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Photoelectron Diffraction: from phenomenological demonstration to practical tool

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The potential of photoelectron diffraction – exploiting the coherent interference of directly-emitted and elastically scattered components of the photoelectron wavefield emitted from a core level of a surface atom to obtain structural information – was first appreciated in the 1970s. The first demonstrations of the effect were published towards the end of that decade, but the method has now entered the mainstream armoury of surface structure determination. This short review has two objectives: First, to outline the way that the idea emerged and the way this evolved in my own collaboration with Neville Smith and his colleagues at Bell Labs in the early years: Second, to provide some insight into the current state-of-the art in application of (scanned-energy mode) photoelectron diffraction to address two key issues in quantitative surface structure determination, namely, complexity and precision. In this regard a particularly powerful aspect of photoelectron diffraction is its elemental and chemical-state specificity.

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1. Introduction: ideas and first demonstrations

When mono-energetic low energy electrons (with energies of $\sim 30\text{-}500$ eV) are scattered from a crystalline solid, the coherent interference of the elastically scattered components leads to a redistribution of the electron flux in space that depends on the structure of the solid. The most obvious manifestation of this is low energy electron diffraction (LEED), in which a collimated incident beam of electrons are scattered into distinct diffracted beams, the directions of which depend on the lateral periodicity of the surface. Similar effects occur, however, if the source of the electrons is in, or on, the solid, as a result of photoelectron or Auger electron emission. In this case the components of the outgoing wavefield that are elastically-scattered by nearby atoms interfere with the directly emitted component (Fig. 1) to give an angular distribution that depends on the location of the emitter atom relative to these surrounding atoms. This is the physical basis of photoelectron, or Auger electron, diffraction. Indeed, insofar as this angular distribution is associated with the interference of a source wave and a set of scattered waves from an object (in this case the atoms surrounding the emitter), it can be described as an electron hologram.

Within the vocabulary of photoemission (or Auger electron emission) this coherent elastic scattering interference is referred to as a final state effect. This distinguishes it from the intrinsic angular dependence that occurs due to the orbital character of the initial occupied state (or states in the case of the Auger process) and the way (in photoemission) they couple to the incident electromagnetic radiation. For the simple case of photoemission from an atomic core level, this initial state angular distribution is governed by the selection rules, usually assumed to be dipolar and thus involving a change in the angular momentum quantum number of 1, i.e. $\Delta l = \pm 1$. For photoemission from an initial s -state ($l=0$), this leads to an outgoing p -wave directed along the polarisation vector of the incident radiation, but for other initial states the outgoing angular distribution of core-level photoemission involves an interference of the outgoing waves of $(l+1)$ and $(l-1)$ character, and the changing relative cross-sections for the excitation of these two components leads to energy-dependent variations in the angular distribution,

characterised by the well-known asymmetry parameter β . For core-level photoemission from an atom at a solid surface the measured angular distribution is thus influenced by both this initial state effect and the final state effect of the elastic scattering of the outgoing wave. The same factors influence photoemission from valence states of a solid surface, although the initial state effect is now more complex.

This issue of the relative importance of initial and final state effects in the angular dependence of photoemission from a solid surface is one that caused some controversy in the early developments of the method. This short review is a report of a talk given at a special session of the VUV-XV conference to celebrate the life of Neville Smith, and my first meeting with Neville coincided with these early years of angle-resolved photoemission and nucleated a collaboration and friendship between us that continued until his untimely death. For me the defining moment in all of these issues was the *Second Interdisciplinary Surface Science Conference* held at the University of Warwick in March 1975 [1], at which I happened to be the local organiser. The timing of this conference was fortuitous in coinciding with the early and rapid development of experimental and theoretical angle-resolved photoemission, and some of the key players in this field presented new results at the conference. On the theory side Bill Gadzuk, who had argued that initial state effects were of greatest importance in determining the angular distribution [2] discussed new results [3] that also incorporated the role of final-state effects that had been stressed in earlier work by Leibsch [4], particularly in the light of their possible utility in surface structure determination. At the same meeting Morton Traum and Neville Smith presented the results of experimental studies of angle-resolved photoemission from the Ta *d*-states of IT-TaS₂ following up on their earlier papers on angle-resolved photoemission from layer compounds [5]. This paper included the results of an azimuthal plot at fixed photon energy and polar emission angle giving a characteristic 'flower pattern' as shown in Fig. 2. With the characteristic humour of these authors the main lobes in this angular pattern were labelled 'ears', 'heads' and 'chins'.

My own contribution to this conference was a paper on angle-resolved Auger electron spectroscopy. Building on an earlier experimental study of clean copper surfaces I

presented the results of model calculations for S on Ni(100) to demonstrate the potential of this method to determine adsorbate structure [6]. I had, however, come to realise that a problem in analysing the data from this technique is the complexity of identifying the proper description of the unscattered outgoing wavefield orbital character due to the complexity of the three-state transition, a problem exacerbated by the fact that the most intense Auger electron peaks are typically of core-valence-valence character. By contrast, core level photoemission is typically dominated by the simple dipole selection rules mentioned above, so photoelectron diffraction looked more promising. This led to discussions with Neville Smith and the beginnings of a long-standing collaboration. Although it is difficult to imagine now, at that time there was a dearth of synchrotron radiation beamlines in the world equipped to deliver monochromated radiation in the 50-200 eV energy range required, and it took another three years to actually complete our first experiments. These were achieved using a beamline on the University of Wisconsin's Tantalus storage ring with a Miyake-West monochromator [7] borrowed from Daresbury Laboratory in the UK in the interregnum between the closure of the NINA electron synchrotron and the opening of the SRS storage ring source. Our first experiments were conducted on another layer compound, InSe, but measuring angle-resolved photoemission from the shallow In 4d and Se 3d core levels. Polar-angle scans showed the dominance of the atomic physics contribution to the angular dependence in terms of the β -factor, but azimuthal scans (with the angle of measurement relative to the incident polarisation vector fixed) showed the 'flower patterns' characteristic of the final state elastic scattering [8]. This was quickly followed by our first demonstration of the utility of photoelectron diffraction to determine surface structure through measurements of azimuthal plots of Te 4d and Na 2p core level photoemission from these two species adsorbed in c(2x2) ordered phases on Ni(100), with the Na data being supported by theoretical multiple-scattering simulations conducted by Brian Holland at Warwick [9]. An example of these (mirror-symmetrised) data is shown in fig. 3.

Of course, as in many areas of science, a set of circumstances and current ideas mean that at specific points in time, a number of people are reaching similar conclusions. 1978 was certainly the year to first demonstrate the potential of photoelectron diffraction as a

means of determining surface structure, and apart from our own work two other groups published key first results of their own investigations. Specifically, the group of Chuck Fadley showed photoelectron diffraction in azimuthal plots of O 1s emission from O on Cu(100) using high-energy forward scattering [10], while that of Dave Shirley demonstrated the same low-energy backscattering effects seen in our work, but in the scanned-energy mode from Se on Ni(100) using Se 3d emission [11].

Following these initial demonstrations, all three groups went on to study new systems and develop further both the experimental and theoretical aspects of the photoelectron diffraction methodology. My own collaboration with Neville Smith and his colleagues at Bell Labs, Mort Traum and Helen Farrell, continued for a few years, but subsequently my collaboration with Neville switched to studies of the electronic structure of solids, the field that was his natural domain, through our work on k-resolved inverse photoemission spectroscopy (KRIPES) (e.g. [12, 13]). At the same time, photoelectron diffraction studies of surface structure became the subject of a new collaboration with Alex Bradshaw at the Fritz Haber Institute in Berlin exploiting the BESSY facility. In the remainder of this short review I will focus on the most recent developments that have emerged from this second phase; the application and exploitation of photoelectron diffraction for surface structure determination.

2. Applications and developments

In general exploiting photoelectron diffraction to determine the structure of adsorbates on surfaces relies on exploiting backscattering (Fig. 1), for which the cross-sections are only adequate at relatively low kinetic energies (below ~500 eV). Small-angle forward scattering can provide adsorbate-substrate registry information in favourable situations, and can provide key information on intramolecular bond directions, but it lacks the ability to be applied successfully more generally. A more detailed discussion of the relative strengths of the different modes of photoelectron diffraction may be found elsewhere (e.g. [14, 15]). As illustrated by two of the first experiments to demonstrate the existence, and potential utility, of the technique [9, 11], photoelectron diffraction effects can be

determined by measuring either the angular distribution of the emitted electrons at fixed energy, or the energy dependence at fixed emission direction. In the early experiments, at a time when there remained some scepticism that photoelectron diffraction effects would prove large enough to be useful, measurements of the azimuthal scans had the advantage that the crystal symmetry provided a valuable check on the integrity of the data. As a basis for a methodology for adsorbate structure determination, however, the scanned energy mode offers some important advantages. One such advantage stems from the fact that, if the emission direction corresponds to 180° backscattering from a near-neighbour substrate atom relative to the adsorbate emitter atom, this near-neighbour backscattering can often dominate the diffraction effects. Thus, as the photon energy, and therefore the photoelectron energy and wavelength, is scanned, this backscattering path switches in and out of phase with the directly emitted wavefield component, leading to modulations in intensity with a period that directly reflects the adsorbate-scatterer bondlength. Measurements in such directions thus offer a particularly direct route to adsorbate site determination, although proper quantitative analysis using multiple scattering calculations from a cluster of scatterer atoms is essential for accurate determination of the interatomic distances. A second advantage relates to the optimisation of one of the key non-structural parameters involved in the data analysis, namely the inner potential, the parameter that defines the difference between the kinetic energy of the photoelectrons inside (where they are scattered) and outside (where they are measured) the surface. For energy-scan spectra the main influence of changes in the inner potential is a small offset in the energy scale, so the effect can instantly be assessed by visual inspection of experimental and theoretical spectra. In angle-scan data, the effect of changing the inner potential is far more opaque, and can only be assessed by many additional calculations of the simulated data at different values of this parameter.

For routine surface structure determination we have therefore adopted the use of modulation spectra in energy-scan photoelectron diffraction (referred to hereafter as PhD), as originally pioneered by the Shirley group [11]. An important aspect of our methodology, however, is to measure (and simulate) such spectra at several (typically 5-

10) different emission directions. The resulting enlarged data set is a key requirement to improve precision and greatly reduce ambiguity in the resulting structures.

Key advantages of photoelectron diffraction in surface structure determination are that the resulting structural information is *local* and is both *element specific* and *chemical-state specific*. The former property arises from the local spherical-wave character of the photoelectron source, together with the influence of inelastic scattering, both of which ensure that it is the locations of relatively near-neighbour scattering atoms to the adsorbate emitter atom that dominate the measured diffraction effects. The second two properties arise because the measurement of the photoelectrons is energy-selective, and the core level photoelectron binding energy is characteristic mainly of the atomic species, but also of the local bonding environment. In particular, if atoms of the same elemental species occur in different local bonding environments within a molecule, in different coadsorbed molecular species, or even in different sites on a surfaces, there are 'chemical shifts' in the measured energy that can be used to separate the emission, and thus the photoelectron diffraction, from these different atoms. It is therefore possible to determine the structural environment of each of these distinct species in a largely independent fashion. We now present a few recent examples of the application of this approach and the novel information that has been gained.

2.1 'Complex' molecular adsorbates

One complication in applying standard methods of electron or X-ray diffraction to molecular adsorbates is that the number of free structural parameters increases sharply as the number of atoms in the molecule is increased, at least in the absence of constraints on the molecular conformation and orientation. Photoelectron diffraction offers the potential advantage that one may attempt to determine the location of the different constituent atoms in a largely independent fashion through the exploitation of the elemental and chemical-state specificity. In such an analysis, a valuable initial assumption, that commonly proves to be sound, is that intramolecular scattering contributes relatively little

to the measured PhD spectra, particularly because most atoms in such adsorbates are of low atomic number and thus are weak electron scatterers.

To explore and exploit this potential we have investigated the structure of two amino acids, glycine [16] and alanine [17], on Cu(110). Glycine, $\text{NH}_2\text{CH}_2\text{COOH}$ is the simplest amino acid, containing the two key ingredients, the amino NH_2 group and the carboxylic acid COOH group. Following deposition on the surface the acid hydrogen atom is lost to form a glycinate species, $\text{NH}_2\text{CH}_2\text{COO}$, which spectroscopic studies indicate may bond either through the carboxylate O atoms alone, or through both these atoms and the amino N atom. The situation is similar for alanine, $\text{NH}_2\text{CH}_3\text{C}^*\text{HCOOH}$, although the fact that one of the H atoms on the central C atom, marked C^* , is replaced by a methyl CH_3 group means that the C^* atom becomes a chiral centre, i.e. that there are inequivalent left-handed and right-handed forms of the molecule. Fig. 4 shows a comparison of the experimental N 1s and O 1s PhD spectra, measured in a range of emission geometries, with the results of multiple scattering simulations for the best-fit structural model of alaninate on Cu(110), which is also shown schematically. Notice that at normal emission the N 1s and O 1s spectra show very similar modulations, although these are substantially stronger for the N emitter. The strong normal emission modulations for the N 1s spectra are characteristic of an emitter in an atop site such that the nearest-neighbour substrate atom directly below is in the favoured 180° scattering geometry. For the O atoms, however, there are two inequivalent positions for each of the two molecules per unit mesh, but as one of these is close to atop, similar modulations occur, but the amplitude is lower due to the effect of the other atoms in sites further removed from the highly-symmetric atop geometry.

Of course, using these two emitter atom species alone does not explicitly provide information on the C atom sites, but the overall geometry may be inferred from this partial information. There are three inequivalent C sites within the molecule in this structure, so there are three chemically-shifted C 1s components [18], but because none of these atoms is close to the strongly-backscattering Cu substrate atoms, their PhD modulations are weak and do not provide a reliable basis for uniquely establishing their

positions. Of course, PhD provides no useful information on the H atoms sites, because H atoms lack any core level and are very weak electron scatterers; the model in Fig. 4 is based on density functional theory (DFT) calculations [19]. Interestingly, while the DFT minimum energy structure generally gives a good description of the PhD data, it did prove necessary to decrease the Cu-O and Cu-N bonding distances by 0.10 Å and 0.08 Å respectively, in order to achieve the good fit shown in Fig. 4. This issue of bondlength determination and experiment-theory discrepancies is discussed further in section 2.3. Notice that a key feature of this study is the large PhD experimental data set used to tackle this complex system.

Very recently, this approach to determining the structure of adsorbed complex molecules has also been applied to the nucleotide base molecule, thymine, adsorbed on the same Cu(110) surface [20]. Fig. 5 shows the basic bonding geometry found for this molecule through the two O atoms and the N(3) atom which is deprotonated by the reaction with the surface. In this case the analysis was based on the O 1s PhD spectra and on the two chemically-shifted N 1s component PhD spectra associated with the protonated N(1) and deprotonated N(3) atoms. In this case, too, the PhD spectra recorded from the N(1) atoms showed weak modulations due to its large distance from the Cu surface atoms, but intramolecular scattering proved sufficient to provide information on the orientation (both tilt and twist) of the molecule relative to the underlying Cu(110) surface.

2.2. Chemical-shift photoelectron diffraction

A key feature of the PhD technique is the ability to exploit the chemical shifts in core level photoelectron binding energies to obtain not only element-specific, but also chemical-state-specific local structural information. One example of this is when an atom of the same element has a different bonding environment within an adsorbed molecule, such as the protonated and deprotonated N atoms in adsorbed thymine on Cu(110) described above. A rather different example is that of oxygen-containing molecules adsorbed on oxide surfaces. While the surfaces and interfaces of oxide materials are known to play an important role in many practical processes, including heterogeneous

catalysis and electronic devices, they have been far less extensively studied than those of metals or semiconductors. In part this stems from the fact that they are typically insulators and thus may charge up in experiments using incident or detected electrons or ions, while UHV surface preparation may also be challenging. Increasing use of ultra-thin epitaxial films, grown *in situ* on conducting substrates, largely overcomes both of these problems. Nevertheless, there remains a dearth of structural studies of oxide surfaces, and particularly of adsorbate on them, even on surfaces of bulk oxides than can readily be made conducting, such as TiO₂. Of course, oxides are strongly ionic in character so it is not surprising that the O 1s photoelectron binding energy in oxides typically differs by more than 1 eV from that in most molecular adsorbates. This effect seems to have been first exploited in a photoelectron diffraction study of the formate species, HCOO⁻, on TiO₂(110) [21, 22] and has subsequently been used more extensively in this same adsorbate system [23] and for OH [23] and H₂O [24, 25] on this same surface.

A third type of chemical shift that can be exploited in photoelectron diffraction is that associated with atoms within identical molecules adsorbed at different sites on a surface. The physical origins of such shifts are, of course, identical to those in the other two examples given above: the constituent atoms are in different bonding environments. In this case, though, the shifts are a specific property of the surface structure and not the constituent molecules or solids, and as such identifying which chemical shift corresponds to which geometry cannot be based on reference spectra from the isolated components (i.e. the molecules and the solids separately). In these cases, therefore, photoelectron diffraction not only exploits the chemical shifts to separate out the structural information from each surface species, but the resulting structural analysis leads to a proper identification of which chemical shift corresponds to which geometry. The classic example of chemical shifts of this type is CO adsorption on Pt(111) for which the different states were observed spectroscopically in early experiments using a laboratory-based X-ray source. Both the C 1s and O 1s show two distinct chemically-shifted states, the relative intensities of which vary with CO coverage on the surface [26]. The two states were attributed to CO molecules in singly-coordinated atop and two-fold-coordinated bridge sites on the surface. More recently, photoelectron diffraction experiments using

these chemically-shifted photoemission signals have confirmed this assignment and provided quantitative structural information for two different surface phases formed at different coverages [27, 28].

2.3 Chemisorption bondlengths

An important feature of photoelectron diffraction relative to photoelectron spectroscopy (and, indeed, other spectroscopic methods) is that it provides *quantitative* surface structural information. Thus, one not only identifies the adsorption sites, but also the associated bondlengths including surface and near-surface reconstruction and distortions. Typically, the most precise structural parameter to emerge is the distance between the emitter atom and the nearest-neighbour (strongly-backscattering) substrate atom. This chemisorption bondlength can generally be determined with a precision in the range 0.02-0.05 Å. This parameter is, of course, intimately related to the bonding strength, and provides an important test of the quality of theoretical descriptions of the surface structure and bonding as obtained from total-energy calculations. In this regard, a number of recent measurements have proved revealing.

Perhaps the most startling example is provided by an early study of CO adsorption on NiO(100) (grown epitaxially on Ni(100)); the Ni-C bondlengths were found experimentally to be 2.07 Å, in sharp contrast to previous theoretical estimates of 2.46 Å and 2.86 Å [29]. While this adsorption system was known to present a substantial challenge to theoretical methods, these huge discrepancies in the structural parameters led to renewed efforts to improve the theory. A more subtle case is that of molecular water on TiO₂(110) [24, 25]. For this adsorption system there has been a long-standing conflict between theoretical and experimental studies as to whether the adsorption is molecular or dissociative. There seems to be a clear experimental consensus that on an ideally-ordered stoichiometric surface water does not dissociate, although dissociation does occur at surface oxygen vacancies. By contrast, most theoretical calculations indicate that dissociation is facile even on the perfect surface. In this regard, the recent PhD study of this system is interesting. While the adsorption site found, with the O atom of the

molecule atop a surface Ti atom, is consistent with all theoretical calculations of this preferred site, and with site determinations based on STM, the Ti-O bondlength found experimentally ($2.21 \pm 0.02 \text{ \AA}$) is shorter than any of the theoretical values. However, in the case of the one theoretical calculation that does predict stable molecular adsorption and also gives a value for this bondlength, the discrepancy in bondlength is only 0.04 \AA . By contrast, calculations that indicate facile dissociation give bondlengths that are $0.07\text{-}0.20 \text{ \AA}$ longer than the experimental value. It seems, therefore, that many calculations may be underestimating the strength of the molecular water bonding strength, and as such incorrectly identifying the relative energies and barriers between the molecular and dissociated states. Note that the effects are probably quite subtle. For the case of adsorption of the formate species (HCOO) on this same surface, the Ti-O chemisorption bondlength found by both experiment and theory is 2.08 \AA , significantly shorter than for the molecular water. Apparently, the theoretical calculations describe the strong chemisorption bond of formate well, but find the weaker bonding of molecular water more challenging. These results further highlight the importance of quantitative experimental structure determinations.

PhD studies of a series of Ni/CO adsorption systems have also provided valuable insight into the relationship between chemisorption energies and bondlengths [30]. On different surfaces of Ni in different structural phases CO bonds in one-fold, two-fold, and three-fold coordinated sites, in all cases with very similar total adsorption energies. PhD measurements reveal that the Ni-CO bondlength increases as the coordination number increases and thus the local bond order decreases, entirely consistent with a Pauling-type bondlength-bond order relationship. However, a comparison of CO bonded in one-fold coordinated atop sites on Ni(100) with and without atom H coadsorption revealed a rather small change in bondlength despite a large change in total adsorption energy. This apparent inconsistency was attributed to the energy cost associated with large substrate relaxations in the coadsorption system that could be the cause of the low total adsorption energy; this interpretation was supported by theoretical total energy calculations.

3. Conclusions

Photoelectron diffraction has progressed very considerably in the last 30 years. In the late 1970s, key experiments performed independently by several groups demonstrated the existence of the phenomenon, and its potential utility for surface structure, and particular adsorbate structure, determination. In this early period there were very few VUV/soft X-ray synchrotron radiation beamlines in existence to perform these studies, and progress was slow, but in the last 20 years huge progress has been made in developing and applying the methodology to a growing number of increasingly complex surface structural problems. The special virtues of the ability to obtain quantitative local structural information that is both element- and chemical-state-specific means it is ideally suited to progress further into studies of more complex surfaces lacking long-range order and involving co-adsorbed species, ensuring it will continue to have an important place in the armoury of surface science.

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Figures

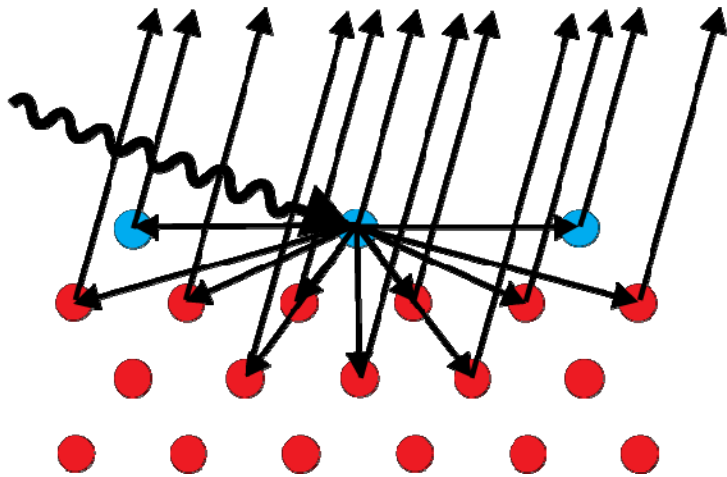


Fig. 1 Schematic diagram showing the directly-emitted and elastically-backscattered electron trajectories that interfere to produce a photoelectron (or Auger electron) diffraction pattern in emission from an adsorbate atom on a surface.

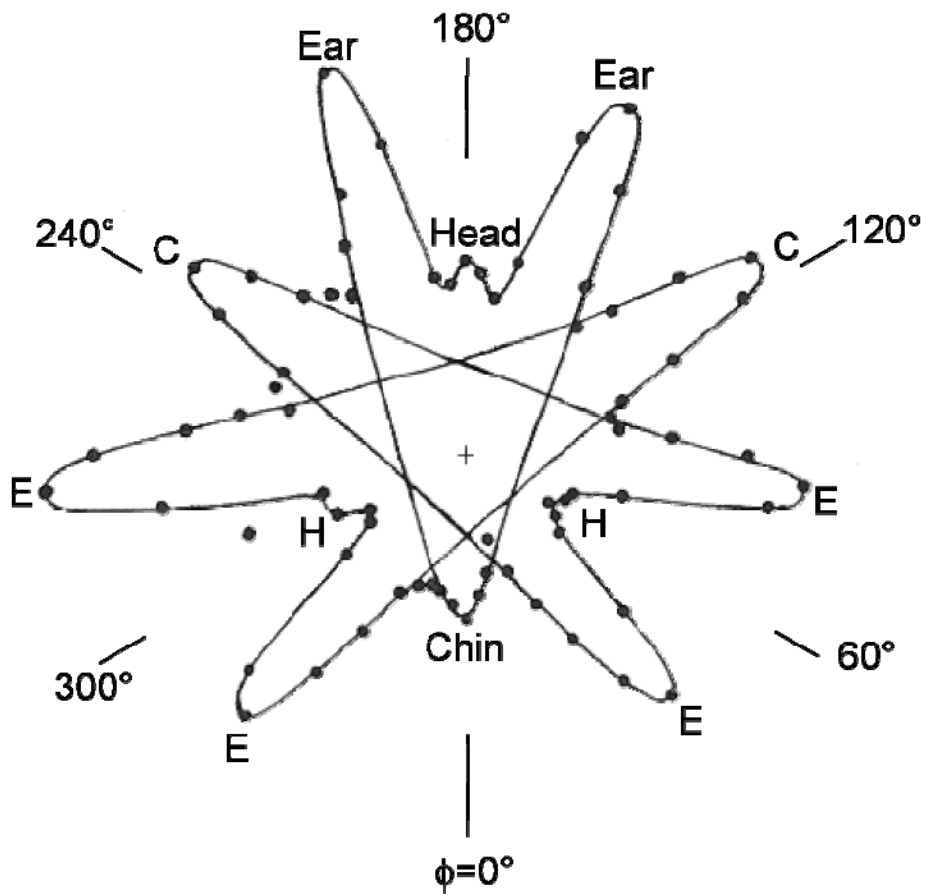


Fig. 2 Azimuthal-angle plot of Ta *d*-state emission from IT-TaS₂ recorded at a polar emission angle of 60° using a photon energy of 21.2 eV, adapted from the work of Traum and Smith [5]

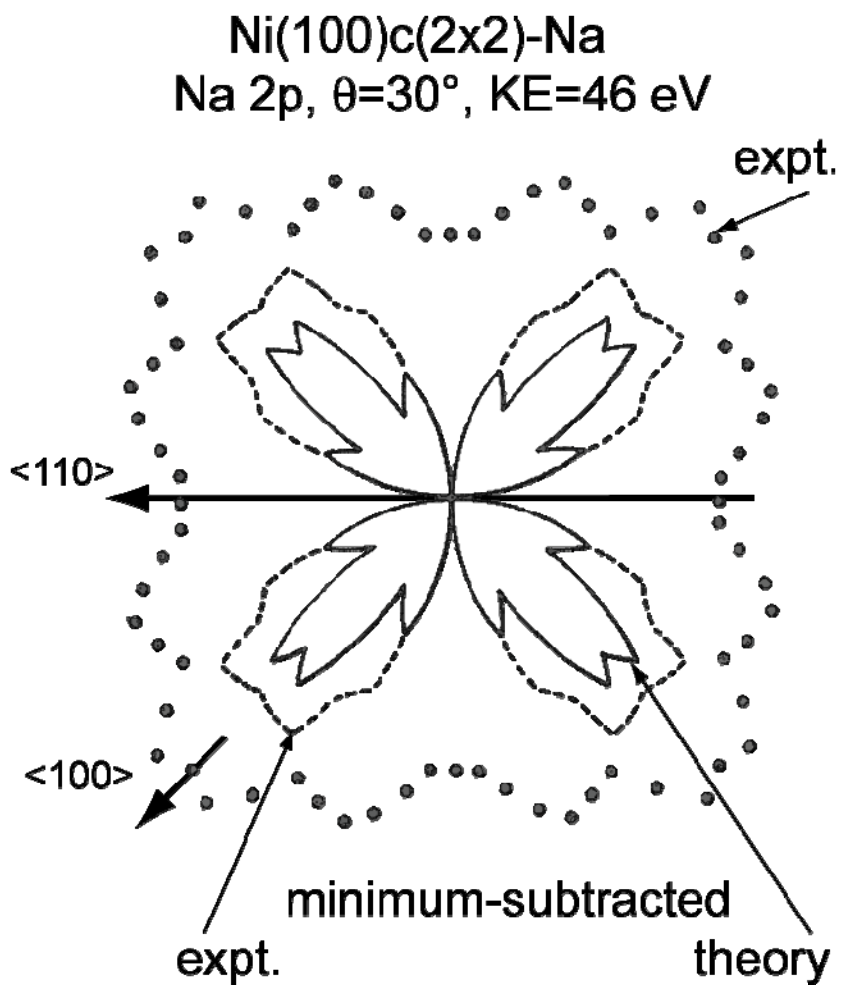


Fig. 3 Azimuthal-angle scan of Na 2p photoemission from a Ni(100)c(2x2)-Na surface compared with a theoretical multiple scattering simulation. Adapted from ref. [9].

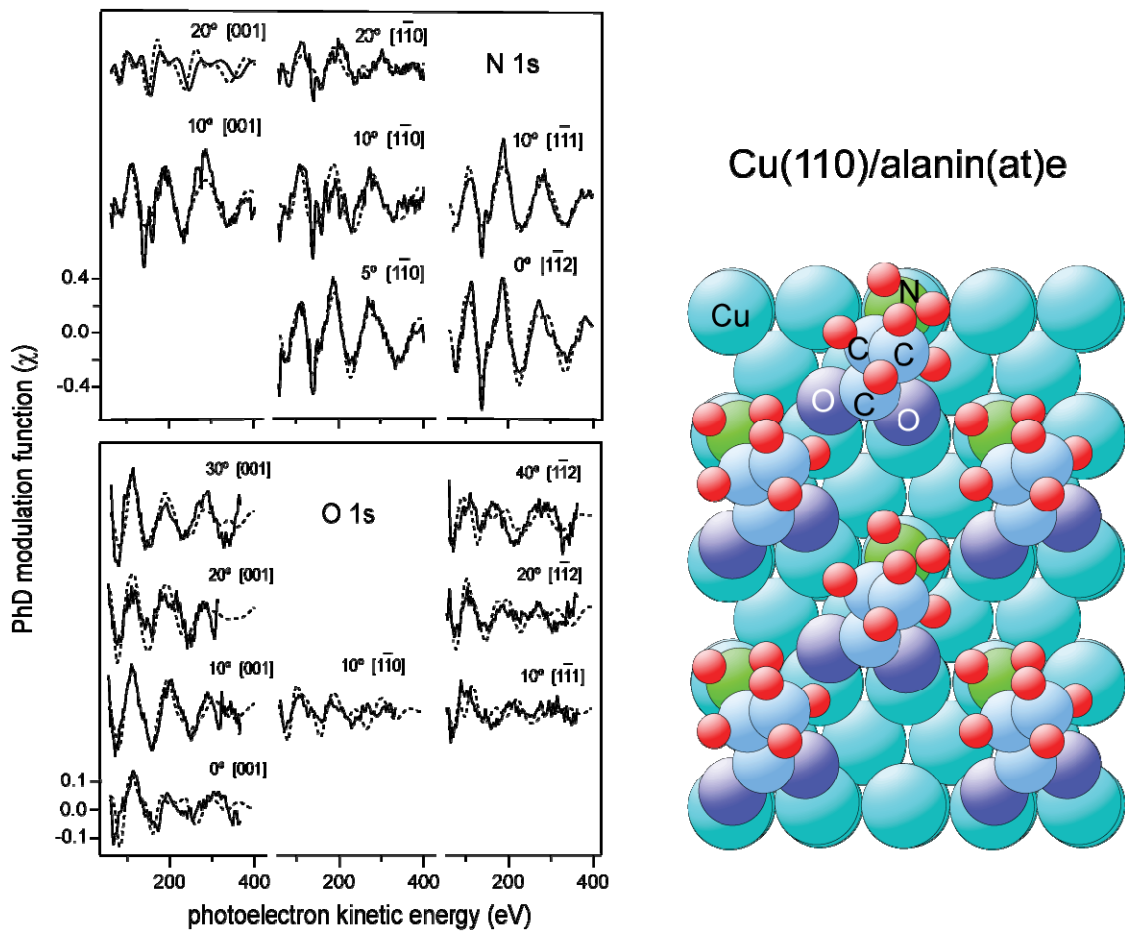


Fig. 4 Summary of the results of a scanned-energy mode photoelectron diffraction (PhD) study of the (3x2) ordered phase of alaninate (deprotonated alanine) on Cu(110) showing the optimised structure and the comparison of the experimental (full lines) and theoretically simulated (dashed lines) PhD modulation spectra for this model [17].

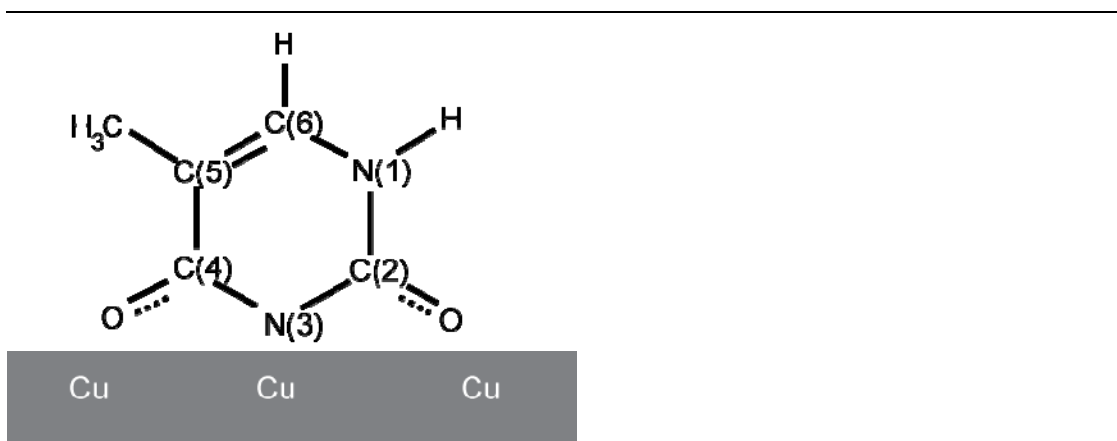


Fig. 5 The deprotonated thymine molecule showing its bonding configuration found in a PhD investigation of its adsorption on Cu(110) [20].