# Structure Determination for Coadsorbed Molecular Fragments Using Chemical Shift Photoelectron Diffraction

K.-U. Weiss, R. Dippel, K.-M. Schindler, P. Gardner, V. Fritzsche, and A. M. Bradshaw
*Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, D 1000 Berlin 33, Germany*

D. P. Woodruff
*Physics Department, University of Warwick, Coventry CV4 7AL, United Kingdom*

M. C. Asensio
*Instituto de Ciencia de Materiales, Consejo Superior de Investigaciones Científicas, Serrano 144, 28006 Madrid, Spain*

A. R. González-Elipe
*Instituto de Ciencia de Materiales, Consejo Superior de Investigaciones Científicas, Apartado 1115, 41071 Sevilla, Spain*

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Chemical shift photoelectron diffraction has been applied to the model system of coadsorbed $PF_x (x=1,2,3)$ species on Ni(111), produced by electron beam fragmentation of a $PF_3$ overlayer, to determine quantitatively and independently the local adsorption site of each species. $PF_3$ is found to occupy atop adsorption sites above the outermost Ni layer atoms at a P-Ni bond length of $(2.07 \pm 0.05)$ Å, $PF_2$ occupies bridge sites at a spacing of $(1.70 \pm 0.05)$ Å, while the PF species occupy both types of threefold coordinated hollow sites, maintaining a constant P coordination throughout the fragmentation.

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A key step in extending our understanding of chemical processes at surfaces, such as those of relevance to heterogeneous catalysis, is developing an ability to obtain detailed information on the local structure of coadsorbed molecular and atomic species, including a range of molecular fragments which may be either reaction intermediates or spectator adsorbates. Although vibrational spectroscopy and core level photoemission can provide excellent fingerprints of such coadsorbed species, no true local structural method has yet been demonstrated to provide a viable solution to such problems. In this paper we describe the successful application of chemical shift photoelectron diffraction to one model system of this type, that of coadsorbates of the type $PF_x$ (with $x=1,2,3$) on Ni(111).

In the scanned energy mode photoelectron diffraction (PD) technique [1,2] used here, the intensity of a core level photoemission signal from an atom in an adsorbed species is measured in fixed emission directions as a function of photon, and thus photoelectron kinetic, energy. Coherent interference between the directly emitted photoelectron wave field and components elastically (back)-scattered from the surrounding substrate atoms causes modulations in this photoemission intensity as the photoelectron wavelength changes, causing the scattering paths to switch in and out of phase. Analysis of these PD spectra by comparison with the results of model calculations for different possible local adsorption structures allows one to make rather accurate quantitative determinations of the local adsorbate geometry. The binding energy of the core levels is characteristic of the atomic species, so PD is intrinsically sensitive to the elemental species. By using the "chemical" shifts in the measured photoelectron binding energy for different local bonding states of the emitter atom, one can also achieve chemical state sensitivity in PD. We have previously demonstrated this potential [3] for chemical shift PD in an experiment on the acetate and trifluoroacetate species on Cu(110), in which the chemical shift in the C 1*s* binding energy between the C atoms in the methyl and carboxyl groups permitted the sites of these two atoms to be determined separately, in addition to the site of the O atoms within these molecular species. Note that other experiments have also been reported which demonstrate the closely similar possibility of *surface* core level shift photoelectron diffraction from clean surfaces [4], but this method is not relevant to the determination of local adsorbate structure.

In the present case we show that chemical state labeling can be used to obtain separate PD spectra, and thus separate local adsorption geometries, for the different molecular fragments obtained on a Ni(111) surface after exposing an adsorbed $PF_3$ layer to electron irradiation. This electron fragmentation process has been previously characterized by ESDIAD (electron stimulated desorption ion angular distributions), which also provided qualitative information on some aspects of the bonding geometry (as well as some important complementary information on the azimuthal orientation of the P-F bonds not considered in the present work) [5]. The basis of our chemical shift PD measurement is clearly shown by the P 2*p* photoelectron energy spectrum recorded at a fixed photon energy of 205 eV from such a surface (see Fig. 1). Also shown on this spectrum is the decomposition of the main peaks into three different chemically shifted spectra, each comprising the P 2*p* spin-orbit split doublet. These three states can be assigned to $PF_3$, $PF_2$, and PF coad-

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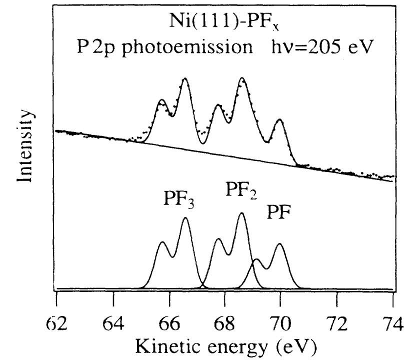

FIG. 1. Photoemission electron energy distribution in the region of the P 2*p* peaks recorded at a photon energy of 205 eV from the fragmented PF$_x$ layer on Ni(111), showing the contributions from the three different species.

sorbed in the partially fragmented layer [6]. Note that intense light illumination (using zero order synchrotron radiation) can cause complete fragmentation to a pure P layer, but this final stage of fragmentation does not appear to occur with the 200 eV electron irradiation used in this experiment. The much lower intensity of the monochromatic radiation used to collect the photoelectron diffraction data was insufficient to produce any significant changes in photofragmentation during the collection of a single data set.

In order to determine the local adsorption site of the three coadsorbed molecular species shown in the spectrum of Fig. 1, measurements were made of this photoelectron energy spectrum at regular photon energy steps in emission directions along the surface normal and at 30° polar emission angle in a ⟨110⟩ azimuth. The three chemically shifted peaks were then separated by a simple peak fitting routine, and their respective areas mapped to provide scanned energy mode photoelectron diffraction spectra of each chemical state for each of the two geometries. Several different methods of data processing were tested in performing the background subtraction and peak separation to ensure that the resulting photoelectron diffraction spectra were not sensitive to the exact method used. The variations found by these different methods form the basis of the error bars shown on the experimental plots of Figs. 2–4. Purely statistical (Poisson) errors fall within the thickness of the lines in the figures. The experiment was conducted by taking synchrotron radiation from the BESSY source in Berlin, using the high energy toroidal grating monochromator [7] of the Fritz Haber Institute. The sample was cleaned by the usual combination of *in situ* argon ion bombardment and annealing, and the quality of the surface was monitored by LEED and core level photoemission. Photoelectron energy spectra were recorded at a fixed angle of 60° relative to the incident photon beam using a 150° deflection hemispherical analyzer (VG Scientific) fitted with three-channel detection. The horizontal plane of incidence and collection means that the **A** vector of the radiation is 30° from the collection direction. The general procedure for the photoelectron diffraction experiment was the same as that reported in previous studies [2,8–10], although in order to separate out the chemically shifted states it was necessary to operate the monochromator and electron energy analyzer at the best practicable energy resolution.

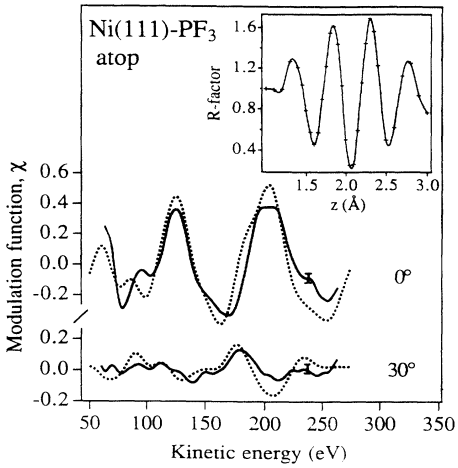

FIG. 2. Comparison of the experimental (full line) and theoretical best-fit (dotted line) P 2*p* PD spectra from PF$_3$ in the mixed layer recorded at emission angles of 0° and 30°. The inset shows the dependence of the two-spectrum *R* factor, which provides a measure of the quality of the fit between experiment and theory for the atop site as a function of P-Ni top layer spacing.

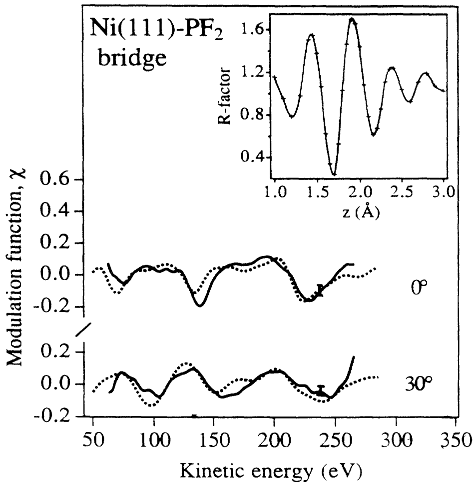

FIG. 3. Experimental and theoretical P 2*p* PD spectra and *R*-factor plot for the PF$_2$ species in the fragmented layer on Ni(111). The adsorption site is bridge; other details as for Fig. 2.

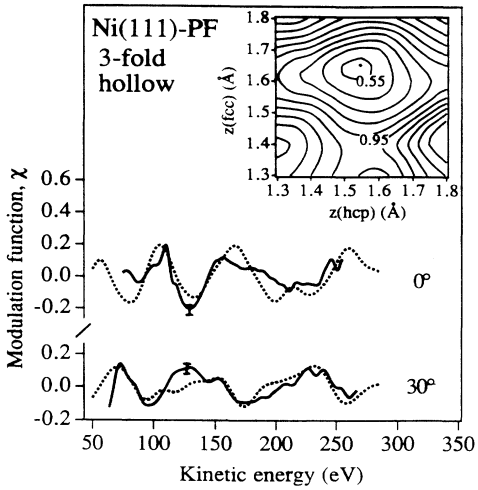

FIG. 4. Experimental and theoretical P 2*p* PD spectra for PF species in the fragmented layer on Ni(111). The adsorption sites are the mixed fcc and hcp hollow sites. The inset shows the dependence of the two-spectrum *R* factor on the P-Ni layer spacings in each site as an *R*-factor contour map.

The highest photon energy at which the peaks could be separated satisfactorily corresponded to a photoelectron energy of approximately 260 eV. The six PD spectra resulting from this procedure are shown in Figs. 2-4.

In order to determine the adsorption sites from these data each spectrum was compared with theoretically computed spectra based on a series of model structures. The calculations were conducted using a full multiple scattering [11,12] simulation computer code, and the experimental and theoretical spectra were compared using reliability factors (*R* factors) as described in further detail elsewhere [2,8-10]. The results of this process are also summarized in Figs. 2-4. In particular, for each data set a range of structures was tested based on adsorption in atop, bridge, fcc hollow, or hcp hollow (i.e., hollow sites above Ni atoms in the third and second substrate layers, respectively) at various P-Ni top layer spacings. In the case of $PF_3$, the best fit was found for atop site adsorption at a layer spacing 2.07 ± 0.05 Å. Figure 2 shows a comparison between the two experimental PD spectra and the results of the theoretical calculations for this best-fit structure. The inset of Fig. 2 shows how the two-spectrum *R* factor based on a normalized square deviation between the experimental and theoretical spectra varied as the layer spacing was changed for this site. Similar curves (with the same local minima) were obtained using an alternative *R* factor based on that proposed by Pendry for LEED analysis [13]. [Actual normal emission theoretical spectra for this range of spacings for Ni(111)/$PF_3$ have been presented in Ref. [9].] This result for the $PF_3$ species is in excellent agreement with the findings of a photoelectron diffraction study of the undissociated molecular layer (Ni-P spacing 2.03 ± 0.03 Å [9,14]), and an independent study of this same adsorption system using standing x-ray wave field absorption and surface extended x-ray-absorption fine structure (SEXAFS) (Ni-P spacing 2.07 ± 0.03 Å [15]).

In the case of the $PF_2$ species in the layer of coadsorbed fragments, the results of the same procedure revealed that this species occupies bridging sites at a P-Ni top layer spacing of 1.70 ± 0.05 Å, a value which implies a P-Ni nearest-neighbor distance of 2.10 ± 0.05 Å, essentially the same as that for $PF_3$. For the PF species, on the other hand, a satisfactory fit of the experimental data could not be obtained for any single adsorption site. We therefore also considered the possibility that both the fcc and hcp hollow sites may be occupied; for many adsorbed species the energy difference between these two sites appears to be very small, and although in many cases of ordered structures there appears to be a clear preference for the fcc hollow [16], there are examples of both disordered [e.g., Ag(111)/I] and ordered [e.g., Ni(111)/H and Ni(111)/NO] systems for which both sites appear to be occupied with essentially equal probability [17-19]. In the case of PF in the coadsorption layer we considered the possibility that there may be some preference in occupation for one of these sites, but the best fit is compatible with equal occupation of both sites (corresponding to an incoherent sum of spectra from the two sites), but with a slight difference in the P-Ni top layer spacing (the spacing being 0.1 Å larger in the fcc site). Even for this optimized geometry the quality of the fit between theory and experiment (as judged visually and by the value of the *R* factor for the best fit) is significantly inferior to that found for the other species. We also noted that there is a slight discrepancy between the optimum layer spacing values for the two experimental spectra of 0.1 Å (although both results show the fcc layer spacing 0.1 Å larger than that for the hcp site). For this reason, the overall best fit (obtained for the minimum in the two-spectrum *R*-factor map as a function of both layer spacings; see inset of Fig. 4) is also slightly worse than the best fit which can be obtained for each spectrum independently. The reason for the poorer quality of the fit to the PF data is not entirely clear, although we should note that the fragmentation of the initial saturation coverage layer of $PF_3$, coupled with an apparent conservation of surface P concentration, must lead to considerable adsorbate-adsorbate interactions in the fragmented layer involving mixed atop, bridge, and hollow sites. It is therefore possible that there is some distortion of the local hollow sites, but the rather short data range makes the exploration of additional areas of parameter range rather unrealistic.

Despite this slight doubt over the more subtle aspects of the PF sites, our results provide a rather clear demonstration of the potential of chemical shift photoelectron diffraction to make quantitative determinations of the local adsorption structure of coadsorbed molecular fragments involving common elemental species. There are currently no alternative means of providing this information in such a specific fashion. In the particular case of the $PF_x$ species in Ni(111), ESDIAD provides clear semiquantitative information, specifically on the azimuthal orientation of the P-F bonds (not obtainable through PD P $2p$ data) and is therefore remarkably successful in indicating that $PF_3$ occupies atop sites and $PF_2$ occupies bridge sites [5]. This technique, however, provides no quantitative structural site information, and the results for PF on Ni(111) could be compatible, on symmetry grounds, with any of the high symmetry adsorbate sites. In the case of vibrational spectroscopy, which is rather successful in fingerprinting coadsorbed fragments, we have previously provided at least one clear example that the practice of using internal stretching frequencies alone as a means of identifying adsorption sites can lead to very misleading results [20].

In summary, we have provided a clear demonstration of the ability of chemical shift photoelectron diffraction to provide quantitative information on the local adsorption structure of coadsorbed molecular fragments, and in the case of $PF_x$ on Ni(111) have shown that there is a progression in local site from atop to bridge to hollow as the $PF_3$ molecule loses successive F atoms, leading to a constant coordination number for the P atoms. With further improvements in spectral resolution and flux, to be expected in third-generation synchrotron radiation sources, we can anticipate the application of this method to problems of increasing complexity, such as the investigation of coadsorbed small hydrocarbon fragments.

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