Using photoelectron diffraction to determine complex molecular adsorption structures

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Abstract. Backscattering photoelectron diffraction, particularly in the energy-scan mode, is now an established technique for determining in a quantitative fashion the local structure of adsorbates on surfaces, and has been used successfully for ~100 adsorbate phases. The elemental and chemical-state specificity afforded by the characteristic core level photoelectron binding energies means that it has particular advantages for molecular adsorbates, as the local geometry of inequivalent atoms in the molecule can be determined in a largely independent fashion. On the other hand, polyatomic molecules present a general problem for all methods of surface structure determination in that a mismatch of intramolecular distances with interatomic distances on the substrate surface means that the atoms in the adsorbed molecule are generally in low-symmetry sites. The quantities measured experimentally then represent an incoherent sum of the properties of each structural domain that is inequivalent with respect to the substrate point group symmetry. This typically leads to greater ambiguity or precision in the structural solutions. The basic principles of the method are described and illustrated with a simple example involving molecule/substrate bonding through only one constituent atom (TiO₂(110)/H₂O). This example demonstrates the importance of obtaining quantitative local structural information. Further examples illustrate both the successes and the problems of this approach when applied to somewhat more complex molecular adsorbates.

1. Introduction
A detailed knowledge of the structure of adsorbed molecules on surfaces is the starting point to understanding the electronic structure, the adsorbate-substrate bonding, and the potential chemical properties. Key aspects are the adsorption site, the extent to which the molecule and/or the underlying surface are structurally modified by the bonding, and the interatomic bondlengths, particularly between the molecule and the surface, but also within the molecule. Heterogeneous catalysis exploits the change in energetics of a reaction between two species when at least one of them is bonded to an ‘active’ surface, so these structural questions underpin any attempt to gain a fundamental understanding of this crucially important aspect of chemistry.

Developments in the techniques of surface science have led to the availability of a range of methods to determine the structure of single crystal surfaces with and without adsorbate species. Conventional diffraction techniques, and low energy electron diffraction (LEED) in particular, have contributed the largest number of structural solutions, but these methods rely on long-range order of the whole surface. For many molecular adsorbate systems, and particularly those involving coadsorption of two or more species, a situation of particular relevance to understanding surface reactions and the role of surface promoters and poisons, the adsorbates lack this long-range
periodicity. To investigate such surfaces one requires a *local* structural probe, and the most successful one has been photoelectron diffraction. This technique exploits the same coherent interference of elastic scattering paths as LEED, but uses a local electron source, namely photoemission from a core level of a constituent atom of the adsorbate species.

Fig. 1 Schematic of the electron scattering paths in photoelectron diffraction from adsorbed atoms

Fig. 1 illustrates the underlying principle. The photoelectron wavefield emerges from the adsorbate atom (shown in Fig. 1 as an isolated atom, but this could equally well be an atom within an adsorbed molecule) and the detected signal outside the surface comprises a coherent sum of the directly emitted wave and components of the same wavefield elastically scattered from the atoms surrounding the emitter, including, in particular, the underlying substrate atoms. Modulations in the detected photoemission intensity are produced as a function of detection angle (which influences the scattering path lengths) or by changing the photoelectron wavelength by varying the photon, and thus the photoelectron, energy. As the phases of the scattering paths depend on the location of the emitter atom relative to its neighbours, the detected modulations are characteristic of the position of the emitter atom. In our investigations we exploit the scanned-energy mode of this technique, to which we have assigned the acronym PhD. The PhD modulation spectra are collected within an energy range of ~50-400 eV, for which elastic backscattering cross-sections are reasonably strong, and are measured at a range of emission angles to enlarge the data set and sample a larger range of electron momentum transfer space. Structure determination is then achieved by a trial and error approach based on a series of ‘guessed’ structures, that are each optimised by adjusting the structural parameters and comparing the results of multiple scattering simulations with the experimental results. This approach is essentially identical to that used in conventional LEED studies, and, indeed, in almost all surface structural techniques. The very first ‘demonstration’ experiments of photoelectron diffraction were performed in 1978\(^2,3,4\), but since that time the method has been developed into a practical tool that has solved ~100 surface structures \(^5\).

PhD has a number of important advantages for determining the local geometry of adsorbed molecules. Firstly, as noted above, it is intrinsically a local technique (resulting from the fact that the initial outgoing electron wave is some sum of spherical harmonics centred on the emitter atom). Secondly, it is element specific. The characteristic core-level binding energies of the different atomic species on the surface means that the PhD modulation spectra from each different elemental atom can be collected independently. Moreover, as most molecular adsorbates are comprised primarily of low atomic number elements (especially C, N, O and H), whereas most substrates of interest have significantly higher atomic number, the dominant elastic scattering contributions are generally from the substrate. This means that the location of each elemental atom on the surface can be determined in a fashion that is largely independent of the location of the other atoms within the molecule, greatly simplifying the structure determination. Intramolecular scattering can generally be added in a second stage of the analysis to refine the structure. Thirdly, PhD is chemical-state specific. If the absorbed species contains the same element in different local geometries, there will be a ‘chemical shift’ in the core level photoelectron binding energy; this effect is an important aspect of the technique of X-ray
photoelectron spectroscopy (XPS) and, indeed, the origin of its original name of ESCA (electron spectroscopy for chemical analysis). Providing the associated chemical shift is large enough to be resolved, this means that the PhD data (and thus the local structure) can be separated for atoms of the same element in different structural environments. For molecular adsorbates this is most commonly exploited to distinguish atoms of the same element in different functional groups in an adsorbed molecule, for example C atoms in methyl (CH$_3$) and carboxylate (COO) species (e.g. in the acetate species$^6$). However, it can also allow distinctions to be made between two identical species coadsorbed in different local sites on a surface, such as CO in atop, bridge and hollow sites.

While all these aspects are positive there are, of course, problems and limitations. These arise, particularly, because the technique works best when the emitter atom occupies a high-symmetry site on a surface. If the adsorption site has a symmetry that is lower than that of the point group symmetry of the substrate, then there will coexist on the surface multiple structural domains that are related by the ‘missing’ symmetry elements of the substrate. The measured PhD modulation spectra will then be an incoherent sum of the modulations from each of the symmetry-related domains, and the resulting modulation amplitude will be attenuated. Typically, in PhD, the strongest modulations are seen when a nearest-neighbour strongly-backscattering substrate atom lies directly ‘behind’ the emitter relative to the detection direction, in part for symmetry reasons, in part because elastic backscattering cross-sections commonly show a peak at 180° scattering angle. It is these strongly-modulated spectra that provide the most reliable basis for the associated structure determination and, indeed, the identification of the detection directions at which such spectra are measured provides a basis for initial identification of the most likely structural model. Low symmetry adsorption sites generally lead to weaker PhD modulations and thus to a more challenging process of structure determination. This is an intrinsic problem of many molecular adsorbate systems. If the molecule bonds to the surface through more than one constituent atom or, as is commonly the case for aromatic molecules, lies flat with its molecular plane essentially parallel to the surface, there is an inevitable mismatch of interatomic distances within the molecule and within the underlying surface. This means that at least some of the constituent atoms of the molecule are bound to occupy low symmetry sites (even if the molecule as a whole occupies a high-symmetry site).

In the remainder of this article a few examples of recent PhD studies are presented that illustrate both successes and challenges in molecular adsorbate studies on surfaces.

2. Molecular bonding through a single atom: TiO$_2$(110)/H$_2$O

When adsorbed molecules bond to a surface through a single constituent atom, any mismatch of intramolecular and interatomic surface bondlengths has no bearing on the way the molecule bonds to the surface, and one generally finds a high-symmetry adsorption site that can be solved relatively easily by the PhD technique. Fig. 2 shows results from such an investigation, notably of molecular water, H$_2$O, on TiO$_2$(110)$^7$.$^8$.

Of course, in this system both the adsorbate and substrate contain O atoms, so it is important to be able to distinguish between emission from these two types of O emitter atoms. As may be seen from Fig. 2(a), which shows the XP spectra from the clean surface and after low-temperature water adsorption (and annealing to 230 K), there is a large chemical shift (3.5 eV) between the photoelectron binding energies of the water and oxide O 1s states. Fig. 2(b) shows a set of PhD modulation spectra recorded from the water O 1s component in 10 different geometries corresponding to different polar emission angles and three different azimuthal planes of incidence and photoelectron detection. The experimental data (full lines) are compared with the results of the multiple scattering simulations (dashed lines) for the best-fit structural model, shown in Fig. 2(c). Clearly the overall agreement is very good, reflected in a low associated reliability factor (R-factor) value of 0.15. One striking feature of the PhD spectra is the strong (~±40%) modulations that appear to have a single dominant period in the normal emission spectra (0° polar angle). This is the behaviour we may expect if the O atom of the water occupies a site directly atop a strongly-scattering substrate atom (such that normal emission corresponds to 180° scattering angle from this atom) and indeed the water is found to occupy a site...
atop the undercoordinated (5-fold coordinated) Ti atoms in the TiO$_2$ surface. The reduced sample temperature (~190 K) used in this study also helps to ensure that the PhD modulations are large, by reducing the Debye-Waller factor in the scattering process.

The adsorption site established in this way, atop an undercoordinated Ti atom, was actually identified in earlier STM (scanning tunnelling microscope) investigations of this surface$^{9,10}$, but a key feature of the PhD investigation is its ability to obtain quantitative information on the associated bondlengths. The TiO$_2$/H$_2$O system is of particular interest because of the possible application of titania as a catalyst for the photochemical production of hydrogen from water$^{11}$, but theoretical modelling of the interaction of water with TiO$_2$(110) has proved challenging. In particular, while it is well-established experimentally that molecular water does not dissociate on a defect-free surface, most calculations in the past have concluded that such dissociation is facile. In this context the value of the Ti-O$_{\text{water}}$ bondlength of 2.21$\pm$0.02 Å found in the PhD study appears to be highly relevant, because in theoretical studies that concluded that dissociation is facile the equivalent bondlength was reported to be very much longer, in the range 2.28-2.41 Å. In effect, it appears that molecular water is significantly more strongly bound to TiO$_2$(110) than these calculations would suggest. This may well be the reason why the barrier to dissociation is calculated to be too low. Experimentally-determined adsorption bondlengths may thus provide a key test of theoretical calculations of this type.

Finally, it is perhaps worth noting that, in the context of PhD structure determination, this adsorption system is particularly simple, because H atoms are such weak electron scatterers that their role in the diffraction process can be safely ignored. As such, from the point of view of the data analysis (but not, of course, from the chemistry), the situation is equivalent to an investigation of a simple atomic (O) species alone.
3. Molecular bonding through two or more constituent atoms
The problem arising from low-symmetry emitter sites emerges when a molecule bonds to a surface through two or more of its constituent atoms, although the scale of the associated problem for PhD structure determination varies. A relatively simple situation arises, for example, in the case of simple carboxylic acids adsorbed on Cu(110). Interaction with the surface leads to deprotonation of the acid, and the resulting carboxylate bonds through the two O atoms in a symmetric fashion. This behaviour has been confirmed for formate (HCOO)$^{12}$, acetate (CH$_3$COO)$^6$ and benzoate (C$_6$H$_5$COO)$^{13}$. In each case the molecular plane is perpendicular to the surface and aligned in a close-packed [110] azimuth centred over a short-bridge site such that the two O atoms occupy symmetrically-equivalent off-atop sites (Fig. 3). The mismatch of the Cu-Cu distance in the surface (2.55 Å) and the O-O distance in a free formate species (2.22 Å) is modest, and indeed the O-C-O bond angle is somewhat flexible, so the two O atoms occupy sites within ~0.15 Å of the exact atop sites and the PhD data analysis does not present a problem.

![Fig. 3 Model of local geometry of formate on Cu(110)](image)

Figure 4. Optimised structural model and subset of the associated experimental (full lines) and simulated (dashed lines) PhD data from an investigation of the structure of thymine on Cu(110) at room temperature$^{14}$. In the model the H atoms have been added for chemical consistency, but their locations were not determined.
A system that might have been expected to be significantly more challenging, illustrated in Fig. 4, is the adsorption of the nucleobase molecule thymine, on Cu(110). When deposited at room temperature XP spectra show two chemically-shifted N 1s peaks, attributed to dehydrogenation of one of the two NH species (notably the N(3) atom) through reaction with the surface to produce the molecular species shown in the schematic diagram of Fig. 4. The PhD structure determination confirms this assignment, because the PhD spectrum from this N 1s component is closely similar to that of the two (equivalent) O atoms, showing a single dominant long period modulation at normal emission characteristic of a (near-) atop site. Thus, the molecule bonds to the surface through the N(3) atom and both the O atoms, all of which occupy off-atop sites. The amplitude of these modulations is about a factor of 2 weaker than those in the TiO2/H2O system, though, attributable to larger vibrational amplitudes (at room temperature) and the fact that the emitter atoms are displaced from the ideal atop sites. Interestingly, as also seen in Fig. 4, the multiple-scattering simulations for this system also reproduce quite well the generally weak modulations from the N(1) N 1s emission component. As this N atom is rather far from the surface these modulations contain a significant contribution from intramolecular scattering.

A rather different set of systems that have led to a lot of valuable information, but expose some constraints of the method, is concerned with simple amino acids on Cu surfaces and, in particular, on Cu(110). The first study was of the simplest amino acid, glycine (NH2CH2COOH) which, as with the simple carboxylic acids, loses its acid hydrogen on interaction with the surface to produce a surface glycinate (NH2CH2COO) species, while this was followed by an investigation of the alaninate species produced by reaction with alanine (NH2CH3C*HCOOH). A key difference is that in alanine one of the central H atoms is replaced by a methyl group, causing the associated (C*) carbon atom to become a chiral centre. Fig. 5 shows why this difference is of special interest in the surface phase formed on Cu(110). In the case of glycine, which is achiral as a free molecule, the glycinate species bond to the surface (through both carboxylate O atoms and the amino N atom) in such a way as to form chiral moieties that are ‘left- and right-handed’, mirror images of one another. These form an ordered (3x2) heterochiral structure. Interestingly, a single enantiomer of alanine also produces a (3x2) ordered phase, but in this case the molecules at the centre of the unit mesh cannot be mirror
images of those at the corners, because this would involve a (forbidden) transition to the opposite enantiomer. The net effect is that the centred molecules in the unit mesh of the alanine structure must have a symmetrically distinct local adsorption structure from those at the corners.

The structure determination of both systems involved the measurement of the N 1s and O 1s PhD spectra in a range of detection directions. All showed clearly that the amino N atom lies close to atop a surface Cu atom, while the O atoms occupy two distinctly different sites that still appear to correspond to single coordination to surface Cu atoms but are up to ~1 Å off atop. The relatively low (2mm) symmetry of the (110) surface, and the mirror symmetry of the whole structure, mean that the number of structural domains over which the measurements average is only two (corresponding to the missing two-fold rotation axis of the surface phase), so quite strong modulations in the O 1s PhD spectra are seen around normal emission despite the large offset from atop. The structure determination provided an unambiguous measure of both the height of the O and N atoms above the surface, and of their lateral offsets from atop in the two principle azimuthal directions. The problem of how these individual atomic positions relate to one another in the whole molecule is not, however, entirely trivial. While it is clear that the O atom offset values in the [001] direction must have the same sign, the sign of the offset of the N atom offset in the [110] is less obvious. For example, for a specific molecule in Fig. 5, is the offset of the N atom from atop to the left or the right? Reasonable assumptions about the molecular conformation, relative to the known properties of the free glycine molecule, provide a rather clear answer to the question, yet this system does highlight a potential limitation of being able to determine the local site of the constituent atoms in a largely independent fashion. The strength offered by the simplicity of this approach can, in some cases, also become a limitation.

For the alanine system the problem of achieving a unique structure determination, based on the PhD data alone, becomes more serious. As discussed above, the four O atoms associated with the two inequivalent adsorbed alaninate species must all have different offset (low symmetry) sites, and obtaining a unique unconstrained solution proved impossible. The initial investigation clearly identified the basic geometry, but the final structural tests were performed on a previously optimised minimum energy structure obtained from density functional theory (DFT) calculations. The very significant outcome was that while the lateral positions and substrate distortions found in the DFT results were consistent with the PhD data, the actual N-Cu and O-Cu bonding distances were not. Only after reducing these by ~0.1 Å was a good fit to the PhD data obtained. From the point of view of the chemisorption bonding, of course, these are the most important structural parameters.

A recent PhD study of furan, C₄H₄O, adsorbed on Pd(111) provides an example of a more significant structural ambiguity. This investigation was greatly hampered by two problems. Firstly, the binding energy of the O 1s state is closely similar to that of the Pd 3p½ state so it proved impossible to extract reliable O 1s PhD spectra from the measurements. The difficulty in separating these components in the photoemission spectra is exacerbated by the fact that the Pd 3p spectra include shifted components associated with the surface layer, and as these are expected to be modified by adsorption, the clean surface spectra cannot be used a basis for separating the O and Pd components in the spectra from the furan-covered surface. The second problem is that the C 1s PhD spectra showed extremely weak modulations. In fact there are two chemically-shifted C 1s components, one associated with the two C atoms bonded to the O atom (the α-C atoms – see Fig. 6). The other with the two β-C atoms that are not bonded to the O atom. Modulation amplitudes of the α-C 1s PhD spectra were only ~±10% or less, but those of the β-C atoms were even weaker; under these circumstances it was felt that the signal-to-noise ratio of the β-C PhD modulation spectra were too low to allow a meaningful analysis, so the structure determination was constrained to the use of the α-C 1s PhD spectra alone. The fact that even these modulations are very weak clearly implies that the site of these C emitter atoms is substantially removed from a high symmetry site. An exhaustive search of possible structural models led to identification of the two basic structures shown in Fig. 6. In fact four optimal models were found, but the other two models only differ from the ones shown in Fig. 6 in being
displaced from fcc hollows to hcp hollows. These two hollow sites (corresponding to positions directly above third and second layer substrate atoms, respectively, only differ with respect to these sub-surface layers, and for a planar molecule lying down on the surface the energetic difference in these pairs of bonding sites is expected (and found\textsuperscript{21,22}) to be essentially negligible. All of these models share a common feature, namely that the β-C atoms are approximately 0.6 Å off atop sites with an associated C-Pd bond length of 2.13±0.03 Å. As the structure is based on the PhD spectra from these β-C atoms, this level of structural identification is not surprising, but of course there are significant differences in the local bonding in the two distinct geometries shown in Fig. 6, so the insensitivity of the limited PhD data to their distinction does not imply that both structures are equally likely in practice. In fact, DFT calculations show that while both of these structures are stable, the ‘hollow’ geometry is energetically preferred by approximately 240 meV\textsuperscript{21,22}.

![Fig. 6 Schematic diagram of the furan molecule (with the H atoms omitted) showing the labelling of the C atoms, and the two basic alternative models found for adsorption on Pd(111).](image)

4. Conclusions

Three decades of development and exploitation of photoelectron diffraction as a means of obtaining quantitative structural information for adsorbates on surfaces have proved very fruitful, and in particular have led to a significant number of structural solutions of molecular adsorbates of increasing complexity. Such complexity does, however, lead to challenges and constraints in determining unique and precise structural solutions. These arise, particularly, due to constituent atoms commonly occupying low-symmetry sites relative to the underlying substrate. Despite these constraints, results continue to provide a necessary complement and challenge to the use of modern (DFT) total energy calculations of adsorbate structures, particularly raising questions regarding the accuracy of computed chemisorption bond lengths in such systems.

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