5×10^{-11} Torr, and it should have been better at the sample position.

Figure 1 shows a series of IRAS spectra for adsorbed CO on Pt(997) at 300 K as a function of exposure. At the initial stage, a peak is observed at 2062 cm^{-1} and the peak shifts to 2071 cm^{-1} with increasing exposure. In the middle stage (25 shots), another peak appears at 2083 cm^{-1}. The former peak can be assigned to atop CO at steps and the latter to atop CO at terraces on Pt(997), compared with the vibrational spectra of CO on stepped Pt surfaces [11,12,14–16]. With further increasing the exposure, the intensity of atop CO at the terrace is increased and the peak position is blueshifted up to 2097 cm^{-1}, but the intensity of atop CO at the step is decreased mainly due to the intensity transfer effect by the dipole-dipole interaction between step CO and terrace CO species [11,12]. In addition, a broad peak is observed between 1850–1880 cm^{-1} above the exposure of 35 shots,

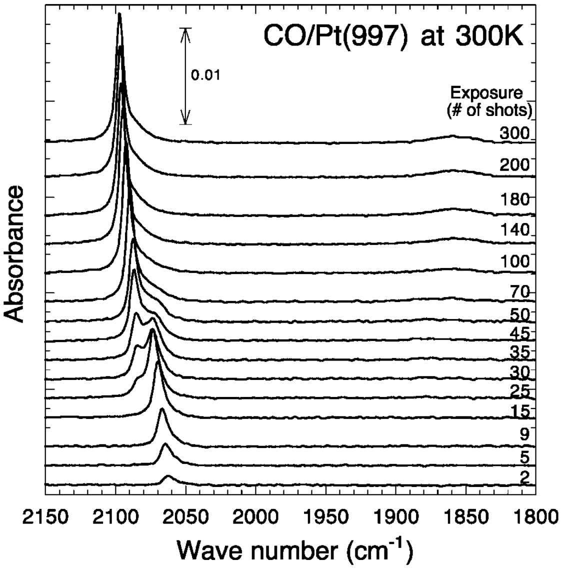

FIG. 1. A series of IRAS spectra of CO on Pt(997) at 300 K as a function of exposure. Exposure was controlled by the number of shots in opening the pulse valve. 2 cm^{-1} resolution. 750 scans for each spectrum. The estimated coverages at 2, 5, 9, and 15 shots are 0.006, 0.015, 0.027, and 0.045 ML, respectively, (1 ML = the number of surface Pt atoms). Here we assume that the saturation of atop CO at the steps on Pt(997) at 300 K corresponds to the CO adsorption on every two atoms at the steps (0.06 ML), and the sticking probability is constant at low coverages as a function of exposure.

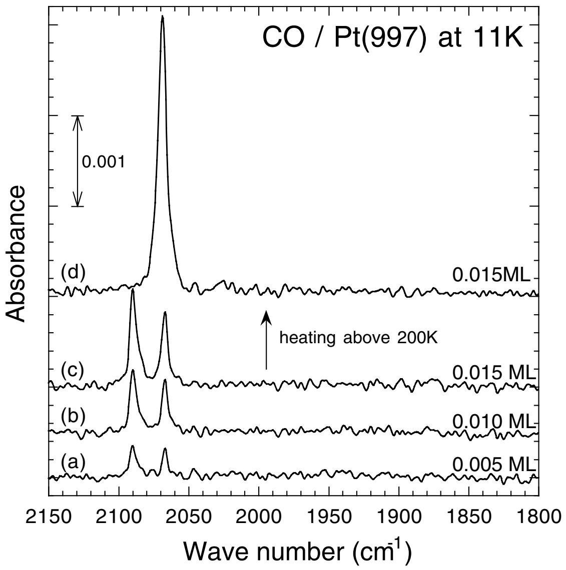

FIG. 2. A series of IRAS spectra of CO on Pt(997) at 11 K. (*a*) 0.005 ML, (*b*) 0.010 ML, and (*c*) 0.015 ML. (*d*) After heating the 0.015 ML CO adsorbed surface above 200 K and cooling to 11 K. 2 cm^{-1} resolution. 750 scans for each spectrum. The coverage was estimated from the exposure and the integrated absorbance of the peaks.

which is ascribed to the bridge CO species on Pt(997) judging from the spectra of CO on other Pt surfaces [12,15,17,18]. Thus, at 300 K the step sites are preferentially occupied at the initial stage, because adsorbed CO species can thermally migrate on the surface and become chemisorbed at thermodynamically more stable step sites. Note that the adsorption energy at step sites is 0.35 eV more stable than that at terrace sites on Pt surfaces [11,13–15].

In contrast, the adsorption behavior is quite different at 11 K. Figure 2, curves (*a*)–(*c*), show a series of IRAS spectra for adsorbed CO on Pt(997) at 11 K at a low coverage region. Two peaks are clearly observed at 2067 and 2090 cm^{-1}, and they are ascribed to atop CO at step sites and atop CO at terrace sites, respectively [11,12,14–16]. With increasing the coverage from 0.005, 0.010, to 0.015 ML (monolayer; see figure caption), two peaks do not shift. In addition, the integrated absorbance of each peak is proportionally increased. These experimental results indicate that adsorbed CO species do not interact with each other, i.e., they are singleton CO species. At 0.015 ML, the integrated absorbance at the 2090 cm^{-1} peak is $I_i(T) = 0.0086$ and that at the 2067 cm^{-1} peak is $I_i(S) = 0.0065$; the ratio is 1.32:1. Note that no bridge CO species was observed at such a low coverage region [14,17,18].

By heating the CO adsorbed Pt(997) surface, thermal migration is activated and all CO species are chemisorbed at step sites. Figure 2(*d*) shows the IRAS spectrum after heating the 0.015 ML CO adsorbed surface above 200 K and then cooling again at 11 K; terrace CO species is not observed and only atop CO at steps is observed at 2069 cm^{-1}. Since no CO molecules are desorbed by 200 K heating [11,13,15], we conclude that all CO species become adsorbed at step sites. Note that the integrated absorbance of this peak is increased to $I_f(S) = 0.0296$. This indicates that the extinction coefficient of atop CO at terrace (α_T) is smaller than that of atop CO at steps (α_S).

Since the total number of adsorbed CO molecules does not change in this heating experiment [Fig. 2, curves (*c*),(*d*)], we can set up four equations:

$$I_i(T) = \alpha_T n_i(T),$$

$$I_i(S) = \alpha_S n_i(S),$$

$$I_f(S) = \alpha_S n_f(S),$$

$$n_i(T) + n_i(S) = n_f(S).$$

Here, $n_i(T)$, $n_i(S)$, and $n_f(S)$ are the number of atop CO molecules at terraces, that of atop CO molecules at steps at 11 K, and that of atop CO molecules at steps after heating, respectively. We can safely assume that the integrated absorbance is directly proportional to the number of adsorbed molecules for each site, because they are singleton CO species and the depolarization effect can be neglected at low coverages. Using $I_i(T) = 0.0086$, $I_i(S) = 0.0065$, and $I_f(S) = 0.0296$, we obtain two important relations: $\alpha_S = 2.7\alpha_T$ and $n_i(T) = 3.6n_i(S)$.

The extinction coefficient of atop CO at the step (α_S) is a factor 2.7 larger than that of atop CO at the terrace (α_T). This agrees well with the previous report for CO on Pt(533) where the ratio was estimated to be 2.7 [11]. Since the extinction coefficient is proportional to the square of the dynamic dipole moment, the dynamic dipole moment of atop CO at the step is a factor 1.6 greater than that for atop CO at the terrace on Pt(997).

Another important result is that the initial occupation ratio between atop CO at the terrace and atop CO at the step is 3.6:1. Figures 3(a) and 3(b) show schematic diagrams for the initial chemisorption at 11 K and the rearrangement after heating above 200 K, respectively. On Pt(997) the number of terrace atoms is a factor 8 greater than that of step atoms. If a gaseous CO collides with the surface randomly and sticks at the first impact point without any migration, the occupation ratio should be 8:1. Since the thermal migration of adsorbed CO is suppressed at 11 K and the kinetic energy of gaseous CO is very small ($2kT \sim 50$ meV) as compared with the adsorption energy (~ 1.3 eV) [11,13,15–18] and the diffusion barrier (0.19 eV) [14,17,18], the transient migration must be considered in order to explain the ratio of 3.6:1. During the transient migration some adsorbed CO molecules reach steps and they are trapped at step sites, and thus the population at steps is increased.

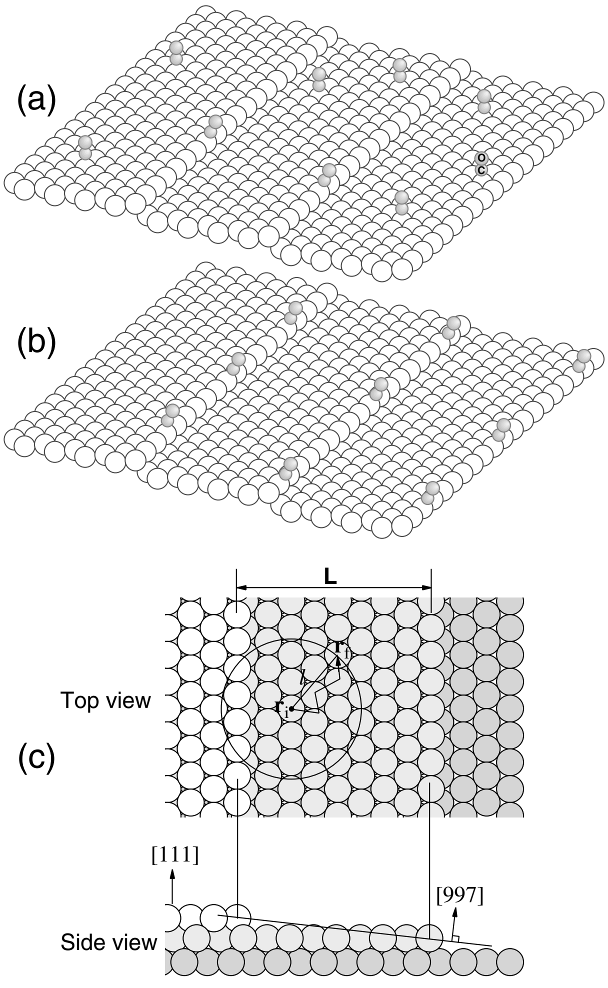

FIG. 3. (a) Schematic model of adsorbed CO on Pt(997) at 11 K and (b) that after heating above 200 K (~ 0.016 ML). (c) An isotropic migration model. $\mathbf{r}_i$: the first impact point. $\mathbf{r}_f$: the initial chemisorption site. l: the mean lateral displacement of the transient mobility. The distance between nearest neighbor Pt atoms (d) = 2.8 Å, and $L = 20$ Å on Pt(997). The estimated mean lateral displacement (6.8 Å) corresponds to $\sim 2.4d$ (see the circle in this figure).

In order to estimate the lateral displacement of transient mobility for CO on Pt(997), we introduce a simple isotropic migration model that includes the following assumptions [see also Fig. 3(c)]. (i) Gaseous CO molecules uniformly collide with the surface, and the first impact point is set to be $\mathbf{r}_i$. (ii) The transient migration occurs randomly on Pt(997), i.e., the adsorption potential is isotropic and an asymmetric potential barrier across the step (Ehrlich-Schwoebel effect) is not significant. After the transient migration, the initial chemisorption site of CO is set to be $\mathbf{r}_f$. Thus, the mean square displacement of transient mobility $l^2 = \langle | \mathbf{r}_i - \mathbf{r}_f |^2 \rangle$. (iii) Once CO moves across a step during the transient migration, it inevitably sticks at a nearby atop site on the step and does not move anymore. This assumption is reasonable because the adsorption energy at step sites is 0.35 eV more stable than that at (111) terrace on Pt surfaces. (iv) The kinetic energy of gaseous CO is neglected.

Using this simple model, the occupation probability at step sites, $P(\text{step})$, is easily calculated to be $2l/(\pi L)$, where L is the distance between steps. In the present experiment, $P(\text{step}) = 1/(3.6 + 1) = 0.217$ and $L = 20$ Å, and thus we can estimate the lateral displacement of transient mobility for CO on Pt(997) to be 6.8 Å.

Several theoretical investigations have reported the adsorption dynamics of CO on metal surfaces. The inelastic scattering and chemisorption of CO on Pt(111) was investigated using a semiclassical model including the substrate temperature and the coupling with phonon by Billing [1]. When the molecule approaches the surface, the large attractive chemisorption potential accelerates the molecule. It is excited to a rotational state and at a closer distance to the surface to a high vibrational state. Later the energy transfer to electron-hole pair (EHP) excitations in the substrate was also included [19]. Kindt *et al.* have investigated the EHP contributions to scattering, sticking, and surface diffusion of CO on Cu(100) using the molecular dynamics with the electronic frictions method [20]. They found that the coupling to EHP excitations causes a significant quenching of transient mobility. They predict that the extent of hot diffusion is limited to several Å, which may be in good agreement with the present experimental estimation. Dobbs and Doren have reported that the hindered rotational mode is most strongly coupled to EHP excitations and it correlates with the translation across the surface [21].

Transient mobility plays a crucial role in molecular manipulation on surfaces. Bartels *et al.* reported that electrons tunneling from the STM tip to an isolated CO molecule on Cu(111) induced a hop of the molecule either to the tip or to an adsite on the surface a few Å [7]. Komeda *et al.* recently reported that the excitation of the CO stretching mode with an inelastic tunneling electron induces lateral hopping of CO along the Pd$[1\bar{1}0]$ row on Pd(110) [8]. They observed the vibrationally excited CO hops over two Pd lattices (2.75 × 2 Å) from the initial position on average. The dissociation of O_2 on Pt(111) causes a nonthermal transient motion of two oxygen atoms, where the average distances are about two Pt lattice constants [22,23]. Note that in the cases of weak chemisorption [9] and physisorption [10,23,24], the length of transient mobility is hundreds of Å. In the case of physisorption, the energy dissipation via EHP excitations may not be efficient. In addition, the migration barrier is usually very small in these cases. Thus, the transient migration ranges over hundreds of Å. On the other hand, little transient mobility was reported on metal-atom adsorption on metals [25].

By taking these results into account, we surmise the scenario of CO adsorption dynamics as follows. An incoming CO molecule to the surface is accelerated by the attractive chemisorption potential and scattered by the corrugated potential at the surface. This causes various excitations including rotation, vibration, and translation. The molecule in such a hot precursor state dissipates its energy further via EHP and phonon excitations. According to the above-mentioned STM study [8], the relaxation of CO stretching energy also induces the lateral hopping by an anharmonic coupling to low energy hindered rotations/translations. Therefore, the estimated lateral displacement by transient migration in the present study includes the scattering by the corrugated potential energy surface and the lateral hopping via the relaxation of CO stretching vibration excited by the collision.

Finally, we note that the present estimation depends on the assumption of the uniform impingement to the surface. In metal deposition on metal surfaces, this assumption may not be appropriate [26,27]. However, according to the low-temperature STM study of CO on Pt(111), the nonuniform adsorption around steps was not observed [Fig. 3(a) in Ref. [23]]. This indicates that a long-range attractive interaction between CO and a step on Pt(111) is not significant. Thus, we assume the uniform impingement as a good approximation.

In conclusion, we have investigated the adsorbed states of CO on Pt(997) at 11 K by IRAS. The initial occupation ratio between atop CO on terraces and atop CO at steps is directly determined to be 3.6:1. With the simple isotropic migration model, we estimate the mean lateral displacement from the first impact point to the initial chemisorption site to be 6.8 Å.

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