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CO-induced restructuring of $Pt(110)-(1 \times 2)$: Bridging the pressure gap with high-pressure scanning tunneling microscopy

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We present an extensive investigation of CO-induced structural transformations occurring on the reconstructed Pt(110)- (1×2) surface while bridging the so-called pressure gap between surface science and industrial catalysis. The structural changes are followed on the atomic scale as a function of CO pressure over 12 orders of magnitude, up to 1 bar, by the use of a novel high-pressure scanning tunneling microscope (HP-STM). The transition between the low-coverage and saturation-coverage structures is found to proceed through local displacements of substrate Pt atoms. The structural transformations of the Pt surface as observed by STM can be explained within a very simple picture governed by the gain in CO binding energy when CO binds to low-coordinated metal atoms. (© 2003 American Institute of Physics. [DOI: 10.1063/1.1540611]

I. INTRODUCTION

A major issue to the catalytic community concerns the validity of applying surface science data obtained under rarified ultra high vacuum (UHV) conditions to "real" catalytic processes occurring at atmospheric pressure and above, often referred to as the surface science approach.¹ Here one typically performs experiments at low temperature (relative to relevant adsorbate desorption temperatures) and low pressures $(10^{-10}-10^{-5} \text{ mbar})$. A number of so-called gaps between surface science conditions and high-pressure/high-temperature conditions in heterogeneous catalysis has been identified, among these:²

- (1) pressure gap;
- (2) materials gap.

The former gap appears due to the high $(1-10^2 \text{ bar})$ pressures and temperatures employed in industrial catalytic processes while the latter gap describes the disparity between oxide-supported cluster catalysts and the corresponding single-crystal model catalysts traditionally investigated in surface science. Model catalysts have to be introduced due to the prohibitively complex structure of real catalysts, which impedes atomic-scale characterization. A general trend in surface science has been—and currently is—to approach, in small steps, real conditions from a direction defined by one of these gaps^{3,4} or even several directions at once.^{2,5}

At the high pressures and temperatures employed in real catalysis, new and unexpected phenomena have been reported as compared to what is observed through the conventional surface science UHV approach.^{6–8} This approach is used extensively to mimic high-pressure situations where a high incoming molecular flux facilitates high adsorbate coverages even well above the adsorbate desorption temperatures. The application of UHV data on the other side of the

pressure gap is necessarily rendered invalid, if the surface science approach fails to emulate processes occurring at high pressures and temperatures. From cases in the literature where relations between the two sides of the pressure gap have been investigated so far,^{3,6–10} it can only be concluded that the high-pressure response is system specific. There is thus a clear need to add to the number of systems considered and from specific cases try to extract general trends.

The system we have chosen to study in detail is CO/ Pt(110). CO adsorption on Pt(110) has been a favorite prototype system for adsorbate-induced structural transformations in the modern surface science era and has been investigated extensively with almost any conceivable theoretical¹¹⁻¹⁵ and experimental UHV technique: low energy electron diffraction (LEED),^{16–23} ultraviolet photoelectron spectroscopy (UPS),^{24,19} thermal desorption spectroscopy (TDS),^{17–20,22} high-resolution electron energy-loss spectroscopy (HREELS),^{19,25–27} angle resolved ultraviolet photoemission spectra (ARUPS),25,28,29 Rutherford backscattering (RBS),^{30,20} nuclear microanalysis (NMA),²⁰ reflec-tion absorption infrared spectroscopy (RAIRS),^{26,22,31,32} x-ray photoelectron spectroscopy (XPS),²¹ work function measurements,^{17,21,23} scanning tunneling microscopy (STM),^{33–35,15} inverse photoemission spectroscopy (PES),³⁶ reflection high energy electron diffraction (RHEED),³⁷ sumfrequency generation (SFG),²⁷ microcalorimetry,³⁸ as well as high-pressure (HP) STM.⁶ In Sec. IV we will show that our HP-STM results differ to some extent form the findings of McIntyre *et al.*⁶

Beside the fundamental interest in platinum, the metal has also been the subject of extensive investigations over the years due to its widespread use of oxide-supported platinumcluster catalysts in, e.g., the automotive three-way catalyst.³⁹ Here platinum has the effect of oxidizing carbon monoxide and uncombusted hydrocarbons.

Crystalline materials usually expose planar low-Millerindex facets at low temperatures due to the high energy required to form structural defects. In the order of 0.25 eV is

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needed to break nearest-neighbor (nn) platinum bonds so very high temperatures (>1080 K) are needed for a sizable fraction of Pt-Pt bonds to be broken spontaneously.⁴⁰ However, with the introduction of CO adsorbates, surface roughening proceeds readily even at room temperature. Here we report on the atomic-scale response of the Pt(110) surface to CO adsorption at temperatures in the 300-400 K range and pressures ranging from 10^{-9} to 1000 mbar. Depending on temperature and CO pressure, the surface structure changes dramatically. In particular, we observe an extremely rough equilibrium structure at intermediate coverages, which transforms into a well-ordered saturation structure under high CO pressure. The seemingly complex behavior of the CO/ Pt(110) system can be explained by a very simple model at all pressures. Furthermore, we shall see that the structure observed at high pressures could have been predicted form UHV data only.

II. EXPERIMENT

The experimental results presented below were obtained on an experimental system combining standard UHV equipment, including UHV-STMs, and a high-pressure (HP) cell containing a STM. Here *in situ* STM investigations at pressures up to 1 bar of pure gases or gas mixtures can be carried out as described in detail in a previous publication.⁴¹

In the present context it is important to point out that special care has been taken to use ultrapure gases. Importantly, a CO-cleaning system designed to avoid nickel–carbonyl (Ni(CO)₄) formation was added. First, exposure of CO to stainless steel components is minimized by using copper tubing. Second, just prior to the inlet to the gold-plated high-pressure cell, the CO is passed through an activated carbon filter heated to ~400 K. Any Ni-carbonyls will dissociate on the high surface-area powder and the Ni is left behind. This cleaning system has proven effective in that no Ni has been detected by AES on the surface under investigation, even after extended CO exposure.

The setup facilitates standard sample cleaning procedures (30 min 800 V Ar⁺ sputtering, 10 min annealing at 800 K in 10^{-7} mbar O₂ to remove residual carbon impurities followed by 2 min annealing at 1000 K in UHV). Once the sample is deemed clean by STM, experiments can be carried out in the UHV chamber at CO pressures up to 10^{-3} mbar (this relatively high pressure does not affect the chamber base pressure significantly).

Experiments at pressures up to 1 bar are carried out in the high-pressure cell equipped with a specially designed HP-STM. A gate valve is closed between the main chamber and the high-pressure cell and the cell is pressurized to 1 bar of pure gas or gas mixtures with a particular CO partial pressure. We always use 1 bar total pressure in order to avoid electric discharges between the closely-spaced piezocontrol electrodes. These electrodes are held at potentials of a few hundred volts relative to each other and total pressures in the 1-100 mbar range are insufficient to dampen an ionization avalanche between the electrodes. Gas mixtures are obtained by first letting in the desired CO partial pressure, pumping out the gas inlet line and adding argon through a check valve



FIG. 1. Missing-row reconstructed Pt(110) surface and the effect of CO adsorption. (a) Model of the missing-row reconstructed Pt(110)-(1×2) surface. Pt coordination numbers for the perfect surface as well as for the various defects are also shown. (b) STM image showing the clean Pt(110)-(1×2) structure. A monatomic step is seen in the upper-left corner (141 ×155 Å²).

up to a total pressure of 1 bar. Ultrapure argon is commercially available (no further cleaning is necessary) and is used for backfilling due to its unreactive nature.

Sample temperatures in the range 90–400 K are accessible in our UHV-STMs and the sample temperature can be varied in the 300–400 K range in the HP-STM by heating and equilibrating the entire HP cell.

In situ HP-STM proves more difficult than conventional UHV-STM in that a higher noise level is evident, mainly due to chemical reaction between gas and tungsten tip, causing tip changes, or stronger coupling of acoustic noise through the gas. Nonetheless, we are indeed able with our setup to record STM images with atomic resolution in both unreactive and reactive gases at pressures up to 1 bar, as illustrated in Sec. III C.

III. EXPERIMENTAL RESULTS

The Pt(110) surface exhibits the well-known (1×2) missing-row reconstruction in its clean state,^{42,43} see Fig. 1. Gas adsorption alters the delicate energy balance between a bulk truncation and the missing-row reconstruction [the total energy per atom of the (1×2) structure is only 0.27 meV/ atom lower than in the (1×1) structure⁴⁴] so the adsorption of CO induces a lifting of the (1×2) reconstruction.^{33,15} The $(1\times 2)\rightarrow(1\times 1)$ transition is readily observable at the atomic scale with STM through the local motion of the Pt atoms. Note that at all coverages below full monolayer coverage $(\theta=1)$, the CO molecules are not detected by STM at room temperature. This has been attributed to the CO molecules'



FIG. 2. STM movie showing homogeneous nucleation and growth of 4-6 membered holes. Size 300×300 Å². $P = 2 \cdot 10^{-9}$ mbar. The relative to the introduction of CO is indicated below each still. The entire movie can be viewed at our web site: http://www.phys.au.dk/camp/movies/co01.mpg



FIG. 3. Appearance of a completely lifted reconstruction at room temperature. The color scale has been repeated to show the emerging atoms of the second layer. As expected, these are shifted by half a [001] spacing, cf. Fig. 1. Image size 138×154 Å².

rapid diffusion and/or the molecules' frustrated motion,⁴⁵ i.e., the ability of the on-top-adsorbed CO molecule to vibrate while still staying bound to a Pt atom. These kinds of motion require very little energy and thus proceed rapidly even compared to the fairly high scanning speed obtainable with our STMs.

A. CO exposure at room temperature

We find a room-temperature behavior similar to that reported previously.^{33,34} Homogeneously nucleated "holes" involving 4–6 atoms are created in the close-packed rows. A STM movie, i.e., a series of sequential STM images,⁴⁶ Fig. 2, shows the homogeneous nucleation and growth of these moieties. The resulting structure of room-temperature CO exposure is seen in Fig. 3. Notice the emergence of second-layer Pt atoms, which become accessible to CO adsorption only after the reconstruction is lifted. The end result is a very rough structure with no kind of ordering except a retained preference for Pt atoms to reside in fourfold hollow sites.

We have studied the evolution of the CO-induced lifting of the reconstruction by varying the CO background pressure and counting the number of holes as a function of time in STM movies. The results are shown in Fig. 4. We see that a



FIG. 5. STM movie recorded at 373 K demonstrating relaxation towards thermodynamic equilibrium. Size 300×300 Å². $P = 2 \cdot 10^{-9}$ mbar. The entire movie can be viewed at our web site: http://www.phys.au.dk/camp/movies/co02.mpg

critical exposure of about 2 L is needed for hole-creation onset.

The question now arises whether this rough structure represents the thermodynamical equilibrium structure. This can be investigated either by simply keeping the sample temperature at an elevated temperature during CO exposure or by flash-annealing the sample after room-temperature exposure, thereby allowing the Pt atoms to equilibrate.¹⁵

B. CO exposure at elevated temperatures

To resolve this issue, we investigated the structural response of the Pt substrate towards CO adsorption at elevated temperatures, here 373 K. Figure 5 shows the evolution, which proceeds in two regimes: First, kinetic limitations dominate through Pt translations akin to those observed at room temperature. Holes form in the close-packed rows, i.e., atoms are displaced from ridges to trough, but the size of the holes is no longer limited to 4-6 atoms since higher thermal activation enables more far-reaching Pt displacements. We note in passing that at 373 K, hole creation commences at a lower exposure (~ 1 L) than at room temperature.

The creation of the rough structure is followed by relaxation towards equilibrium. We see how short close-packed Pt strings line up *perpendicular* to the close-packed rows, see last still in Fig. 5. The same kind of equilibrium structure can be produced by flash-annealing the sample in UHV after room-temperature exposure, as seen in Fig. 6.¹⁵ Again a channel-like structure lined up in the [001] direction is formed. In both cases discussed above, desorption will occur, as the lower of the two CO desorption peaks lie at ~375 K.¹⁹ The CO coverage will thus be below saturation coverage $(\theta=1)$.



FIG. 4. Number of holes as a function of time for different CO background pressures. Number of holes as a function of time. $\Box: P_{\rm CO} = 5.0 \times 10^{-9}$ torr. $\diamond: P_{\rm CO} = 1.5 \times 10^{-9}$ torr. Image size: 275×307 Å².



FIG. 6. The effect of a flash-anneal to 400 K. (a) 200 $\times 200$ Ų; (b) 500 $\times 500$ Ų



FIG. 7. Imaging of CO molecules in the (2×1) -*p2mg*-2CO structure. (a) 50×50 Å². (b) Ball model of the structure. The substrate atoms diameter (2.78 Å) and CO molecule van der Waals diameter (3.2 Å) are shown in correct relative proportions. Unit cells of the bare substrate and (2×1) overlayer are indicated. The glide line and mirror symmetries belonging to the *p2mg* space group are indicated by dashed and full lines, respectively.

It is, however, also possible to form an equilibrated saturation structure in UHV. Cooling down from 600 K to room temperature in a 10^{-7} mbar CO background creates a (2×1) p2mg-2CO structure also found for several other transitionmetal (110) terminations, e.g., Ni.⁴⁵ In this case, the CO overlayer is so densely packed that the molecules' frustrated motion is impeded and the CO molecules, opposite to the low-coverage case, themselves are imaged as also discussed in the beginning of this section. STM images show a characteristic zig–zag CO structure, identical to that observed previously by STM,³⁵ covering the entire surface, see Figs. 7(a) and 7(b) for a simple ball model.

From the results presented above, one realizes that a substrate temperature of 373 K is high enough to sufficiently invigorate substrate Pt atoms to approach their equilibrium structure at a given coverage. Intermediate coverage ($0 < \theta < 1$) structures are easily accessible but a special treatment has to be implemented to produce the full coverage structure in UHV.

Another question then arises as to the effect of even higher CO pressure than the maximum of 10^{-7} mbar employed above. To this end, our novel HP-STM design allows us to follow the changes in the atomic-level surface morphology at progressively higher pressures up to 1 bar, as discussed in Sec. II. We are thus able to *bridge the pressure gap* at the atomic scale. This will be the subject of the next section.

C. Elevated-temperature high-pressure CO exposure

The entire pressure range from UHV pressures to 1 bar could be covered by going to 10^{-3} mbar in the UHV chamber and from 10^{-2} mbar to 1 bar in the HP cell. As described in Sec. II, a high-pressure experiment is always conducted at 1 bar total pressure composed of a given CO partial pressure backfilled with Ar. The CO partial pressure can thus not be adjusted while performing STM measurements so only batch experiments are possible. To ensure that only thermodynamic-equilibrium structures are created, all HP experi-



FIG. 8. STM images of CO–Pt(110) at different CO pressures: (a) 10^{-7} mbar CO, (300×300 Å²), (b) 10^{-6} mbar CO, (300×300 Å²); (c) 10^{-5} mbar CO, (1000×1000 Å²); (d) 10^{-2} mbar, (700×700 Å²); (e) 1000 mbar CO (900×900 Å²); and (f) 1000 mbar CO (28×28 Å²). All images were obtained at 373 K.

ments reported in the following were carried out at 373 K. This was accomplished by heating the entire HP cell externally.

Even though CO desorption takes place at a sample temperature of 373 K, we expect to reach progressively higher adsorbate coverages when increasing the CO background pressure. Raising the CO pressure, and thus the incoming molecular flux, puts the adsorption system in surface-gas phase equilibrium where a free site created by a desorbed molecule is quickly reoccupied by an incoming molecule. This is where high-pressure experiments differ from UHV experiments at low temperature. At low temperature, no replenishment from the gas phase is needed to maintain a high adsorbate coverage.

Figure 8 shows the resulting structures at a range of CO partial pressures. We see how at low pressures the displaced Pt atoms order into the same channel-like structure ordered along the [001] direction described above. The [001] steps are characterized by a low kink density. Higher CO pressures, however, result in kink formation, and consequently

step edges smoothen, see Fig. 8(d). The transition from kinkfree step edges is found to take place at a CO partial pressure of $\sim 10^{-3}$ mbar where also the first hint of the high-coverage (2×1) *p2mg* zig–zag structure is observed (not shown). At a CO pressure of 1 bar the channel-like structure has been replaced by islands elongated in the [110] direction. A zoom-in [in Fig. 8(f)] reveals the (2×1)-*p2mg* zig–zag structure also observed in UHV on both first and second-layer areas. As will be discussed further below, it thus appears that the CO structure observed at 373 K and high pressures from 10^{-3} mbar to 1 bar is indeed identical to the one observed at low pressure.

IV. DISCUSSION

To disentangle the multitude of details presented above, the following discussion is divided into two natural parts treating low and high-coverage structures, respectively.

The observed structures and accompanying transformations depend on CO coverage in a fairly complex way. However, as will be shown below, a simple model in which the CO binding energy depends in a linear fashion on the coordination number of the Pt atom to which it binds, is able to account for all the STM results.

A. Low-coverage behavior

The overall effect of CO exposure is the creation of lowcoordinated Pt atoms. The van der Waals diameter of CO is ~3.2 Å, significantly larger than the Pt nn distance of 2.78 Å, so $\theta = 1/4$ (one CO per two top-layer Pt atoms) is the highest coverage possible when imposing the criterion of preferred on-top adsorption in the top Pt layer. This is in accord with previous studies in that at RT lifting is found to commence when $\theta \approx 0.2$. The concept of a critical coverage is also found in Fig. 4 where we measure a critical *exposure* of ~2 L since the CO molecule elude detection at submonolayer coverage.

For CO adsorption to continue, CO/Pt complexes have to "squeeze out" from the ridges to accommodate more CO and indeed previous studies show that the lifting process is completed—no (1×2) areas are detected—when $\theta \approx 1/2$. These steps only require displacements ranging a few lattice spacings and are readily observed at room temperature. As we have seen above, however, at room temperature the resulting structure is metastable and higher temperatures are needed to form the equilibrium structure. As shown in Sec. III B and a previous publication,¹⁵ a temperature of 373 K is, however, sufficient to facilitate the creation of thermally equilibrated structures.

The driving force behind the lifting of the (1×2) reconstruction can be explained within the so-called *d*-band model.¹³ Density functional theory (DFT) calculations show that CO binds more strongly to low-coordinated metal atoms. The qualitative trends in this observation are simple to understand: When any atom lowers its coordination number, the orbital overlap with neighboring atoms is lowered as well—in other words, the atom turns more "free-atomlike." Lower orbital overlap with neighboring atoms results in band narrowing and in order to maintain the band filling degree, the *d*-band center shifts upwards in energy, towards the



FIG. 9. Ball model of the kink formation process showing the coordination number of the Pt atoms involved. (Left) Kink-free step edge. When the CO coverage is less than 1 ML, CO is only adsorbed on the low-coordinated sites (<8 nearest neighbors), and the kink-free configuration is therefore the energetically favored configuration. (Right) Kink formation. When the CO coverage is close to 1 ML the energy difference between the two configurations is close to zero and the higher entropy of the kinked step edge is therefore favored at finite temperatures.

Fermi energy. The CO adsorption energy depends strongly on the relative positions of the molecular orbitals involved in bonding (here the 5σ HOMO and $2\pi^*$ LUMO) and the energy of the metal *d*-states. The closer in energy, the stronger are the orbital overlap and adsorbate binding. In absolute numbers, CO binds more strongly to a 5-coordinated adatom than to a 7-coordinated ridge atom by 0.45 eV,¹⁵ incidentally exactly equal to the energy required to rupture two Pt nn bonds. This explains the preference and ability of CO to create its own low-coordinated adsorption site and lift the (1×2) reconstruction.

As an aside to the above energy considerations, we mention that most previous studies of the CO-induced lifting of the Pt(110)-(1×2) reconstruction,³² have been interpreted in terms of a CO adsorption energy difference between the (1×2) and (1×1) clean Pt substrate phases. This is conceptually different from the discussion above where the driving force behind the lifting process is interpreted in terms of single CO molecules gaining binding energy. It should be noted, however, that the microscopic explanation presented here in the end has the same (macroscopic) thermodynamic implications as the broader view proposed earlier.

B. High-coverage behavior

The considerations above only consider coordination number changes in top-layer Pt atoms. When the (1×2) reconstruction is lifted, however, the next Pt layer is made available for CO adsorption. At most half of the second layer is exposed because the top layer Pt atoms effectively constitute half a monolayer when compacted into the (1×1) phase. The exposed part of the second layer is a full (1×1) layer with a Pt coordination number of 7; higher coordination numbers (8-10) are found at step edges, as seen in Figs. 1(a) and 9. Even while the lifting process occurs, adsorption must take place on both first and second-layer atoms, initially at coordination number 7 sites. At ever higher coverage, adsorption is forced to take place at less energetically favored 8-10-coordinated sites, see Figs. 1(a) and 9. Here we recognize the driving force behind the line-up of short, closepacked Pt rows along the [001] direction observed at intermediate coverages (see Fig. 6): The lined-up structure does not contain a lower number of step (coordination number 5-6 in the top layer) atoms than would a structure with no kind of ordering of the short close-packed rows. It rather minimizes the average coordination number of occupied Pt sites in the second layer.

For coverages close to saturation, the energy gained in the kink-free channel structure vanishes due to adsorption on second-layer, high-coordinated Pt atoms. Entropic effects (higher disorder) are then manifested as kinked or "rounded" step edges, as was observed at a pressure of 10^{-2} mbar in Fig. 8(d). The formation of a kink is illustrated in Fig. 9, where we recognize the higher average coordination number of a kinked structure. At even higher pressures, channels coalesce to form extended (1×1) substrate areas with the characteristic zig–zag (2×1)-*p2mg*-2CO pattern seen in Figs. 7 and 8(f).

Our results shed new light on a previous high-pressure STM study of the CO/Pt(110) system.⁶ This being a pioneer experiment in the area of high-pressure STM, the design did not enable atomic resolution. Furthermore, McIntyre *et al.* made use of a transfer cell between crystal cleaning and HP imaging which raised the background pressure during transfer to 10^{-5} mbar. After heating at 425 K for 5 h in 1 bar CO, McIntyre *et al.* observed large flat terraces displaying no missing-row reconstructions separated by multiple-height steps and groups of steps with a corrugation amplitude of 42 Å. Due to the lack of atomic resolution, no further details could be extracted of the atomic structure on the flat terraces.

We also observe extended terraces at high pressures and the mechanism for their creation was presented above. Atomically-resolved images of the (2×1) -p2mg-2CO structure created on the flat terraces allow us to confidently conclude that the pressure gap has indeed been bridged for this system. Contrary to the findings of McIntyre *et al.* we do, however, not observe any large-scale changes, i.e., the wellknown mesoscopic "corrugated-iron" structure^{47,48} is not modified even after overnight exposure to 1 bar CO at 373 K. The level of gas cleanliness may be the point where the study of McIntyre *et al.* differs from the present study and could explain the discrepancies.

V. CONCLUSIONS

The classic prototype system for adsorbate-induced substrate transformations, CO/Pt(110), was investigated in detail with STM in the 300–400 K temperature range and 10^{-9} –1000 mbar pressure range. The overall behavior is summarized well by the step-density plot in Fig. 10: At first, adsorption at top-layer Pt sites dictates a step density increase through the adsorbate's preference for lowcoordinated sites. When second-layer Pt atoms become exposed, adsorption continues here as well, and adsorption on high-coordinated second-layer sites is minimized by forming the low-kink-density channel structure. This continues until a CO coverage of $\theta \approx 0.7$ where adsorption on highcoordinated second-layer Pt sites removes the preference for the low-kink-density structure. Finally, the energetically favored structure at saturation consists of low-step-density



FIG. 10. Step density calculated from Monte Carlo simulations at 300 K based on DFT parameters from a previous publication (Ref. 15) shown as a function of CO coverage. A step atom is defined as an atom with coordination number 5 or 6. Reproduced from Ref. 15.

 (1×1) substrate areas with a close-packed (2×1) -p2mg-2CO layer on top. This transition to a (1×1) substrate is also explained by the strong dependence of the CO binding energy on the coordination number of the Pt atom to which it binds.

A temperature of 373 K was shown to facilitate the formation of equilibrated structures. At intermediate coverages, a rough structure was observed but the Pt substrate heals at saturation (θ =1). At pressures above ~10⁻³ mbar, a saturated (2×1)-*p2mg*-2CO layer adsorbed on a (1×1) substrate is formed. This structure can also be formed in UHV by cooling from 600 K in a 10⁻⁷ mbar CO background. As a common feature at all coverages, substrate transformations are found to proceed through minimal displacements. In particular, a given Pt atom is found to remain on its native terrace.

In conclusion, we emphasize that no new CO phase was observed when bridging the pressure gap, i.e., by raising the CO pressure to 1 bar. The Pt(110) surface thus responds identically to CO under UHV and high-pressure conditions. For this system, however, raising the pressure is *not* exactly equivalent to lowering the temperature since at low temperature the rearranging Pt substrate atoms would not be sufficiently thermally activated to form the equilibrium structure at a given coverage. The high-coverage equilibrium structure can, however, be formed under UHV conditions by cooling the sample in a CO background pressure as discussed above. In the present case, UHV data are adequate to predict the surface structure at high pressure and elevated temperature. In general one must thus take into account pertinent activation barriers, e.g., substrate equilibration when making conjectures as to the high-pressure response of an adsorption system.

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