

Displacement of chemisorbed ^{12}CO from Pd{110} by adsorbing hot precursor ^{13}CO molecules

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The dynamic displacement from CO precovered Pd{110} surface by incident CO is investigated as a function of surface temperature and translational energy by employing a molecular beam surface scattering technique with supersonic molecular beams of isotopically labeled ^{13}CO . A strong and kinetically prompt displacement of preadsorbed ^{12}CO by incoming ^{13}CO molecules is observed. The displacement kinetics are found to be only weakly dependent on the translational energy. The activation energy of desorption for CO in an adlayer of 0.65 ML is found to decrease from 1.3 eV to 52 meV due to the presence of gas phase CO. Direct collision induced desorption, thermodynamic displacement, and dynamical displacement processes such as collisions with hot precursors, local hot-spot formation, and electronic nonadiabaticity are discussed.

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I. INTRODUCTION

In the past, the mechanisms of CO adsorption and desorption have been extensively investigated on a wide variety of transition metals. This interest stems from the central role that CO plays in several technologically important surface processes such as automotive and process catalysis or more recently in fuel cell technology where CO acts not as a reactant but a reaction inhibitor. As a result, the kinetics and dynamics of CO adsorption and desorption are well known from experiments conducted under ultrahigh vacuum (UHV) conditions. However, under UHV conditions the gas phase molecules have large mean-free paths and hence, their energetics are determined by the ambient temperature of the surroundings (i.e., UHV chamber walls), which often equals to ~ 300 K. This has obvious implications on how well we can relate molecular level information obtained in UHV experiments to the results from experiments conducted at elevated pressures, where the number of highly energetic molecules is non-negligible and the low rates of highly activated processes are compensated by the high molecular flux to the surface.

In the early “isotope jump” experiments by Yamada *et al.*^{1–3} it was observed that the dynamic equilibrium between the gas phase CO and the CO adlayer on Rh, Ru, and Pd surfaces was maintained by an exchange process in which the incident gas phase CO induced desorption from the adlayer. These experiments were, however, carried out in a background pressure of CO and consequently, only a limited amount of information about the kinetics of the exchange mechanism or molecular level detail was obtained. A pioneering molecular beam study of NO adsorption on CO/Ni{100} by Hamza *et al.*⁴ demonstrated that extremely detailed information concerning displacement mechanisms can be obtained in UHV by employing supersonic molecular beams. The use of a nearly monoenergetic and highly collimated supersonic beam allowed the energy selective probing of the displacement process up to the high-energy tail of the Maxwell-Boltzmann distribution of the gas phase molecules without the need for high pressures or temperatures.

Since then other molecular beam investigations have shown that not only desorption of molecules^{5–12} but a wide

variety of surface processes are activated by the interaction between the gas phase species and adsorbates. Atoms and molecules incident from the gas phase facilitate surface processes such as dissociation of molecules,¹³ recombinative desorption of atomic species,¹⁴ migration of adsorbates,¹⁵ and even chemical reactions between two coadsorbed species.¹⁶ It is evident that the interactions between gas phase species and the adlayer can affect virtually every elementary surface reaction step and more experiments are required in order to better understand when these interactions need to be taking into account and how they may modify surface processes.

In this manuscript we employ a supersonic molecular beam and isotopically labeled CO to investigate the effect of ^{13}CO molecules impinging on a ^{12}CO precovered Pd{110} surface. We find that the incident ^{13}CO molecules effectively disrupt the adlayer, leading to rapid ^{12}CO displacement and subsequent ^{13}CO adsorption. The displacement mechanism is operative both at low (27.4 meV) and high (276 meV) translational energies (E_T) of the incident CO molecules and only weakly dependent on the surface temperature (T_S). Based on our experimental results we argue that the CO displacement is driven by a dynamic displacement mechanism involving a hot-precursor state for CO molecules.

II. EXPERIMENT

We employed in our experiments a supersonic molecular beam apparatus described in detail elsewhere.¹⁷ The 9 mm \times 9 mm Pd{110} single crystal surface (Metal Crystals and Oxides, Ltd.) was cleaned by Ar⁺-ion bombardment at 900 K followed by annealing at 1050 K and reactive oxygen treatments.¹⁸ The CO beam flux (~ 0.1 ML s⁻¹, 1 ML = 9.4×10^{14} cm⁻²) was calibrated with a capillary calibrated leak of a known flux. E_T of the molecular beam was varied in the range of 24.7–276 meV by seeding CO in He, Ar, or Kr at a constant nozzle temperature of 300 K. The E_T distribution of the molecular beam was determined for every experiment by using the time-of-flight (TOF) technique. The rotational temperature of CO molecules was also determined from the width of the E_T distribution¹⁹ and was always found to be less than 50 K. Prior to each measurement Pd{110} was saturated with ^{12}CO at 350 K by backfilling the chamber with

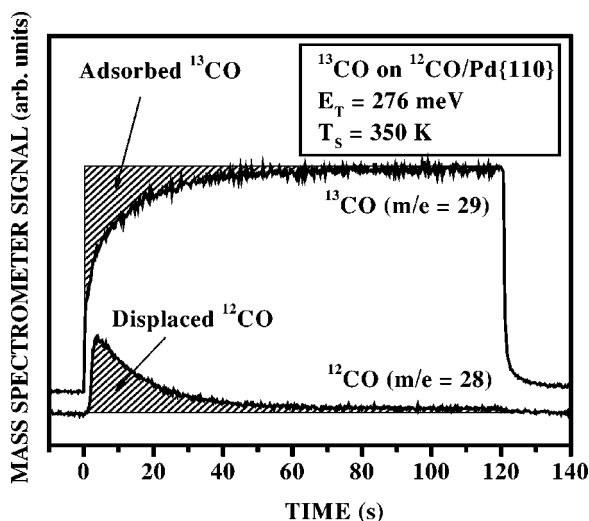


FIG. 1. An experiment showing strong ^{12}CO ($m/e=28$) displacement from a saturated $^{12}\text{CO}/\text{Pd}\{110\}$ by an incident ^{13}CO ($m/e=29$) molecular beam as determined by quadrupole mass spectrometer (QMS). The surface temperature (T_s) was 350 K and the translational energy (E_T) of ^{13}CO molecules was 276 meV. Hatched areas correspond to ^{13}CO uptake and the displaced ^{12}CO .

^{12}CO . The saturation coverage at 350 K is 0.65 ML leading to the formation of a $\text{Pd}\{110\}c(4\times 2)\text{-CO}$ phase²⁰ which was confirmed by low-energy electron diffraction (LEED). Subsequently, the ^{12}CO atmosphere was pumped off prior to setting the surface temperature for the experiment and switching on the ^{13}CO beam for 120 s. Both ^{12}CO and ^{13}CO signals were measured simultaneously during the ^{13}CO exposure. A variable aperture plate in our beam apparatus allowed experiments to be performed both on the entire sample area ($\varnothing_{\text{beam}}=1.6$ cm) and only on the central part of the sample ($\varnothing_{\text{beam}}=0.8$ cm). All displacement experiments were conducted by utilizing the 0.8 cm beam. Temperature programmed desorption (TPD) experiments were carried out after each beam experiment in order to determine the final ^{12}CO and ^{13}CO coverages and to detect any CO dissociation. Potential beam patch effects in adsorption and displacement kinetics as well as in TPD spectra were controlled by repeating some experiments with 0.8 and 1.6 cm beams. Our experimental setup did not permit angle-resolved measurements. All sticking probabilities (S_0) reported in this manuscript have been determined by using the direct reflectivity method by King and Wells.²¹ Reaction gases ^{12}CO (99.9%) and ^{13}CO (99% isotopic purity), He (99.9999%), Ar (99.9999%), and Kr (99.995%) were supplied by AGA, Ltd. (Finland).

III. RESULTS

Figure 1 shows a typical experiment in which a beam of ^{13}CO ($E_T=276$ meV) seeded with He is directed at a ^{12}CO precovered $\text{Pd}\{110\}$ surface ($\theta_{^{12}\text{CO}}=0.65$ ML and $T_s=350$ K) at normal incidence while the mass spectrometer signals for $m/e=29$ (^{13}CO) and $m/e=28$ (^{12}CO) are simultaneously monitored. At $t=0$ s the beam shutter is opened

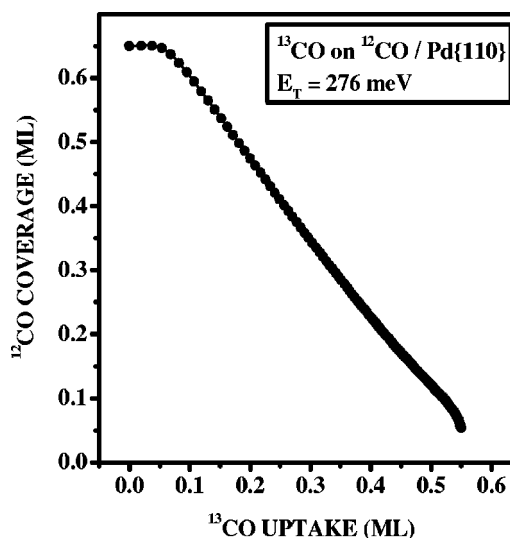


FIG. 2. ^{12}CO coverage as a function of ^{13}CO uptake during the ^{13}CO beam exposure on a saturated $^{12}\text{CO}/\text{Pd}\{110\}$ at 325 K. Translational energy of ^{13}CO molecules was 276 meV.

and the ^{13}CO molecules impinge on the surface. The beam shutter is closed at $t=120$ s. The uptake of ^{13}CO and the desorption of ^{12}CO are indicated by the hatched areas. The most striking feature in Fig. 1 is the kinetically prompt and continuous desorption of ^{12}CO during ^{13}CO exposure. ^{12}CO desorption rate peaks at the beginning of the experiment and subsequently decreases in an exponential fashion. The ^{13}CO uptake is also significant. The high S_0 (~ 0.6) for ^{13}CO adsorption on the precovered $^{12}\text{CO}/\text{Pd}\{110\}$ is interesting, considering that the surface was initially saturated with CO. This high S_0 and the rate at which ^{12}CO desorption proceeds during the beam exposure are clear evidence of a dramatic disruption of the $c(4\times 2)$ ^{12}CO adlayer by incident ^{13}CO . The analysis of the uptake curve reveals that the adsorption kinetics for ^{13}CO on $^{12}\text{CO}/\text{Pd}\{110\}$ are Langmuirian: S_0 decreases linearly with the increasing ^{13}CO coverage and does not exhibit the Kisliuk-like behavior unlike on the clean $\text{Pd}\{110\}$.^{18,22}

Figure 2 presents the ^{12}CO coverage ($\theta_{^{12}\text{CO}}$) as a function of the ^{13}CO uptake coverage ($\theta_{^{13}\text{CO}}$) on $\text{Pd}\{110\}$ at 325 K as determined for the initial ^{12}CO coverage of 0.65 ML. E_T was 276 meV. ^{12}CO is displaced at a relatively constant rate and the total coverage remains constant at 0.65 ± 0.05 ML. The constant total CO coverage and the linear trend can be considered as evidence of a displacement mechanism in which, on average, each ^{13}CO molecule induces the displacement of one ^{12}CO molecule. The plateau in the low ^{13}CO coverage regime (up to 0.05 ML) is most likely caused by the different detection limits for ^{12}CO and ^{13}CO . Due to higher background level of ^{12}CO , our detection limit is close to 0.05 ML for ^{12}CO , whereas the detection limit for ^{13}CO is lower by order of magnitude. After a sufficiently long ^{13}CO exposure, the entire ^{12}CO adlayer is eventually displaced and the surface is entirely covered by the ^{13}CO molecules.

The temperature programmed desorption (TPD) spectra in Figures 3(a) and 3(b) were measured following a ^{13}CO beam exposure ($E_T=276$ meV) on a $^{12}\text{CO}/\text{Pd}\{110\}$ surface at 300

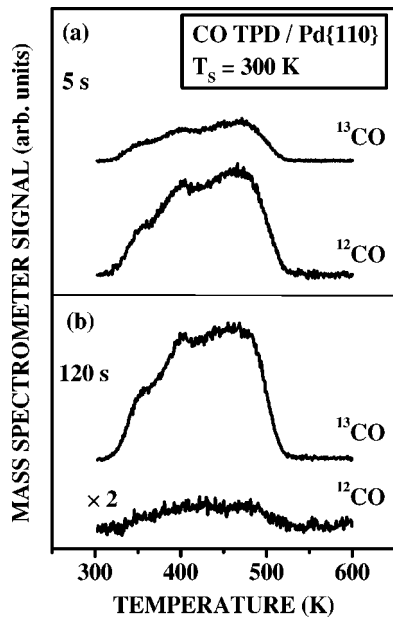


FIG. 3. Temperature programmed desorption (TPD) experiments conducted after a saturated $^{12}\text{CO}/\text{Pd}\{110\}$ surface was exposed to a 276 meV ^{13}CO molecular beam at 300 K for (a) 5 s and (b) 120 s. A linear heating rate of 3 K/s was employed.

K ($\theta_{^{12}\text{CO}} = 0.65 \text{ ML}$). In the Fig. 3(a) $^{12}\text{CO}/\text{Pd}\{110\}$ was exposed to ^{13}CO for 5 s. The subsequent TPD shows that most of the ^{12}CO adlayer is still intact, but a buildup of ^{13}CO can already be seen. Exposing the $^{12}\text{CO}/\text{Pd}\{110\}$ surface to ^{13}CO for 120 s led to the displacement of most of the ^{12}CO layer as shown by Fig. 3(b). Both experiments confirm that the thermal desorption from the coadsorbed $^{12}\text{CO}-^{13}\text{CO}$ adlayer exhibits the same TPD features that have been reported previously from the pure ^{12}CO adlayer.²³ No new desorption features or shifts in the peak positions can be seen. Furthermore, the 5 s exposure and the subsequent TPD demonstrate that the adsorbed ^{12}CO molecules are not being selectively

replaced by ^{13}CO from any particular adsorption sites. No formation of CO_2 or other carbon compounds was observed, thus confirming that no CO dissociation had occurred during the experiments.

Figure 4 shows the effects of T_S and E_T on the ^{12}CO displacement by ^{13}CO on Pd{110}. Experiments were conducted at $T_S = 200\text{--}350 \text{ K}$ for $E_T = 27.4 \text{ meV}$ and $E_T = 276 \text{ meV}$. Displacement experiments could not be performed above 350 K due to the thermal desorption of ^{12}CO . As was already seen in Fig. 1, the results in Fig. 4 do not exhibit any discernible delay between the onset of the displacement and the opening of the beam flag. High T_S was found to increase the rate of ^{12}CO displacement. This can be attributed to the weakening of the CO-Pd bond at higher temperatures. For high E_T the initial displacement of ^{12}CO is fast, whereas low E_T yields somewhat lower initial rates and slower decay.

This data set allows us to estimate the cross section for the preadsorbed ^{12}CO displacement by the incident ^{13}CO molecules by employing the rate-equation model by Takagi *et al.*²⁴ In Takagi's kinetic model, the desorption of adsorbed CO can proceed via two pathways: (i) isothermal desorption into vacuum and (ii) desorption induced by the gas phase CO. Desorption is accompanied by adsorption at a vacant site or by the displacement of a preadsorbed CO molecule. The model consists of following three rate equations for preadsorbed ^{12}CO coverage (θ_{28}), impinging CO coverage (θ_{29}) and total coverage (θ),

$$-\frac{d\theta_{28}}{dt} = k\theta_{28} + \frac{1}{2}\sigma\theta_{28}F_{29}, \quad (1)$$

$$\frac{d\theta_{29}}{dt} = -k\theta_{29} + \frac{1}{2}\sigma\theta_{28}F + s(\theta)F_{29}, \quad (2)$$

$$-\frac{d\theta}{dt} = k\theta - s(\theta)F, \quad (3)$$

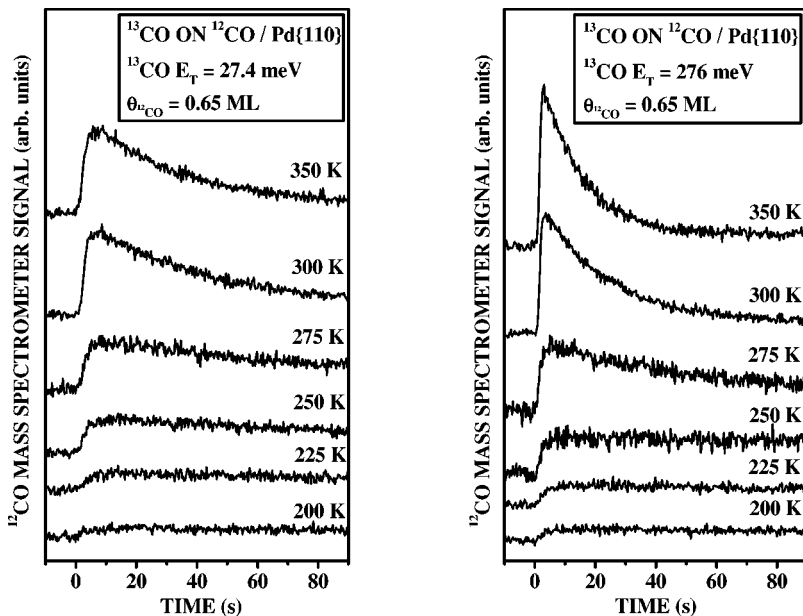


FIG. 4. CO displacement transients showing ^{12}CO mass spectrometer signal as a function of ^{13}CO exposure time on a saturated $^{12}\text{CO}/\text{Pd}\{110\}$ at 200–350 K for ^{13}CO translational energies of 27.4 and 276 meV.

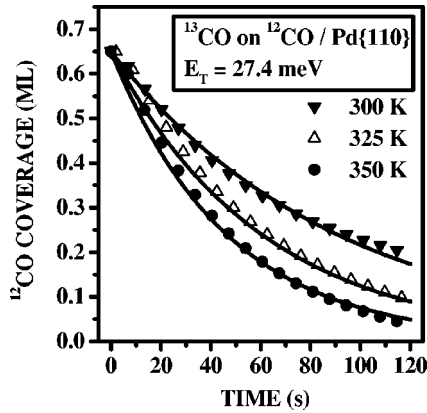


FIG. 5. Selected plots of the ^{12}CO coverage as a function of ^{13}CO ($E_T=27.4$ meV) exposure time on a saturated $^{12}\text{CO}/\text{Pd}\{110\}$ at 300 (▼), 325 (△), and 350 K (●). Solid lines correspond to fits to a Polanyi-Wigner function.

where F is the incoming flux (molecule/cm 2 s), σ is the cross section (cm 2 /molecule) for displacement, k_1 is the rate constant for isothermal desorption of CO, and $s(\theta)$ is the coverage dependent sticking probability of CO. The molecular beam flux was known and $s(\theta)$ was experimentally determined. The unknown parameters (k_1 and σ) were obtained by fitting the Takagi's model to the experimental data shown in Fig. 4. Figure 5 shows the quality of the fit at selected surface temperatures for $E_T=27.4$ meV. Similar results were obtained for the higher translational energy.

Figure 6 presents the cross-section (σ) for ^{12}CO displacement by ^{13}CO on Pd{110} as a function of inverse surface temperature for incident E_T of 27.4 meV and 276 meV. The solid lines represent fits of the Polanyi-Wigner function $\sigma = \sigma_0 \exp(E_D/RT)$ to the data where σ_0 is the preexponential factor, E_D the activation energy of desorption, R the gas constant, and T_S the surface temperature. The cross section for ^{12}CO displacement at 300 K is almost the same at low and high E_T with $\sigma(27.4$ meV) = 3.73×10^{-16} cm 2 /CO molecule and $\sigma(276$ meV) = 3.30×10^{-16} cm 2 /CO molecule. It can be seen that the cross section for $^{12}\text{C}^{16}\text{O}$ induced desorption from $^{13}\text{C}^{18}\text{O}/\text{Ni}\{100\}$ (Ref. 24) is one order of magni-

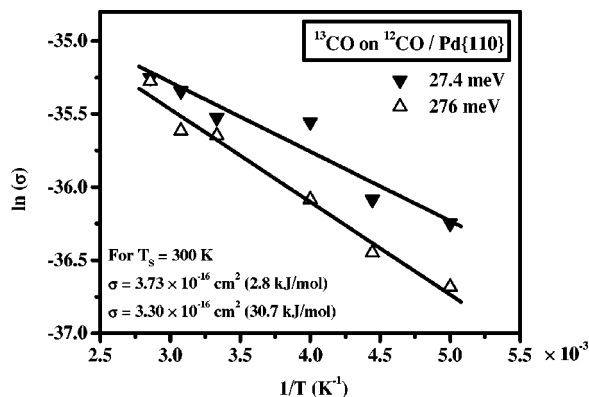


FIG. 6. Cross-section (σ) of ^{12}CO displacement on $^{12}\text{CO}/\text{Pd}\{110\}$ as a function of the inverse surface temperature (T_S) for 27.4 meV (▼) and 276 meV (△) ^{13}CO molecules.

tude higher ($3.5-6.6 \times 10^{-15}$ cm 2 /CO molecule) than our result for CO/Pd{110}, although their results were obtained at $T_S=368-400$ K. A better agreement is found with cross sections obtained from other systems such as Kr+N $_2$ /Ru{001} (2.5×10^{-15} cm 2 /Kr atom), 10 H+CO/Cu{111} ($\sim 1 \times 10^{-16}$ cm 2 /H-atom), 7 and D+N $_2$ /Ru{001} (7.6×10^{-16} cm 2 /D atom). 25 The fits yield an E_D of 44 meV which is dramatically less than that of ~ 1.1 eV reported by Raval *et al.* for CO/Pd{110} without the gas phase CO. 20 In comparison, on CO/Ni{100} the presence of the gas phase CO reduced the activation energy of desorption from 1.4 eV to 224 meV. 24

IV. DISCUSSION

The major finding of this work is the rapid and eventually complete displacement of the CO chemisorbed layer on Pd{110} by gas phase CO. Furthermore, our energy selective molecular beam experiments show that the displacement mechanism is almost equally effective at high incident energies as well as for the low E_T CO molecules typically found in a Maxwell-Boltzmann gas at room temperature. As the displacement process does not significantly depend on the E_T of the impinging molecules, it seems likely that the displacement process is as efficient with Maxwell-Boltzmann gas (for instance, in the case of backfilling the chamber with CO) as it is in our molecular beam experiments. In the discussion below, we consider the following mechanisms: (i) direct collision induced desorption, (ii) thermodynamic displacement, (iii) dynamic displacement by hot-spot formation, hot-precursors, or electronic nonadiabaticity.

In collision induced desorption either a direct collision of incident ^{13}CO with preadsorbed ^{12}CO or a collision between the impinging ^{13}CO and a neighboring Pd atom results in the desorption of a chemisorbed ^{12}CO molecule. This displacement mechanism has been found to be operative, in particular at high incidence energies, for CO+O $_2$ /Pt{111} (Ref. 11) and Xe+O $_2$ /Ag{110}, 13 Ar+CH $_4$ /Ni{111}. 6 If the ^{12}CO desorption transient observed in Fig. 1 were collision induced, a heavy inert atom with a sufficiently high E_T should induce a similar desorption transient. This collision induced desorption mechanism was investigated by repeating the experiment shown in Fig. 1 by using a high-energy Kr beam ($m_{\text{Kr}}=84$ a.m.u., $E_T=1.03$ eV) instead of ^{13}CO . The direct mechanical energy transfer between the Kr atoms in the molecular beam and the chemisorbed CO molecules was estimated to be 75% of the translational energy of the Kr atoms in the Baule (impulsive) limit. 26 Similarly, in a Kr-Pd collision 98% of the E_T of the Kr atom is transferred to a Pd atom. These values are already close to chemisorption energy of the CO molecules on Pd{110} (~ 1.1 eV). 20 Yet, energetic Kr atoms did not induce any detectable ^{12}CO desorption. This indicates that the rapid ^{12}CO desorption shown in Fig. 1 cannot be attributed to the direct collision induced desorption mechanism or to the mechanical disruption of the lattice near the adsorbate as was suggested for Xe-induced recombinative desorption of D from Ni{111}. 27 However, this experiment leaves open the role of internal degrees of freedom of impinging molecules, which will be discussed later.

In the thermodynamic displacement mechanism, the desorption of the adsorbed species is facilitated by the strongly bound adsorbate forcing the more weakly bound species to a local higher coverage in which the increasing lateral interaction eventually becomes repulsive. This mechanism has been previously associated with the displacement of Xe from Pt{111} by CO adsorption.²⁵ However, since we employed chemically identical CO species in our experiments such compression mechanism is not very plausible. Bending and tilting of the adsorbed ^{12}CO by incident ^{13}CO could, conceivably, increase the strength of lateral interactions. However, we note that no new features or shifts can be seen in the TPD spectra in Figs. 3(a) and 3(b). The absence of shifts suggests that the mixed ^{12}CO - ^{13}CO adlayer is not significantly compressed. Also, if the lateral interactions play a critical role one would expect to see preferential displacement of the more weakly bound ^{12}CO . This would result in the population of the low temperature TPD state by ^{13}CO at ~ 400 K. However, both the high temperature TPD feature at 475 K and the low-temperature shoulder are equally occupied as seen in Figs. 3, thus providing us strong enough evidence against the thermodynamic displacement mechanism.

Dynamic displacement mechanisms are characterized by the nonthermal manner by which an incident gas phase molecule removes surface bound species. Dynamic mechanisms have been previously associated with the displacement of mostly molecular adsorbates (N_2 , CO, and O_2) by reactive atoms (O, N, and H) (Refs. 7, 8, 10) although displacement by incoming molecules has also been reported.^{5,11} The details of the energy transfer process are still largely unknown and several explanations ranging from hot precursors and local hot spots to the creation of electron-hole pairs have been proposed.

The creation of electron-hole pairs in general is known to require large charge transfers and the formation of the strong CO chemisorption bond could certainly involve such processes. Upon CO chemisorption on Pd charge is transferred both from molecule's 5σ orbitals into the surface with concomitant back donation from the metal into $2\pi^*$ orbitals of the CO molecule. In their elegant paper Diekhöner *et al.*²⁵ employed H and D atoms to distinguish between the effects of electronic nonadiabaticity and hot precursors in the displacement of N_2 on Ru{0001}. In their experiments, a different isotopic effect was expected depending on whether the electron-hole pair creation played an important role or if mechanical energy transfer (hot spot or hot precursor) dominated. Unfortunately, relatively heavy molecules such as CO render any isotopic effects negligible and thus we cannot employ Diekhöner's method to determine the extent of nonadiabatic electronic effects on Pd{110}.

In both hot-precursor and hot-spot mechanisms the energy required for displacement is supplied by the thermalization of the incident molecule and these mechanisms essentially differ only in how fast the thermalization process is.²⁵ A local hot spot is created when the thermalization occurs in a time scale comparable to the lattice relaxation times. The released energy disrupts the bonds between the surface and the neighboring adsorbates leading to displacement.

Displacement mediated by a hot-spot formation on a saturated $^{12}\text{CO}/\text{Pd}\{110\}$ surface would require efficient trapping of ^{13}CO into an extrinsic precursor state before it could migrate to an adsorption site and chemisorb. The existence of an extrinsic precursor state would also support the high S_0 in seen Fig. 1 and such a process has, in fact, been suggested to account for the NO adsorption on a saturated $\text{CO}/\text{Ni}\{100\}$.⁴ Therefore, a similar explanation could in principle be invoked here. However, we find S_0 for ^{13}CO chemisorption on $^{12}\text{CO}/\text{Pd}\{110\}$ and the displacement cross section (see Fig. 6) to be independent on E_T . This is in contrast to the results from $\text{NO}+\text{CO}/\text{Ni}\{100\}$ where the presence of a precursor state resulted in decreasing S_0 with increasing E_T .⁴ Thus our results would seem to rule out the existence of the classical precursor state and consequently the hot-spot mechanism.

A hot precursor, on the other hand, is characteristic of systems featuring highly corrugated adsorbate-surface potential energy surfaces (PES). In this mechanism, a significant amount of the molecule's incident energy is converted by the convoluted PES into parallel motion along the surface and/or into the rotational and vibrational states of the molecule *before the impact*. In our previous investigation we found that the CO chemisorption on a clean Pd{110}, particularly at low E_T , is dominated by a steering-mediated hot-precursor channel.²⁸ It is conceivable that a similar hot precursor could play a role in the efficient ^{12}CO displacement. Although the thermalization of a hot-precursor molecule is slow and the energy transfer to the lattice at each point of impact is small in comparison with the hot spot mechanism, the parallel momentum increases the probability of a collision with a nearby adsorbate and thus promotes displacement. Furthermore, unlike an approaching CO molecule which will strongly prefer to point its carbon end towards Pd{110} upon adsorption, a cartwheeling hot-precursor molecule on top of the CO adlayer will inevitably end up in highly unfavourable configurations where the oxygen ends of the two CO molecules point towards each other. The resulting mutual repulsion would certainly further enhance the displacement rate of the chemisorbed CO molecules. A similar argument was recently made by Möller *et al.* to account for the CO displacement from Ni{100} by NO.⁵ In our opinion, this is the only remaining mechanism that is consistent with our experimental observations. Therefore, we argue that a hot-precursor mediated process, similar to the one we previously observed for CO chemisorption on a clean Pd{110}, is indeed responsible for the efficient displacement kinetics seen in Fig. 1.

V. SUMMARY AND CONCLUSION

The present study shows that a strong and kinetically prompt displacement of preadsorbed ^{12}CO is induced by incident ^{13}CO molecules. ^{13}CO molecules readily adsorb on $^{12}\text{CO}/\text{Pd}\{110\}$ with $S_0 \sim 0.6$ eventually displacing the entire adlayer. The displacement process is found to be operative both at low and high incident translational energies of CO. Thus, the CO displacement may be an important reaction step on Pd{110} and possibly other Pd surfaces under high pressure reaction conditions. We find the displacement to be dependent on surface temperature which is a result of the

CO-Pd bond weakening with the increasing surface temperature. The activation energy of desorption for CO in an adlayer is found to decrease from ~ 1.1 eV to a mere 44 meV in the presence of adsorbing CO. Direct collision induced desorption, thermodynamic displacement, and dynamical displacement processes such as hot precursors, local hot-spot formation and electronic nonadiabaticity are discussed. Hot precursors possibly combined with nonadiabatic electronic effects are found to be responsible for the observed displacement phenomenon. In order to further elucidate the role of the electronic structure and indeed the exact nature of the dynamic displacement mechanism, detailed calculations

would be required. Ideally one should seek to determine the potential energy surface for a CO molecule approaching a saturated CO/Pd{110} surface followed by classical molecular dynamics (see Ref. 29) with which the dynamics of the displacement process could be observed and correlated with the surface electronic structure.

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