

SURFACE SCIENCE LETTERS

ABSOLUTE COVERAGES OF CO AND O ON Pt(111); COMPARISON OF SATURATION CO COVERAGES ON Pt(100), (110) AND (111) SURFACES

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Nuclear microanalysis (NMA) has been used to determine the absolute coverages of oxygen and CO adsorbed on Pt(111). The saturation oxygen coverage at 300 K is $3.9 \pm 0.4 \times 10^{14}$ O atoms cm^{-2} ($\theta = 0.26 \pm 0.03$), confirming the assignment of the LEED pattern as $p(2 \times 2)$. The saturation CO coverage at 300 K is $7.4 \pm 0.3 \times 10^{14}$ CO cm^{-2} ($\theta = 0.49 \pm 0.02$). The low temperature saturation CO coverages on Pt(100), (110) and (111) surfaces are compared.

The accurate determination of adsorbate coverages on well defined metal surfaces is an important goal of surface science. For example, if there is ambiguity in the number of adsorbed molecules or atoms in the unit cell of an overlayer responsible for a particular LEED pattern, this greatly increases the effort involved in a dynamical calculation since more models must be tested.

Recently [1], Hollins and Pritchard have published a reassignment of a LEED pattern that appears when CO is adsorbed on Cu(111). This pattern occurs at a coverage between 0.33 monolayer (corresponding LEED pattern is $(\sqrt{3} \times \sqrt{3})R30^\circ$) and saturation (0.52 monolayer; (1.39×1.39) hex). At the intermediate coverage the positions of the overlayer beams are close to those of a $c(4 \times 2)$ structure which could correspond to a coverage of 0.50. By careful relative coverage measurements, Hollins and Pritchard have been able to demonstrate that the coverage at which this pattern is most intense is 0.44 monolayer and that the pattern is actually $(1.5 \times 1.5)R18^\circ$. Pritchard [2] has suggested that the CO/Pt(111) system also should be re-examined to determine whether the structure designated $c(4 \times 2)$ [3] requires reassignment.

A second and separate problem relates to the exposure of a clean Pt(111) surface to O_2 : at temperatures in the range $200 < T < 350$ K a LEED pattern of the symmetry shown in fig. 1 is eventually produced. This was usually assumed to be a $p(2 \times 2)$ pattern, corresponding to a coverage (θ) of 0.25 (a θ of 1 corresponds to 1.5×10^{15} adsorbate particles cm^{-2} on Pt(111)). However,

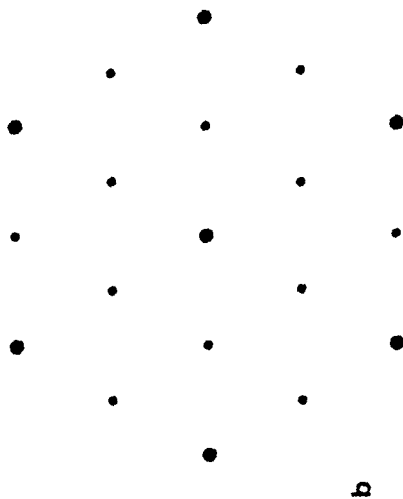
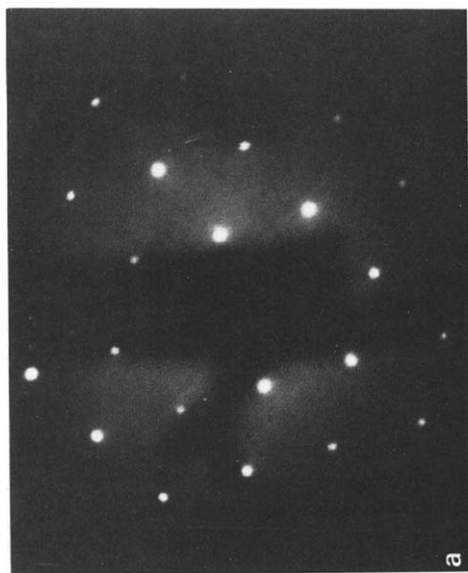


Fig. 1. (a) LEED pattern of an adsorbed oxygen overlayer on Pt(111); $T \approx 300$ K, O_2 pressure $\approx 10^{-4}$ Pa. (b) Schematic of LEED pattern. Larger spots, integral order beams from the substrate.

the symmetry of the LEED pattern would also be consistent with the presence of 3 domains of (2×1) symmetry rotated by 120° with respect to each other, which corresponds ideally to a coverage of 0.5 monolayer.

There is thus a need to determine the absolute coverages of CO and O on Pt(111) and the technique of nuclear microanalysis (NMA) is ideally suited to yield such coverage data. In this Letter we report new measurements of the coverages of oxygen and carbon monoxide on Pt(111) and compare the resulting data with our previous NMA measurements of CO coverages on Pt(100) and (110) surfaces. These absolute coverage data can serve as reference standards and the coverages of other oxygen or carbon containing species on platinum can then be determined by using other more conventional surface science techniques, such as LEED, photoemission, thermal desorption spectroscopy, etc.

The NMA measurements were carried out in a UHV chamber interfaced to a 2.5 MV Van de Graaff accelerator. This system has been fully described elsewhere [4]. The crystals were cut from two Materials Research Corporation boules, oriented to within 1° of the desired planes and polished by standard metallographic techniques. The annealing and cleaning procedures, which have already been described in detail [5], involved high temperature sputtering and oxidation (sometimes both simultaneously) followed by annealing at $T \sim 1600$ K. The surfaces were then observed to be clean by XPS standards (~ 0.01 monolayer). The LEED measurements were carried out with a VG 4-grid LEED optics at beam currents of the order of $1 \mu\text{A}$. Careful tests indicated that beam-induced desorption was not a limitation in these measurements.

The sample temperature was measured with a W-Re thermocouple to an accuracy of ± 2 K. The ion gauge was calibrated to $\pm 10\%$ against an MKS model 146 H Baratron capacitance pressure manometer.

The reactions used to measure the O and C coverages simultaneously were the $^{12}\text{C}(\text{d}, \text{p})^{13}\text{C}$ and $^{16}\text{O}(\text{d}, \text{p})^{17}\text{O}$ reactions. The principles involved and the calibration of this technique have been described previously [6]. Briefly, the accuracy originates from the use of an in-situ Ta_2O_5 standard and knowledge of the relative cross sections of the $^{16}\text{O}(\text{d}, \text{p})^{17}\text{O}$ and $^{12}\text{C}(\text{d}, \text{p})^{13}\text{C}$ reactions. Counting rates of $\sim 1 \text{ s}^{-1}$ are readily achievable so that a statistical precision of a few percent is obtainable with counting times in the order of 10–20 min. The technique probes the top few tenths of a micron of the sample.

On freshly cleaned surfaces carbon and oxygen were usually below the detection limits ($\lesssim 1 \times 10^{13}$ C atoms cm^{-2} and $\lesssim 2 \times 10^{13}$ O atoms cm^{-2} in the top 0.1–0.2 μm of the sample); the one exception was the (110) sample in which a trace of oxygen was detectable ($\sim 7 \times 10^{13}$ O atoms cm^{-2}). This oxygen is almost certainly buried through the top few tenths of a micron of the sample, since it was undetectable by Auger spectroscopy. The origin of this sub-surface oxygen contamination in the (110) sample is not known, but it is significant that the total time during which the crystal was maintained in

vacuum at $T \gtrsim 1600$ K was shortest for the (110) crystal.

In all cases where LEED data were obtained, the diffraction pattern was checked before and after the microanalysis; no evidence of any ion-beam desorption effects was ever detected.

To investigate the oxygen overlayer, NMA measurements were made on a surface exhibiting the LEED pattern described above (fig. 1) under a variety of experimental conditions. Our first method of preparing the $p(2 \times 2)$ -O overlayer was to saturate the surface with oxygen at 300 K and then cool in vacuum to ~ 160 K during the NMA determination. The purpose of this cooling procedure was to minimize the reactive removal of adsorbed O by CO or H_2 present in the ambient vacuum. The total O coverage (θ_o) always lay in the range 0.22 to 0.28 monolayer; in those cases where $\theta_o > 0.25$, carbon was also detected in amounts corresponding to the presence of a few hundredths of a monolayer. It is probable that the excess O was present as CO adsorbed during the cool down and/or the subsequent NMA analysis. A more satisfactory method was to saturate the crystal surface at 300 K in 10^{-4} Pa O_2 ; then, after the adsorbed layer was annealed at 425 K in $\sim 10^{-4}$ Pa O_2 , the sample was again cooled to 300 K before determination of θ_o in the presence of $\sim 10^{-4}$ Pa O_2 . This procedure produced the sharpest and most intense LEED pattern, illustrated in fig. 1. The coverage so determined was 0.26 ± 0.03 monolayer, thus confirming the assignment of the pattern as $p(2 \times 2)$.

To investigate the CO overlayers at 300 K, we made NMA measurements of the saturation coverage and of the coverage at which visual observation indicated a maximum in the intensity of the (nominally) $c(4 \times 2)$ pattern. The results are shown in table 1. It is seen that the saturation coverage at 300 K, stable to prolonged pumping, is 0.49 ± 0.02 monolayer; this value is in reasonable agreement with other recent measurements [7,8]. At saturation coverage, a rather diffuse LEED pattern is visible which exhibits the symmetry previously designated $c(4 \times 2)$. Upon warming to 320 K, the LEED pattern sharpened but, without measurements of the integrated intensity, we cannot definitely state whether this sharpening was accompanied by an intensity change. This pattern is illustrated in fig. 2, which also shows a schematic of the pattern. The positions of the diffraction beams are consistent with a $c(4 \times 2)$ pattern, and the measured coverage is now 0.47 ± 0.02 monolayer. Further heating of this surface in vacuum to 330 K decreased the coverage slightly to 0.44 ± 0.02 monolayer and also decreased the intensity of the LEED beams without measurably changing the symmetry or sharpness of the pattern. Hence, the observed coverage of 0.47 ± 0.02 at maximum sharpness is, within the error limits, consistent with either the $c(4 \times 2)$ or the $(1.5 \times 1.5)R18^\circ$ structure, but the positions of the beams strongly support the assignment as $c(4 \times 2)$.

Finally, measurements were made at 160 K in flowing CO at $\sim 10^{-4}$ Pa to determine the saturation coverage under conditions equivalent to those used in ref. [3]. The same sequence of LEED patterns was observed and the coverages

Table 1
CO coverages on Pt(111)

Adsorption and measurement temp. (K)	Annealing temp. (K)	P (Pa)	Coverage ($\times 10^{15}$ molecules cm^{-2})	Fractional coverage, θ	LEED pattern
300	300	$< 10^{-8}$	0.74 ± 0.03	0.49 ± 0.02	Relatively diffuse $c(4 \times 2)$
300	320	$< 10^{-8}$	0.71 ± 0.03	0.47 ± 0.02	Sharp, intense $c(4 \times 2)$
300	330	$< 10^{-8}$	0.66 ± 0.03	0.44 ± 0.02	Weak, $c(4 \times 2)$
160	160	$\sim 10^{-4}$	0.96 ± 0.04	0.64 ± 0.03	Complex compression

Note: Coverages determined at 300 K were stable to prolonged pumping.

Table 2
Saturation coverages of CO on Pt(100), (110) and (111) surfaces

Plane	T (K)	P (Pa)	Coverage ($\times 10^{15}$ molecules cm^{-2})	Fractional coverage, θ	LEED pattern	Expected θ from LEED pattern
(100)	190	$< 10^{-8}$	0.99 ± 0.04^a	0.77 ± 0.03	$c(4 \times 2)$	0.75
(110)	160	$< 10^{-8}$	0.92 ± 0.04^b	1.00 ± 0.04	$(2 \times 1)p1g1$	1.00
(111)	160	$< 10^{-8}$	0.96 ± 0.04	0.64 ± 0.03	Complex compression	Consistent with LEED pattern

^{a)} From ref. [5].

^{b)} From ref. [9].

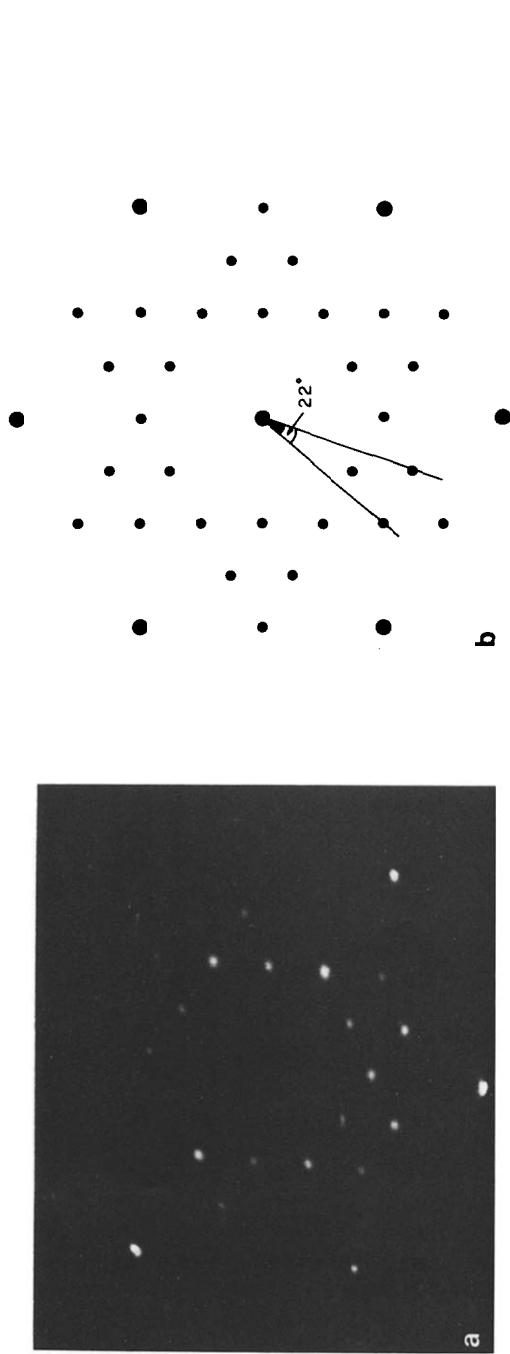


Fig. 2. (a) LEED pattern of an adsorbed CO overlayer on Pt(111) produced by adsorption at 300 K followed by a brief anneal to 320 K; $\theta = 0.47 \pm 0.02$ monolayer. (b) Schematic of LEED pattern showing relevant angle = 22° . Ideally this angle = 21.8° for $\alpha(4 \times 2)$ and 24° for a $(1.5 \times 1.5)R18^\circ$ structure.

are in good agreement with those calculated from the symmetry of the LEED patterns. However, we were not able to produce a surface exhibiting a uniform LEED pattern characteristic of the highest coverage achieved by Ertl, Neumann and Streit [3]. Since the LEED pattern is extremely sensitive [3] to coverage in the range $0.60 \leq \theta \leq 0.68$, our LEED observations are consistent with an *average* coverage somewhat lower than that achieved by Ertl and co-workers; i.e. < 0.68 monolayer. We thus believe that although the coverage may locally be as high as $\theta = 0.68$ (we observe small areas exhibiting the LEED pattern characteristic of $\theta = 0.68$) our NMA-determined saturation coverage of 0.64 ± 0.03 is characteristic of an ordered overlayer with a coverage slightly less than 0.68. The precision of our NMA measurements does not permit us to draw this conclusion unambiguously. Furthermore, at the present time we cannot be certain that the LEED gun electron beam (~ 1 mm diameter) and the NMA beam (~ 1 mm diameter) probe exactly the same spot.

The low-temperature saturation coverages of CO adsorbed on the (100), (110) (data from refs. [2] and [9], respectively) and (111) surfaces of platinum are compared in table 2. The observed coverages are in excellent agreement with those determined by inspection of the LEED patterns.

The saturation CO coverages for all three surfaces are similar and correspond to packing densities in which the CO-CO spacing is 0.32 to 0.34 nm, i.e. not too different from the sum of the Van der Waals radii. Within our statistical accuracy of ± 0.03 monolayer, the saturation densities of CO adsorbed on Pt(100) and (111) surfaces are identical. The marginally smaller observed coverage for the (110) surface may indicate that this coverage is limited by the 6% smaller number of available sites rather than by the CO packing density.

In summary, we have used nuclear microanalysis to confirm that the $p(2 \times 2)$ -O overlayer on Pt(111) corresponds to a fractional coverage of 0.25. The low-temperature saturation CO coverages on the (100), (110) and (111) surfaces are in excellent agreement with those determined by inspection of the LEED patterns. Possibly they are controlled by CO-CO interactions on the (100) and (111) surfaces and by the number of available adsorption sites on Pt(110). The CO overlayer structure formed by CO adsorption on Pt(111) at 300 K is believed to be $c(4 \times 2)$.

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