Photoelectron Diffraction: Early Demonstrations and Alternative Modes

D. Phil Woodruff[1]

[1]Physics Department, University of Warwick, Coventry CV4 7AL, UK

Electronic mail: d.p.woodruff@warwick.ac.uk

A brief review is presented of the early demonstrations of the utility of photoelectron diffraction to determine the structure of surfaces, contrasting the two fundamentally different approaches of high-energy forward scattering and low-energy backscattering, and the alternative angle-scan and energy-scan different modes of data collection in backscattering experiments. The development and applications of the high-energy angle-scan XPD (X-ray photoelectron diffraction) version of the technique by Chuck Fadley and coworkers is contrasted with those of low-energy backscattering photoelectron diffraction, with particular emphasis on studies of molecular adsorption using the energy-scan mode (PhD).

I. INTRODUCTION

The earliest technique developed for the quantitative determination of surface structure was low energy electron diffraction (LEED). The diffraction pattern formed by incidence of electrons in the low energy range (~30-300 eV), for which atomic backscattering cross-sections are high, provides a direct indication of the surface periodicity, but simulation of the diffracted beam intensities as a function of accelerating voltage ('I-V spectra') for different model structures, using multiple scattering theory, provides a full quantitative structure determination. Although quantitative LEED using this approach has proved able to solve many surface structural problems, and is generally regarded as the benchmark technique for this purpose, it relies on the surface having good long-range order and is sensitive to the elemental character of the surface atoms only via differences in their atomic scattering cross-sections.

Photoelectron diffraction exploits the same underlying physics of LEED, namely coherent interference of components of an incident electron wavefield elastically scattered by the surface atoms, but by using photoemission from a core level of a surface atom as the source wave, rather than the incident plane wave from outside the surface used in LEED, the technique is intrinsically more sensitive to the location of these emitter atoms relative to their surroundings. Moreover, photoelectron diffraction requires only short-range order (all chemically equivalent atoms must occupy identical local sites) and can be used to obtain the local site of chemically distinct surface atoms of the same atomic species by exploiting their different photoelectron binding energies.

The first clear evidence that photoelectron diffraction can be used to determine surface structures, and specifically the identification of the local geometry of adsorbed atoms on a single-crystal surface, was provided by three papers from three independent groups published in *Physical Review Letters* in 1978[1,2,3]. In the following section an analysis of these three papers is presented leading to the identification of two distinctly different modes of photoelectron diffraction, namely high-energy forward scattering, and low-energy backscattering. The high-energy forward scattering technique developed by Chuck Fadley and his coworkers will doubtless be the subject of several articles in this special edition of *JVST A*, so the focus of the latter part of this short review will emphasise the further development and exploitation of the low-energy backscattering mode.

II. FIRST RESULTS – FORWARD SCATTERING AND BACKSCATTERING

Two of these first three demonstrations of the utility of photoelectron diffraction for surface structure determination[1,2] exploited the same backscattering processes and the same low electron energy range as those exploited in LEED, although the mode of data collection differed. Both studies used synchrotron radiation in the very soft X-ray energy range up to photon energies of a few hundred eV. The study resulting from a collaboration between the University of Warwick and Bell Labs[1] measured the variation of the intensity, at fixed polar emission angle, as the sample was rotated azimuthally, of Na 2p and Te 4d photoemission from c(2x2) phases of these two adsorbates on Ni(100). Measurements at three different photoelectron kinetic energies in the range ~40-70 eV were compared with the results of multiple scattering calculations to identify the

adsorption sites and their heights about the surface. The paper from the group of Dave

Shirley in Berkeley[2] studied Se adsorption on Ni(100) in both c(2x2) and p(2x2) phases,

measuring the intensity of the Se 3d emission along the surface normal as a function of

the photoelectron energy in the range ~30-190 eV; the adsorption site and height above

the surface were identified by matching the peak energies in these modulation spectra to

those of model calculations. These two experiments, both exploiting the coherent

interference of the backscattering paths shown in Figure 1(a), differ mainly in the mode

of data collection: angle-scan and energy-scan, respectively. The latter mode, of course,

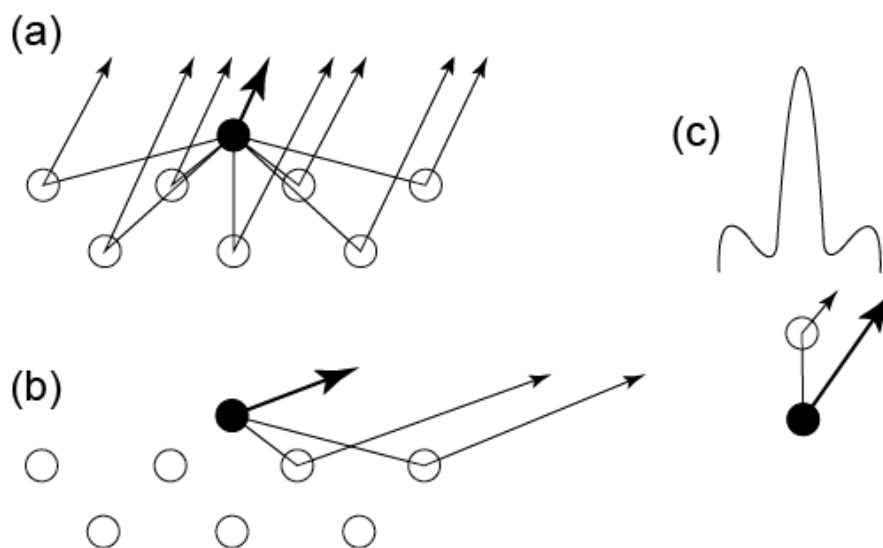is essentially the same as the mode of intensity measurements (I-V spectra) in LEED.

Figure 1 Schematic diagram showing the elastic scattering pathways (small arrows) that interfere with the directly emitted photoelectron path (large arrows) to lead to photoelectron diffraction modulations from an adsorbed atom (filled circles) in the (a) low energy backscattering and (b) high energy forward scattering modes. (c) shows the photoelectron diffraction polar-angle dependence in near-forward scattering from a single atom pair; the main peak is due to zero order diffraction, but the weaker sidebands are due to first (and higher) order diffraction

By contrast, the other report in 1978 from Chuck Fadley and co-workers[3]

(preceded by a preliminary report of some of their experimental data alone[4]), is of an

investigation of O adsorption on Cu(100), performed at a much higher (O 1s)

photoelectron energy of 951 eV generated by a standard laboratory-based Al Kα X-ray source, recording data in the azimuthal scan mode. This led to the acronym XPD (X-ray Photoelectron Diffraction) for this type of experiment. At this higher energy the Cu elastic scattering cross-section is strongly peaked in the forward (zero scattering angle direction) and backscattering is weak, but by detecting the photoemission at grazing emission angles (particularly at 7° grazing) very significant intensity modulations were observed as a function of azimuthal detection angle and could be reconciled with single-scattering simulations for O atoms occupying 4-fold coordinated hollow sites almost coplanar with the outermost. Cu layer. In this case the photoelectron diffraction modulations can be attributed to the near-forward (small angle) scattering pathways of Figure 1(b). As is clear from this figure, strong near-forward scattering from the atoms of the underlying surface is only possible is the adsorbed emitter atoms lie low in the surface. In this regard, the choice of O adsorption on Cu(100) was rather fortuitous. It now seems to be generally accepted that the nominal phase c(2x2) phase thought to have been studied in this experiment does not exist as a well-ordered phase (despite many reports to the contrary, including some by the present author) but a well-ordered (√2×2√2) *does* exist, reconstructed such that every third close-packed Cu <110> row is missing, allowing O atoms to occupy sites near-coplanar with the outermost Cu layer. Any further O atoms adsorbed *above* the surface in disordered areas[5] would have contributed little to the observed photoelectron diffraction modulations. Nevertheless, later use of XPD to determine the location of adsorbed atoms has shown that even at quite high photoelectron kinetic energies there is sufficient backscattering to identify an adsorbate site higher above the surface[6].

Of course, the fact that these three groups independently reached the point of completing a first proof-of-principle experiment in the same year is not entirely coincidental. The general idea had been around for a few years and these experiments were based on other preliminary results. Chuck Fadley had shown several years earlier that the angular dependence of Au 4f photoemission from an Au(111) surface showed peaks corresponding to well-defined bulk crystallographic directions[7]. For my part, an investigation of the angular dependence of Cu $M_{2,3}M_{4,5}M_{4,5}$ Auger electron emission from Cu(111) and Cu(100) surfaces revealed strong variations, while parallel multiple scattering calculations showed the magnitude and character of the experimental results were consistent with Auger electron diffraction[8], indicating that such measurements ought to be useable for adsorbate structure determination[9]. However, the difficulty of describing the initial unscattered partial wave character of CVV Auger emission made us appreciate that to a generally useful structural tool we needed to move from Auger electrons to core level photoemission with its simple dipole selection rules. Moreover, in 1974 Ansgar Liebsch had published a paper calculating the angle- and energy-dependence of emission from an adsorbed atom (albeit only at rather low photoelectron energies), effectively predicting the utility of the backscattering mode of photoelectron diffraction[10]. In the case of the low energy backscattering studies a further factor determining the timing of these experiments was that synchrotron radiation monochromators in the vacuum ultraviolet/soft X-ray energy range from a few tens to a few hundreds of eV were just becoming available.

I first met Chuck Fadley at a Faraday Discussion meeting in Vancouver in 1975, although neither of us presented work directly related to our later photoelectron

diffraction experiments. Chuck did present a paper on the angular dependence of XPS[11], but with a focus on the effects of surface morphology on the use of XPS for surface analysis (his paper does also refer to his earlier work on Au(111)[7]). My contribution to this conference related to evaluation of a proposed simplified treatment of quantitative LEED data[12]. We certainly had some discussions at the meeting, but I do not recall any explicit discussion of photoelectron diffraction, although we certainly had such discussions subsequently; 1975 was perhaps a little too early for this.

The dominance of forward scattering at high electron energies does offer a particularly simple structural probe if the geometry being studied allows a zero-angle forward scattering photoemission signal to be observed outside a surface. One such situation is an adsorbed diatomic molecule. The detected emission from one end of the molecule should peak in the direction corresponding to the molecular axis, and thus to forward scattering from the atom at the other end of the molecule. This was elegantly illustrated by Chuck Fadley and co-workers in a study of CO adsorption on Ni(100) reported[13] only one year later; CO adsorbs through the C atom bonded to the surface, with its axis perpendicular to the surface, so a polar angle scan of the C 1s emission shows a peak along the surface normal not present in the O 1s data. The same approach has subsequently been used to determine the orientation of larger molecules such as C_{60}[14] and tartaric acid[15] adsorbed on surfaces. The schematic diagram of Figure 1(c) shows clearly that this forward scattering can be regarded as a zero-order diffraction peak, corresponding to zero path length between the directly emitted and 0° forward scattered component of the photoelectron wavefield. Notice, though, that unlike in simply light optics (e.g., from a diffraction grating), there is a phase difference between these two

components at the zero-order forward scattering condition, due to the complex atomic scattering factor, despite the absence of a path length difference. However, at high energies this phase shift is small, and the forward scattering interference is constructive.

Of course, in structural problems in which the emitter atom lies below the surface, an angle scan of the emitted photoelectrons may be expected to show peaks in directions corresponding the alignment of the emitter atom with scatterer atoms closer to the surface due to true (0°) forward scattering, providing valuable information on the structure of interfaces and in the growth of epitaxial thin films. The fact that the scattering cross-section of atoms is strongly peaked at 0°at high energies means that these atomic-alignment forward scattering peaks would appear in data even without the coherent interference of 'photoelectron diffraction', but quantitative analysis of the amplitude and angular width of these peaks is influenced by this 'diffraction' effect, which can be simulated by computational modelling. Modelling of the scattering is even more important (indeed essential) to interpret intensity variations at non-zero emission angles. Simple single scattering calculations have proved to be quite effective in many cases at high electron energies, although in the case of forward scattering along chains of crystallographically aligned atoms, multiple forward scattering can be very important. In the lower photoelectron energy backscattering studies multiple scattering is always important, so the associated calculations are generally more computationally demanding.

III. ANGLE-SCAN v ENERGY-SCAN MODES

The relative phases of the scattered components of the emitted photoelectron wave that interfere to determine the variations in the intensity of the emission due to photoelectron diffraction are determined by two factors, namely the pathlength differences of these different components, and the photoelectron wavelength. These

relative phases differ at different angles of detection, and at different photoelectron energies, respectively. Both angle-scan and energy-scan modes of data collection therefore offer a basis for determining surface structures. In the case of the higher photon energy XPD using the characteristic 'line' emissions of laboratory X-ray sources (most commonly Kα emission from Mg or Al targets), however, the available photon energies are severely constrained and not freely variable, so only the angle-scan mode is possible. Moreover, at higher photoelectron energies one would need to scan over a wider energy range to achieve significant fractional changes in the associated wavelength. At lower photoelectron energies using synchrotron radiation, however, both modes can be exploited. In the early Warwick/Bell Labs experiments the angle scan mode was used. At that time, this mode had the advantage that it was possible to establish whether the observed intensity modulations were consistent with the surface point-group symmetry; in this case the modulations could clearly be attributed to photoelectron diffraction. Demonstrating that this was the case was a significant issue at a time when there was some scepticism that such an effect could be detected. However, the energy-scan mode first adopted by the Shirley group has an important advantage when comparing experimental data with the results of multiple scattering theory. This is because, as in quantitative LEED structure determinations (which also compares experimental and computed modulations of the diffracted intensity as a function of electron energy), one non-structural parameter that must be optimised in such theory-experiment comparisons is the inner potential – the difference in electron kinetic energy (and thus wavelength) inside and outside the surface. Although the approximate value of this parameter (typically in the range ~10-20 eV) for many materials is known, small changes in its value, thereby shifting the kinetic energy and associated wavelength inside the sample surface, can change apparent interatomic distances in the model structure used in the scattering calculations to match the experimental data. For data in the energy-scan mode (particularly at normal emission), changing the inner potential simply causes an offset in the experimental and computed energy scales. In the angle-scan mode, the method of optimising the inner potential is less straightforward, because the inner potential causes refraction of the emitted electrons at the surface. Of course, at high photoelectron kinetic energies (~1 keV) the impact on angle-scan data of changing the inner potential by a few

eV is marginal, but this is an added complication in analysing low energy angle-scan data.

Experiments in the low energy backscattering mode initially performed on photoemission from shallow core level were subsequently followed by the same (Shirley) group using the deeper 1s core levels of elements of the second row of the Periodic Table, most notably S 1s with a binding energy of ~3 keV, using standard double-crystal monochromators that can be readily scanned over a wide energy range. In a series of such studies the technique was referred to by this group as ARPEFS, Angle-Resolved Photoelectron Extended Fine Structure (e.g. [16]), reflecting the similarity of the data and the mode of data analysis to EXAFS (Extended X-ray Absorption Fine Structure). In both techniques, modulations of the recorded intensity as a function of photoelectron energy arise from the coherent interference of different scattering paths, the relative phases changing due to the changing electron wavelength. A key difference is that in EXAFS the dominant single scattering pathways all involve round trips from the emitter atom to a near-neighbour scattering atom and back to the emitter with associated scattering angles of 180° (Figure 2(a)). In effect the emitting atom is also the detector of the associated absorption. In ARPEFS (energy-scan photoelectron diffraction) the photoemission detector is outside the surface, the contributing scattering paths involve a range of scattering angles, while the scattering path differences are also influenced by the direction of detection. Nevertheless, the data analysis of these ARPEFS experiments exploited a somewhat similar Fourier Transform and filtering technique to that used in EXAFS to extract the modulations arising from scattering from specific substrate atoms, bondlengths being determined from modelling of these scattering paths.
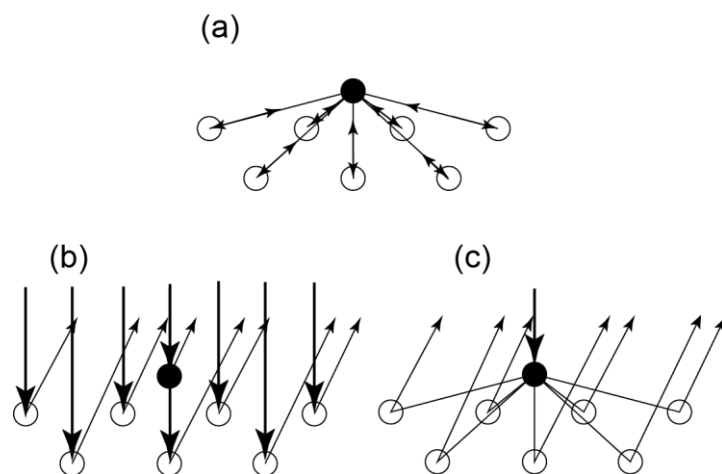
Figure 2 Schematic diagram showing the elastic scattering paths contributing to (a) EXAFS, (b) LEED single scattering (c) LEED double scattering following initial scattering by an adsorbed atom.

By contrast, my own continued exploitation of low energy backscattering photoelectron diffraction has also been based on the energy-scan mode (using the acronym PhD), but extracting the underlying quantitative structural information using full multiple scattering cluster calculations. This was initiated through a new Warwick-Berlin collaboration in the early 1980s with the group of Alex Bradshaw at the Fritz Haber Institute using the BESSY (and BESSY II) synchrotron radiation facilities and new multiple scattering computational codes developed by Volker Fritzsche[17,18,19]. This work focused on the use of C, N and O 1s photoemission from adsorbed small molecules and some of the associated results are summarized in section V.

IV. MULTIPLE SCATTERING, FOURIER TRANSFORMS AND PHOTOELECTRON HOLOGRAPHY

As described above, the use of the energy dependence of low energy electron elastic scattering as a mode of surface structure determination by photoelectron diffraction and by EXAFS was preceded by LEED, the first technique successfully developed for this purpose, and some comparison of the contributing scattering events and the resulting method of data analysis deserve comparison. In LEED it was established at an early stage that multiple scattering events were extremely important.

While the fact that the elastic backscattering at low energies is reasonably strong, a key requirement for the viability of the technique and an important factor contributing to the surface specificity of LEED, is that forward scattering is even stronger, so the dominant multiple scattering events in LEED typically involve a single backscattering together with one or more forward scattering events. To understand the importance of multiple scattering in backscattering photoelectron diffraction relative to LEED, it is important to recognize that the single-scattering events in LEED (Figure 2(b)) are dominated by interference between scattering from substrate atoms by the incident plane wave. The double scattering events in LEED that involve initial scattering from the adsorbate atoms (Figure 2(c)) are equivalent to the single scattering events in backscattering photoelectron diffraction (Figure 1(a)). This, of course, accounts for the higher sensitivity to the location of the adsorbed atom, but also why higher order scattering events are generally less important in photoelectron diffraction than in LEED. Despite this, the use of Fourier transform methods of data analysis in both techniques are intrinsically less successful than in X-ray diffraction. Under most conditions X-ray scattering cross-sections are (almost) real, so the relative phases of the different scattering pathways are dominated by the scattering pathlengths and not by scattering phase shifts. In the case of electron scattering the associated scattering phase shifts are dependent on the energy, the scattering angle, and the atomic species, scrambling the structure-related relative scattering phases. Multiple scattering adds to this complication. Despite this there have been various attempts to apply Fourier transform methods to LEED intensity-energy data. Indeed, one such attempt[20] was reported at the 1975 Faraday Discussion meeting mentioned above where I first met Chuck Fadley, though no successful applications of this particular approach emerged. Fourier transforms prove valuable in EXAFS because all the (strongest) near-neighbour scattering contributions involve the same scattering angle of 180° and multiple scattering only contributes for more distant neighbours that are aligned with near-neighbours, the condition corresponding to one backscattering event plus one 0° forward scattering. To some extent this also accounts for the relative success of this approach in the ARPEFS analysis of the Shirley group in that if the scanned-energy mode photoelectron diffraction is measured in a geometry such that a nearest-neighbour substrate scattering atom is close to the 180° scattering geometry, this

12

path tends to dominate the modulations. Later work by our Warwick/Berlin collaboration on many different adsorbate systems showed that this near 180° scattering geometry from a nearest-neighbour substrate atom typically leads to the simplest modulation spectra due to the dominant influence of this single backscattering interference path, so identifying these spectra via Fourier transforms from a large data set recorded in diffraction directions can be an aid to an initial identification of a preferred structural model[21].

Interest in direct methods in photoelectron diffraction (as opposed to trial-and-error structural modelling) was greatly increased by a conference paper by Szoke[22], followed up by Barton[23], which pointed out that a complete photoelectron diffraction angle scan is effectively a photoelectron hologram; the 'reference wave' of the hologram is the initial outgoing photoelectron wave while the scattering 'object' is the surrounding crystal. Inversion of this hologram would therefore result in an image of the local emitter geometry. Of course, achieving this inversion (numerically) is the challenging problem, with all the complications referred to above in the context of Fourier transforms, but a range of methods were proposed and explored by a number of different groups including several papers from Chuck Fadley and colleagues (e.g.[24,25]). One common conclusion of these investigations is that to in order to achieve conclusive structural solutions, the input data must provide adequate sampling of k-space by the use of photoelectron diffraction data, not only at many different emission directions, but also at several photoelectron energies. Many of these investigations were based on processing model simulated data rather than experimental data and very few claims have been made to solve unknown structures. One example aimed at achieving this, using low energy backscattering data, was the holographic inversion of data from ethylene (C_2H_4) and acetylene (C_2H_2) adsorbed on Si(100) to determine the local adsorption sites. Figure 3 shows a plan view of a Si(100) surface with a pair of carbon atoms to represent the two molecules (photoelectron diffraction is 'blind' to the weakly-scattering H atoms) in four alternative adsorption sites.
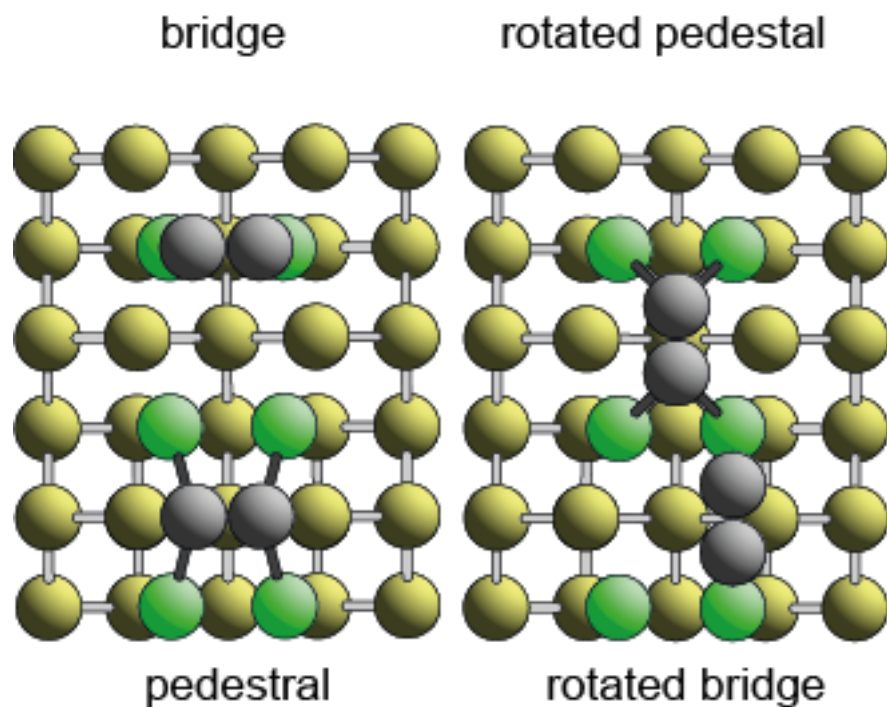
Figure 3 **Plan view of the Si(100) surface showing possible adsorption sites of C_2H_4 and C_2H_2 adsorbed on the surface. The molecules are represented by a pair of (black) C atoms, the H atoms being omitted. The bulk Si atoms are shown yellow, but the outermost dimerised Si atoms of the clean surface (1x2) reconstruction are shown green.**

In the case of ethylene adsorption, the holographic inversion study[26] favoured the bridge geometry of Figure 3, a conclusion consistent with a slightly earlier independent investigation in which the structure determination was achieved by the traditional fully quantitative trial-and-error structural search using multiple scattering simulations[27]. However, a similar holographic investigation of acetylene adsorption[26] favoured adsorption of this molecule in the pedestal geometry of Figure 3, whereas another study using multiple scattering simulations[28] concluded that acetylene adopts the same bridging geometry as ethylene. Subsequent investigations of this adsorption system, particularly by scanning tunnelling microscopy (STM), provided evidence for possible co-occupation in more than one geometry which may be temperature dependent, different sample temperatures possibly causing the different conclusions of the two photoelectron diffraction studies. This led to a new investigation at different temperatures, also using full multiple scattering simulations[29]. This concluded that co-occupation of two or more sites is involved, that temperature does influence the occupation of these sites, and that while at low temperature the bridging site is clearly favoured, at higher temperatures

some partial occupation of pedestal sites may be involved; however, the pedestal geometry favoured by the holography study could be excluded.

This example provides evidence of both the success and failure of one method of holographic inversion, but it also highlights some important challenges for both direct and indirect methods of data analysis of photoelectron diffraction from molecular adsorbates. Very many of the early applications of these techniques based on simulated and real experimental data, concerned identifying adsorption sites of single atomic species. In this cases, high symmetry adsorption sites are to be expected. For molecular adsorbates, however, the mismatch of interatomic distances within the molecule and in the underlying substrate means that the local sites of individual atoms within the adsorbed molecule often occupy low symmetry sites. In this case, measurement of photoelectron diffraction in directions away from the surface normal necessarily averages over several distinctly different local sites that are related by the point group symmetry of the substrate. At best this is likely to lead to reduced precision in the site identification, but it is also possible that it can lead to incorrect site identification. A test of some significantly simpler direct methods applied to 30 different adsorbate/substrate experimental data sets[30] highlights this problem of correctly identifying low-symmetry sites, although using the methods of this particular publication no false sites were identified but, in some cases, no clear site identification could be achieved. Of course, the Si(100)-C_2H_2 example also highlights another potential problem, that in some cases several distinctly different sites may be co-occupied. The first challenge in data interpretation is therefore to be sure to consider this higher level of complexity in the analysis, a problem that is common to all surface structural techniques using both trial-and-error modelling and direct methods.

V. MOLECULAR ADSORPTION STRUCTURES AND CHEMICAL SHIFT PHOTOELECTRON DIFFRACTION

One particular advantage of photoelectron diffraction in investigating the structure of molecular adsorbates on surfaces is the ability to distinguish emission from atoms of the same element in different bonding environments through the chemical shifts in their photoelectron binding energies. This allows one to obtain structural data that is

not only element specific, but also chemical state specific, and this has proved particularly valuable in the Warwick-Berlin collaboration; many examples up to 2007 are summarised in a review of that year[31]. An example from shortly afterwards that illustrates the benefit of this approach is of adsorption of the nucleobase molecule, thymine (Figure 4), on Cu(110)[32]. Polarisation-direction dependent NEXAFS data showed that the molecule adsorbs on this surface with its molecular plane essentially perpendicular to the surface lying in a close-packed <110> azimuthal direction of the surface. Adsorbed at room temperature the O 1s XP spectrum shows a single peak, whereas the N 1s spectrum shows two components separated by ~1.7 eV. The implication of these spectroscopic results is that one, but only one, of the N atoms in the molecule is deprotonated by interaction with the surface, while the two O atoms (essentially equivalent in the free molecule) must experience similar bonding interactions with the Cu surface. Scanned-energy mode photoelectron diffraction modulation spectra provide a much more detailed picture of the adsorption structure.
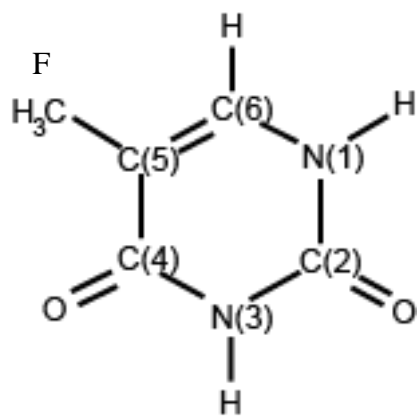

Figure 4 Fig. 4 Chemical structure of thymine. Note the labelling of the two N atoms used in the structural study of these species shown in Figure 5.

Figure 5 shows a small sub-set of these spectra, specifically corresponding to normal emission, from the O 1s and the two separate chemically-shifted N 1s photoemission peaks. Superimposed on the experimental spectra are the results of multiple scattering simulations for the structural model that gave the best fit to the

16

complete set of 24 such spectra recorded in different emission directions. Two structural

conclusions can be drawn from a simple visual inspection of the spectra in Figure 5.

Firstly, the modulations for emission from the O 1s and N(3) 1s signals are very similar,

and both are dominated by a single strong modulation frequency (strictly in k rather than

energy). This implies that the local geometries of this N atom and the O atom relative to

the backscattering Cu substrate are very similar, but also that these adsorption sites are

likely to be close to atop surface Cu atoms, leading to a dominant 180° scattering path. A

further observation is that the modulations for the N(1) 1s signal are much weaker and of

higher frequency, consistent with this atom being much further from the strongly

backscattering Cu atoms. Figure 5 also shows a simple ball-model of the optimised

structure (H atoms omitted), in which precise values for the Cu-O and Cu-N bondlengths
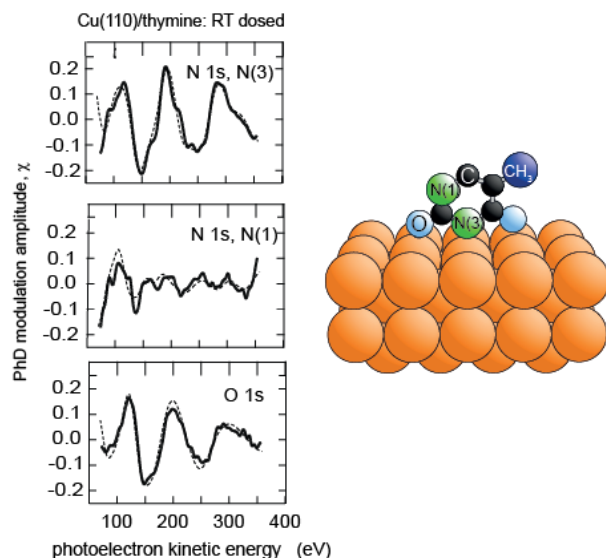
were determined.

Figure 5. Experimental (bold lines) scanned-energy mode N 1s and O 1s photoelectron diffraction modulation spectra recorded at normal emission from thymine adsorbed onto Cu(110) at room temperature, compared with the results of multiple scattering simulations (dashed lines) for the optimised structural model, which is also shown

A rather different application of chemical shift PhD is in the study of oxygen-containing

molecules on oxide surfaces, there being a significant chemical shift in the O 1s

photoelectron binding energy between the bulk oxide and the adsorbed molecules. One example of this is in the study of water adsorption on the (110) surface of rutile TiO_2. The outermost layer of this surface comprises rows of O atoms bridging Ti atoms in the layer below, but it proves to be challenging experimentally to produce a perfectly stoichiometric surface and in general there are some bridging oxygen vacancies. H_2O can adsorb intact on this surface at low temperatures, occupying sites with the O atom bonded atop Ti atoms, but it is also well-established that water can dissociate at these oxygen vacancies, an OH species thereby occupying the vacancy site while the released H atom can adsorb at a bridging oxygen atom; the resulting surface then gains two OH species occupying the bridging sites, OH_{br} in Figure 6.
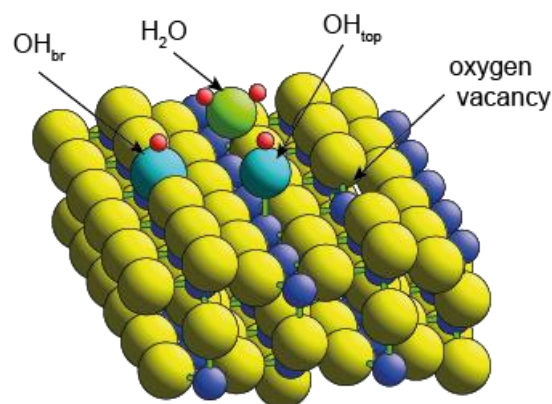

Figure 6 Schematic diagram showing the structure of the rutile $TiO_2(110)$ surface and states produced by its interaction with molecular water. O atoms of the oxide are shown yellow, but those of intact H_2O and OH are shown green and blue indicating their different O 1s photoelectron binding energies

Figure 6 shows a schematic representation of this surface including the different possible species resulting from water interaction. The O 1s photoelectron binding energy of adsorbed molecular water is some 3.5 eV higher than that of the O atoms in the bulk oxide, while a smaller intermediate shift characterises the OH species. Exploiting these shifts in O 1s backscattering photoelectron diffraction allows the exact adsorption geometries of H_2O[33] and OH_{br}[34] to be determined. The conventional wisdom for some time had been that water will only dissociate at these oxygen vacancy sites, but evidence from STM indicated that some dissociation on a perfectly stoichiometric surface can

occur at reduced temperatures leading an OH species occupying Ti atop sites (OH$_{top}$), while the displaced H can adsorb on bridging O atoms to create a matching OH$_{br}$ species. Careful monitoring the O 1s photoemission from OH species as a function of temperature by Walle *et al.*[35] confirmed that an OH species can occur due to H$_2$O adsorption onto a perfect surface at low temperatures. However, though the chemical shift associated with this species was the same as that from OH$_{br}$ formed by water dissociation at bridging oxygen vacancies, so this spectroscopic information could not identify a distinctly different species. Energy-scan photoelectron diffraction, however, did allow this second (OH$_{top}$) species to be demonstrated by its different adsorption site[36]. Multiple scattering modelling of the measured OH O 1s PhD modulation spectra for different degrees of co-occupation of the OH$_{br}$ and OH$_{top}$ sites was found to correspond to the known initial defect density of the surface, thereby identifying the OH$_{top}$ site and its associated Ti-O bondlength.

VI. **STRUCTURAL PRECISION AND RELIABILITY**

Essentially all techniques capable of providing quantitative surface structure determination use trial-and-error fitting of experimental data by simulations of these data based on different structural models. Direct methods may aid identification of the best structural models but lack the precision to produce a complete reliable structure determination. Two key questions arise from this approach: what is the structural precision, but also what is the reliability or uniqueness of the solution? The second of these questions is ultimately the more challenging one to answer, because while one can test a range of structural solutions and see which gives the best agreement with experiment, it impossible to know if there is not a fundamentally different model that gives an even better fit. The general solution to these problems is to define an objective quantitative reliability factor or *R*-factor that provides a measure of the level of theory-experiment agreement. By exploring the variation of the *R*-factor with changes in structural parameter values one can estimate the precision of these values, while the absolute value of *R*, compared with the best values achieved in a range of studies of

different structures with the same technique, gives some indication of the likely reliability of the determined structure.

The first technique developed to determine surface structures, and thus the first technique to address these issues, was quantitative LEED [37]. As mentioned in the introduction, the experimental data in this technique comprises measurements of the intensity of different diffracted beams as a function of the electron energy (and thereby the applied voltage) – so-called I-V plots. Most commonly the measured intensities are not absolute (i.e they are not normalised to the incident beam current) but relative, so the core structural information arises from the energies at which peaks in these I-V plots occur. While a range of different LEED R-factors were explored, the one most widely used now is that proposed by Pendry[38], which compares not the measured and calculated intensities, I, but a quantity

$$Y(E) = L^{-1} / (L^{-2} + V_{0i}^2)$$

that is a function of the logarithmic derivatives of I, $L(E) = I' / I$, a quantity sentive to peak position but not to absolute intensity. This led to an R-factor definition

$$R = \frac{\sum_g \int (Y_{gth} - Y_{g\exp})^2 dE}{\sum_g \int (Y_{gth}^2 + Y_{g\exp}^2) dE}$$

The summation is over different diffracted beams, g, while the integrals are over the energy range of each measured diffracted beam. V_{0i} is the imaginary part of the inner potential that describes the effect of the inelastic scattering that influences the widths of peaks I the I-V spectra. A significant advantage of this R-factor is that is allows one to define a double reliability factor, RR, which determines the significance of the best-fit value of R, but also a variance that can be used to define the significance of changes of R as a function of changes in structural parameter values, thereby defining their precision.

For energy-scan photoelectron diffraction, the experimental data are also in the form of spectra as a function of energy, but in this case the variable is the modulation, $\chi(E)$, of the intensity. The absolute value of this quantity (defined relative to the average intensity

being measured), *is* measured experimentally, so an appropriate *R*-factor can be defined[39] as

$$R = \frac{\sum (\chi_{th} - \chi_{exp})^2}{\sum (\chi_{th}^2 + \chi_{exp}^2)}$$

The summations being over all the discrete value of χ measured at different energies and in different emission directions. This definition also allows a variance to be defined as in Pendry's LEED R-factor, to determine the precision of different structural parameters. The larger is the variance, the worse the precision, but the magnitude of the variance decreases as the number of experimental data points increases, so better precision can be achieved by a larger data set, as one might expect. Notice that this *R*-factor is defined such that perfect agreement between theory and experiment leads to a value of 0, while a value of 1 implies there is no correlation between the theoretical experimental values and a value of 2 implies anti-correlation between theory and experiment. Experience from studies of many different adsorption systems indicates that the best theory-experiment fits can lead to values of *R* of ~0.2 or less, although for very complex structures or when the signal-to-noise ratio of the $\chi(E)$ measurements is worse, such low values cannot be achieved. The precision achievable in structural parameter values is typically in the range ±0.02-0.05 Å.

The equivalent situation in XPD is variable, depending on the details of the experiments and the data obtained. As described in the introduction, XPD experiments were originally performed only with laboratory X-ray sources and highlighted the role of the strong forward scattering peak. Quite a number of applications of XPD, such as in studies of the local morphology of epitaxial growth, focussed on the emission angle of this forward scattering peak to gain structural information, without recourse to detailed quantitative simulations. However, many experiments using this technique have collected the angular distribution of the emission over most of or all the 2π steradians of emission (a complete photoelectron 'hologram') and have compared these with scattering calculations for model structures, commonly using single scattering calculations. Clear comparison on the relative precision of XPD and PhD is further complicated by the fact that the XPD

acronym has been used by some authors to describe angle-scan photoelectron diffraction at lower photon and photoelectron energies, blurring the distinction made at the beginning of this article between high energy angle-scan and low energy-scan measurements. Of course, angle-scan data, with suitable normalisation, also comprises measurements of a modulation amplitude at different emission directions (and in some cases at different energies). As a result the same *R*-factor as that defined for PhD has also been used in XPD and combined XPD/PhD studies, such as a recent investigation into the corrugation of an h-BN nanomesh monolayer grown on Rh(111)[40]. In this example, too precision as low as ±0.03 Å was seen in the most sensitive structural parameters, although the data were significantly less sensitive to some other parameters.

VII.　SUMMARY AND CONCLUSIONS

This short review of photoelectron diffraction has traced the early development of the technique and described the key differences between the (largely) high energy forward scattering XPD version of the technique first developed by Chuck Fadley and the lower energy backscattering technique. The relative merits of angle-scan and energy-scan detection modes are discussed, together with a slightly more detailed survey of developments and applications in the latter mode, from its early beginning with the group of Dave Shirley to the extensive exploitation of the approach to determine molecular adsorption structure by the Warwick/Berlin collaboration. Photoelectron diffraction, with its ability to determine *local* structure in a quantitative fashion exploiting both its elemental and chemical-state sensitivity clearly has a continuing valuable and largely unique role in the armoury of methods available for quantitative surface structure determination.

The development in recent years of so-called near ambient pressure (NAP) XPS highlights the possibility of using photoelectron diffraction to perform *in operado* structural studies of the surfaces of model heterogeneous catalysts. A proof-of-principle experiment has been reported[41], but these are challenging experiments requiring careful control of steady-state reactions in an accessible pressure range, so it remains to be seen how important this technique will prove to be.

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DATA AVAILABILITY

This paper involves no new original data.

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FIGURE CAPTIONS

FIG. 1 Schematic diagram showing the elastic scattering pathways (small arrows) that interfere with the directly emitted photoelectron path (large arrows) to lead to photoelectron diffraction modulations from an adsorbed atom (filled circles) in the (a) low energy backscattering and (b) high energy forward scattering modes. (c) shows the

photoelectron diffraction polar-angle dependence in near-forward scattering from a single

atom pair; the main peak is due to zero order diffraction, but the weaker sidebands are

due to first (and higher) order diffraction

FIG. 2 Schematic diagram showing the elastic scattering paths contributing to (a)

EXAFS, (b) LEED single scattering (c) LEED double scattering following initial
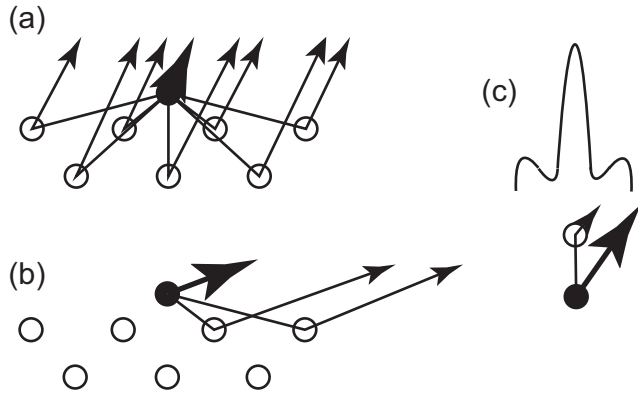
scattering by an adsorbed atom.

FIG. 3 Plan view of the Si(100) surface showing possible adsorption sites of C_2H_4 and C_2H_2 adsorbed on the surface. The molecules are represented by a pair of (black) C atoms, the H atoms being omitted. The bulk Si atoms are shown yellow, but the outermost dimerised Si atoms of the clean surface (1x2) reconstruction are shown green.

FIG. 4 Chemical structure of thymine. Note the labelling of the two N atoms used in the structural study of these species shown in Figure 5.

FIG. 5. Experimental (bold lines) scanned-energy mode N 1s and O 1s photoelectron diffraction modulation spectra recorded at normal emission from thymine adsorbed onto Cu(110) at room temperature, compared with the results of multiple scattering simulations (dashed lines) for the optimised structural model, which is also shown

FIG. 6. Schematic diagram showing the structure of the rutile $TiO_2(110)$ surface and states produced by its interaction with molecular water. O atoms of the oxide are shown yellow, but those of intact H_2O and OH are shown green and blue indicating their different O 1s photoelectron binding energies

(a)

(b)   (c)

bridge   rotated pedestal

pedestral   rotated bridge

Cu(110)/thymine: RT dosed

N 1s, N(3)

N 1s, N(1)

O 1s

PhD modulation amplitude, χ

photoelectron kinetic energy   (eV)