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Theoretical Aspects of the Nature of the Surface Chemical Bond [and Discussion]

J. B. Pendry, M. W. Roberts, J. Wong and T. B. Grimley

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Theoretical aspects of the nature of the surface chemical bond

By J. B. Pendry, F.R.S.

The Blackett Laboratory, Imperial College, London SW7 2BZ, U.K.

The determination of surface chemical bonds has involved an interplay between theory and experiment. Two major techniques, l.e.e.d. and s.e.X.a.f.s., are discussed and some of their limitations analysed. Finally, I look forward to the development of other methods that will further extend our powers to unravel surface chemical bonding.

Surface crystallography is now an established discipline. It rests on a number of techniques for characterization of the surface and there are several methods available for the actual measurement of bond lengths. By far the most important of these is low energy electron diffraction (l.e.e.d.), which can now be used to study moderately complex molecules at surfaces (Koestner *et al.* 1982). The technique can be illustrated by the simple example of CO adsorbed on a Cu (001) surface (Anderson & Pendry 1980). Experimental intensity–energy measurements of diffracted beams are the starting point for the determination. Theory is then used to predict the $I(E)$ spectra for a number of trial structures.

One problem with determination of molecular structures at surfaces is the large number of configurations that are possible. The evaluation of many sets of theoretical l.e.e.d. curves becomes increasingly tiresome and some automated criterion for evaluation of the quality of agreement with experiment is needed. Zannazzi & Jona (1977) have suggested using a reliability factor analogous to those used in evaluation of X-ray crystal structures. A new reliability factor defined by comparison of Y-functions was proposed by Pendry (1980):

$$Y = L^{-1}/(L^{-2}+V_{0i}^2), \quad L = I'/I, \quad I' = \mathrm{d}I/\mathrm{d}E,$$

where I is the intensity of a diffracted beam and V_{0i} the imaginary part of the potential. The R factor is then

$$R = \sum_g \int (Y_g(\text{th.}) - Y_g(\text{ex.}))^2\,\mathrm{d}E \Big/ \sum_g \int (Y_g^2(\text{th.}) + Y_g^2(\text{ex.}))\,\mathrm{d}E,$$

where the integration is over the energy range measured in each beam, and the summation is over beams. Abbreviations th. and ex. refer to theory and experiment. R is normalized to unity for uncorrelated data and is designed to be insensitive to the intensities in a curve. The correlation improves with decreasing R, and $R = 0$ is perfect correlation. It can be statistically analysed to show that

$$RR = \operatorname{var} R/\bar{R} \approx (8V_{0i}/\delta E)^{\frac{1}{2}},$$

where δE is the total range of energy spanned in all beams. For the data sets used here $RR \approx 0.3$, thus any variation of R below 0.7 is statistically significant. A minimum in R of 0.42 would give 95% confidence that the correlation was not spurious. Experience indicates that these estimates err on the conservative side.

In the analysis of copper we first noted the similarity between the copper spectra and the nickel spectra. This tells us that the structures must be very similar but with some small changes in atomic spacings. Accordingly we plotted an R-factor contour map with the C–O spacing as x-coordinate and the Cu–C spacing as y-coordinate in the configuration with CO standing vertically above the copper atoms in the last layer, carbon end downwards. The minimum was then optimized with respect to the muffin-tin zero in the CO layer, V_D, and α, the exchange parameter. The optimized R-factor is shown in figure 1, calculated with the (01), (11), $(\frac{1}{2}\frac{1}{2})$, $(\frac{3}{2}\frac{1}{2})$ beams, but excluding the (00) beam, which was not available at normal incidence.

The minimum $R = 0.39$ occurs at

$$d(\mathrm{CO}) = 0.113\ \mathrm{nm},$$
$$d(\mathrm{CuC}) = 0.190\ \mathrm{nm},$$

and can be precisely located to two decimal places with the aid of the contours. Our statistical analysis of R gives for

$$\mathrm{var}\ R_{\mathrm{min}} - 0.3R_{\mathrm{min}} \approx 0.1.$$

Therefore, in another set of calculations or experiments it is statistically conceivable that the minimum could shift away from its present location out as far as the present $R = 0.5$ contour. In this way we fix error bars on our determination of ±0.01 nm for both $d(\mathrm{CO})$ and $d(\mathrm{CuO})$.

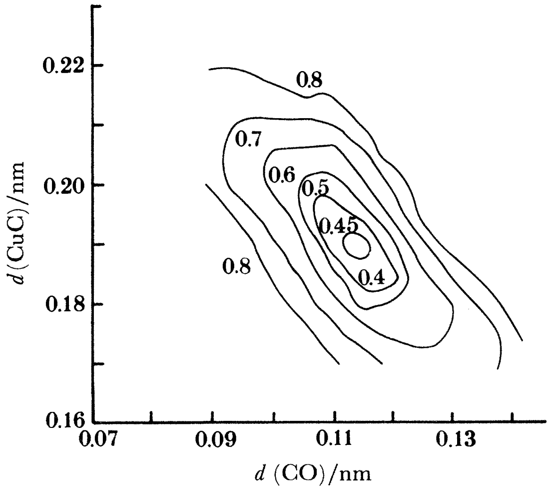

FIGURE 1. The reliability factor contours for $c(2\times2)$ CO/Cu(001) plotted with the Cu–C and C–O bond lengths as variables.

A technique that complements l.e.e.d. is surface extended X-ray absorption fine structure measurement (s.e.X.a.f.s.) (see Lee 1976, Citrin *et al.* 1979, Stohr *et al.* 1978). Here the surface in question is irradiated by X-rays of sufficient energy to eject one electron from the K shell of an adsorbed atom. The wavelength of the *electron* wavefunction depends on the energy available for the X-ray photon over and above the threshold for K-shell excitation. The electron has its escape impeded by the atoms surrounding the emitter and characteristic modulations of the absorption cross section are produced by diffraction effects. These are used to extract radii to neighbouring shells of atoms. Typically the cross section is monitored by measuring the total yield of electrons emitted from the surface, which further enhances the surface sensitivity.

The great virtue of s.e.X.a.f.s. is the relative simplicity with which the bond lengths can be extracted and its has, in consequence, become a popular tool now that high-intensity X-rays are available from synchrotron sources. The information is less complete than that provided by l.e.e.d., being confined to bond lengths around the absorbing atom. Also, there are limitations on applicability of the technique: occurrence of multiple sites for the same sort of atom confuses the signal and the experiment is less convenient for the catalytically important light atoms such as carbon, because the K-shell excitation energy lies in the soft X-ray region. Nevertheless, in favourable circumstances s.e.X.a.f.s. is a useful technique for obtaining a picture of the coordination of atoms adsorbed on surfaces.

In contrast to a l.e.e.d. experiment, s.e.X.a.f.s. requires no long-range ordering of the surface, and in this respect is more flexible than l.e.e.d. The s.e.X.a.f.s. technique does have its limitations. It cannot easily look at the reconstruction of clean surfaces because all the crystallographically inequivalent atoms have the same X-ray edge and the s.e.X.a.f.s. spectrum is a mess of superimposed signals. It is not very good with complex organic molecules for the same reason. But in circumstances where an appropriate 'clean' edge can be found it is an effective tool. Perhaps the ideal situation in which to apply s.e.X.a.f.s. would be the case of a single atom or a molecule containing a unique atom adsorbed on a clean perfect surface. This situation gives clear s.e.X.a.f.s. signals and, so far, has been resistant to l.e.e.d. analysis. However l.e.e.d. experiments on disordered overlayers of molecules contain, in the diffuse scattered intensity, information that is similar to that obtained from s.e.X.a.f.s., and this information can be extracted with no more effort than that needed to a l.e.e.d. calculation from the perfect clean surface without the adsorbate, plus the calculational effort required to interpret an e.X.a.f.s. experiment in the appropriate energy range (Pendry & Saldin 1984).

Very briefly, the idea is equivalent to observing that instead of using X-rays to inject an electron near the adsorbed atom, we can use an external electron gun. The external beam can be diffracted by the clean surface before it reaches the adsorbate, but this is easily calculated. Once the electron reaches the adsorbate the same process that characterize s.e.X.a.f.s. take place and provide the same sort of information. Finally, the electron is detected after escaping from the adsorbate, and again we can correct for the interaction with the clean surface. Provided that the surface is clean and well ordered except for the adsorbate, we know that any diffusely scattered electron must have interacted with an adsorbate molecule. The pre- and post-s.e.X.a.f.s. stages, far from being a nuisance in the interpretation, provide additional valuable information about the orientation of the molecule relative to the clean surface. In this way we can do what is, in essence, a s.e.X.a.f.s. experiment without X-rays.

We can, in fact, do it better than s.e.X.a.f.s., partly because of the additional information present in the diffuse scattering, but much more importantly for the following reasons. S.e.X.a.f.s. suffers from the severe limitation that there is one and only one data set available for the system, or three if a polarized source is available. Thus in s.e.X.a.f.s., information about the surrounding atoms falls rapidly with the distance of the atom from the absorber. Also, there are just not enough data to resolve the structure in a really complex coordinating shell, for example, if we were studying a chlorobenzene molecule on a W(110) surface. For diffuse l.e.e.d., more data can be accumulated at will by changing the angle or energy of incidence and observing the new diffuse pattern. Each pattern of itself contains a wealth of information even at low energies. Furthermore there are few restrictions as to systems for the diffuse l.e.e.d. experiment. It can as easily handle benzene or even toluene on a clean surface as chlorobenzene, whereas s.e.X.a.f.s. would need to have the single chlorine atom present to have a 'clean' spectrum to interpret.

The new technique is not without its pitfalls. The measurement of diffuse as opposed to discrete beams imposes much stronger constraints on the system. The diffuse intensities are much weaker per unit solid angle and require efficient detectors. They also are susceptible to interference from other mechanisms that produce diffuse scattering such as defects, steps and thermal vibrations, all of which must either be eliminated or accurately subtracted. Fast low-intensity data-taking techniques (Heinz & Muller 1980) will be essential, especially in systems susceptible to electron-beam desorption, and checks on the importance of inelastic background contributions must be made to establish their importance.

Thus surface chemical bonds need no longer be subject to speculation in the way that they have sometimes been in the past. Several hundred surface structures have already been determined and published, with more being added every year. The established techniques of l.e.e.d. and s.e.X.a.f.s. are being used in increasingly ingenious ways at the same time as new methods are being experimented with. Perhaps the most interesting of these is the possibility of using X-ray diffraction to study surfaces. This requires very high intensity X-rays, but preliminary experiments have indicated that there may be a possibility of atomic resolution despite the difficulty of the experiment. We can be confident of a steady flow of information on chemical bonds in a widening range of surface systems.

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Discussion

M. W. ROBERTS (*Department of Chemistry, University College, Cardiff, U.K.*). Professor Pendry has given us some interesting ideas on the role of poisons in terms of the extent to which they protrude above the surface. Adsorbed sulphur is known to inhibit CO dissociation at an iron surface. This was interpreted (Kishi & Roberts 1975) as due to sulphur withdrawing electrons from neighbouring surface ion atoms, thereby decreasing back-bonding to the $2\pi^*$ orbital of CO(ads). Do Professor Pendry's calculations exclude this possibility? Furthermore, what model has he used for *sub-surface* modifiers? We have been inclined to think along the lines of a ligand-effect, the sub-surface 'modifier' controlling the electron density (charge) on the surface atoms (Blake *et al.* 1982). Each modifier influences up to ten metal atoms.

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J. B. Pendry. Our model is entirely consistent with sulphur withdrawing electrons from the $2\pi^*$ levels.

J. Wong (*Department of Physical Chemistry, Cambridge University, U.K.*). Professor Pendry gave an example of micro-cracks of N on a W(100) surface under tension and the possibility of surface pressure (compression) of Si(111). Does he think that it is generally the case for covalent solids that their free surfaces are under compression, while metallic surfaces, like W, are usually under tension to produce micro-cracks?

J. B. Pendry. I should emphasize that it is the presence of the N that induces the cracks. I do not think that a general rule can be deduced on the basis of a surface being metallic or covalent.

T. B. Grimley (*Donnan Laboratories, University of Liverpool, U.K.*). In general, there are no symmetry considerations of the Woodward–Hoffman type operating in chemisorption because outside a metal surface, there are enough electrons in orbitals of the right symmetries to form bonds with the valence orbitals of almost any adsorbate. To be more precise, consider an adsorbate with frontier orbitals $|\mathrm{HOMO}\rangle$, and $|\mathrm{LUMO}\rangle$, and a metal with valence orbitals $|\mu\rangle$ of energies ϵ_μ. For an assumed adsorption geometry we form the spectral densities of the frontier orbitals in the metal eigenstates

$$\rho_{\mathrm{HOMO}}(\epsilon) = \sum_{\mu} |\langle \mathrm{HOMO}|\mu\rangle|^2 \, \delta(\epsilon-\epsilon_\mu),$$

$$\rho_{\mathrm{LUMO}}(\epsilon) = \sum_{\mu} |\langle \mathrm{LUMO}|\mu\rangle|^2 \, \delta(\epsilon-\epsilon_\mu).$$

If ρ_{HOMO} has negligible density above the Fermi level ϵ_{F}, and ρ_{LUMO} has negligible density below ϵ_{F}, the conditions for chemisorption are unfavourable because of symmetry factors. For ethene adsorbing on Al(100) in the on-site geometry, I have made calculations for a tight-binding slab of the metal, which reveal ϵ_{HOMO} and ϵ_{LUMO} as broad resonances spanning ϵ_{F} so that the above conditions are *not* met, and there are no symmetry factors inhibiting chemisorption. I find a similar situation for nitrogen monoxide on Pt(100) in many different geometries. On the other hand, for the 'chemisorption' of ethene by butadiene, i.e. the cycloaddition to form vinylcyclobutane, the situation is quite different. The above conditions *are* met, and the reaction is symmetry-forbidden, as is well known. The difference between butadiene and a metal in this context is that, in butadiene, there simply is not the wealth of orbitals and symmetries that are available at a metal surface.