Surface adsorption structure determination using backscattering photoelectron diffraction

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ABSTRACT

Following a brief historical introduction, the distinction between two modes of photoelectron diffraction, high-energy forward scattering and low energy backscattering, and two modes of data collection, angle-scan and energy-scan, is explained. This is followed by a review of energy-scan backscattering photoelectron diffraction (PhD). Examples are presented of atomic adsorption and molecular adsorption on metal surfaces and molecular adsorption on oxide surfaces. The paper ends with a brief survey of future prospects for the application of the PhD technique.

1. Introduction

The idea of using photoelectron diffraction – the coherent interference of an emitted photoelectron wavefield with components of the same wavefield elastically scattering by surrounding atoms – first emerged in a series of published experimental papers in the late 1970 s, albeit preceded by a few related theoretical and preliminary experimental papers. This early history has been described recently elsewhere [1] and will therefore be touched upon only briefly in this paper. However, one important aspect of these early experiments that needs to be repeated is the distinction between two rather different modes of exploiting the phenomenon, namely high-energy forward scattering and low energy backscattering. One important factor determining these different modes is the scattering-angle dependence of the cross-section for (elastic) electron scattering by atoms at different energies. Fig. 1 shows this dependence for a Cu atom at electron energies of 100 eV and 1100 eV. At both energies the maximum scattering cross-section is in the forward ($0°$ scattering angle) direction but, while the cross-section for $180°$ backscattering is only about a factor of 3 less than that for forward scattering at 100 eV, backscattering is comparatively very weak at 1100 eV.

The fact that backscattering is strong at low energies is the key factor exploited in low energy electron diffraction (LEED), using typical energies ~30–300 eV. At electron energies of ~1 keV and higher, elastic scattering of atoms is strongly peaked in the forward direction. This was the effect exploited by Chuck Fadley and co-workers for X-ray photoelectron diffraction (XPD) using the standard laboratory photon sources of X-ray photoelectron Spectroscopy (XPS), namely Mg Kα and Al Kα, at photon energies of 1254 eV and 1487 eV. By contrast, to exploit backscattering in photoelectron diffraction lower photoelectron energies are

required, so to access a range of atomic core levels with binding energies in the range of tens to a few hundred eV, it is necessary to have an energy-tuneable photon source, as provided by synchrotron radiation.

Fig. 2 summarises the specific scattering geometries relevant to photoelectron diffraction for the determination of surface structures. On the left is shown the direct emission from an atom adsorbed on a surface together with the elastic backscattering paths of components of the photoelectron wavefield that interfere with the direct component to produce photoelectron diffraction. The conditions for constructive and destructive interference depend on the scattering pathlengths and the photoelectron wavelength, so these can be explored either by measuring the emitted signal at different angles or at different energies (and thus at different wavelengths). This leads to two alternative experimental measurement modes of photoelectron diffraction: angle-scan or energy-scan. On the right of Fig. 2 is shown the direct and scattered photoelectron paths in the case of emission from one atom of a diatomic molecule, together with a schematic polar diagram of the resulting angle-scan photoelectron diffraction. At high photoelectron energies at which forward scattering dominates, this angular dependence shows a strong forward scattering peak in the direction corresponding to the molecular axis. In this direction the pathlength difference between the direct and scattered wavefield components is zero, so this corresponds to a zero-order diffraction peak. At some larger value of the emission angle a first-order diffraction peak occurs, when this pathlength difference equals the photoelectron wavelength. The zero-order forward scattering peak provides direct information on the molecular orientation, but to determine the intramolecular bondlength one must measure the emission angle of the first (or higher) order diffraction peaks, provided by angle-scan data. Notice that energy-scan measurements are only an effective way of sampling the structural information provided by
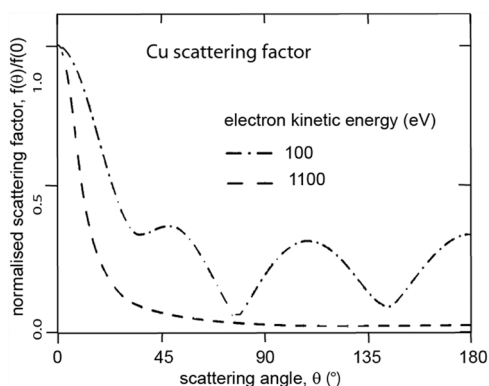
Fig. 1. Relative atomic scattering factor of electrons by a Cu atom as a function of scattering angle, at two different energies, normalized to the values for 0° forward scattering.
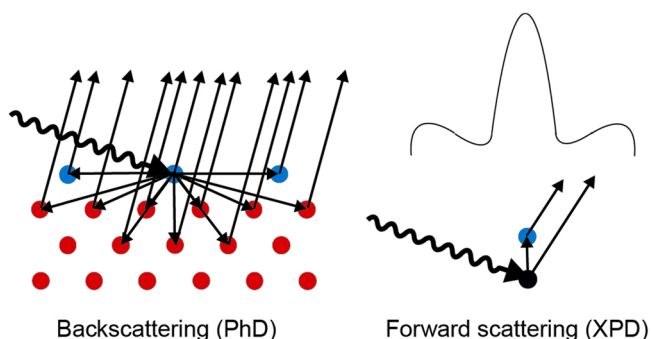

Fig. 2. Schematic diagram showing the interfering scattering paths of emitted photoelectrons in backscattering from an adsorbed atom and in forward scattering from the non-emitting atom of a diatomic molecule.

photoelectron diffraction if the changes in energy lead to significant changes in the photoelectron wavelength. In the backscattering mode using low photoelectron energies, values of ~30–300 eV (as used in LEED) provide variations in the wavelength of a factor of 3 or more across this energy range. By contrast, using higher photoelectron energies at which forwards scattering dominates, very large energy variations would be required; for example, a kinetic energy range of 500–2000 eV is required to produce a wavelength change of a factor or 2. High energy forward-scattering photoelectron diffraction measurements are therefore invariably measured in the angle-scan mode leading to the technique known as XPD. Measurements of backscattering photoelectron diffraction can be (and have been) measured in both modes, but the energy-scan mode, when the technique is commonly referred to as PhD, has been used more extensively. Recently a few backscattering studies using both modes have been reported (e.g. [2]); in some cases the data collected in the angle-scan mode is referred to, somewhat confusingly, as XPD. Notice that it is the energy of the photoelectrons, not of the photons, that distinguishes the backscattering and forward scattering modes. Using 'hard' X-rays to access deeper core levels is actually advantageous for PhD as the atomic photoionisation cross-section falls off more slowly with increasing photoelectron energy. Evidently, XPD is well-suited to determinations of interatomic orientations in systems where scattering atoms lie between the detector and the emitter, not only in oriented molecules, but also in studies of epitaxial films. Notice that XPD can be used to determine the location of scattering atoms below emitter atoms by exploiting the near-forward scattering that occurs in the situation depicted in the left of Fig. 2 at grazing emission angles; near-forward scattering then occurs from some substrate atoms (this was demonstrated in Chuck Fadley's first XPD study [3]), but in general determining adsorbate atom locations on a surface is

performed at lower photoelectron energies.

The focus of this short review is on the development and achievements of the PhD technique. A more detailed description of the technique including citations of related publications to 2007 may be found elsewhere [4].

2. Atomic adsorption

In the early period of development of the first techniques to provide quantitative surface structure determination, initially by quantitative LEED (QLEED), but then by exploration of a range of other methods, the first challenge in studies of surface adsorption was to determine the structure of simple atomic adsorption systems, specifically aimed at identifying the adsorption site and local interatomic distances. The first such adsorption structure determinations (by QLEED) were of Ni(100)c (2 × 2)-Na [5,6,7] and the Ni(100)c(2 × 2) phases formed by adsorption of the chalcogens O, S, Se and Te [8]. The first demonstrations of backscattering photoelectron diffraction were performed on three of these same systems, Ni(100)c(2 × 2)-Na and Ni(100)c(2 ×2)-Te [9], and Ni(100)c(2 × 2)-Se [10]. While the latter study used the energy-scan mode, comparing the energies of peaks in the intensity modulations with those of model calculations, the former investigation was performed in the angle-scan mode. The rationale for this use of the angle-scan mode, at a time when some scepticism was expressed that photoelectron diffraction would lead to significant intensity modulations, was that the angle-scan mode provides a symmetry check on the likely reliability of the data. Fig. 3 shows a comparison of the experimental data of Na 2p emission from the Ni(100)c(2 × 2)-Na surface recorded at one photon energy with the results of multiple scattering simulations for the structural model obtained in the earlier QLEED studies. Notice that all of these early backscattering studies were performed using emission from relatively shallow core levels (binding energies < 60 eV) using photon energies below 250 eV.

While relatively soft X-rays have been widely exploited more recently, particularly for providing access to low photoelectron energies from photoemission the 1 s states of C, N, and O, the group of David Shirley followed their early low photon energy study of the Ni(100)c (2 × 2)-Se system [9] with a number of investigations using harder X-ray energies to access the 1 s states of heavier atoms, and particularly of S, leading, for example, to a structural investigation of another of the
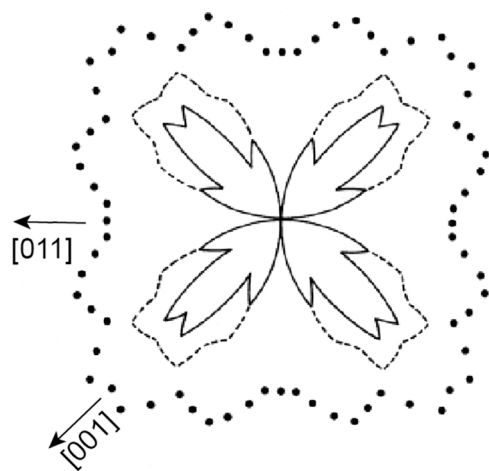

Fig. 3. Comparison between theory and experiment for azimuthal angle dependence of the intensity of Na 2p emission from a Ni(100)c(2 × 2)-Na surface at a polar emission angle of 30°and a photoelectron energy of 46 eV. The filled circles show the calculated intensities while the full curve shows the same data with the minimum value subtracted. The dashed curve shows the corresponding mirror-symmetrised experimental data.
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systems addressed in 1973 by QLEED, namely Ni(100)c(2 × 2)-S [11].

The conclusions of most structural studies of atomic adsorbates on low-index metal surfaces, is that the adsorbate occupies the highest local coordination site with little modification of the metal surface structure apart from small changes in the outermost layer spacings, but there are several cases in which adsorption leads to more significant modification of the metal surface structure. One example of this is the adsorption of atomic C on the Ni(100) surface, together with a closely similar structure formed by N adsorption. An early QLEED study [12] indicated that the C atoms occupy hollow sites with a c(2 × 2) periodicity (as also seen for adsorption of the chalcogens on this surface), but the C atoms are almost coplanar with the outermost Ni atoms, leading to a distortion of the lateral positions of the nearest-neighbour Ni atoms. Fig. 4 shows a schematic diagram of this structure, with superimposed arrows indicating the directions of the surface Ni atoms tangential lateral displacements. Notice that these displacement around the central C atom are clockwise, while those around the corner C atoms are anticlockwise. This inequivalence leads to a (2 × 2) unit mesh rather than the c(2 × 2) mesh defined by the C atoms alone; the nature of the Ni atom displacements leads to the structure commonly being referred to as a 'clock reconstruction. The initial identification of this reconstruction was achieved in the early QLEED study, greatly aided by the fact that some 'missing' diffracted beams showed the space group to be 4 pg [11], while a later QLEED study significantly refined the details of the structure [13]. The lateral displacements of the surface Ni atoms lead to an enlargement of the 4-fold coordinated 'hole' in the surface and help to account for the fact that the C atoms are only 0.1 Å higher above the surface than these Ni nearest-neighbours. As is clear from Fig. 4, this reconstruction involves coordinated movements of large numbers of surface Ni atoms, which form a long-range ordered structure, so an interesting question is: what is the adsorption structure at much lower C coverage than the 0.5 ML of the ordered phase? Part of the answer appeared to be provided by scanning tunnelling microscopy (STM) constant-current images, which showed dark spots at 4-fold coordinated hollow sites but no clock reconstruction [14]. However, these images were interpreted as providing evidence for radial movements of the nearest-neighbour Ni atoms by 0.15 Å away from these C atoms. PhD is well-suited to test this idea, because (unlike QLEED) it determines the *local* adsorption geometry even in the absence of long-range order.

Fig. 5 shows the results of such an investigation [14]. In the PhD technique the measurements of the photoemission intensity *I(E)* in a particular direction as a function of the photoelectron energy, *E*, are converted into modulation spectra $\chi(E) = (I(E) - I_0(E)/I_0(E))$, where $I_0(E)$ is the intensity variation due to instrumental effects and changes in the photoionisation cross-section; in practice this function is extracted from a stiff spline through the experimental data. While a full structure determination involves comparison of these experimental modulation spectra with multiple scattering simulations for an iterative series of trial structures, there are some characteristic features of the raw data that can guide the structure determination. In particular, if a strongly backscattering atom (such as Ni) lies directly behind the emitter relative to the detector, the modulation spectra are generally dominated by strong modulations that are periodic in electron wavevector (i.e. periodic in $\sqrt{E}$) due to the dominance of the single backscattering pathlength. As Fig. 5 shows, this condition is met for emission at a polar angle of 80° in the < 100 > azimuth from the surface with a low C coverage, consistent with the C emitter being in an undistorted four-fold coordinated hollow site, when the C atom is about 0.2 Å above the neighbouring Ni atom. Notice that this strong modulation is damped in the same emission direction from the higher-coverage (2 × 2) phase due to the lateral displacements of the Ni atoms in the clock reconstruction. Comparison of the experimental data with results of full multiple scattering calculations (Fig. 5) show that while the C atoms are only 0.1 Å above the top Ni layer in the reconstructed surface, this height is 0.2 Å in the low-coverage unreconstructed surface. Qualitatively the PhD and STM results agree about the adsorption site at both coverages, but the PhD results clearly show that the radial displacements of adjacent Ni atoms in the low coverage structure do not occur to a precision of ± 0.03 Å. This clearly does not agree with the conclusions of the STM study, but is consistent with the known difficulty of extracting quantitative atomic displacements from STM. Note that, as in QLEED, it is important to demonstrate the ability to fit PhD modulation spectra for a significant range of emission geometries to ensure that the structural solution is unique.

3. Molecular adsorption

While the competing structural technique of QLEED has proved to be extremely effective in determining surface structures involving atomic adsorption, many molecular adsorbates can prove to be more challenging. The simplest systems involve diatomic molecules such as CO and NO (and CN), which often also form structures with the good long-range order essential for the application of any conventional diffraction technique. The fact that PhD provides *local* structural information overcomes this constraint (as in the low-coverage Ni(100)-C system described above), which can be important in applications to molecular adsorbates, in part because long-range order may be less common. There is a further important difference. Particularly for larger molecules a LEED simulation must explore different conformations of an adsorbed molecule as well as its lateral position, height above the surface and orientation. The fact that most molecules of chemical interest are largely composed of the weakly scattering C, N and O atoms means that QLEED may be relatively insensitive to subtle changes in the molecular conformation and orientation. By contrast, PhD with its intrinsic elemental specificity (through the atomic core level photoelectric binding energies) offers the possibility to determine the location of the constituent atoms in a largely independent fashion; intramolecular scattering does have some influence, but is generally quite weak, so the PhD modulations are dominated by the backscattering from the underlying near-neighbour substrate atoms. An early example exploiting this effect is a study of CO [16] on Cu(110), in which both C 1 s and O 1 s PhD data allowed information to be obtained rather directly on both the Cu—C and C—O bonding distances. Indeed, the PhD technique has also been used to obtain very precise Ni—C bonding distances on different Ni surfaces to establish the relationship between these bondlengths and the adsorption site coordination [17], similar to the Pauling rules in chemistry. PhD has also been used to determine the differences in local adsorption bondlengths for the formate species, HCOO, on different
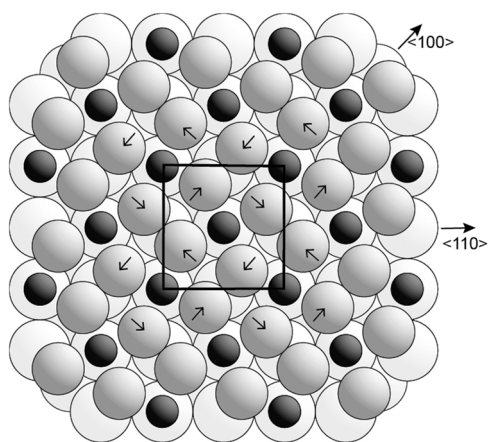

Fig. 4. Schematic representation of the Ni(100)(2 × 2)-C 'clock reconstruction'. The (2 × 2) unit mesh is superimposed while the arrows indicate the direction of displacements of the outermost Ni atoms from their clean surface positions. The surface layer Ni atoms are shown with slightly smaller radii and a darker shading than the underling bulk Ni atoms. The C atoms are shown as smaller with the darkest shading.
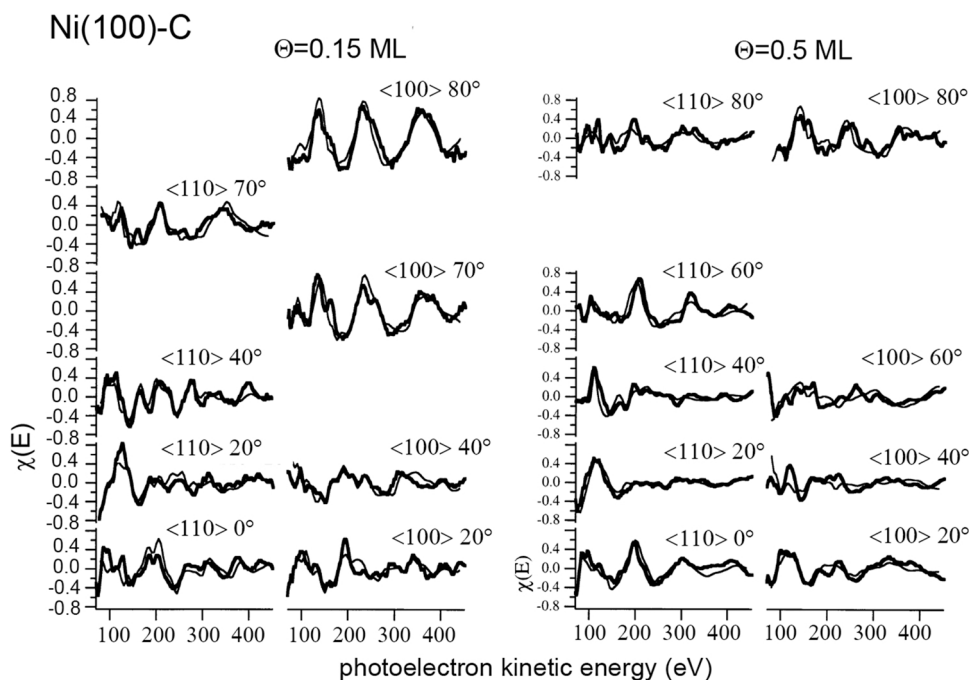
Fig. 5. PhD modulation spectra recorded in several emission directions from the Ni(100)-C surface at low C coverage and from the Ni(100)(2 × 2)-C 'clock' phase at a coverage of 0.5 ML. the bold lines are experimental results while the thinner lines are theoretical simulations for the best-fit structures. Reprinted from Terborg et al. [15] with permission from Elsevier.

crystal faces of Cu [18].

While the elemental specificity of PhD is important in allowing the locations of different atomic species within adsorbed molecules to be determined, the 'chemical shift' found in photoelectron binding energies for atoms of the same element in different chemical environments provides a valuable source of additional specificity in investigations of slightly larger molecular adsorbates. Indeed, these chemical shifts can also prove value in some very simple small molecules. The adsorption on N_2 on Ni(100) is an example of this; although the nitrogen molecule is a homo-nuclear diatomic, it adsorbs on Ni(100) with its molecular axis perpendicular to the surface, so the local chemical environments of the two N atoms, one 'inner' N atom bonded to the surface and the second 'outer' N having no direct bonding interaction with the surface, leads to two distinct N 1 s photoelectron binding energies differing by approximately 1.3 eV, as shown on the right of Fig. 6 (note that the large different in amplitude of the two components is due to transfer of much of the intensity of the inner atom emission to a satellite feature at lower kinetic energies). Comparison of the experimental PhD spectra from each of these components with the results of multiple scattering simulations for the best-fit model structure provides identification of the bonding site, orientation and Ni-N and N-N bondlengths [19]. Notice that the two normal emission spectra show strong modulations with a single periodicity in $\sqrt{E}$ due to backscattering from the Ni atom lying directly below the molecule; the $\sqrt{E}$ periodicity is shorter for the outer N emitter due to the longer distance from this Ni atom. This Ni atom receives an enhanced photoelectron flux from the outer N due to forward scattering by the inner N, leading to the stronger modulation amplitude.

A more typical benefit of chemical-state specificity in PhD studies of molecular adsorbates arises in the case of somewhat larger molecules that contain atoms of a specific element (typically C, N and/or O) in chemically distinct bonding states within the molecule. Several investigations of the adsorption geometry of relatively small biologically-related molecules such as amino acids and nucleobase molecules in DNA and RNA illustrate this effect. Of course, if there are two or more chemically shifted peaks in the photoemission spectrum from a single core level, one challenge is to identify which peak corresponds to the atomic species in which part of the molecule. PhD data from these
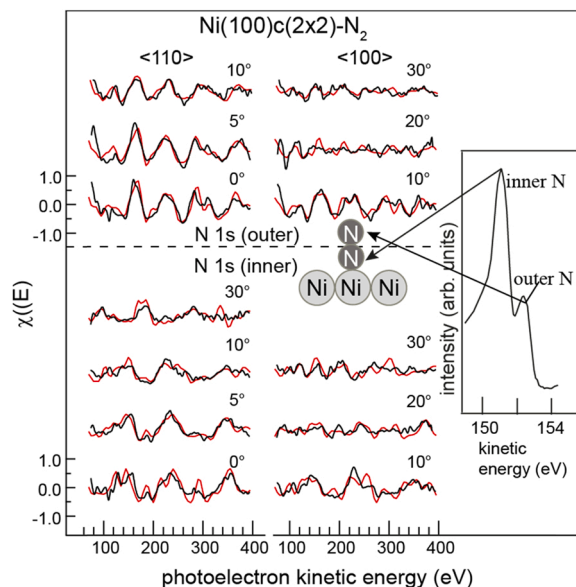

Fig. 6. Results of a PhD study on the Ni(100)c(2 × 2)N$_2$ surface. In the centre is a schematic diagram of the adsorption geometry while on the right is part of the N 1 s photoelectron spectrum recorded at a photon energy of 557 eV. Experimental PhD modulation spectra (black) for the two chemically inequivalent N 1 s emission components, are compared with the results of the multiple-scattering simulations for the best-fit structure, shown in red.

different components can actually assist these assignments. To illustrate this consider the cases of the two nucleobase molecules thymine [20] and cytosine [21] adsorbed on Cu(110). Fig. 7 shows the molecular structure of these two species, also defining a numbering convention for the different N and C atoms that is used below. Photoemission spectra recorded from thymine deposited at room temperature show a single O 1 s peak but two N 1 s peaks separated by ~1.7 eV. Annealing the surface to ~520 K, or deposition at this higher temperature also leads to a
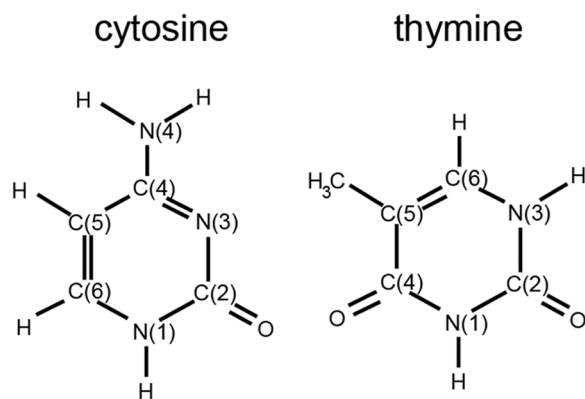
Fig. 7. Molecular structure of cytosine and thymine showing the labelling convention used in this paper for the different N and C atoms.

single O 1 s peak (but shifted by ~0.8 eV to lower photoelectron binding energy), while the N 1 s spectrum becomes dominated by a single peak at a binding energy close to that of the lower binding energy components of the room temperature two-peak spectrum. The implication of these observations is that the two O atoms of the molecule occupy similar bonding environments at both temperatures, but the initial adsorption at room temperature leads to the N(1) and N(3) atoms becoming more chemically distinct, while heating leads to these two N atoms having more similar chemical environments. The simplest way in which this change might occur is if first one NH species is deprotonated and then, on heating, the second NH species is also deprotonated. What might one infer about the adsorption structure? The single O 1 s peak and the implied deprotonation of one of the NH groups can most readily be reconciled with the two O atoms and the (deprotonated) N(1) peak all being bonded to the Cu surface, the two O atoms occupying sites of similar coordination. Heating then leads to deprotonation of the N(3) atom. Even simple qualitative evaluation of the O 1 and N 1 s PhD spectra provides clear support for this interpretation.

Fig. 8 shows the final optimised structure of thymine on Cu(110) following room temperature deposition obtained from comparison of a full set of 15 PhD modulation spectra with the results of multiple scattering for the best-fit model structure. However, qualitative evaluation of only a small subset of the PhD modulation spectra clearly points to the main features of this structural model as shown in Fig. 9(a). This figure compares the normal emission PhD modulation spectra from the O 1 s and the two chemically distinct N 1 s components. Notice that the O 1 s and N 1 s N(1) spectra are almost identical and both are dominated by a single periodicity in $\sqrt{E}$, consistent with a single Cu surface atom lying directly behind (i.e. in 180° scattering geometry) the emitter; as the detection direction is along the surface normal this implies that these two emitter atoms occupy atop (or close to atop) adsorption sites. By contrast the modulations from the other (N(3)) emitter are much weaker and of higher frequency, consistent with an emitter significantly further
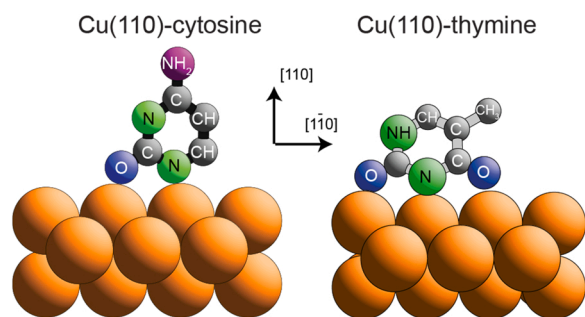
from the surface.

Turning to the case of cytosine adsorption, the free molecule contains three N atoms, all of which are chemically inequivalent. In the N 1 s photoelectron spectrum recorded immediately after deposition there are two main components separated by ~ 2 eV, the lower binding energy component having a significant higher intensity; prolonged annealing to 420 K leads to some attenuation and energy shift of the higher binding energy component, while further heating eventually largely removes this component. This initial lower-temperature heating effect was attributed to the removal of a partial second layer on the basis of comparison with published spectra from multilayer deposition. The initial conclusion regarding the assignment of these components is that the more intense low binding energy peak is due to emission from the N(3) and deprotonated N(1) atoms whereas the high binding energy peak originates from the N(4) (NH₂) atom. This assignment and the adsorption geometry of Fig. 8 are clearly supported by the normal emission PhD spectra shown in Fig. 9(b). Notice that the O1s spectrum from this surface is almost identical to O 1 s modulation spectrum from Cu(110)-thymine shown in Fig. 9(a), consistent with the O atoms occupying atop sites. Moreover, the PhD modulations of the low binding energy N 1 s are also closely similar, consistent with the strong modulation expected from the N(1) emitter, also occupying an atom site. As the N(3) emitter may be expected to lead to much weaker modulations (as in the case of adsorbed thymine) this modulation contribution to this combined N(1) and N(3) emission would be weak. Fuller details including a comparison of experimental and simulated PhD spectra for a range of emission directions provided full justification of the adsorption geometries shown in Fig. 8 together with their associated bondlengths and molecular tilt angles [19,20].

4. Adsorption on oxide surfaces

While most investigations of molecular adsorption have been on metal surfaces, there is certainly significant interest in the properties of oxide surfaces that play a key role in some reactions as heterogeneous catalysts. In this regard the chemical state specificity of PhD is valuable in investigating the adsorption of oxygen-containing molecules on oxide surfaces, exploiting the significant chemical shift in the O 1 s photoelectron binding energy that may occur between the oxide and the molecule. However, a PhD investigation of the adsorption of CO and NO on NiO(100) focused on the emission from the C and N atoms that bond to the surface rather than the O atom emission; the results of this study [22] revealed very large discrepancies between the experimentally determined Ni-C and Ni-N bonding distances relative to the results of theoretical calculations at that time. Standard DFT methods were known to give a poor description of the electronic structure of NiO, but the PhD adsorption bondlength results led to a debate as to the underlying problems in use of standard DFT for the determination of adsorption structure, and to developments that improved the level of theory/experiment agreement (e.g. [23,24]).

A system of molecular adsorption on oxide surfaces that has proved to be of great interest for many years is that of water adsorption on TiO₂, and while it appears that the structural phase of TiO₂ most relevant to the photocatalytic dissociation is anatase, many model studies have been performed on the rutile (110) surface for which good crystals are readily available. A general consensus appeared to be that water does not dissociate at a perfect (stoichiometric) rutile TiO₂(110) surface but does dissociate at the sites of oxygen vacancies on this surface. However, a careful temperature-dependent soft X-ray photoelectron spectroscopy investigation [25] provided evidence that dissociation to H and OH species can occur at low temperatures (~230 K), these components recombining and desorbing as the temperature is raised. A subsequent O 1 s PhD investigation provided further evidence of this interpretation, identifying OH species at both hollow and bridge sites and extracting Ti-O bondlengths for each species [26].
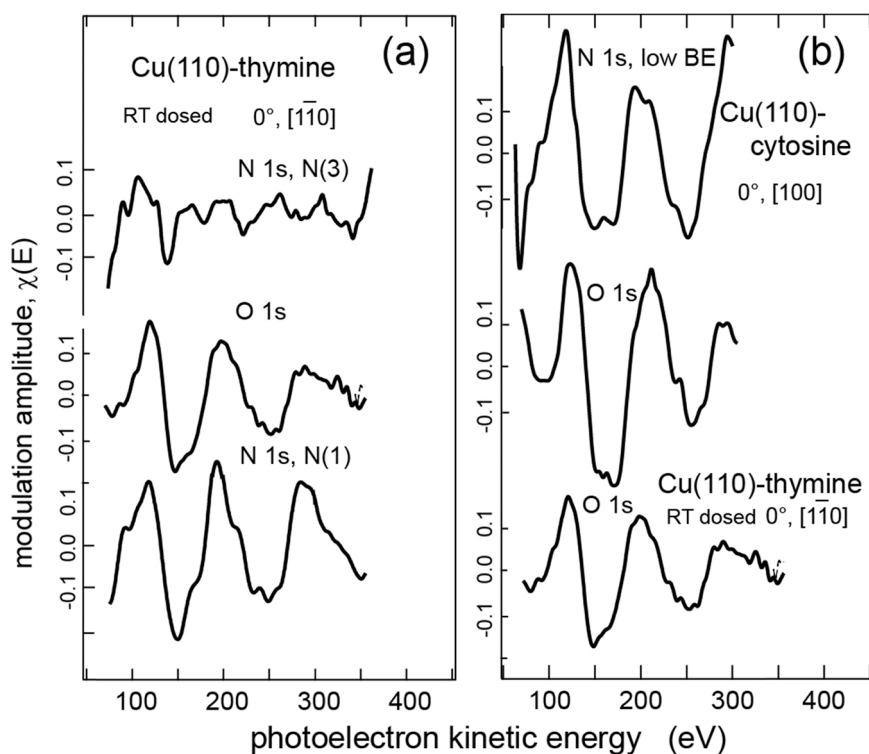

Fig. 8. Side views of the optimised structures of cytosine and thymine adsorbed on Cu(110).

Fig. 9. Normal emission PhD modulation spectra recorded from O1s and N 1 s components from thymine and cytosine adsorption on Cu(110).

5. Future prospects

The successful application of the PhD technique to solve more than 100 adsorbate/substrate structural problems, only a very few of which are described in this short review, clearly demonstrates the utility of the technique to obtain precise quantitative surface structural information on systems of increasing complexity in terms of molecular size but also (not described here) in coadsorption systems. In extending the application of PhD to determine the adsorption structures of larger or more complex molecules, two factors act as constraints. One is the need for these molecules to contain a small number of elementally or chemically distinct atoms that can act as distinct emitters, the adsorption sites of which can be determined. For example, the method is unlikely to prove to be as incisive in studies of large planar hydrocarbon molecules, which contain many C atoms in equivalent chemical sites within the molecule but different local sites on the surface. PhD has been applied successfully to the adsorption of benzene lying down on Ni(111) and Ni(110), but much larger planar hydrocarbons are likely to be challenging. This example also serves to illustrate the second constraining factor. The technique works well if the emitter atom of interest occupies a local high-symmetry site on the surface, but if its site is significantly displaced from a high-symmetry site, PhD spectra recorded at non-normal emission angles must average over multiple substrate-symmetry related local molecular locations, significantly attenuating the measured diffraction modulations. In a large flat-lying planar molecule there are likely to be several different local low-symmetry adsorption sites of constituent atoms due to the mismatch of intramolecular bondlengths with the substrate surface interatomic distances.

On the positive side, the significant developments in recent years of parallel detection of photoemission spectra at different emission angles through the use of 2-D detectors in the exit plane of concentric hemispherical analysers means that experimental data can be collected much faster; for angle-scan data the so-called momentum microscope also provides such data in a 'single shot'. Nevertheless, despite the huge advances in low-cost high-power computing facilities, the need for trial-and-error searching for optimal structural models using multiple

scattering simulations remains a discouraging factor to many researchers. Various 'direct methods' aimed at avoiding this trial-and-error approach have been explored, as discussed briefly elsewhere [1, 3], but as yet have failed to offer a realistic alternative to achieve full structure determination. The advent of scanning probe microscopies with sub-atomic real-space imaging has led to these becoming the most widely reported methods of surface science in recent years. The value of these techniques is clear, particularly in providing previously unimagined information on surface heterogeneity, but these methods can be misleading in terms of their apparent information on local quantitative structure. The dominance of these imaging techniques has led to a trend away from truly quantitative surface science studies [27].

One further instrumental development in recent years in surface science is to enable X-ray photoelectron spectroscopy of samples being exposed to partial pressures of interacting gases well above the usual requirements of ultra-high vacuum. Commonly referred to as ambient or near-ambient pressure XPS (NAP-XPS), albeit with pressures typically at least 2 orders of magnitude less that true ambient pressure, these instruments do allow one to follow heterogeneous catalytic reactions, including detection of surface catalytic intermediates as well as gas-phase reaction products, in favourable reactions. One further advance in the use of such instruments would be to extract PhD data from the surface species during the reaction, providing valuable structural information on the reaction mechanisms. One proof-of-principle experiment of this type has been reported [28], but the need for stable steady state reaction conditions over the time required for PhD data collection remains a significant challenge to its further development.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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