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Electronic Structure of Surfaces and of Adsorbed Species [and Discussion]

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Phil. Trans. R. Soc. Lond. A 1992 **341**, 293-300
doi: 10.1098/rsta.1992.0102

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Electronic structure of surfaces and of adsorbed species

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Electrons are the main probe for determining surface crystallography. Existing methods have already established an impresive list of completed structures but, such is the demand for structural information at surfaces, new ways of interpreting diffraction data are being explored with a view to extending the power and flexibility of tools available to us.

1. Electronic structure and crystallography

Electronic structure has many roles to play at the surface: bonding, transport, spectroscopy, and determination of surface crystallography. In this paper I shall concentrate on the last of these. The arrangement of atoms at surfaces must be their most fundamental property, and until we can provide that we have no microscopic description of the surface. Although it is true that bonding provided by valence electrons determines the crystallography, as a means of actually determining the arrangement of atoms, electronic structure calculations remain an ideal just as they are in the bulk of a solid. That is not to say that they do not have a fundamental role, simply that their role is one of explanation and understanding rather than of providing details of individual structures. Elucidation of surface crystallography is largely done by diffraction of electrons with energies in the 50 eV to 500 eV range, and by subsequent interpretation of the often complex data.

Determination of surface crystallography is so important an issue that many different approaches have been tried. One of the earliest to give atomic positions was field-ion microscopy (Müller & Tsong 1969), which images atoms by ionizing helium in the intense electric fields generated by a sharp tip held at a high voltage. Remarkable images of surfaces are seen, but the technique languishes under several disadvantages: only extremely strong materials can withstand the strong electric fields, and even in these cases there is debate about whether the fields distort atomic arrangements. Only the top layer of atoms is visible and we now know that surface rearrangements can take place several layers deep into the surface. These disadvantages combined with the low resolution of the technique prevent it from occupying centre stage, but nevertheless elegant contributions are made by this technique from time to time (Fink 1986).

Sharp tips made a reappearance in surface crystallography with the scanning tunnelling microscope (STM) (Binnig & Rohrer 1982). This technique has taken the world of surface science by storm: unlike the field ion microscope (FIM) STM can study a wide range of materials, and it has the great advantage of producing real-space images of the surfaces which can be viewed and interpreted almost instantaneously. Overwhelmingly its application has been to surface *topography* rather than to

Phil. Trans. R. Soc. Lond. A (1992) **341**, 293–300
Printed in Great Britain
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crystallography, making a vital contribution on this mesoscopic scale where diffraction methods run into problems of interpretation. As a surface crystallographic technique it has many of the disadvantages of the FIM: restriction to the outer layer of the surface and low resolution. The STM image of a single atom adsorbed on a surface is at least 5 Å† across, and interpretation of structure on a finer scale than this involves some wishful thinking. Yet in many ways the STM is an ideal companion to diffraction techniques, filling the gaps they leave.

The workhorses of surface crystallography are low-energy electron diffraction, photoelectron diffraction, high-energy ion scattering, and X-ray diffraction. Of the known surface structures, the overwhelming majority have been determined by low-energy electron diffraction.

2. LEED: the workhorse of surface crystallography

Electrons with energy in the range 50–500 eV penetrate only 5–10 Å into the surface, presenting us with ideal sensitivity for surface crystallography: most surfaces become bulk-like at depths greater than these. Their wavelength is around 1 Å, enabling resolutions approaching 0.01 Å to be achieved in deal circumstances. Traditional methodology involves acquisition of data for several diffracted beams over a range of several hundred eV, with the assumption that the surface has a well-ordered periodic structure (Pendry 1974; Van Hove & Tong 1979; Heinz & Müller 1982). The complex diffraction intensities contain all the information necessary to find the structure: it is doubtful whether any other technique is capable of generating such a volume of information. Unfortunately extraction of this information is not trivial and proceeds via trial and error. We guess a structure, calculate the diffracted intensities and compare with experiment. The latter step is done by means of an R-factor measuring overall quality of agreement with experiment for the trial structure. Agreement is never perfect, but R-factors as low as 0.25 represent 'good agreement' with experiment, on a scale where 0 is perfect agreement and 1 is no agreement at all. This method is effective for simple surfaces and something like 500 to 1000 structures have been determined in this fashion (MacLaren *et al*. 1987). With increasing complexity trial and error becomes more and more time-consuming, as the possibilities grow exponential with system size. Nevertheless it has proved possible to determine some fairly complex structures.

An early example by Andersson & Pendry (1980) is shown in figure 1: CO is adsorbed on a Cu(100) in a C(2 × 2) structure. This was the first surface molecular structure to be determined, and is typical of the molecular phase of interaction with surfaces. The CO molecule is relatively weakly bound, perched high above the surface on top of a copper atom as befits a molecule whose bonding arrangements are already well satisfied. The molecular bond length at the surface is within experimental error of the gas-phase value, also reflecting the weak nature of the bonding. In contrast, atomic carbon or atomic oxygen typically bury themselves deeply in the surface, presumably to saturate their bonding requirements.

Similar sorts of results can be achieved with photoelectron diffraction and surface EXAFS, both of which share the electron as active ingredient, and have similar advantages and disadvantages.

Surface crystallographers are presently in the position that protein crystallographers were some years ago: their experimental data contain all the

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† $1\ \text{Å} = 10^{-10}\ \text{m} = 10^{-1}\ \text{nm}$.

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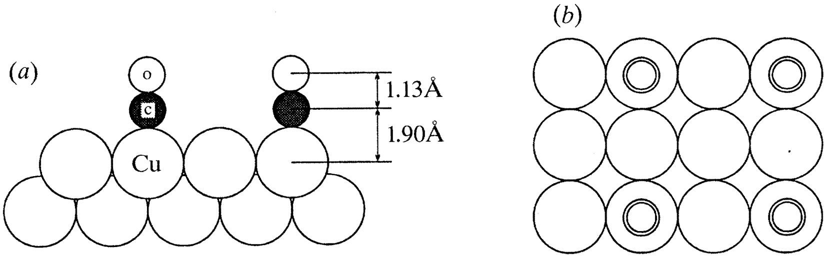

Figure 1. The structure of C(2 × 2) CO adsorbed on a Cu (100) surface after Andersson & Pendry (1980): (*a*) side view and (*b*) top view. The molecule adsorbs carbon end down, standing vertically on top of a copper atom.

information necessary to determine the surface structure, but inadequacies in methodology stand in the way of comprehensive exploitation of this information. Much development in the field in the past few years has been directed to removing this restriction, with some notable successes, and many ideas for future improvements.

3. Multiple scattering: the dragon of surface crystallography

If surface crystallography is imprisoned in the data by the dragon of multiple scattering, who will play St George?

One candidate is the *tensor-LEED* method developed by Philip Rous and myself (Rous 1992). Its original aim was to speed comparison of a given trial structure to experiment, but it has also spawned other more radical approaches to the problem. At the core of tensor-LEED lies the following idea. Suppose we make a reasonable guess at the trial structure, calculate the expected diffraction intensities, and compare with experiment, but find that the fit is not perfect. In the old method we simply start again with a new trial structure, but in tensor-LEED the first trial calculation is used to make a perturbation expansion with the original structure as a *reference structure*. Much of the computational work has already been done, and the perturbation can be accomplished very rapidly. The vicinity of a given structure can be explored at little computational cost. For structures where many coordinates are to be adjusted, some perhaps by only a small amount, this can be extremely valuable. An instance might occur when an adsorbate reconstructs the substrate. Motion of substrate atoms is often vital in obtaining an accurate and reliable structure, yet often substrate atoms move by no more than 0.1 Å. An example is given in figure 2, showing the P(2 × 2) C_2H_3 structure on an Rh (111) surface (Wander *et al.* 1991, 1992). In each unit cell there are two adsorbate atoms (discounting the hydrogen) and eight substrate atoms whose positions are to be adjusted. Without tensor-LEED this would be an almost impossible task, but it can now be accomplished in a routine manner.

One further step has been taken in developing tensor-LEED. Perturbation theory, on which the whole idea rests, expresses the change in diffracted amplitudes in terms of a matrix element of the change in scattering potential,

$$\delta A_g = \sum_j Y\langle \boldsymbol{k}+\boldsymbol{g}; \mathrm{out}\,|\,\delta t(\delta \boldsymbol{R}_j)\,|\,\boldsymbol{k}; \mathrm{in}\rangle = \sum_j M_{gj} f(\delta \boldsymbol{R}_j), \qquad (1)$$

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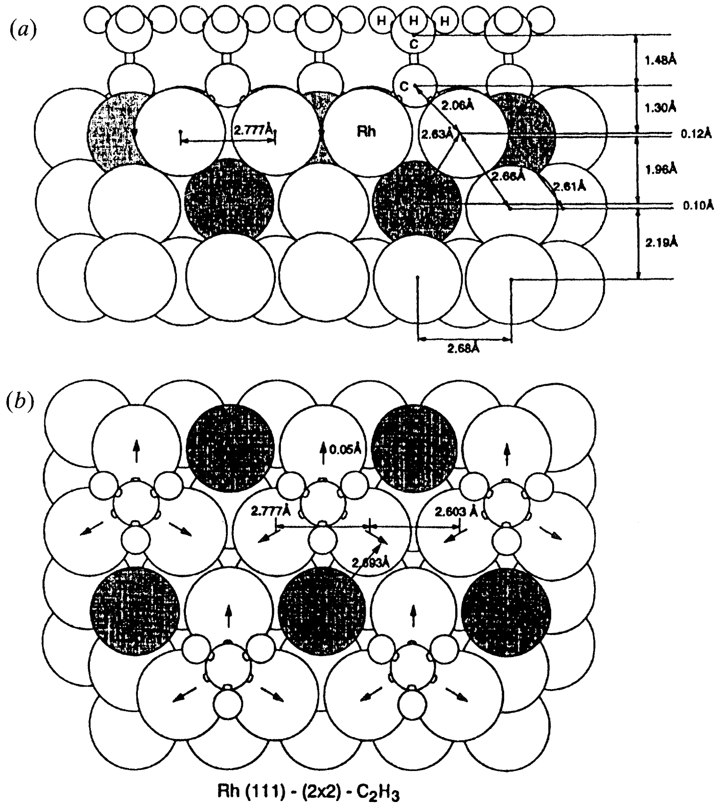

Figure 2. The structure of P(2×2) C_2H_3 adsorbed on an Rh (111) surface after Wander *et al.* (1991): side view (top panel) and top view (lower panel). Note the reconstruction in the Rh substrate.

where $f(\delta \boldsymbol{R}_j)$ is a function of the displacement of the jth atom and M_{gj} is a matrix, or tensor, that is independent of $\delta \boldsymbol{R}_j$. Once M_{gj} is computed for a reference structure, $f(\delta \boldsymbol{R}_j)$ can easily be calculated for each new structure and diffracted amplitudes evaluated by simple matrix multiplication. Hence the original power of the method. Aside from simplicity, equation (1) has another property: there is a linear relation between the structural information contained in the $f(\delta \boldsymbol{R}_j)$ and the diffracted amplitudes, δA_g. In essence we can say that each atom has a characteristic contribution to δA_g which is linearly independent of the other atomic displacements.

This concept of linear independence opens new methods for interpretation of data. To see why it is so important consider a simple analogy. Suppose that we lose the keys to a safe containing some vital information. One possibility would be to call the manufacturers and borrow their bunch of replica keys. This could prove a very time-consuming solution: suppose that the lock has three tumblers and each has ten different positions, there would be 10^3 trials to be made. The other possibility is to contact a locksmith with a set of skeleton keys. He will need three, one for each tumbler, and provided that each tumbler is independent of the rest he will have ten possibilities to try for each tumbler, a total of only 30 for the lock as a whole. He will open the safe before we have barely started on the bunch of replica keys!

The moral for our problem is that we must extract independent contributions to the diffracted amplitudes and fit them one by one. In some experiments this is easily

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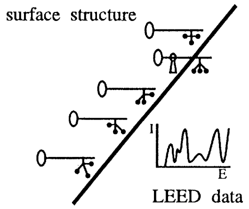

Figure 3. Traditionally LEED data are interpreted by trial-and-error methods which become time-consuming for complex structures. Adjusting the coordinates of atoms in a trial-and-error process is time-consuming, particularly when there are many atoms.

done. For example, in an EXAFS experiment atoms in each shell contribute a given Fourier component of the absorption cross-section, which can be extracted by Fourier transformation and its intensity related to occupancy of that shell. We observe that sine waves are not the only waveform that can be extracted from data, and even more complex signals occurring in multiple scattering can be extracted. The overriding requirement is one of linear independence.

Some progress towards this objective has been made in developments of direct methods (Pendry & Heinz 1990) and exploited by Wander *et al.* (1992) to simplify structure determination. In a recent paper they took the $P(2\times 2)\,C_2H_3$ structure on a Pt(111) surface, similar to the corresponding Rh(111) structure shown in figure 2, as a test bed for their calculations. The diffracted intensities were calculated for a zero-order reference structure that consisted of the unreconstructed substrate with the $P(2\times 2)\,C_2H_3$ adsorbed on top. In addition three other hypothetical structures were considered: in the first the $P(2\times 2)\,C_2H_3$ was raised by 0.5 Å, in the second the uncoordinated surface Pt was moved by 0.5 Å, and in the third both the $P(2\times 2)\,C_2H_3$ and the Pt were moved by 0.5 Å. To test whether the principle of linearity holds for this system, the intensities for the third structure were also calculated by adding together the changes in amplitudes found for structures one and two, on the assumption that the amplitudes combine linearly. The resulting diffracted intensities were compared with the conventional calculation which makes no assumptions and found to agree extremely well: the R-factor was less than 0.09. This new method, linear LEED as it has been christened, adds yet another refinement to the speed of conventional analysis while offering the possibility of more direct analysis of the data.

4. Future possibilities

The techniques that we have discussed so far are part of the present reality of structure analysis, in the process of being applied to numerous complex structure determinations. More exotic possibilities are under investigation which if realized would transform surface crystallography, but have some way to go before they are accepted as a practical means of data analysis.

Szöke (1986) followed by Barton (1988) first proposed an analogy between photoemitted electrons and holography. Figure 4 shows the principles involved in holography. Compare figure 4 with figure 5, where we show a photoemission experiment in which an electron is ejected from the inner core of an adsorbed atom. The outgoing wave divides itself between a component heading directly out of the surface, and a second component that first scatters from atoms in the later below. Interference between the two components generates a hologram-like structure.

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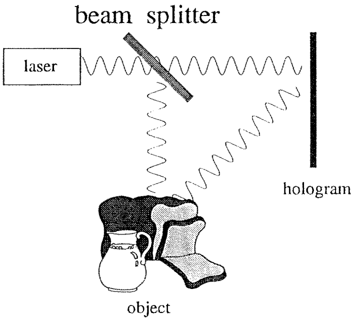

Figure 4. The principle of holography: a coherent beam of radiation, a laser in this instance, is split into two beams: one travels directly to the screen, the other illuminates the object.

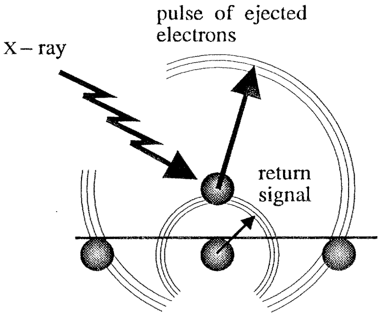

Figure 5. An electron-wave ejected from an adsorbed atom by an X-ray divides itself between a component escaping directly from the surface and a component that first scatters from atoms in the layer below, making an analogy with the holography experiment shown in figure 4.

Having drawn the analogy with holography, Szöke and Barton proposed to create an image of the surface by holographic reconstruction from the photoelectron diffraction pattern. That is a strong statement, and to what extent it can be made a reality is not clear.

There is one instance in which the idea has already been in use for some time. Suppose that figure 5 corresponds to a surface EXAFS experiment in which the interference pattern is measured at the emitting atom itself. The absorption cross-section as a function of energy is a one-dimensional hologram of the radial distribution function. It has long been recognized that Fourier transformation for EXAFS signals does yield a reasonable radial distribution function provided that one does not look beyond the first few shells, and that not too great an accuracy is required.

A clever extension of the one-dimensional (1D) hologram concept has been made by Wang *et al.* (1991). They observed that nearly all atoms have a strong peak in their scattering factor in the backwards direction. Hence diffracted intensity at a given angle of emission is dominated by direct emission plus any scattering from atoms immediately behind the emitter. They neglect all other contributions. Measuring the intensity as a function of energy at a given angle of emission gives a 1D hologram along a line immediately behind the emitter, in line of sight to the detector. Wang *et al.* convincingly make their case by Fourier transforming their 1D holograms taken at various angles of emission (figure 6) and show that they can

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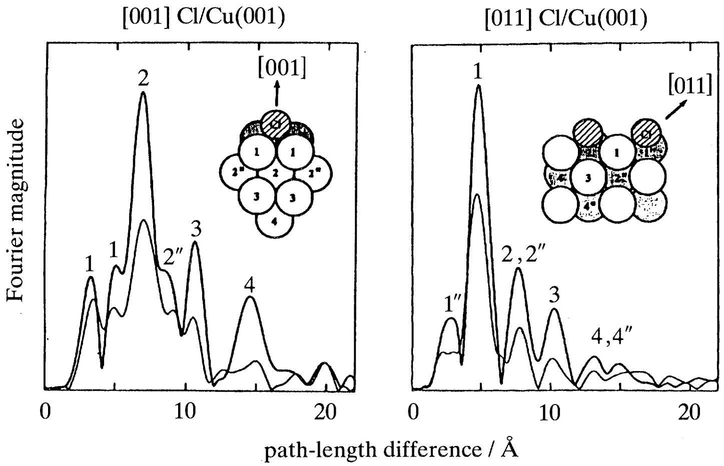

Figure 6. Fourier spectra for the C(2 × 2) Cl structure on Cu (100), after Wang *et al.* (1991). The data for this figure were taken with electrons in the [100] direction (left-hand figure) and [110] direction (right-hand figure). Data were taken at 110 K and 300 K, and each numbered peak is associated with a scattering path-length difference for a numbered atom in the inset. Note how changing the emission direction emphasizes those atoms behind the line of sight to the detector.

emphasize the signal from one or other of the surface atoms by aligning them with the back-scattering direction.

5. Conclusions

Quantitative surface crystallography is currently producing many new results on a diverse set of systems. The simplest of these can easily be handled by long-established techniques, but the more complex ones require help from recent advances. Such is the appetite of surface science for ever more information on the location of surface atoms that there is strong pressure for yet more advances in our ability to interpret data. Some of the more radical ideas such as electron surface holography are certainly in the developmental stage, but offer future possibilities for flexible on-line interpretation of diffraction data.

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Discussion

A. M. Stoneham (*Harwell Laboratory, Didcot, U.K.*): Do diffraction methods give any information on properties of surfaces as well as their structure? Is it that direct real space methods (e.g. STM), even if cruder, are preferred on the issue of mechanisms?

J. B. Pendry: The STM gives information on a larger length scale than the crystallographic, which can be equally relevant to mechanisms.