

## Experimental evidence on molecular interaction in desorption and adsorption of CO molecules on metal surfaces

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**Abstract.** Adsorption and desorption of CO on Ni(100) and Pt(111) surfaces are presented. At the thermodynamic equilibrium, the site occupation between the terminal and the bridged sites are described with the free energy of the system, including the vibrational entropy. Adsorption of CO onto a cold surface as 20 K has also been studied by infrared reflection absorption spectroscopy (IRAS). The occupation ratio of bridged CO to terminal CO species on Ni(100) at 20 K ranges from ~2.8 to 0.7 at the total coverage from 0.003 to 0.15 ML. Such strong coverage dependence of the occupation ratio even at small coverages suggests that the interaction between CO molecules operates at relatively long range ( $> 10 \text{ \AA}$ ). The isotope experiments suggest that there is substantial interaction between preadsorbed (accommodated) CO species and incoming (mobile) CO species. Desorption process is also affected by the interaction between the adsorbed CO and the incoming species. The effect of temporal bimolecular CO interaction on the desorption kinetics is also discussed.

**Keywords.** CO; Ni(100); Pt(111); adsorption; IR; desorption.

### 1. Introduction

Carbon monoxide (CO) on transition metal surfaces is one of the prototype systems in the studies of thermodynamic properties, adsorbed states, adsorption/desorption kinetics and dynamics (Yates 1994). A microscopic picture of adsorption process of CO on a metal surface may be summarized as follows. When gaseous CO approaches the surface, the molecule interacts with adsorption potential. The potential depth (adsorption energy,  $E_{ad}$ ) of chemisorbed CO on transition metal surfaces is typically about 0.5–2 eV (Somarjai 1994). When the CO molecule collides with the surface, although a small part of molecules is going apart from the surface, the kinetic energy (adsorption energy + kinetic energy of gaseous CO) is transferred into various kinds of internal excitations (vibrational, rotational, electronic, phonon, etc). Usually the molecule does not stick on the surface by the first collision, and it travels on the surface ('mobile precursor states'), dissipating its kinetic energy further (Billing 1984; Doren and Tully 1991). Finally it is trapped at one of the potential minima (i.e. a certain adsorption site). After an adsorbed molecule is thermalized at the surface temperature, thermal motions of the adsorbed molecule can be excited by the heat of substrate. The statistical thermodynamic equilibrium of total adsorption system may be reached through the surface migration (hopping) of adsorbed molecules.

There are several possible adsorption sites for CO on transition metal surfaces, i.e. a terminal site, a bridged site and hollow sites. Under thermal equilibrium, the

occupation probability of each site is controlled by the free energy of adsorption (adsorption energy and entropy of the system at a certain temperature) (Schweizer *et al* 1989; Grossman *et al* 1993a, b; Yoshinobu *et al* 1993, 1994). If the surface temperature is too low to activate the surface migration, non-equilibrium adsorbed states, where molecules are initially trapped at a certain local potential minimum, may be observed. Namely, on a low temperature surface, the adsorption site occupancy is determined by the elementary adsorption dynamics and not by thermodynamic equilibrium (Yoshinobu and Kawai 1996). On the other hand, when we observe the adsorption of CO at higher temperature (e.g. room temperature), thermodynamic equilibrium between the adsorption sites is quickly achieved. Therefore, the knowledge about the initial adsorption sites at low temperature would give some new information about the probability of adsorption at a certain site.

Chemical reactions on solid surfaces are usually carried out under complex conditions of coexisting reactant and product gas molecules with high pressure ranges. One of the key phenomena to the approach of 'real surfaces' is the surface event under the existence of gaseous molecules. Even the most simple surface reaction as desorption of CO molecules from metal surfaces are known to be enhanced in the presence of gas phase CO (Yates and Goodman 1980; Yamada *et al* 1983, 1985; Yamada and Tamaru 1984a, b, 1985; Lambardo and Bell 1991; Song *et al* 1994). This effect can be explained by the temporal and local interaction of CO molecules under the equilibrium between the adsorbate and the gas phase.

## 2. Experimental

The experiments were carried out in an ultrahigh vacuum chamber, which was equipped with a three-grid retarding-field analyzer for low energy electron diffraction and Auger electron spectroscopy, a quadrupole mass spectrometer for thermal desorption spectroscopy (TDS), and gas delivering systems. The base pressure was  $< 4 \times 10^{-11}$  Torr. The details of the apparatus has been published elsewhere (Yoshinobu and Kawai 1993). The clean surfaces of Ni(100) were prepared by Ar-ion bombardment, annealing and flashing cycles and, with the oxidation cycle for Pt(111). The sample crystal was cooled down to 20 K by a cryogenic refrigerator and was heated up to 1400 K by electron bombardment from the rear. Gaseous CO was introduced onto the sample through a pulsed gas doser or a continuous gas doser (impinging rate of  $1.6 \times 10^{12}$  molecules  $\text{cm}^{-2} \text{s}^{-1}$ ), where the gas temperature was room temperature. The averaged incident angle of the doser is set about  $45^\circ$  to the surface normal. The coverage is determined from the integrated area of TDS peaks, assuming that the coverage of  $c(2 \times 2)$ -CO on Ni(100) is 0.5 ML [1 ML =  $1.6 \times 10^{15}$  molecules  $\text{cm}^{-2}$  on Ni(100)] and that of  $c(4 \times 2)$ -CO on Pt(111) is 0.5 ML [1 ML =  $1.5 \times 10^{15}$  molecules  $\text{cm}^{-2}$  on Pt(111)]. The IRAS spectra were taken with a Fourier transform infrared spectrometer (Mattson RS-1) using a mercury-cadmium-telluride detector. The clean surface is served as a background reference for an absorption spectrum.

## 3. Potential energy surface (PES) of Co on Ni(100) and Pt(111)

Terminal CO and bridged CO species are observed on Pt(111) and Ni(100) surfaces.

At thermodynamic equilibrium, the occupation probability of each site is given by minimizing the free energy of the system. When the binding-energy difference between the possible sites is large, the energetically stable site is predominantly occupied. Namely, the binding energy  $E$  controls the free energy  $F = E - TS$  in the system. However, when the difference is small the entropy factor plays an important role (Schweizer *et al* 1989; Yoshinobu *et al* 1993, 1994; Grossman *et al* 1993a, b).

Figures 1a and b show the cross sections of PES between a terminal CO and a bridged CO on Pt(111) and Ni(100), respectively, assuming harmonic curves (Schweizer *et al* 1989; Hähner *et al* 1990; Yoshinobu *et al* 1994). The curvatures are obtained from the scattering measurements and normal mode calculations (Hähner *et al* 1990). The adsorption energy difference are obtained from IRAS studies (Schweizer *et al* 1989; Yoshinobu *et al* 1993). In the case of CO on Pt(111), the microscopic migration barriers between adsorption sites have been studied. From a bridged site to a terminal site, the barrier is estimated to be 91 meV (Nekrylova and Harrison 1994), and that from a terminal site to a terminal site, the barrier is reported to be 173 meV (Reutt-Robby *et al* 1990). These values agree remarkably well with the barriers estimated from the PES assuming harmonic curves in figure 1a. However, the diffusion barriers measured by macroscopic methods are reported to be  $\sim 260$ – $550$  meV (Kwansniewski and Schmidt 1992; Croci *et al* 1993). In the case of Ni(100), the macroscopic diffusion barriers have been obtained using laser induced thermal desorption, where Roop *et al* (1987) have reported that the diffusion barrier is 200–278 meV. This value is much larger than the estimated barrier from figure 2b. Recently, the microscopic diffusion barrier of CO on Ni(100) has been reported to be  $\sim 30$  meV using quasielastic helium atom scattering (QHAS) measurement (Hofmann *et al* 1996; Bertino *et al*, to be published). The QHAS measurements are sensitive only to the diffusion process on a length scale less than about 3 nm and thus the value is considered to be the microscopic diffusion or hopping barrier of CO on Ni(100). The value is close to the diffusion barrier shown in figure 1, or even smaller. Unlike the macroscopic diffusion measurements, the microscopic diffusion experiments give the barrier height close to the harmonic curves presented in figure 2 both for Ni(100) and Pt(111) cases. In figure 1, the potential curves are plotted as a function of one direction, i.e. parallel to the surface from a terminal site to bridged site. Along the other parallel direction containing a three-fold (or four-fold) hollow site, experimental information is too scarce to describe the PES, because of the lack in the knowledge about CO species on hollow sites.

#### 4. Initial site occupation at low temperature

When the temperature is too low to activate the surface migration of the adsorbed molecules, the site occupation of the adsorbed CO may reflect the elementary adsorption dynamics rather than the thermodynamic equilibrium.

Gaseous CO was pulse-dosed on Ni(100) at 20 K and the IRAS spectra were observed. Below 20 K, no observable change in the spectra was detected within  $\sim 600$  s after the adsorption at  $t = 0$  s, indicating that the surface migration of adsorbed CO on Ni(100) at 20 K is negligibly small. Two bands are observed at  $\sim 2019$ – $2029$   $\text{cm}^{-1}$  and at  $\sim 1863$ – $1875$   $\text{cm}^{-1}$ , which are assigned to CO stretching

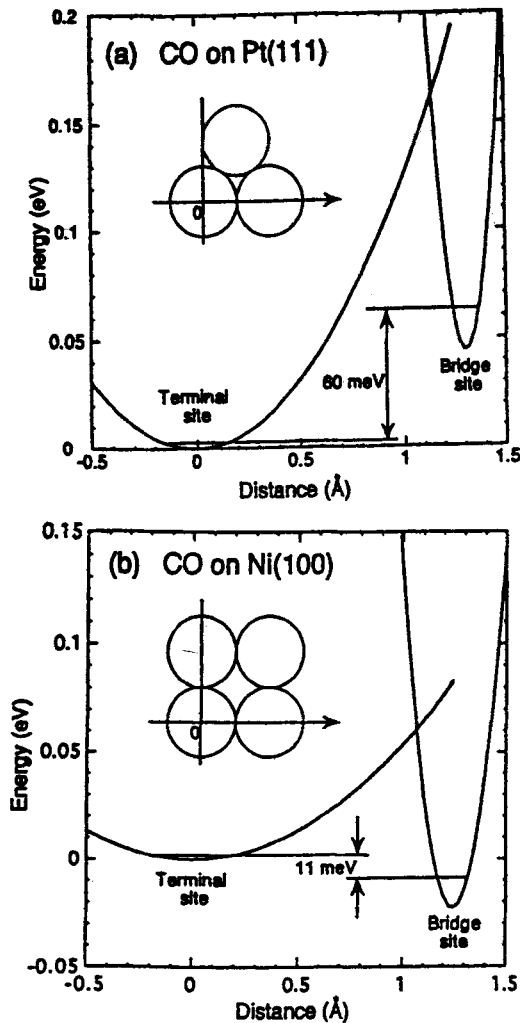


Figure 1. PES of adsorbed CO between the terminal site and the bridged site on Pt(111) (Schweizer *et al* 1989; Hähner *et al* 1990) (a) and on Ni(100) (Yoshinobu *et al* 1994) (b), assuming harmonic curves.

modes of terminal CO and bridged CO species, respectively. Since the ratio of the dynamic dipole moment of terminal CO to that of bridged CO is  $\sim 1.1$  (Grossman *et al* 1993a; Yoshinobu *et al* 1993), the fractional coverage of each site is estimated from the integrated absorbance of each CO stretching band. Figure 2 shows the ratio between the fractional coverage of bridged CO and that of terminal CO on Ni(100) at 20 K as a function of total coverage. At a very low coverage ( $\theta_{\text{total}} = 0.003$  ML), the ratio is located at  $\sim 3.1$ . With increasing  $\theta_{\text{total}}$ , the ratio rapidly decreases to 1:1 at  $\theta_{\text{total}} = 0.05$  ML, and it gradually decreases to about 0.9 above  $\theta_{\text{total}} = 0.1$  ML. Note that the observed occupation ratio is completely different from the equilibrated state, where at 20 K almost all the CO should locate at the bridged site.

There are several factors which affect the elementary adsorption dynamics, such as (1) the potential energy surface (PES) of the adsorption system, (2) the initial conditions of incident gas molecules (kinetic energy, internal energy, incident angle,

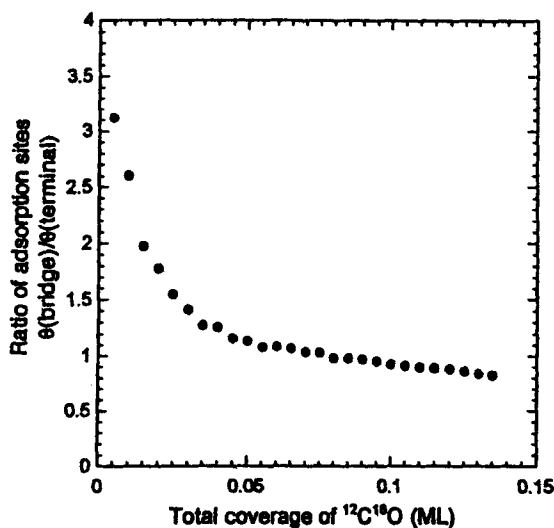


Figure 2. Occupation ratio of adsorption sites, bridged CO to terminal CO on Ni(100) at 20 K, as a function of total coverage.

etc), (3) the energy dissipation processes and (4) the surface temperature. In the case of gaseous CO molecules ( $\sim 300$  K) approaching the Ni(100) surface at low temperature, the potential energy surface and the energy dissipation processes are important, because the adsorption energy ( $> 1$  eV) is much larger than the thermal kinetic energies and also the substrate heat, which may induce the migration of adsorbed CO, is negligibly small.

One may expect that a mobile molecule just before the accommodation at a certain site prefers the site with higher density-of-states (DOS) including hindered motions and phonons, because energy could be dissipated more effectively, resulting in being accommodated in the potential well. Although the multi-dimensional PES should essentially be considered (Tully 1994), it seems that the terminal sites are occupied more than the bridge sites, judging from the shape of PES. However, in the case of Ni(100), the probability of terminal CO is less than that of bridged CO below  $\theta_{\text{total}} = \sim 0.07$  ML (figure 2). These results suggest that the above simple low-dimensional DOS picture does not explain the phenomena. In the case of CO on Pt(111), the terminal sites are more favourably occupied at low coverages (Nekrylova *et al* 1993; Nekrylova and Harrison 1994, 1996; Yoshinobu and Kawai 1996), on the contrary, where the binding-energy for the terminal site is larger than the bridge site. As far as the above two cases tell us, at the zero-coverage limit, CO molecule seems to predominantly occupy the site with larger binding-energy (Kawai and Yoshinobu 1996; Yoshinobu and Kawai 1996).

## 5. Indirect adsorption at low coverage region

As shown in figure 2, the occupation ratio of adsorption sites between terminal and bridged site changes drastically at very low coverage region. If the sticking probabilities at terminal and bridged sites are changing with CO coverage, then the site occupation ratio should differ between the preadsorbed CO and post dosed

CO. This can easily be tested by using different isotopes for preadsorbed and post dosed CO. First, 0.015 ML of  $^{12}\text{C}^{16}\text{O}$  (or  $^{12}\text{C}^{18}\text{O}$ ) was adsorbed on Ni(100) at 20 K. Then, this preadsorbed surface was exposed to 0.015 ML  $^{12}\text{C}^{18}\text{O}$  (or  $^{12}\text{C}^{16}\text{O}$ , respectively) to give  $\theta_{\text{total}} = 0.03$  ML (figure 3). The results show that these two final spectra resemble each other and almost complete mixing about adsorption sites takes place, indicating that there is substantial interaction between accommodated CO and incoming CO molecules on Ni(100) even at 20 K.

This is an indication of 'indirect adsorption' even at low coverages. In the direct adsorption mechanism, the elementary adsorption dynamics is controlled only by the interaction between the incoming molecule and the surface. On the other hand, 'indirect mechanisms' involve the interactions between adsorbate-adsorbate and/or between adsorbed molecules and incoming molecules. Once the molecules are accommodated on a low temperature surface, the self migration is suppressed. However, it is possible that transient 'mobile' molecules interact with the molecules already accommodated on the surface and induce the site-change. The interaction

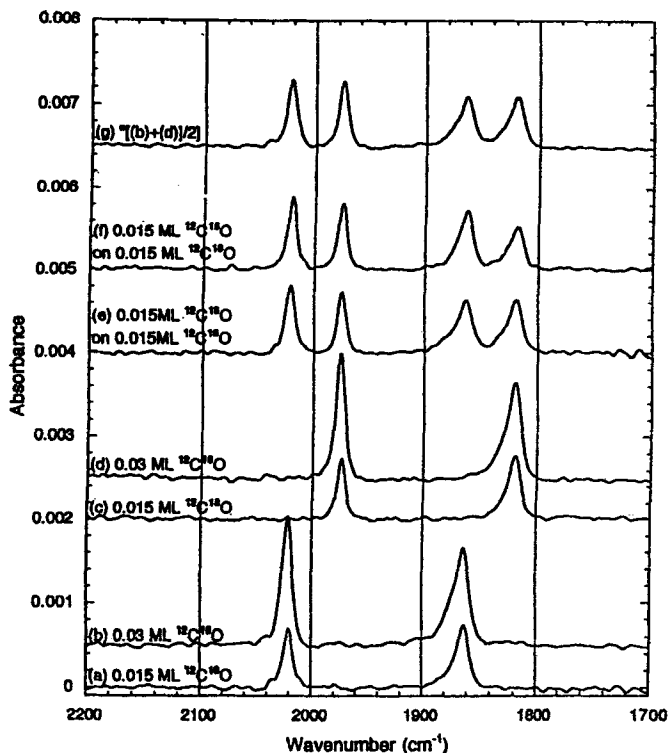


Figure 3. IRAS spectra of adsorbed CO on Ni(100) at  $\sim 20$  K. Absorption bands at  $\sim 2020$   $\text{cm}^{-1}$  and  $\sim 1860$   $\text{cm}^{-1}$  are due to the  $^{12}\text{C}^{16}\text{O}$  stretching vibration of terminal CO and bridged CO, respectively (a and b). These two bands are observed at  $\sim 1980$   $\text{cm}^{-1}$  and  $\sim 1820$   $\text{cm}^{-1}$  for  $^{12}\text{C}^{18}\text{O}$  (c and d). It is clear that the intensity ratio between the terminal and bridge CO is different when the coverages increases from 0.015 ML to 0.03 ML (a, b and c, d). Spectrum (e) represents 0.015 ML  $^{12}\text{C}^{18}\text{O}$  adsorbed on 0.015 ML  $^{12}\text{C}^{16}\text{O}$  preadsorbed surface and (f) represents the other way round. Artificially convoluted spectrum of (b) and (d) is shown in (g). See the similarity in spectra (e), (f) and (g).

probability depends on the cross-section and the life time of such mobile state, i.e. the travelling length. As a result of the interaction (or collision on the surface), lateral translational energy of transient mobile CO could be dissipated effectively near the adsorbed CO site, and thus it is finally accommodated in close proximity to the adsorbed CO on the surface. In this situation, the site-conversion of the preadsorbed CO may also take place by the interaction with mobile CO molecules. Based on 'indirect mechanisms', the isotope mixing between preadsorbed CO and post dosed CO can be explained (Kawai and Yoshinobu 1996). Similar collisional site conversion of adsorbed CO from terminal site to bridged site has been reported on Pt(111) (Nekrylova and Harrison 1996).

## 6. Desorption of CO under the existence of gas phase

Interaction between the adsorbed and incoming CO molecules also play an important role during the desorption as well. Direct observation of dynamical equilibrium between the preadsorbed CO and gas phase CO exhibited that the desorption path induced in the presence of gas phase CO is described by

$$\sum \sigma_i \theta F^i,$$

where  $\sigma_i$  is the desorption probability when the temporal CO clusters are formed between the adsorbed CO molecule and the CO molecules incident from the gas phase to the adsorbed phase (flux induced desorption). Under a dilute flux condition ( $F < 10^{-1}$  ML  $s^{-1}$ ) the higher terms ( $i \geq 2$ ) in the summation can be neglected and the reaction becomes bimolecular. For CO molecules on Ni(100) and on Pt(111) surfaces the temporal bimolecular CO cluster, adsorbed at nearby sites, exhibits repulsive interaction resulting in the enhancement in the desorption rate. At higher surface temperature region, accommodation time of the adsorbed CO decreases and the effective temporal cluster formation becomes negligible (Kawai *et al* 1966; Takagi *et al* 1994).

## 7. Summary

At the thermodynamic equilibrium, the site occupation between the terminal and the bridged sites on Ni(100) is described with the free energy of the system, including the vibrational entropy. On low temperature surfaces, surface migration of adsorbed CO molecules is effectively suppressed, and thus the occupation of adsorption sites is controlled by elementary adsorption dynamics and not by equilibrium thermodynamics. The occupation ratio of bridged CO to terminal CO species on Ni(100) at 20 K ranges from  $\sim 3.1$  to 0.8 at the total coverage from 0.003 to 0.15 ML. It seems suitable to consider contributions of two different surface processes. When CO molecules approach the surface without any encounter with adsorbed molecule, molecule seems to be trapped preferentially to the site with larger binding-energy ('direct adsorption'). On the other hand, when a molecule happens to encounter the preadsorbed molecule or sites perturbed by the preadsorbed molecule, interaction between the adsorbed molecules may induce the stabilized

preadsorbed molecules to hop to a different site ('indirect adsorption'). Desorption of CO from Ni(100) and Pt(111) surfaces under the existence of gas phase CO is found to be enhanced by the formation of temporal bimolecular CO cluster, adsorbed at nearby sites, exhibiting repulsive interaction resulting in the reduction of the adsorption potential.

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