Comment on "High Pressure Adsorbate Structures Studied by Scanning Tunneling Microscopy: CO on Pt(111) in Equilibrium with the Gas Phase"

In a previous Letter [1], Jensen *et al.* investigated the high-pressure (200–750 torr) response of the Pt(111) surface towards carbon monoxide using scanning tunneling microscopy (STM). A new hexagonal CO overlayer structure was found, quite different from the structures formed at similar coverages under low pressure and temperature conditions, and Jensen *et al.* concluded that their results illustrated the inequivalence between studies of surfaces in catalytic conditions of high pressure and surface science studies carried out in high vacuum.

In this Comment, we present atomically resolved STM images obtained at room temperature with a novel high-pressure STM described elsewhere [2]. Our results differ from those obtained by Jensen *et al.* in several respects: At 1 bar of CO, we detect two rotational domains of a hexagonal CO Moiré pattern with a periodicity of 11.8 ± 0.4 Å
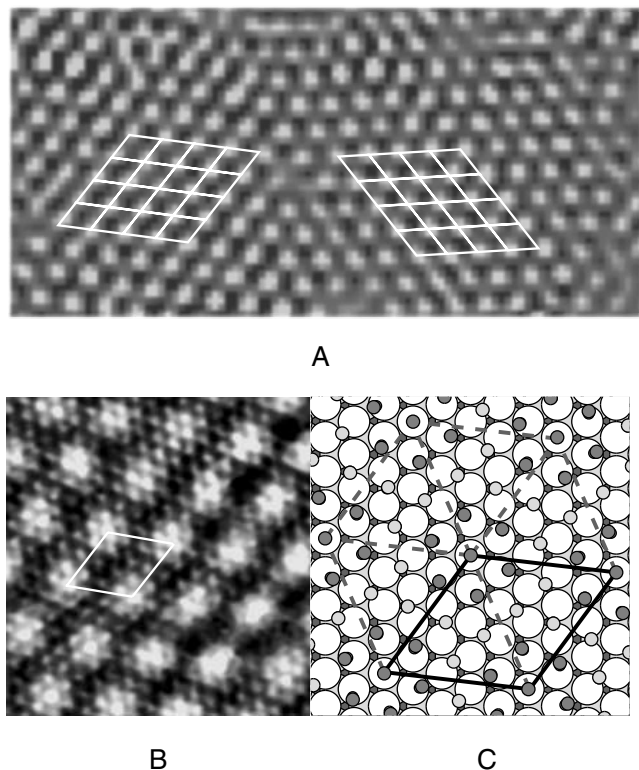

A

B   C

FIG. 1. (A) STM image (240×125) Å^2 of two rotational domains of the Moiré pattern formed at 1 bar CO. (B) High-resolution STM image (55×51) Å^2 of the CO overlayer obtained at 1 bar CO. (C) The $(\sqrt{19} \times \sqrt{19})R23.4°$-13 CO structure. One CO molecule in the unit cell has been fixed in the on-top position. If, alternatively, the CO molecule is fixed to the bridge or fcc position, the energy is raised by about 0.4 eV per unit cell (three-layer Pt slab). The unit cell of the pattern is indicated with the solid line. Dark balls represent CO molecules adsorbed in nearly on-top sites (see text).

rotated $\Psi = 24 \pm 2°$ with respect to the underlying substrate (see Fig. 1A). This alone invalidates the model proposed in [1] consisting of a nonrotated CO overlayer. Furthermore, we resolve the individual CO molecules of the overlayer structure and find that the Moiré pattern arises from a $(\sqrt{19} \times \sqrt{19})R23.4°$-13 CO unit cell, corresponding to a surface coverage of 0.68 ML (Fig. 1B). From an interplay between our STM results and density functional calculations, we arrive at the lowest-energy structural model shown in Fig. 1C with 13 CO molecules per unit cell. The brightest protrusions in Fig. 1B are associated with CO in on-top adsorption sites.

At low pressure and temperature conditions (170 K), we moreover observe the exact same CO Moiré structure when the Pt(111) surface is saturated with CO. This result is consistent with earlier low-temperature LEED studies [3]. 170 K is thus a sufficiently high temperature to overcome the CO diffusion barrier and facilitate long-range ordering, and yet sufficiently low to form high-coverage saturation structures. (At 90 K we observe a kinetically hindered domain structure.)

Comparing the high-pressure CO structural model presented in Fig. 1C with the $c(4 \times 2)$-2CO room-temperature UHV saturation structure ($\theta = 0.5$ ML), a 47% on-top occupancy increase is found. In this way our STM results are in excellent agreement with a recent sum-frequency generation study by Rupprechter *et al.,* who observed a $\sim$40% on-top occupancy increase when the CO pressure was raised from low to high pressure [4].

With respect to the so-called pressure gap, we thus conclude that raising the pressure is equivalent to lowering the temperature as long as the thermodynamical equilibrium structure remains kinetically accessible [1], as previously observed for other systems [5].

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