

# Photoemission Studies of Adsorbates on Metal Surfaces

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A brief review is presented of the general field of synchrotron radiation photoemission of adsorbates on well characterized metal surfaces, contrasting some of the earliest work of the 1970s with more recent experiments, and highlighting some of the likely future developments that may derive from the use of third-generation synchrotron radiation facilities. Four general types of study are identified: shallow core-level photoemission either for the fingerprinting of the chemical state, or for quantitative structural studies *via* photoelectron diffraction, and valence-level photoemission either to study the two-dimensional band structure of adsorbate-induced surface-localized states, or to investigate the orientation of molecular adsorbates through the use of symmetry selection rules.

**Keywords:** photoemission; adsorption; surfaces of metals; electronic structure; surface structure; photoelectron diffraction.

## 1. Introduction

The object of this short review is to briefly survey the range of applications of (synchrotron radiation) vacuum ultraviolet (VUV) photoelectron spectroscopy to the study of adsorbates on metal surfaces, looking back over the last 20 years or so but also considering some of the more obvious routes which this work might be expected to follow in the near future. This review arises from a meeting held to celebrate the '21st birthday' of the Miyake grazing-incidence monochromator (Howells, Norman, Williams & West, 1978) which was actually first ordered for installation on the existing 'Synchrotron Radiation Facility (SRF)' at Daresbury Laboratory, 21 years ago. Because of this, I will particularly highlight some scientific problems to which we contributed through the use of this instrument. There are, of course, many other groups who have done far more work in this field, and references to a few of these are included, but the review is certainly not exhaustive. It is intended to be representative of past work in character, but not necessarily in terms of relative contributions of different researchers. In discussing future opportunities, I will particularly emphasize some of the potential benefits of the new third-generation VUV synchrotron radiation sources (such as the ALS in the USA and ELETTRA and BESSY-II in Europe) which are now coming on stream.

Within the relatively narrow range of application covered here, I identify four main types of work, two concerned with photoemission from core levels, and two with photoemission from valence states. In the first two, I distinguish the general use of shallow core-level spectroscopy using synchrotron radiation, commonly referred to as soft X-ray photoelectron spectroscopy [*i.e.* soft XPS or SXPS; the distinction between VUV and soft X-rays (SXR) is a fine one and largely a matter of perspective], from photoelectron diffraction (PhD) which is also based on

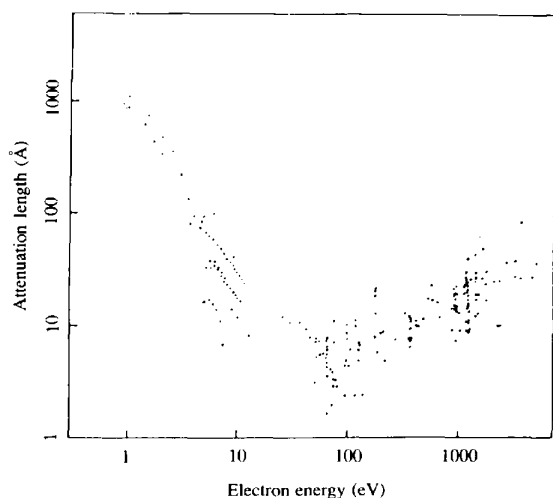
core-level spectroscopy but has a rather different scientific objective. In the case of valence-level spectroscopy, I distinguish between studies concerned with two-dimensional band mapping of adsorbate-induced states, from the study of more localized states associated with adsorbed molecular species; both of these applications are commonly referred to under the acronym of ARUPS (angle-resolved ultraviolet photoelectron spectroscopy).

## 2. SXPS

The power of conventional XPS (using *in vacuo* laboratory Al and Mg  $K\alpha$  X-ray sources) is widely recognized in surface science (Briggs & Seah, 1992; Woodruff & Delchar, 1994). Apart from the utility of the method for identifying the elemental character of the surface species through their characteristic core-level binding energies, and the extension of this information to quantify the surface composition through the relative intensities of the photoemission peaks, the exact photoelectron binding energies can be used to fingerprint the 'chemical' character of each element present. This capability led to the original name for the technique of ESCA (electron spectroscopy for chemical analysis). There are at least two limitations to the method for the study of adsorbates at surfaces, however, which can be overcome by using synchrotron radiation. These concern the degree of surface specificity, and the energy resolution. The surface specificity of XPS is governed by the electron attenuation length [the distance below the surface from which an electron has a reasonable (1/e) chance of escaping without significant energy loss] and this is determined by a combination of inelastic and elastic scattering cross sections (Woodruff & Delchar, 1994). The attenuation length is material dependent, but typically as the electron energy is increased from very low energies, the attenuation length

falls steeply to a very broad minimum around 50–100 eV (with a value *ca* 5 Å), before rising slowly (roughly proportional to  $E^{1/2}$ ) as the energy is increased further. Fig. 1 shows a compilation of experimental values of this parameter collected from a range of materials given by Seah & Dench (1979) which demonstrates this general trend. The maximum surface specificity can thus be achieved if a photon energy is chosen which gives the photoelectrons from the core level of interest a kinetic energy in this range. This clearly necessitates the use of a 'tunable' energy source of radiation, *i.e.* the combination of a synchrotron radiation source and a suitable monochromator. By contrast, the fixed and relatively high (1254, 1487 eV) photon energies used in conventional XPS typically lead to photoelectron kinetic energies in the 500–1400 eV range for which the attenuation length is substantially larger (10–20 Å). This ability to 'tune' to the maximum degree of surface specificity was a key theme of much of the early work on SXPS using synchrotron radiation in the 1970s, and is, of course, still exploited today. Indeed, one of the very first experiments which we did on the Miyake monochromator when it was installed at the SRF on the NINA electron synchrotron at Daresbury at this time was to try to measure the energy dependence of the attenuation length in some specific materials by exploiting this 'tuning' capability (Norman & Woodruff, 1977, 1978*a*).

The second advantage of SXPS over conventional XPS, however, concerns energy resolution. In both XPS and SXPS the experimental energy resolution is determined by the combination of photon and photoelectron instrumental energy widths. In conventional XPS, the intrinsic linewidth of the  $K\alpha$  lines used as photon sources is almost 1 eV, although some instruments incorporate a monochromator to improve on this value for the photons delivered to the sample. Nevertheless, it is a general truth of both photon monochromators and electron spectrometers that the energy resolution is improved as the energy is reduced – typically



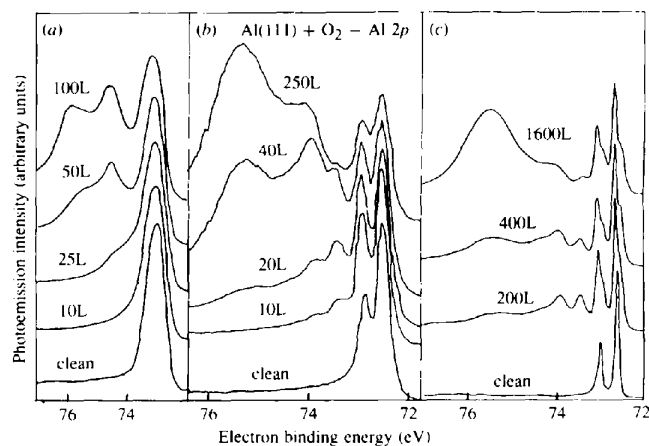
**Figure 1**  
Electron attenuation lengths as measured in a range of materials (after Seah & Dench, 1979).

in both cases, it is the resolving power ( $E/\delta E$ ) which is fixed by the instrument, so there is a linear gain in resolution as the energy is decreased. For shallow core levels (*i.e.* with binding energies in the range *ca* 30–200 eV) there is therefore a very substantial potential gain in using monochromated synchrotron radiation with a photon energy of some 50 eV above the photoemission threshold. Not only is the surface specificity improved, but also both the photon and electron kinetic energies are very substantially reduced relative to conventional XPS, leading to major potential gains in resolution. Indeed, a further advantage, at least for core levels having low associated angular momenta, is that the photoionization cross section, and thus the sensitivity, is also greatly improved.

The enhanced spectral resolution combined with the enhanced surface specificity has continued to yield new and important information from SXPS throughout the last two decades of interest to us here. One of the earliest examples of this advantage for adsorbates on metals came from studies of oxygen chemisorption on Al surfaces. Again, one of our own early studies using the SRF (NINA) facility was on oxygen adsorption on *in situ* evaporated films of both Al and Mg (Norman & Woodruff, 1978*b*); the existence of large ( $\approx 2.5$  eV) chemical shifts on the  $2p$  photoemission peaks of these materials associated with true oxidation was already well established from XPS, but the SXPS data, even at rather poor resolution, gave strong indications of an intermediate chemically shifted state associated with oxygen chemisorption preceding the true oxidation. As an aside, it is perhaps worth remarking that it is a measure of both the novel potential of SXPS experiments, as well as of the experimental difficulties of working in a parasitic mode on the electron synchrotrons of this period, that polycrystalline films were still regarded as of interest in synchrotron radiation experiments at a time when laboratory-based surface science was already dominated by single-crystal studies. In fact, on Al at least, the chemisorption state is found only on the (111) face amongst the three low-index faces, and an experiment on this single-crystal surface, performed at much the same time at SSRL, provided substantially clearer evidence of this intermediate chemically shifted state with a chemical shift relative to the metallic state of some 1.4 eV, see Fig. 2(*a*) (Flodström, Martinsson, Bachrach, Hagström & Bauer, 1978). A key factor in these experiments, of course, was the enhanced surface specificity which allowed the emission from the outermost Al atomic layer bonded to the chemisorbed O atoms to dominate the Al  $2p$  photoemission spectrum. We returned to this system some 10 years later, again using the Miyake monochromator, but now installed on the dedicated Synchrotron Radiation Source (SRS) storage ring at Daresbury, and with improved resolution discovered that the system is even more complex than had been supposed (McConville, Seymour, Woodruff & Bao, 1987). Rather than one intermediate chemically shifted Al  $2p$  state between the metallic and oxidic states, it transpires that there are three such states, with chemical shifts of approximately

0.5, 1.0 and 1.5 eV; the fact that the separation of these states is rather similar to the spin-orbit splitting of the Al 2*p* photoemission spectrum (0.42 eV) leads to a somewhat misleading impression of only two such states at first glance (Fig. 2*b*). Quite simple curve fitting of the data, however, such as the example in Fig. 3, shows the existence of the three intermediate states and it now seems to be generally accepted that these three peaks correspond to Al atoms bonded to one, two and three O atoms in the chemisorbed layer as the O atoms fill up the (f.c.c.) threefold coordinated hollow sites to form ultimately an ordered (1 × 1) overlayer as we proposed. A comparison of the old (1978) SSRL experimental data and the 1987 higher-resolution spectra shown in Figs. 2(*a*) and 2(*b*) shows rather clearly how the earlier identification of only a single intermediate state arose as a result of lower spectral resolution.

Of course, the old Miyake monochromator no longer represents the state-of-the-art in monochromator design for this spectral region, and many better instruments are now in use. Probably the most extensive use of high-resolution SXPS for adsorbate studies on metal surfaces in recent years has emerged from a beamline at MAX-lab in Lund (Andersen *et al.*, 1991). This station also incorporates a high-resolution high-transmission Scienta electron-energy analyser, and the performance of this combination has led to some striking new applications of SXPS. Indeed, this instrument has also been used to revisit the Al(111)/O system (Berg *et al.*, 1993), but while the chemisorbed states are more clearly resolved (see Fig. 2*c*), the only new feature to emerge from this study is a further high-binding-energy shoulder state attributed to Al atoms at the metal/oxide interface when true oxide growth is initiated.

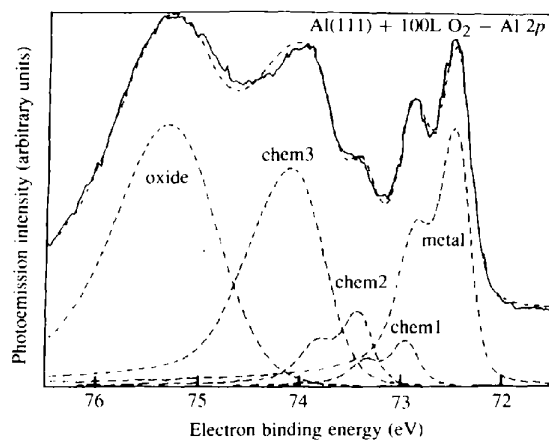


**Figure 2**

Al 2*p* photoemission spectra recorded from Al(111) surfaces subjected to different exposures of oxygen from (a) Flodström *et al.* (1978), (b) McConville *et al.* (1987) and (c) Berg *et al.* (1993). The binding-energy scales are as given in the original papers and indicate some differences in calibration. In addition, the large differences in exposures to achieve oxidation probably reflect differences in different vacuum chamber designs as well as differences in surface perfection. The principal differences in the three data sets, however, are associated with differences in spectral resolution.

Quite new results, however, have emerged from studies of a range of alkali metals on Al surfaces using this new beamline. This work has clearly identified several Al 2*p* chemically shifted states, first for Na on Al(111) (Andersen, Qvarford, Nyholm, van Acker & Lundgren, 1992), but latterly for several other adsorbate/substrate orientation combinations (Andersen, Lundgren, Nyholm & Qvarford, 1992, 1993), when the deposition occurs at room temperature or the samples are warmed after low-temperature deposition. These have been interpreted as indicative of alkali-aluminium intermixing, a surprising conclusion in view of the fact that all of these combinations are immiscible in the bulk. Full structural studies of the Al(111)/Na system by several techniques [surface-extended X-ray absorption fine structure (SEXAFS; Schmalz *et al.*, 1991), normal-incidence X-ray standing wavefield absorption (NIXSW; Kerkar *et al.*, 1992), low-energy electron diffraction (LEED; Burchhardt, Nielsen, Adams, Lundgren & Andersen, 1994)] have confirmed this basic conclusion and provided a more detailed understanding, but the high-resolution SXPS 'fingerprinting' provides a particularly convenient means of following the transitions and certainly was the first to identify the generality of the effect. A key result of considerable interest which emerges from the later structural studies is that for both K and Rb adsorption on Al(111), ( $\sqrt{3} \times \sqrt{3}$ )R30° absorption phases are seen both after low-temperature and room-temperature preparation, but while the low-temperature phases have the alkalis atop top-layer Al atoms, the room-temperature phases involve alkalis in substitutional sites (Stampfl *et al.*, 1992; Nielsen, Burchhardt, Adams, Lundgren & Andersen, 1994; Scragg *et al.*, 1994).

A further area of application of this SXPS facility in Lund is the work of the Uppsala group on CO adsorption on metal surfaces. Historically, the most successful

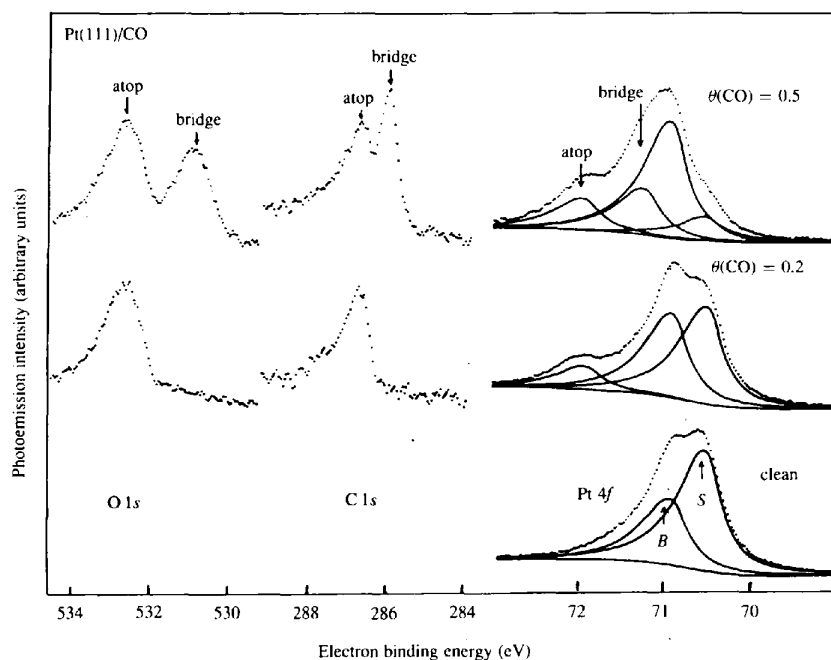


**Figure 3**

Al 2*p* photoemission spectra recorded from an Al(111) surface subjected to 100 L exposure of oxygen as shown in Fig. 2(*b*) but showing the separate chemically shifted components due to the metallic substrate, Al surface atoms bonded to 1, 2 and 3 chemisorbed O atoms (chem1, chem2, chem3) and Al atoms in the surface oxide (after McConville *et al.*, 1987).

fingerprinting of molecular adsorbates on surfaces has been found to be by vibrational spectroscopy although electronic structural probes (notably valence-level photoemission, see below) have proved of value. In the case of CO adsorption in particular, it has even become common to assign local adsorption sites for CO on a surface on the basis of the measured C—O internal stretching frequency. This procedure has been based on the extensive structural and vibrational data on coordination compounds which show how this mode softens as the CO—metal coordination increases. More recently, true structural studies of a number of such molecular adsorption systems have highlighted the dangers of extending the interpretation of such vibrational frequencies too far (Asensio *et al.*, 1992; Schindler *et al.*, 1993; Davila *et al.*, 1994). Nevertheless, it is clear that spectral fingerprinting has real advantages in characterizing the phenomenology of adsorption systems, and the information on the number of distinct states is a valuable source of input to any proper structural study (as, indeed, in the alkali/aluminium case described above). With this background in mind, the photoemission data, such as those from CO adsorption on Pt(111), provide a pointer to an important new potential. Fig. 4 summarizes the key results of this study (Björneholm *et al.*, 1994). Several different CO adsorption phases (corresponding to different coverages) were studied on Pt(111) and the figure shows the Pt 4*f*, C 1*s* and O 1*s* spectra recorded from the clean surface and two different CO adsorption phases. Vibrational data indicate that at lower coverages [e.g. the

(4 × 4) phase corresponding to a coverage of 0.2 ML, *i.e.* 0.2 CO molecules per surface-layer Pt atom] all CO molecules occupy atop sites, whereas in the 0.5 ML c(4 × 2) phase both atop and bridge sites are occupied; this latter result is known to be correct from a quantitative LEED analysis (Ogletree, Van Hove & Somorjai, 1986). On this basis the ‘chemical’ shifts in the C and O 1*s* XPS data shown in Fig. 4 can be assigned to fingerprints of the atop and bridge adsorbed species. Similar chemical shift fingerprints are also seen in the Pt 4*f* spectra, although in this case the interpretation is further complicated by the fact that even in the clean-surface spectrum there are two spectral components corresponding to emission from ‘bulk’ or subsurface atoms, and from the surface layer of atoms (not bonded to CO molecules) which show a ‘surface chemical shift’. As CO is adsorbed onto the surface, increasing proportions of the ‘surface’ peak are replaced by new features at different energies associated with Pt atoms bonded to atop or bridge CO molecules. We should note that in this case the Pt 4*f* data, which require low kinetic energies to achieve high surface specificity, were measured by SXPS at MAX-lab. The very high resolution C and O 1*s* spectra, on the other hand, were actually achieved using the conventional XPS technique, albeit with a high-power (rotating-anode) X-ray source and monochromator, and the very high resolution electron spectrometer (now commercialized by Scienta) (Nilsson & Mårtensson, 1989). For studies of chemical shifts in the adsorbate core levels, of course, surface specificity



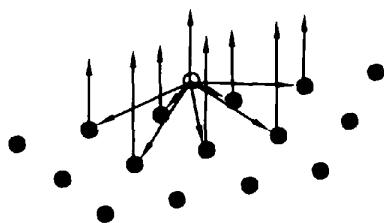
**Figure 4**

O 1*s*, C 1*s*, and Pt 4*f* photoemission spectra recorded from clean Pt(111), Pt(111)(4 × 4)-CO (at a CO coverage of 0.2 ML) and Pt(111)c(4 × 2)-CO (at a coverage of 0.5 ML). The signals associated with C and O atoms in atop CO, and Pt atoms bonded to atop CO, are labelled ‘atop’, while emission from atoms associated with bridge-bonded CO are labelled ‘bridge’. The contribution to the Pt 4*f* emission from subsurface or ‘bulk’ Pt atoms is labelled B, and that from surface Pt atoms not bonded to CO is labelled S. Adapted from Björneholm *et al.* (1994).

is guaranteed by the elemental specificity, and the only immediate advantage of synchrotron radiation is to make the high-resolution measurement easier by offering lower energies. Whilst these results show that such high resolution can be achieved with special laboratory sources, they also point the way to the exciting possibilities offered by the combination of a similar electron spectrometer with a high-resolution monochromator on a soft X-ray undulator of a third-generation synchrotron radiation source. Indeed, very recent test results on this same Pt(111)/CO adsorption system, recording C 1s spectra at a photon energy of 400 eV at the new ELETTRA facility, do indeed show huge electron count rates at even higher spectral resolution (Comelli, 1995). It is perhaps worth noting that while these high-resolution SXPS data show the potential to fingerprint different CO adsorption states in a fashion similar to that seen in vibrational spectroscopy, a major advantage is likely to be that the relative intensities of the different chemically shifted states should be a quantitative guide to the relative occupation of the different states, a situation which does not generally hold in vibrational spectroscopy.

### 3. Photoelectron diffraction

A quite different application of synchrotron radiation core-level photoemission is the exploitation of the phenomenon of photoelectron diffraction. In this case, the objective is specifically to gain quantitative structural information, rather than to infer structural effects through fingerprinting of 'chemical' (electronic) structure effects. The basic phenomenon is the coherent interference of the directly emitted component of the photoelectron wavefield emitted from an adsorbate atom with components of the same wavefield scattered elastically from surrounding (especially substrate) atoms (Fig. 5). The path-length differences involved in these scattering processes are governed by the local adsorption geometry, so a study of either the angular dependence or the photoelectron kinetic energy dependence of this adsorbate core-level emission contains information on the local adsorption geometry which can be extracted from theoretical modelling of the data. More complete reviews of the technique and its application (Woodruff & Bradshaw, 1994; Bradshaw & Woodruff, 1995), and even of the historical development of the method (Woodruff,

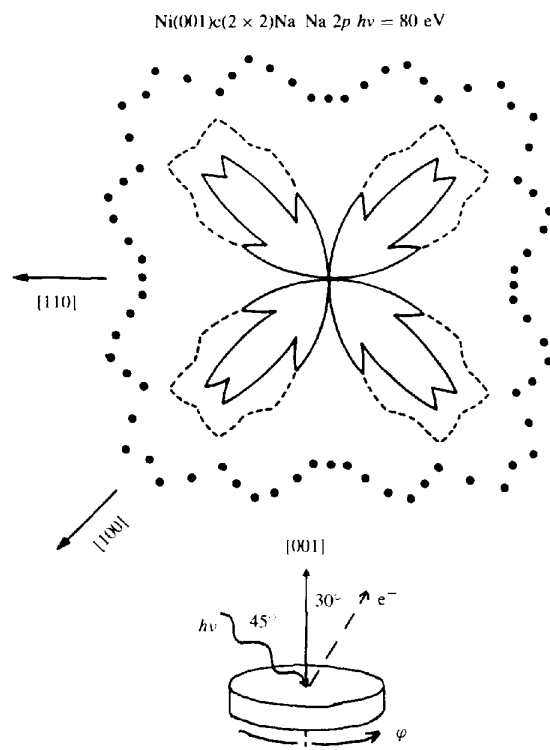


**Figure 5**

Schematic diagram showing the elastic scattering events from substrate atoms (filled circles) which interfere with the direct photoemission wavefield component from an adsorbate atom (open circle).

1994a), have been given elsewhere. Particularly apposite to the present review, however, is that one of the first pieces of work to demonstrate both the existence and utility of the idea (Woodruff *et al.*, 1978) was performed on the Miyake monochromator when it was installed on the Tantalus storage ring at the University of Wisconsin-Madison, following the closure of NINA at Daresbury, and prior to the installation of the SRS. It is a measure of the scarcity of even quite low-energy grazing-incidence monochromators at that time that such a trans-Atlantic 'loan' of the instrument was deemed a worthwhile exercise.

An example of the data from these first experiments (Woodruff *et al.*, 1978) is shown in Fig. 6 in the form of the intensity of the Na 2p photoemission signal from a Ni(100)c(2 × 2)-Na surface as a function of azimuthal emission angle at a fixed polar emission angle of 30° and a fixed photon energy of 80 eV. At the time (Woodruff, 1994a) there was considerable doubt about the magnitude of the photoelectron diffraction effect in backscattering, and the azimuthal scan mode of data collection is particularly attractive for demonstrating the phenomenon. In this mode the incident light and emitted electron directions are held fixed and the sample is rotated about its surface normal; any measured modulation which reflects the symmetry of



**Figure 6**

Azimuthal angle dependence of Na 2p photoemission from Ni(100)c(2 × 2)-Na. The lower diagram shows the experimental geometry as the sample is rotated about its surface normal to vary the azimuth,  $\varphi$ . The filled circles show the theoretically simulated data on a polar diagram, the full line repeats these theoretical results after subtraction of the minimum value, and the dashed line shows similarly background-subtracted experimental data (after Woodruff *et al.*, 1978).

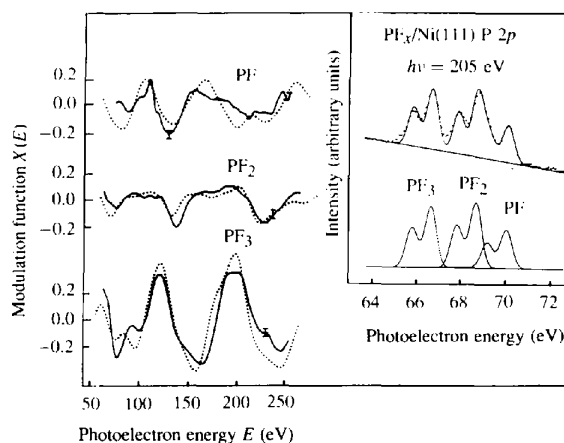
the crystal substrate under these conditions must result entirely from photoelectron diffraction. Fig. 6 also shows the results of theoretical modelling calculations based on the known structure of this adsorption phase, providing an early demonstration of the potential to use the effect to determine adsorbate structures in a quantitative fashion.

Of course, unique quantitative structure determination requires a much larger database than one azimuthal scan. Indeed, the need to measure the intensity of an adsorbate core-level photoemission spectrum as a function of either energy or angle over a wide enough range of conditions, in order to accumulate PhD data rich enough to guarantee a unique structural assignment, requires the collection of very many spectral intensities (typically, in recent applications of the method, 500–1000); for such a study, high photon fluxes are of considerable advantage. For this reason, and because for metal adsorption systems there is a high level of motivation to study C-, N- and O-containing molecules on metal surfaces, our own work on the exploitation of this technique has used the high-energy toroidal grating monochromator (HETGM) of the Fritz Haber Institute on the BESSY storage ring. These experiments, in a collaboration with Alex Bradshaw's group at the Fritz Haber Institute, have exploited the scanned energy, rather than scanned angle, mode of the technique [this was the method first used by Kevan, Rosenblatt, Denley, Lu & Shirley (1978)] and the high flux of this beamline over the energy range from some 200–1000 eV or more is ideally suited to energy-scan experiments (at photoelectron kinetic energies from *ca* 100–400 eV) from the C, N and O 1s states. This arrangement has allowed a wide range of quantitative structure determinations of small molecular adsorbates to be conducted over the last few years (Woodruff & Bradshaw, 1994; Bradshaw & Woodruff, 1995).

Despite this success, existing (second generation) synchrotron radiation facilities are of marginal adequacy for one of the most interesting potential developments in this area, which involves exploiting the combination of PhD and high-resolution SXPS. In particular, while conventional PhD allows structural information to be obtained in an element-specific fashion, by measuring the diffraction effects on photoelectron peaks from different elemental species, one would ideally like to distinguish the structural environment of atoms of the same element in different geometries. One important example of this situation is the case of co-adsorbed molecular fragments resulting from a surface reaction, a particularly demanding but potentially important case being that of hydrocarbon fragments on a heterogeneous catalyst used in a range of hydrocarbon processing reactions (reforming, combustion, alcohol production *etc.*). Changes in the C 1s photoelectron binding energy in this example for different species (*e.g.* CH<sub>3</sub>, CH<sub>2</sub>, CH) should allow photoelectron diffraction data to be collected from each chemically shifted component of the C 1s spectrum, providing local structural information on each of the C species independently. This chemical shift photoelectron diffraction (CSPHD) offers a unique potential

for the detailed quantitative study of complex structural problems of potentially increasing chemical significance. Indeed, the data presented in the previous section for CO occupying two different sites on Pt(111) also offers a further example in which far clearer structural information could be provided by this method.

The key requirement for this experiment, of course, is high photon flux combined with high spectral resolution. For this reason, current instrumentation, such as the BESSY HETGM facility, has allowed only demonstrator experiments of CSPHD to be performed on systems displaying rather large chemical shifts. Two rather different examples illustrate the potential of the method rather clearly. In one case (Weiss *et al.*, 1992), the local geometry of the two inequivalent C atoms in an acetate species (CH<sub>3</sub>COO<sup>-</sup>) adsorbed on Cu(110) have been determined by exploiting the chemical shift in the C 1s photoelectron peak recorded from the methyl and carboxyl species. In a second example (Weiss *et al.*, 1993), the local adsorption sites of co-adsorbed PF<sub>3</sub>, PF<sub>2</sub> and PF on Ni(111) produced by electron-irradiation-induced fragmentation of adsorbed PF<sub>3</sub> have been found by CSPHD of the P 2p photoemission signal; the results (Fig. 7) show the P atom shifts from atop, to bridge, to threefold coordinated hollow sites as the F atoms are successively removed, retaining a fourfold coordination for the P atom (Fig. 8). More general application of CSPHD will require new light sources, however, and undulators on third-generation synchrotron radiation facilities are ideally matched to the combination of high spectral resolution and flux. Of course, if such a source is to be used for scanned-energy mode PhD, it will be necessary for the user to have simultaneous scanning of the undulator and



**Figure 7**

Summary of results of a photoelectron diffraction determination of the structure of co-adsorbed PF<sub>x</sub> (*x* = 1, 2, 3) species on Ni(111) from Weiss *et al.* (1993). In the right-hand panel is shown the P 2p spectrum at a single photon energy separated into the three chemically shifted components. On the left are shown the comparison of theoretically simulated (dotted lines) and experimentally determined (full lines) normal emission scanned-energy mode photoelectron diffraction spectra from the three different components. The theoretical simulations are based on the adsorption geometries shown in Fig. 8.

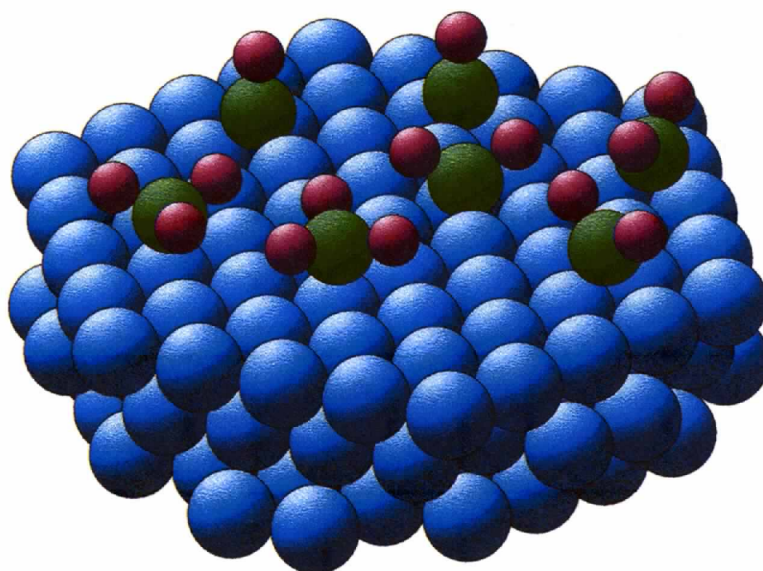
monochromator. It remains to be seen how easy this will prove to be in practice, and whether compromises such as tapering of the undulator will prove necessary.

#### 4. ARUPS – two-dimensional band mapping

In the general area of solid-state physics, one of the very special features of valence-band photoemission is the fact that not only energy, but also electron momentum (and spin) are conserved; this means that if the energy and direction (and thus electron wavevector  $\mathbf{k}$ ) of the photoemitted electron are determined in an angle-resolved experiment, it is possible to establish in an experimental fashion the  $E$ - $\mathbf{k}$  relationship of the occupied electron states from which the photoemission occurs; *i.e.* it is possible to map experimentally the occupied band structure of the solid. This procedure is actually not as simple as this description might suggest, particularly because the final (photoemitted) electron states will only be truly free-electron-like at high energies; it is therefore common to use rather more subtle methods for internal calibration, such as triangulation from two or more surfaces or some kind of experiment-theory interaction. Nevertheless, this ability to provide broad-brush band structure information is unique, and has had a particularly strong impact in recent years on attempts to develop an understanding of 'high-temperature' superconductors. In such three-dimensional 'band mapping' experiments, the tunability of the photon energy offered by synchrotron radiation is crucial to mapping large regions of  $\mathbf{k}$  space along crystal symmetry directions (see, for example, Woodruff & Delchar, 1994).

Ordered adsorbate overlayers on surfaces can also produce two-dimensionally itinerant electron states through adsorbate-adsorbate coupling, and lead to two-dimensional

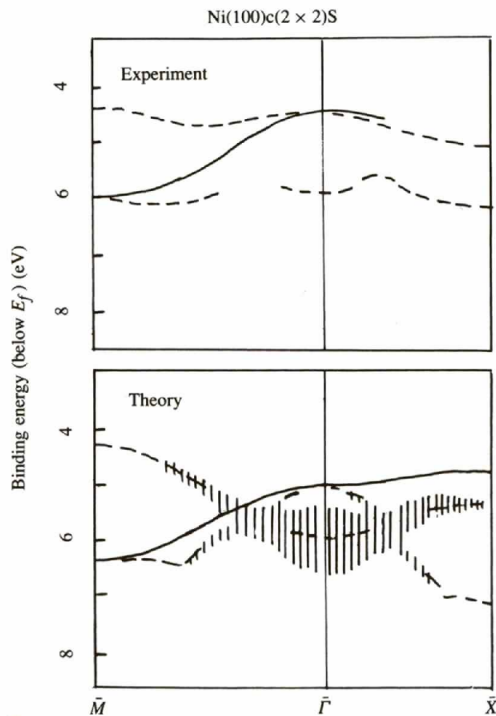
electron bands which can be investigated in a similar fashion. In this case, however, the states are one-dimensionally localized (perpendicular to the surface) and only the component of electron momentum parallel to the surface is conserved. This means that it is actually possible to map adsorbate bands using a single photon energy, and as the bands of principal interest are within a few eV of the Fermi level, a conventional He I gas-discharge line source ( $h\nu = 21.2$  eV) provides ready access to these states. Indeed, most of the early studies of adsorbate-induced surface-localized bands, and indeed intrinsic clean-surface, surface-state bands, were based on such sources. Nevertheless, there are important advantages to the use of synchrotron radiation for such work which was also recognized at quite an early stage. One of these stems simply from the fact that it is much easier to distinguish surface-localized from bulk states if the photon energy can be varied; surface-localized states do not disperse as the perpendicular component of the electron momentum is changed, so as the photon energy is changed they remain at the same location in the parallel component of momentum. By contrast, bulk (three-dimensionally itinerant) states do disperse in the perpendicular component of momentum. Changing the photon energy thus allows bulk-related and surface-related spectral features to be distinguished, and allows optimum energies to be selected for the study of the surface bands, both to avoid overlap as well as to optimize signal levels through the energy dependence of the photoemission cross section. In addition, however, the selective (normally linear) polarization of synchrotron radiation can be of enormous value in identifying the symmetry of the surface bands, and distinguishing states of different symmetry. In particular, by studying emission into a mirror plane of the surface (for which photoemission intensity can only be observed into



**Figure 8**

Schematic diagram showing the local adsorption geometries (hollow, bridge, atop) of co-adsorbed  $\text{PF}_x$  ( $x = 1, 2, 3$ ) species on Ni(111) based on the photoelectron diffraction study of Weiss *et al.* (1993).

states of even parity relative to this mirror plane), one can vary the direction of the incident radiation electric vector and thus distinguish initial states of the excitation of either odd or even parity relative to the mirror plane.

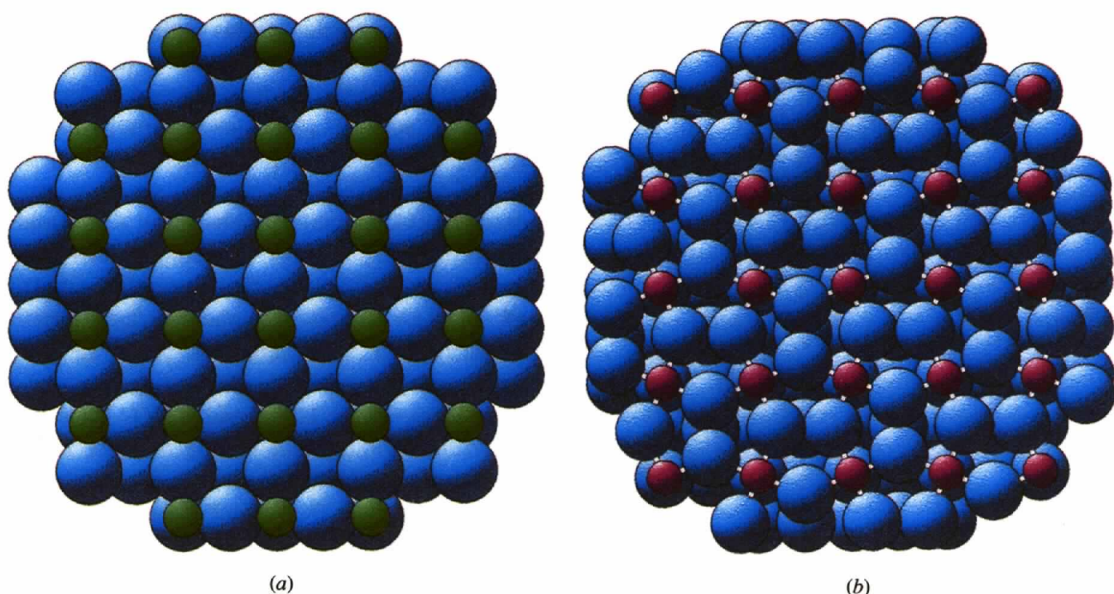


**Figure 9**

Comparison of theoretical and experimental adsorbate-derived two-dimensional band structure for Ni(100)c(2 × 2)-S from Plummer *et al.* (1980). The dashed lines correspond to states of even parity, the full lines to states of odd parity. The hatched region indicates the calculated one-electron width of the *p* levels in the region where they overlap the projection of bulk occupied states.

Some of the first and most extensive applications of this methodology to adsorbate bands on metal surfaces was by the group of Plummer who also pioneered applications in the electronic structure of some bulk materials. A particular example was a study of S adsorption on Ni(100) (Plummer, Tonner, Holzwarth & Liebsch, 1980) in which the S-induced valence bands of the (2 × 2) and c(2 × 2) phases were mapped for both odd and even parity states relative to the mirror planes of the surface structure. This early work did much to aid the general understanding of adsorbate-induced surface bands, and indeed provided rather excellent agreement between theory and experiment (Fig. 9). Somewhat perversely, perhaps, this early success and the fact that much of the qualitative behaviour can be understood in rather simple terms has meant that this area of study has not attracted a high level of activity in the last few years. On the other hand, a continuing theme of two-dimensional band mapping at surfaces on clean surfaces has been investigations of intrinsic surface states and the possible role of electronic effects as the driving force for the phenomenon of intrinsic clean-surface reconstructions (*e.g.* Smith & Kevan, 1991). Some of this work has placed rather high demands on both energy and parallel electron momentum resolution, another combination for which new third-generation synchrotron radiation sources must eventually prove of importance. Although this more recent work has concentrated on studies of clean-surface reconstructions, it is worth noting that the phenomenon of adsorbate-induced reconstruction of surfaces is becoming recognized as far more widespread than had hitherto been supposed and, as such, one might anticipate a resurgence of work in this area.

In fact, one detailed ARUPS band-mapping study of such adsorbate-induced reconstruction was undertaken by us a



**Figure 10**

Schematic diagrams showing plan views of (a) the Ni(100)c(2 × 2)-O, and (b) Ni(100)(2 × 2)-C (*p4g*) [or Ni(100)(2 × 2)-N (*p4g*)] structures, each associated with 0.5 ML coverage adsorbate layers.



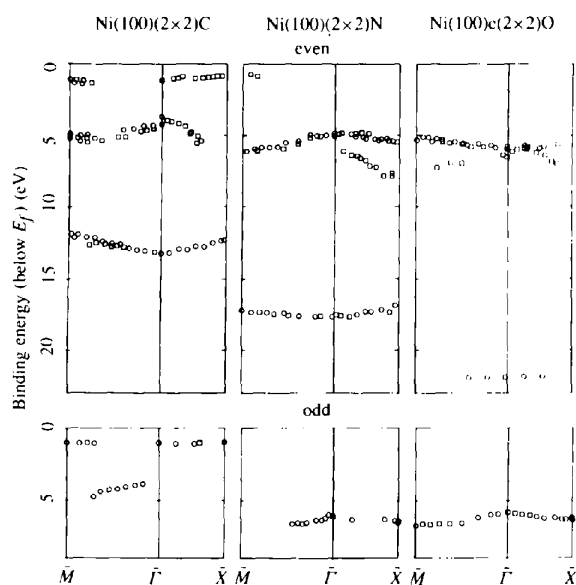
few years ago using the beamline originally established by Steve Kevan at the NSLS at Brookhaven National Laboratory (McConville, Woodruff, Weinart & Davenport, 1986; Kilcoyne, Woodruff, Rowe & Gaylord, 1989). The motivation for this work was to try to see if one could establish an electronic structure 'signature' of the reconstruction induced by C and N adsorption on Ni(100). One of the very first examples of a successful structure determination of an atomic adsorption system was Ni(100)c(2 × 2)-O, which involves a half monolayer of O atoms occupying simple overlayer hollow sites with little distortion of the substrate atom positions. By contrast, the same coverage of C or N atoms on this surface induces a reconstruction of the outer layers of the substrate; in particular, although the adsorbate atoms are again found to occupy the fourfold coordinated hollow sites, the four Ni atoms around the hollows move outwards from the hollows, with associated alternate clockwise and counter-clockwise rotations, allowing the C and N atoms to penetrate the outer layer and occupy sites which are almost coplanar (Woodruff, 1994b). Fig. 10 shows the resulting structure schematically, compared with that for O which does not generate the reconstruction. Fig. 11 shows a comparison of the two-dimensional bands induced by the adsorbate in these three surfaces. Apart from obvious and rather trivial differences between the three adsorbates, such as the increasing dispersion of the 2s-derived state as the binding energy and thus degree of localization decreases from O to C, there do appear to be subtle differences in the vicinity of the Fermi level, as well as in the detailed form of the 2p-derived bands; similar changes in the unoccupied anti-bonding 2p states have been seen in inverse

photoemission and discussed in terms of the possible role of the reconstruction (Hayden, Pervan & Woodruff, 1994).

## 5. ARUPS – molecular adsorbate studies

A quite different area of application of valence-level photoemission to surface science which was recognized in the early 1970s was to provide a *molecular* fingerprint of adsorbate species through the characteristic valence binding energies of the molecular orbitals. The transferability of most of the relative binding energies and relative photoionization cross sections from the free gas-phase molecule to the adsorbed species reflects the relatively minor interaction of the substrate with most of these orbitals, and indeed the observation of a differential energy shift in one or two levels can commonly be attributed to those orbitals which do suffer substrate bonding interactions; identification of these orbitals provides additional information on the likely character of the molecule–substrate bond, and indeed offers some indication of the probable molecular orientation. A key demonstration of this molecular fingerprinting was provided by the work of Demuth & Eastman (1974) who used the method to follow the dehydrogenation of adsorbed ethylene to adsorbed acetylene on Ni(111); this was the first use of a surface spectroscopy to follow a simple catalytic reaction on a well characterized single-crystal metal surface. In general, of course, such work does not necessitate synchrotron radiation, as a simple He discharge lamp provides access to the necessary spectral range of initial occupied states (although the extended range to binding energies of some 30 eV or more below the Fermi level provided by the He II line at 40.8 eV has some advantages over the more intense He I line). However, as in two-dimensional band mapping, the tunability of synchrotron radiation, as well as the controlled polarization, does offer some significant advantages.

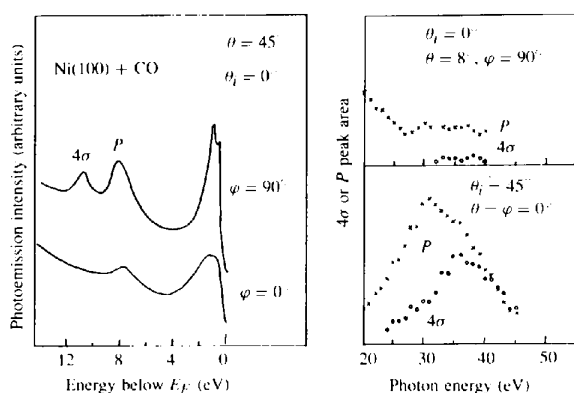
An early example of this utility came in studies of CO adsorption on metal surfaces; despite the fact that CO must be by far the most studied molecular adsorbate in surface science, understanding much of the detail of CO–metal interactions has proved far from easy. In the case of ultraviolet photoelectron spectroscopy studies of adsorbed CO, an early problem was that while gas-phase CO shows three shallow molecular-orbital states, the 4σ, 1π and 5σ, with ionization potentials of 19.72, 16.91 and 14.01 eV, ultraviolet photoelectron spectroscopy of CO adsorption on a range of metal surfaces typically shows only two peaks (at binding energies relative to the Fermi level of *ca* 11 eV and 8 eV). Clearly, there is a differential binding shift of one of these orbital energies on adsorption, but the exact ordering of the levels is far from clear and was the subject of early controversy (Lloyd, 1974; Brundle, 1974; Fuggle & Menzel, 1974). As the CO molecule adopts an orientation with its symmetry axis perpendicular to the surface of most substrates, however, the polarization selection rules described in the previous section can be used with considerable effect to separate



**Figure 11**

Comparative experimental adsorbate-induced two-dimensional band structures obtained from the three half-monolayer structures of C, N and O on Ni(100) (see Fig. 10). After Kilcoyne *et al.* (1989).

out the two overlapping orbitals ( $5\sigma$  and  $1\pi$ ) and establish their proper ordering. At the same time, the photon-energy dependence of the photoemission cross section proved of further value in understanding the behaviour of adsorbed CO. In particular, as was already known from studies of gas-phase photoemission from molecules, 'shape resonances' corresponding to strong enhancement in the cross section can be observed at certain final-state energies from certain molecular states. These resonances are due to intramolecular scattering within the potential of the molecule, and the final states also have a well defined symmetry. For example, the  $4\sigma$  level of CO shows a shape resonance at a photon energy of 32 eV in the gas phase which, because of its  $\sigma$  symmetry, can only be excited when the electric vector of the light lies along the C–O molecular axis. This property was exploited in variable energy and variable polarization experiments on CO adsorbed on Ni(100) by Allyn, Gustafsson & Plummer (1977) to establish both the perpendicular geometry of the C–O axis relative to the surface and the presence of the overlapping  $5\sigma$  and  $1\pi$  levels. Fig. 12 shows some of the results of this experiment; in particular, the actual photoemission spectra recorded under conditions which favour observation of  $\sigma$ - and  $\pi$ -symmetry states for a perpendicular molecule are shown, as are the photon-energy dependence of the two main peaks (the  $4\sigma$  and the overlapping pair of peaks labelled simply 'P') for two different polarization geometries. Note that the absence of any shape resonance in the  $4\sigma$  photoemission intensity when the light is normally incident on the surface



**Figure 12**

Composite summarizing some of the main results of an angle-resolved photoemission study of CO adsorbed on Ni(100) from Allyn *et al.* (1977). On the left are shown the photoelectron-energy spectra recorded in two different geometries [the same polar incidence ( $\theta_i$ ) and emission ( $\theta_e$ ) angles, but different azimuthal angles ( $\varphi$ )]. The two main peaks are labelled  $4\sigma$  and P, the latter being associated with overlapping CO  $5\sigma$  and  $1\pi$  states, and the two geometries are chosen to favour emission from  $\sigma$ - and  $\pi$ -symmetry states, respectively, from a perpendicularly oriented CO molecule. On the right are shown the photon-energy dependence of the amplitude of these two peaks for two different incidence and emission geometries. Note the  $\sigma$ -symmetry final-state shape resonance seen only when the incident light has a component of its electric vector along the surface normal, again indicating a normally orientated CO molecular axis.

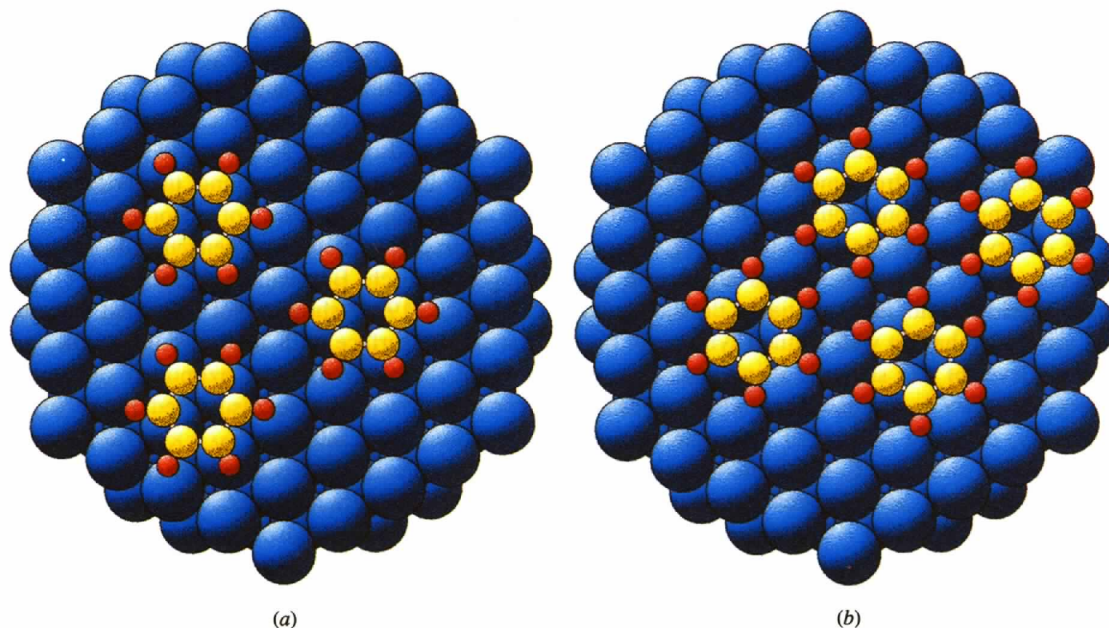
(polarization vector parallel to the surface) is a key result indicating the perpendicular geometry of the molecule.

More recently, the application of polarization selection rules has been applied to a number of more complex molecular adsorption systems and has led to surprisingly specific information regarding the orientation (including the azimuthal alignment) of adsorbed molecular species. For example, in a study of benzene adsorption on Ni(111), Huber, Zebisch, Bornemann & Steinrück (1991) (see also Steinrück, 1994) showed not only that the molecule lies flat on the surface with its molecular plane parallel to the surface, but also that the azimuthal orientation changes from the low coverage disordered phase (up to 80% of saturation) to the saturation ( $\sqrt{7} \times \sqrt{7}$ )R19° ordered phase. This assignment has recently been proved to be correct in a C 1s PhD study (Schaff *et al.*, 1995) which also established the (different) local adsorption sites associated with these two adsorption phases shown schematically in Fig. 13.

## 6. Future prospects

The new third generation of synchrotron radiation sources now being built or coming into routine user operation offer some impressive improvements in potential. The very high spectral brilliance offered by these sources, particularly using undulators, means that substantial increases are possible in photon flux delivered to experiments, but much greater benefits are available for those experiments which seek these flux increases coupled to increases in spectral or spatial resolution. In this brief survey of photoemission from adsorbates on metals, the potential utility of spatial resolution has not been discussed, although experiments using photoemission electron microscopy (PEEM) based on conventional laboratory sources have shown important applications in adsorbate/metal systems, notably in the study of 'reaction fronts' in reactions between gas-phase chemicals catalysed by the metal surface (*e.g.* Mundshau *et al.*, 1990; Rottermund, Engel, Jakubith, Vonoertzen & Ertl, 1991). One can envisage that coupled to synchrotron radiation to provide elemental and chemical specificity, there could be an entirely new area of application opened up by these new facilities.

In the context of the application areas discussed here, however, the most obvious benefit which could accrue from a combination of higher photon flux and higher spectral resolution is in shallow core-level spectroscopy. The recent work at MAX-lab and using laboratory X-ray sources at Uppsala provides a clear indication that far more can be achieved in SXPS studies of adsorbate–surface interaction fingerprinting, and already results from one of the new sources is confirming this potential. These data provide a striking illustration of the fact that major improvements in spectral resolution commonly open up entirely new areas of application. Even more demanding of flux combined with resolution is C1s PhD, and the potential here to obtain quantitative local structural information on complex co-adsorption systems may well be unique in surface science,



**Figure 13**

Schematic diagrams showing the geometry of benzene adsorbed at (a) low coverage, and (b) saturation coverage yielding an ordered  $(\sqrt{7} \times \sqrt{7})R19^\circ$  phase on Ni(111). The azimuthal orientations of the two phases were deduced from angle-resolved photoemission studies by Huber *et al.* (1991). The actual local adsorption sites were obtained in a very recent photoelectron diffraction study by Schaff *et al.* (1995).

and has great importance if surface science is to fulfil its promise to tackle issues of increasing complexity and relevance to heterogeneous catalysis. It remains to be seen how the CSPHD methodology will evolve on third-generation sources bearing in mind the (at least short-term) difficulties of routine wide-range tuning of undulators under user control.

For valence-level spectroscopy of adsorbed atoms and molecules, the gain to be offered by the next generation of light sources may be more quantitative than qualitative. Higher fluxes should permit studies at lower coverages, and of course in all areas offers the possibility of 'time-resolved' measurements, or more properly, higher-speed measurements of controlled time-varying experiments (*i.e.* studies in which the rates of change are externally controlled – such as by varying coverage or temperature – rather than experiments identifying intrinsic time scales of physical phenomena). For most adsorbate studies, especially molecular adsorbates, the evidence is that instrumental resolution is not a limiting factor in the experiments, and little is to be gained in improving spectral resolution. For bulk solids, of course, there are key experiments for which much higher spectral resolution would be of great interest; for example, in studies of superconductors, or even heavy-fermion systems. As yet there is no evidence that such narrow gap phenomena are important in adsorbate systems. On the other hand, increased photon fluxes from undulators on existing storage rings have already shown the benefit for spin-resolved photoemission, and indeed have indicated that not only surface magnetism, but also aspects of adsorbate-substrate interactions may be better understood by such

experiments (Brookes, Clarke & Johnson, 1989). Even here, therefore, there is evidently a subset of experiments for which very real gains may open up new opportunities and the identification of new physics.

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