Adsorption Site Determination by Means of Surface Core Level Shift High Energy Photoelectron Diffraction: Pd{110}(2 × 1)$p2mg$-CO

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We propose a novel application of the photoelectron diffraction method for determining the adsorption site of an adsorbate, based on the diffraction of high kinetic energy photoelectrons originating from the topmost layer of the substrate. Sensitivity to the topmost layer is achieved by working at grazing emission angle and by means of the adsorbate induced surface core level shift. A simple single scattering theory is shown to be adequate to interpret the data. We apply the method to the Pd{110}(2 × 1)$p2mg$-CO system and provide clear evidence that CO adsorbs in the short bridge sites.

Photoelectron diffraction (PD) is a well-established technique for the determination of surface structures [1–3]. In PD the intensity of a core level photoemission peak is measured as a function of the emission angle and/or the photoelectron kinetic energy. The resulting pattern is due to the interference between the directly emitted photoelectron wave portion and the wave portions scattered by the atoms surrounding the emitter. To determine the geometrical parameters, the experimental data are usually compared to theoretical calculations obtained with trial geometries and tabulated atomic properties. The structural model that yields the best agreement (usually evaluated by means of reliability factors) is accepted as the correct one.

For a system with many atoms, such as a solid surface, many different scattering events can in principle contribute to PD. Indeed for low (≤ 500 eV) photoelectron kinetic energy, multiple scattering plays a crucial role. On the other hand if the electron kinetic energy is high enough, single scattering has proved to be adequate for the calculation of PD patterns because of the relatively low elastic scattering cross section. Moreover, for fast electrons the scattering factor is strongly peaked in the forward direction, thus giving a straightforward tool to identify bond directions [1–3]. This property is the base of several studies in which the orientation of molecules chemisorbed on single crystal surfaces is accurately determined by measuring the PD of a core level of the molecule bonding atom as a function of the emission angle [3]. In this case though, PD has a very low sensitivity to the chemisorption site [4], as a backscattering event is required for the scattering electron to reach the detector.

Sensitivity to atoms that are "behind" the emitter (and therefore to the chemisorption site) can be achieved by working in the low energy regime [5]. Moreover, under these conditions the surface sensitivity is highest, as the electron mean free path has a minimum in most solids in the 20 to 150 eV kinetic energy range [6]. These facts make low energy PD a powerful tool to determine the complete surface structure of clean or adsorbate covered surfaces. The enhancement of surface sensitivity offers the further possibility of using the topmost substrate atoms as emitters when the surface core level shift (SCLS) can be resolved. The price to pay is that many multiple scattering paths must be included in the simulations, requiring a highly sophisticated theory. This is why even though the potentiality of low energy PD in conjunction with the use of SCLS was shown a few years ago [7, 8], only very recently has an adequate theory become available, allowing us to actually determine surface structural parameters [9, 10].

In this Letter we show that high kinetic energy PD can be used as a tool for determining the molecule adsorption site. By monitoring the surface shifted component of the substrate atom core level photoemission peak we place the emitter "behind" the adsorbate and therefore achieve sensitivity to the adsorption site in the forward scattering conditions. In this way the data can be interpreted in the framework of the simple single scattering cluster (SSC) theory [11]. The surface sensitivity required to highlight the signal from the topmost layer is obtained in our case by measuring azimuthal angle scans at very grazing polar angles.

We tested the technique by applying it to the Pd{110}(2 × 1)$p2mg$-CO chemisorption system, for which recently a CO "atop" adsorption site has been proposed from dynamical low energy electron diffraction (LEED) studies [12], in contrast to the "short bridge" site suggested earlier on the basis of vibrational spectroscopies [13, 14]. An independent structural determination is therefore needed for this interesting case. This system is particularly suitable to our technique as the CO-induced SCLS of the Pd $3d_{5/2}$ core level in the low temperature saturation (2 × 1)$p2mg$ phase is known to be 0.98 eV [15], making it easy to separate the bulk from the surface contribution.

The experiment has been performed with an ultrahigh vacuum chamber equipped with standard surface science

experimental facilities [16]. A 150 mm mean radius electron energy analyzer (VSW Scientific Instruments Ltd) with variable magnification, variable entrance slit, and multidetector was used to collect electrons emitted by the sample illuminated by a monochromatized Al $K\alpha$ source (VSW). With the slit and magnification settings we have used during the PD experiments the angular resolution was 3° FWHM. The sample was a Pd(110) single crystal mounted on a computer controlled 6 axis manipulator (Fisons Instruments). Data acquisition and sample movement control were performed by a computer program described elsewhere [17] which allows us to align the sample surface *in situ* by LEED and to keep the alignment during the PD experiment to within 0.3° for scans around any of the three rotational axes. The Pd(110) sample was cleaned *in vacuo* by standard techniques following the procedure described elsewhere [16].

A sharp $(2 \times 1)p2mg$ LEED pattern was obtained by exposing the Pd{110} to 10 L [1 L (Langmuir) = 10^{-6} Torr s] of CO at 150 K. Figure 1 shows the Pd $3d_{5/2}$ peak from this surface together with a fit obtained as a sum of two Doniach-Sunjič [18] peaks convoluted with a Gaussian to take into account the experimental resolution. A SCLS of 0.93 eV was found, in excellent agreement with Ref. [15].

A series of photoemission spectra has been measured at fixed polar emission angle (80° from the surface normal) as a function of the azimuthal angle, measured from the $[1\bar{1}0]$ direction. The sample was kept at 150 K during the experiment, and the quality of the LEED pattern was checked at the end.
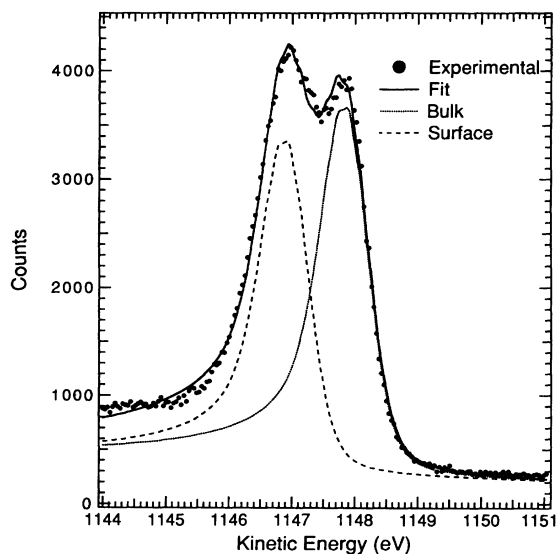
The bulk and surface photoelectron diffraction curves have been separated by fitting each spectrum as described above, keeping constant the line shape parameters and allowing intensities of the bulk and surface components to vary. The bulk and surface photoelectron diffraction scans measured in this geometry are shown in Fig. 2 as solid curves in the top and bottom panel, respectively.

We used SSC plane wave (SSC-PW) theory to simulate the experimental curves and determine the adsorption site. The experimental angular resolution was also taken into account in the calculation by a two dimensional Gaussian averaging. Applicability of this theory was checked by simulating the bulk PD curve. The result is shown in Fig. 2 in the top panel. The agreement is excellent, confirming the adequacy of the simple theoretical approach for our experimental conditions. It is important to note here that multiple scattering events are more likely to happen in the bulk than at the surface, as the number of atoms surrounding the emitter is much higher. We therefore calculated with confidence the PD curves for different adsorption geometries using the same approximation. Different models were tried, with CO molecules adsorbed in both "atop" and "short bridge" sites, varying the C-Pd distance and the α angle (see Fig. 3, top panel). The agreement between experimental and simulated curves was judged on the basis of the reliability factors R_1 and R_4 defined in Ref. [19], which express the agreement between the intensities and the derivatives, respectively, of the theoretical and experimental curves. In
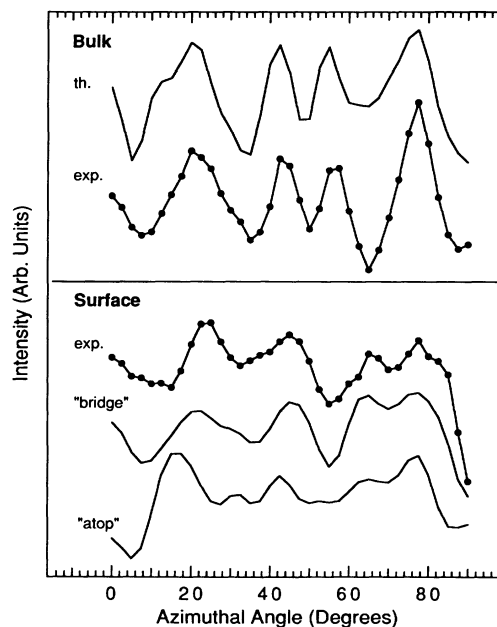

FIG. 1. Pd $3d_{5/2}$ photoemission spectrum (points) and fit (solid line) from the Pd{110}(2 × 1)$p2mg$-CO system, measured at 80° polar angle and 0° azimuthal angle (corresponding to electrons emitted in the {1$\bar{1}$0} plane). Surface and bulk components of the fit are shown.

FIG. 2. Intensity of the Pd $3d_{5/2}$ peak from the Pd{110}(2 × 1)$p2mg$-CO structure as a function of the azimuthal angle at 80° polar angle (solid line with points). Top panel: bulk component; bottom panel: surface component; theoretical curves are shown as solid lines.
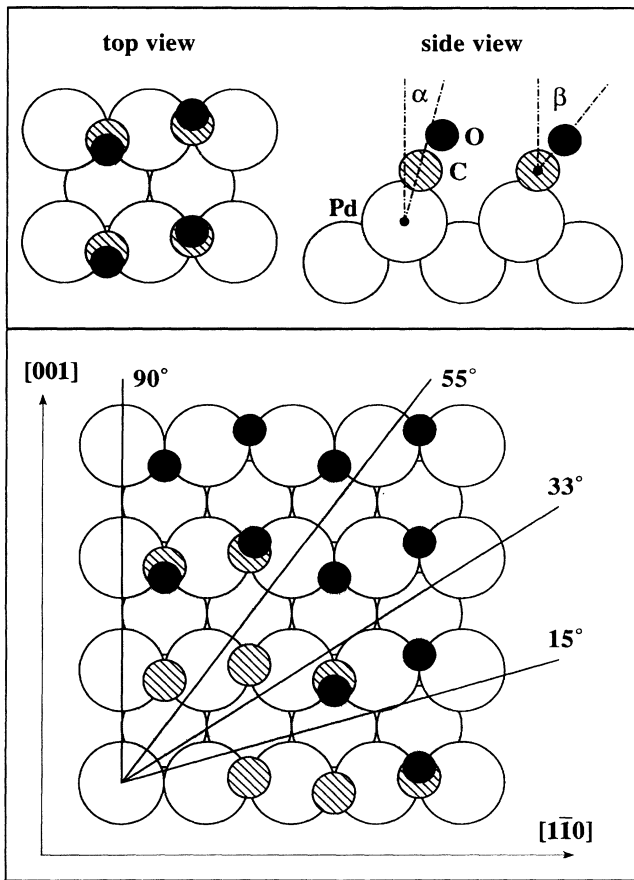
FIG. 3. Top panel: Hard sphere structural model of the Pd{110}(2 × 1)p2mg-CO system. Lower panel: Carbon (dashed circles) and oxygen (dark circles) atoms of the adsorbate layer which contribute to the forward scattering at 80° polar angle. The emitter is the Pd atom in the lower left corner. The lines represent the azimuthal directions of the main minima of the experimental data (see Fig. 2, bottom panel).

all the models we kept the β angle constant at 24° a value that has been determined independently by PD of the C 1s core level [20]. We tried the effect of variations of the β value on the simulations and found that they changed very little when β was varied in the range 18°–30°. This can be understood considering that at 80° polar angle, for CO adsorbed nearly upright, the forward scattering from a Pd emitter involves C and O atoms of different CO molecules, the O atom being much further away from the emitter than the C atom and therefore contributing much less to the diffraction pattern. This is evidenced in Fig. 3, bottom panel, where we have drawn only the atoms of the adsorbed molecules which are involved in the forward scattering process at 80° polar angle. The emitter is the Pd atom in the bottom left corner. We have also indicated the azimuthal directions corresponding to the main minima in the experimental curve. It is apparent that these

directions correspond exactly to the corridors existing in the bridge-bonded CO layer.

The curves with the best theoretical simulations for the atop and bridge CO adsorption sites are reported in the bottom panel of Fig. 2. The latter already by visual inspection appears to be the only one consistent with the experimental data. This is further confirmed by the R factors for the two geometries summarized in Table I. For comparison, we also report the R factors for the bulk curve and for the curve calculated using the atop structural parameters proposed in Ref. [12] for this system.

Our data strongly support a short bridge adsorption site. The structural parameters we obtained are summarized in Table II and compared with the dynamical LEED values and with the parameters recently determined by surface extended x-ray absorption fine structure [21] and PD [22] for CO adsorbed on Ni(110) in the same low temperature compressed phase.

Our result is in clear contradiction with the model proposed by Wander, Hu, and King [12], both in the adsorption site assignment and in the C-Pd nearest neighbor distance. The C-Pd distance we determined is in good agreement with the values for metal carbonyls found in the literature [23]. While simple carbonyls of Pd do not seem to be known, typical values for the metal-CO distance in Fe and Ni carbonyls (where the CO molecule behaves as a monodentate ligand) are ~1.8 Å, and slightly larger values (~1.9 Å) are found for carbonyls where CO bridges between two metal atoms. Our determination of the adsorption site agrees with previous assignments [13, 14], and indicates that the adsorption geometry for CO on the Pd(110) and Ni(110) surfaces is similar. It is noteworthy that the same bridge adsorption site has been recently proposed for CO in the closely related Rh{110}(2 × 1)p2mg-CO system on the basis of the O 1s binding energy [24].

In conclusion we propose a new, very powerful and relatively simple method for the determination of adsorption sites by means of surface core level shift high energy PD. With respect to the chemical shift low energy PD, the technique we propose has the advantage of being interpretable within the framework of the much simpler SSC-PW theory, still yielding clear and reliable information about the adsorption geometry. Also, the ex-

TABLE I. Comparison of the reliability factors as defined in Ref. [19] obtained for the bulk and surface Pd $3d_{5/2}$ photoemission peak.

Experimental data	Model	R_1	R_4
Bulk	Bulk 80°	0.073	0.665
	Best bridge	0.065	0.627
Surface	Best atop	0.111	1.214
	Atop Ref. [12]	0.129	1.429

TABLE II. Comparison of the structural parameters obtained for Pd{110}(2 × 1)$p2mg$-CO and for the related system Ni{110}(2 × 1)$p2mg$-CO. See Fig. 3 for the definitions of α and β.

System	Adsorption site	α (degrees)	β (degrees)	C-metal Distance (Å)
CO/Pd{110} (this work)	Bridge	5(±5)	⋯	1.8(±0.1)
CO/Pd{110} [20]	⋯	⋯	24(±3)	⋯
CO/Pd{110} [12]	Atop	11(±4)	13(±5)	2.11(±0.06)
CO/Pd{110} [21]	Bridge	19(±3)	21(±5)	⋯
CO/Pd{110} [22]	Bridge	16(±2)	19	1.94(±0.02)

periment can be performed using conventional monochromatized x-ray sources, even though the higher resolution achievable with synchrotron radiation allows applicability to systems with smaller SCLS's. By applying this technique we have clear evidence that the CO adsorption site in the Pd{110}(2 × 1)$p2mg$-CO system is the short bridge, thus solving the contradiction in the previous literature.

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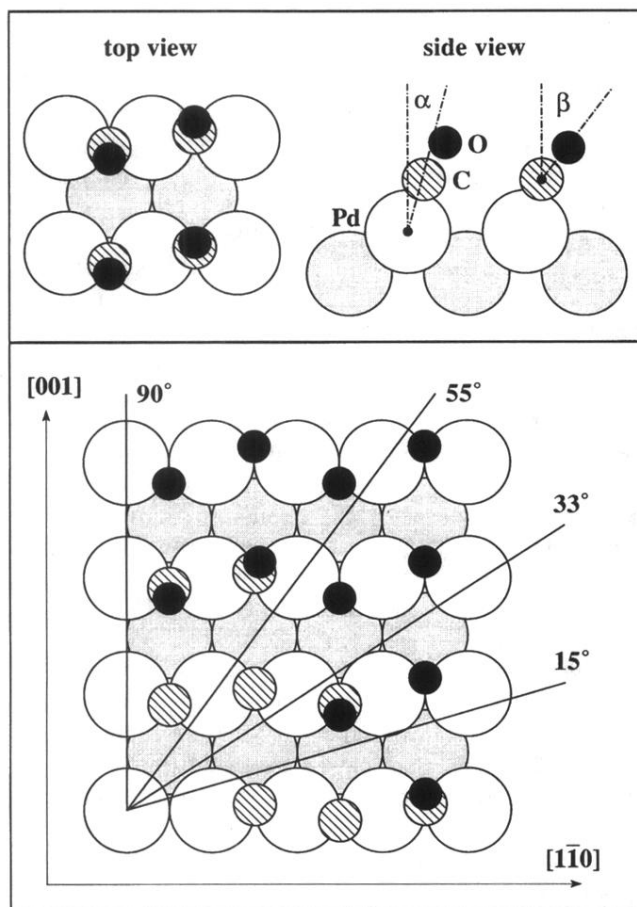[24] V. R. Dhanak, A. Baraldi, G. Comelli, G. Paolucci, M. Kiskinova, and R. Rosei, Surf. Sci. **295**, 287 (1993).

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