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# SFG spectroscopy from $10^{-8}$ to 1000 mbar: less-ordered CO structures and coadsorption on Pd(1 1 1)

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## Abstract

Vibrational sum frequency generation spectroscopy was employed to study "less-ordered" phases resulting from low-temperature CO exposure on Pd(1 1 1). Such imperfect structures may also occur under catalytic reaction conditions up to 1000 mbar and originate from the superposition of ordered structures when the CO mobility and flux were insufficient. The effect of coadsorbed hydrogen and water was also examined.

*Keywords:* Sum frequency generation; Catalysis; Vibrations of adsorbed molecules; Palladium; Carbon monoxide; Low index single crystal surfaces

## 1. Introduction

The interest to connect surface science and catalysis has promoted surface-sensitive techniques that operate in the mbar range, such as sum frequency generation (SFG) vibrational spectroscopy [1,2]. Because SFG provides adsorbate vibrational spectra from sub-monolayer quantities in ultrahigh vacuum (UHV) up to ~1 bar, adsorbate structures under UHV and elevated pressure can be directly compared. It has been argued that at high pressure UHV saturation coverages may be exceeded thus leading to adsorbate geometries not existing under UHV. However, our SFG studies of CO on Pt(1 1 1) and Pd(1 1 1) have shown that identical high coverage structures were present under UHV and at 500–1000 mbar, with "regular" CO adsorption sites (on-top, bridge, and hollow bonded) [3,4].

Despite these results, the "pressure gap"—of course—still exists. High coverages are typically attained under UHV at low temperature ($\leqslant 100$ K) where the reduced mobility of adsorbed molecules may lead to less-ordered ("non-equilibrium") structures. Furthermore, when elevated temperatures (>300 K) are required to stimulate reactions between molecules, typical UHV pressures ($10^{-9}$–$10^{-6}$ mbar) may produce only low surface coverages that may not be relevant for a specific reaction. Changes in surface morphology and composition at high pressure comprise another complication [5,6].

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In this paper we address issues that could not be answered in previous publications [4,7]. We specifically discuss the relevance of less-ordered phases under UHV and high pressure. Because coadsorbed molecules such as $H_2$ and $H_2O$ cannot be avoided when long-time UHV experiments are carried out, we have also examined their interaction with CO.

## 2. Experimental

The experiments were performed in a UHV surface analysis system combined with an SFG-compatible UHV-high pressure cell [4,8]. Pd(1 1 1) was prepared as described in [4] and characterized with low energy electron diffraction (LEED), Auger electron spectroscopy (AES) and temperature programmed desorption (TPD). For details about SFG spectroscopy we refer to the literature (e.g. [2,4,8–12] and references therein).

## 3. Results and discussion

Although CO/Pd(1 1 1) is a "simple" system it exhibits a rich behavior. SFG spectra of CO/Pd(1 1 1) from $10^{-8}$ to 1000 mbar and 100–500 K were presented in preceding papers [4,7]. In agreement with earlier studies ([4] and references therein), several well-ordered structures were observed, the most prominent being a $(\sqrt{3} \times \sqrt{3})$R30°-1CO at 0.33 ML, a $c(4 \times 2)$-2CO at 0.5 ML, a $(4\sqrt{3} \times 8)$rect at 0.63 ML and a $(2 \times 2)$-3CO at 0.75 ML.

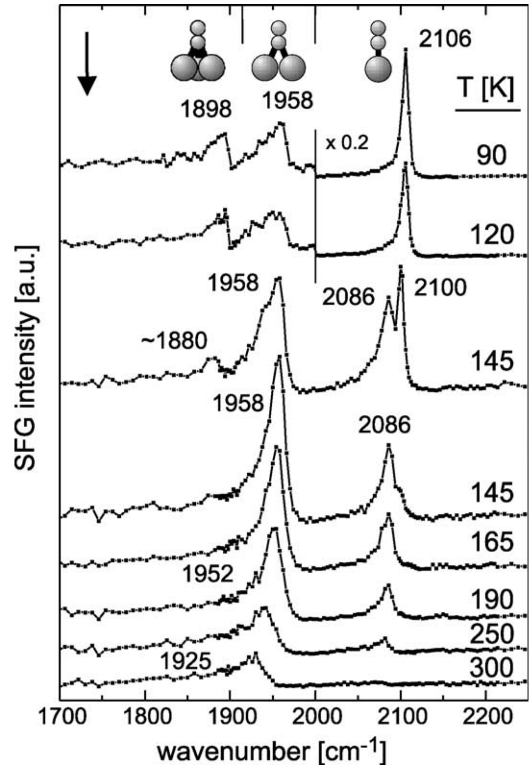

Fig. 1. SFG spectra of CO on Pd(1 1 1): after saturating the surface at 90 K, the crystal was annealed as indicated. Approximate frequency ranges of hollow, bridge, and on-top CO are also shown.

Each structure exhibited a characteristic SFG spectrum (see Fig. 2 of [4]). CO adsorbed in fcc threefold hollow sites with stretching frequencies around 1850 cm$^{-1}$ at 0.33 ML. At 0.5 ML a peak at 1925 cm$^{-1}$ was observed (cf. the 300 K spectrum in Fig. 1). In a recent STM study Rose et al. [13] were able to resolve both CO molecules within the $c(4 \times 2)$ unit cell and could show that two types of $c(4 \times 2)$ structures coexisted. One with CO in fcc and hcp threefold hollow sites and one with bridge bonded $c(4 \times 2)$. Above $\theta = 0.6$, CO was bridge bonded (1955 cm$^{-1}$) with a small amount of linear (on-top) CO at ~2085 cm$^{-1}$ (cf. the 190 K spectrum in Fig. 1). If the coverage was increased, the SFG bridge site intensity decreased, the on-top signal increased and a rearrangement (transition) from a bridge/on-top to a hollow/on-top structure occurred [14]. At saturation ($2 \times 2$, $\theta = 0.75$), two bands at 1895 and 2106 cm$^{-1}$ (fcc and hcp hollow and on-top CO) were observed (cf. uppermost spectrum in Fig. 2).

However, the well-ordered structures were only obtained upon cooling Pd(1 1 1) from ~300 to 100 K in $10^{-6}$ mbar CO ([4,7], see also [14,15]). When CO was dosed at 90 K, a less-ordered saturation structure was obtained, exhibiting hollow, bridge and on-top CO (Fig. 1), presumably due to the reduced CO mobility. Such structures may be important in low-temperature UHV surface reaction studies and it seems worthwhile to investigate whether they originate from a specific adsorbate structure, from antiphase domain boundaries

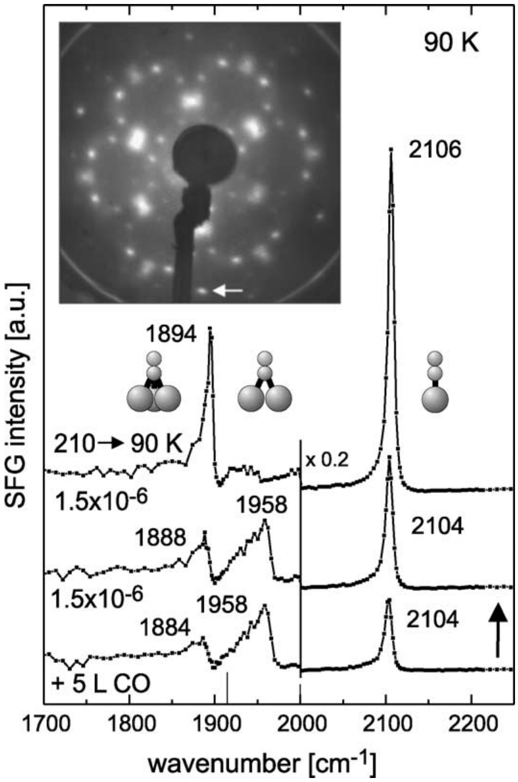

Fig. 2. SFG spectra of CO on Pd(1 1 1): saturation at 90 K, exposure to $1.5 \times 10^{-6}$ mbar, and cooling in $1.5 \times 10^{-6}$ mbar CO from 210 K to 90 K. The inset shows a LEED image revealing a superposition of 0.63 and 0.75 ML domains. An arrow marks one Pd reflection.

[13,15], or from a superposition of well-ordered domains.

The 90 K spectrum in Fig. 1 shows a less-ordered CO saturation structure (>10 Langmuir), with peaks at 1898 $\text{cm}^{-1}$ (hollow), 1958 $\text{cm}^{-1}$ (bridge) and 2106 $\text{cm}^{-1}$ (on-top). Heating to 145 K strongly reduced the on-top intensity and split the on-top peak into two components (2086 and 2100 $\text{cm}^{-1}$) while hollow CO also decreased and bridged CO increased. The concomitant intensity changes suggest a rearrangement of the adsorbate. In fact, the 145 K spectrum represents a superposition of a 0.63 ML structure (1958 and 2086 $\text{cm}^{-1}$) and of a 0.75 ML structure (1880 and 2100 $\text{cm}^{-1}$). Waiting longer at the "transition" temperature (~145 K) allowed more CO to desorb and formation of the 0.63 ML structure. Heating to 165 K and higher produced spectra that were identical to the well-ordered spectra obtained upon cooling Pd(1 1 1) in $10^{-6}$ mbar CO (cf. Fig. 2 of [4]).

Subsequent cooling to 90 K and saturation with CO (Fig. 2) again produced a superposition of the 0.63 and 0.75 ML structures (1884, 1958 and 2104 $\text{cm}^{-1}$). Increasing the background to $1.5 \times 10^{-6}$ mbar increased the on-top and hollow peak, but did not produce a $(2 \times 2)$. Only after heating in $1.5 \times 10^{-6}$ mbar CO to 210 K and cooling back to 90 K, a well-ordered $(2 \times 2)$ was formed (annealing in $10^{-8}$–$10^{-7}$ mbar CO produced less-ordered structures).

Rose et al. [13] and Bourguignon et al. [15] reported antiphase boundaries between $(2 \times 2)$ domains with CO in various (low symmetry) sites. Although certainly present, such structures play only a minor role here. Our parallel LEED studies of less-ordered structures also indicated a superposition of a $(4\sqrt{3} \times 8)$rect (0.63 ML) and a $(2 \times 2)$ (0.75 ML) structure (inset in Fig. 2, obtained after cooling Pd(1 1 1) from 300 to 90 K in $10^{-7}$ mbar CO). Such long-range ordering can hardly occur for domain boundaries with low symmetry sites. We conclude that the formation of a well-ordered $(2 \times 2)$ structure requires a sufficiently high CO mobility (temperatures of ~150 K to overcome the CO diffusion barrier) and a sufficient CO flux at the transition temperature (~$10^{-6}$ mbar at 150 K) to avoid "quenching" of domains with lower coverage.

We now focus on the role such less-ordered structures may play under catalytic reaction conditions, i.e. at near-atmospheric pressure (Fig. 3). At $10^{-6}$ mbar and 190 K, 1955 $\text{cm}^{-1}$ (bridge) and 2087 $\text{cm}^{-1}$ (on-top) peaks indicated a 0.63 ML structure that turned into the 0.75 ML structure (hollow/on-top CO) with increasing pressure. However, at $10^{-4}$–$10^{-3}$ mbar the two on-top species (2087/2099 $\text{cm}^{-1}$) and the coexistence of bridge and hollow peaks indicated a superposition of 0.63 and 0.75 ML domains. A well-ordered $(2 \times 2)$ structure with hollow/on-top occupancy was only reached at 1 mbar. At 300 K, such non-equilibrium structures were observed between 400 and 1000 mbar CO [4]. Summarizing, the saturation structures under UHV and high pressure were identical, but at slightly lower coverage less-ordered

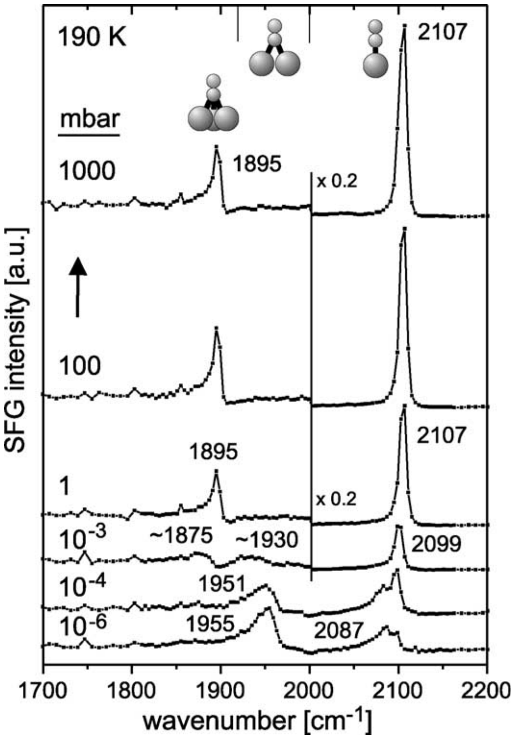

Fig. 3. SFG spectra of $10^{-6}$ to 1000 mbar CO on Pd(1 1 1) at 190 K.

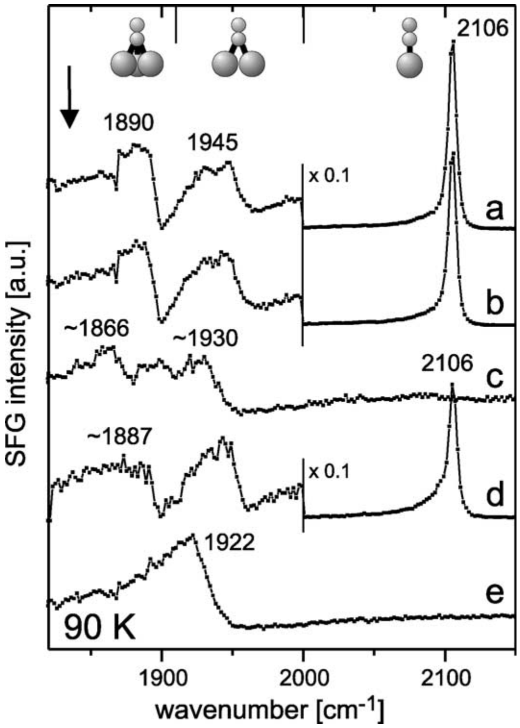

Fig. 4. SFG spectra of coadsorption on Pd(111) at 90 K: (a) 100 L CO, (b) +50 L $H_2$, (c) clean surface + 25 L 50/50% CO/$H_2$, (d) clean surface + 50 L CO, +100 L $H_2O$, (e) clean surface + 10 L 50/50% CO/$H_2O$.

structures may be present with possible impact on catalysis.

Previously [4,7] we have observed that the on-top intensity decreased above 300 mbar CO. We suggested this effect to be related to the IR normalization of the SFG signal and not to reflect a real disappearance of on-top CO [3,4]. Using an improved IR normalization that utilizes the (non-resonant) SFG signal from a thin $Al_2O_3$ film on NiAl(1 1 0) as reference, the high pressure spectra were re-examined (Fig. 3). In agreement with our suggestion we confirm that the on-top intensity remains constant up to 1000 mbar.

Coadsorbed $H_2$ or $H_2O$ preventing "merging" of well-ordered CO domains may be another reason for less-ordered structures. Fig. 4(a) displays an SFG spectrum after adsorbing 100 L CO at 90 K, producing a less-ordered phase. Upon subsequent exposure to 50 L $H_2$, no changes occurred (Fig. 4(b)) indicating that preadsorbed CO effectively blocks $H_2$ adsorption (as corroborated by TPD and LEED and in agreement with previous coadsorption studies on Pd, Ni and Ir(1 1 1) [16–18]). This also holds for lower coverages of preadsorbed CO (0.5 and 0.63 ML). Vice versa, preadsorbed $H_2$ strongly inhibited CO adsorption (no CO LEED pattern or SFG spectrum could be obtained). When a 50–50% CO/$H_2$ mixture was used (Fig. 4(c)), hollow and bridge CO were present but on-top CO was absent, demonstrating the blocking of on-top CO by hydrogen. Because on-top CO was dominant in the less-ordered phases, a significant influence of $H_2$ contamination can be ruled out.

Fig. 4(d) shows an SFG spectrum after adsorbing 50 L CO, followed by 100 L $H_2O$. According to TPD, adsorbed $H_2O$ was present but no differences to the pure CO spectrum were observed (the same is true for a 0.63 ML CO starting structure). This indicates that preadsorbed CO layers were not influenced by adsorbed $H_2O$. However, dosing a 50–50% $CO/H_2O$ mixture at 100 K (Fig. 4(e)) resulted in a single hollow peak at 1920 $cm^{-1}$, different from both the less-ordered and well-ordered saturation structure. The CO frequency suggests a 0.5 ML coverage but the elucidation of this structure needs further experiments including higher CO exposures. In any case, a significant influence of water contamination on SFG experiments with pure CO (Figs. 1–3) can be excluded.

## 4. Conclusions

SFG spectroscopy was applied to study less-ordered CO structures on Pd(1 1 1). These structures were identified as superposition of two ordered structures (0.75 and 0.63 ML). Such phases were also observed at elevated temperature/pressure and may be of importance during catalytic reactions. Using an improved scheme to normalize high pressure SFG spectra for IR gas phase absorption, we have confirmed our previous suggestion that the intensity of on-top CO remains almost constant between 100 and 1000 mbar CO. When CO adsorption was followed by $H_2$ or $H_2O$, no influence on the CO spectrum was observed. Mixtures of $CO/H_2$ or $CO/H_2O$ typically led to SFG spectra without on-top CO.

Our SFG studies on Pt(1 1 1) and Pd(1 1 1) have shown that the same adsorbate species were present under UHV and high pressure. Recent high pressure STM data support this finding [19]. However, to closely connect surface science and catalysis one has to make sure that both types of studies are carried out under conditions where identical surface coverages and adsorbate structures are present. If this is guaranteed the total gas pressure may be of small relevance, given that mass transport limitations are absent.

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