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Surface Science Prospective

Should surface science exploit more quantitative experiments?

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Abstract

In recent years two particular methods, scanning probe microscopy and theoretical total energy calculations (based, particularly, on density functional theory), have led to major advances in our understanding of surface science. However, performed to the exclusion of more 'traditional' experimental methods that provide quantitative information on the composition, vibrational properties, adsorption and desorption energies, and on the electronic and geometrical structure, the interpretation of the results can be unnecessarily speculative. Combined with these methods, on the other hand, they give considerable added power to the long-learnt lesson of the need to use a range of complementary techniques to unravel the complexities of surface phenomena.

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Modern surface science, based on all-metal ultra-high vacuum systems and the study of well-characterised (mainly single crystal) solid surfaces, has now been around for more than 40 years, and a veritable armoury of new methods has been developed during this period and been incorporated into these studies. Using incident and/or emitted electrons, photons, ions, atoms and molecules, methods have been developed to study the composition, structural, electronic and vibrational properties of surfaces. A key feature of the successful application of these methods to elucidate the properties of surface phenomena of increasing complexity (as typified by the work that led to the award of the 2007 Nobel prize in Chemistry to Gerhard Ertl [1]) has been the use of several complementary methods; rarely in surface science can a single technique provide all the information one requires. The great majority of the available methods are able to provide quantitative information. In the case of surface composition, very considerable efforts have gone into making the associated techniques quantitative and to define the sources of error and the likely precision; this has proved to be particularly relevant to surface analysis of complex surfaces in a range of practical ('real-world') situations. Electronic and vibrational spectroscopies provide absolute values of electron binding and vibrational energies. Thermal desorption and microcalorimetry can determine desorption and adsorption energies. Fully quantitative surface structure determination, with relative atomic positions typically determined to a precision in the range 0.02-0.05 Å, can be achieved by a number of methods such as quantitative low energy electron diffraction (QLEED), surface X-ray diffraction and photoelectron diffraction [2].

Despite this great potential to obtain, experimentally, quantitative information regarding the properties of surfaces, a survey of the papers now being presented at a major conference in the field of surface science, or indeed now to be found in a typical issue of this journal, shows a high proportion of work which makes little or no use of this potential. This is a new trend that has emerged in the last decade or so. Its origins can be traced to a combination of two factors: (1) the increasing use of scanning probe microscopy, SPM (mainly scanning tunnelling microscopy, STM) as the primary (or in many cases, the only) technique, and (2) the increasing number of studies of geometrical or electronic structure (or chemical reactivity) based wholly or primarily on the use of total energy calculations, mainly using density functional theory (DFT). Within the group of SPM-dominated studies are a growing number

directed to inhomogeneous surfaces, particularly those falling in the fashionable (but also potentially very important) area of nanostructuring

Of course, both STM and DFT have made huge positive contributions to our current understanding of the properties of nominally homogeneous surfaces. Moreover, if one wishes to study surfaces that are inhomogeneous on a nanometre scale, STM (or one of the other SPM methods, which generally have lower spatial resolution, but are advantageous in some situations) is almost the only way to gain information in a spatially-resolved fashion. STM can provide information on the morphology of the surface and the nature of its heterogeneity, and may even, in favourable circumstances, identify the atomic-scale periodicity of individual regions which may be only of nanometre dimensions. This information cannot be obtained by standard, spatially-averaging, surface methods. STM is not, however, able to identify the elemental character or composition of these different regions and is only rarely used to obtain spatially-resolved electronic or vibrational structure information. The *combination* of STM and standard spatially-averaging techniques *is* capable of obtaining some of this information, but such combinations are often not employed in these studies. The conclusions drawn from such studies would undoubtedly be more reliable if this type of combination of methods was applied more routinely.

STM is also used as the primary (or only) technique in studies of far more homogeneous surfaces. Indeed, the full power of STM to provide imaging on a sub-atomic resolution scale is most commonly achievable on atomically-flat low-Miller-index single crystal surfaces. Images of this type are extremely seductive. One appears to be 'seeing atoms', and as such to be 'determining the surface structure'; in this area of application, however, there are many potential pitfalls, and essentially no study of this type leads to a truly quantitative structure determination. Atomic-scale protrusions do not always correspond to atomic positions, particularly in surfaces containing two or more elemental species, there is no generally-applicable way of distinguishing different atomic species, the amplitude of the surface corrugation in the images does not generally correspond to height variations in atomic coordinates; even the lateral positions of atoms cannot be inferred reliably from these images [3].

If the preceding statements read like an assault on the utility of STM in the study of surfaces, this is certainly not the intention of this article. STM has had a profound and positive effect on the progress of surface science. At the most basic level STM experiments have shown that even the simplest low-index single crystal surfaces are rarely truly homogeneous, as was implicitly assumed in much earlier work. Perhaps even more importantly, STM studies have provided unique information on the character of structural change on surfaces and surface dynamics. A classic early example of this is the case of the modification of the Cu(110) surface by the adsorption of oxygen to produce a (2x1)-O surface phase. That such a change in the lateral periodicity occurred was well-established from qualitative LEED (low energy electron diffraction) observations, but the detailed structure of this phase was the subject of some controversy. One structural model (which subsequently proved to be correct) was the 'missing row' model in which alternate Cu atoms along the close-packed <110> rows are 'missing' relative to the bulk-terminated clean surface structure, with the O atoms occupying long-bridge sites between the remaining surface Cu atoms to produce Cu-O-Cu-O chains along the <100> direction within the surface. One objection that was aired to such 'missing-row' models of metal surfaces (including (1x2) clean surface reconstructions of a few fcc(110) surfaces) was: where do the missing atoms go to?

In fact the equilibrium structure first proposed on the basis of early *static* STM images was a different (incorrect) structural model [4]; instead, conventional structural methods based on ion scattering [5] and SEXAFS (surface extended X-ray absorption fine structure) [6] identified the correct structural model while LEED [7] provided a full quantitative structure determination. However, dynamic STM studies, performed during oxygen dosing, as the structural transformation occurred, provided a graphic illustration of how the structure forms (as described more fully in ref [8]) . Specifically, as the dosing progressed, <100> atomic chains were found to grow out from (or near to) atomic steps on the Cu(110) surface onto the lower terraces, the upper terrace being eroded. This mechanism is illustrated schematically in fig. 1. The results of these studies led to the realisation that the mechanism of formation of the (2x1)-O phase is by the *addition* of <100> Cu-O-Cu-O chains to produce what should perhaps be correctly described as an 'added-row' structure. Of course, the static structures produced by adding or removing alternate Cu atoms rows is the same, but

the STM experiments answer the question 'where do the *missing* atoms go *to*' by turning it around – the answer is the *added* atoms come *from* the steps at the terrace edges. Coincidentally, this investigation also showed just how mobile Cu atoms can be on a Cu surface at room temperature.

Despite the preceding negative comments regarding the ability of STM studies to determine static surface structures, this technique can also play a valuable role in such investigations, but *only* when complemented by more quantitative methods. A general problem in all quantitative experimental surface structural methods is that the ultimate method of structure determination relies on a trial-and-error approach in which a range of 'guessed' structural models are refined to achieve the best agreement between the experimental data and simulations of the data expected from the trial structures. The structure giving the best fit (of an acceptable quality) is deemed to be the true structure. An obvious limitation of this approach is that if the correct structural model is not tested, the true structure is not found. For complex structures, particularly involving large unit mesh sizes and two or more elemental species, it is particularly difficult to be sure that all plausible structural models have been tested; the method is limited by the imagination of the researcher. In such cases, particularly, atomic-scale STM images can help to provide ideas of possible structural models, although in doing so it is important to bear in mind all the caveats listed above regarding possible pitfalls in interpreting STM images in terms of atomic coordinates.

In the context of surface structure determination, a particular interest of mine, quantification is certainly an important issue. There are well-established experimental methods for achieving this objective, but also good reasons why they are not always applied. Not all surfaces display long-range order, precluding the use of standard diffraction methods such as low energy electron and surface X-ray diffraction. Local quantitative structural probes, such as scanned-energy mode photoelectron diffraction and SEXAFS require access to synchrotron radiation, clearly of limited availability. As such, spectral fingerprinting of local adsorbate coordination (most notably through vibrational spectroscopy, but also through photoelectron binding energy shifts) can play a valuable role. Of course, these methods rely on a solid database of known systems, and even then caution is required. Much the most widely used and documented example of this approach is in identifying the coordination of CO

adsorption sites through the absolute value of the C-O stretching vibrational frequency, a method used in studies of dispersed catalysts at high pressures for many years [9]. Even application of such a well-documented method has not been without its difficulties, however. For example, for many years vibrational spectroscopy from CO adsorbed in a c(4x2) phase on Ni(111) and Pd(111) had led to a clear identification of two-fold coordinated bridging sites as associated with the c(4x2) phase, and an attractive structural model was based on this assignment in which the CO molecules occupy rotationally-inequivalent bridge sites on a regular sub-mesh (see fig. 2). Only after true quantitative structural methods had shown the adsorption sites to be the two inequivalent three-fold coordinated hollow sites (fig. 2) [10, 11, 12, 13] did reassessment of the vibrational data lead to a realisation that there had been a kind of ‘creep’ in the frequency range correctly assigned to bridging CO, and a failure to take adequate account of the influence of intermolecular coupling in the vibrational frequencies.

Of course, quantitative structure determination can provide detailed bondlength information not available from spectral fingerprinting, thus giving far more insight into the nature of chemisorption bonding, for example. Even if this additional information were not necessary, however, this CO adsorption case highlights the fact that this kind of experimental structure determination has an important role in re-referencing the methods of spectral fingerprinting, in order to ‘keep them honest’. This same role is perhaps even more important in addressing the other important trend in surface science papers presented or published in the last few years, namely the considerable growth in the application of DFT calculations as a means of 'determining' surface structures. The viability and effectiveness of these calculations has certainly grown considerably, and there is no doubt that they now play an invaluable role in modern surface science, giving insight into electronic and energetic changes that underpin many surface phenomena. In part, the increasing use of DFT calculations is due to the important developments in the methods themselves. Other important factors are the increasing availability of low-cost high-speed computing facilities, and the maturity of several computer codes to perform these calculations that are being made available to a wider range of users, including those previously involved only in experimental studies. While the use of different functionals and approximations appears to have a significant effect on calculated binding energies,

including those associated with atomic and molecular adsorption on surfaces, the structural parameter values associated with the minimum energy structures are often rather insensitive to these aspects of the calculations. In cases in which detailed comparisons of theory and experiment have been conducted, these structural parameter values often agree to within a few hundredths of an Ångström unit, a fact that has led to some suggestions that DFT calculations could *replace* quantitative experimental structure determination. This is not, fortunately, a universally-held view, nor is the underlying assumption of invincibility of the methods universally true. There are quite a number of examples now in which the theoretical chemisorption bondlengths differ by ~0.10 Å or more from experiment (e.g. for alanine on Cu(110) [14] and for water on TiO_2(110) [15]), differences that are certainly very significant in chemical terms; assuming the experimental values are correct, this certainly suggests a failure in the theory to describe correctly the true nature of the bonding. There are also examples of DFT calculations leading to the wrong minimum energy structure; the best-known cases, identified by several of the most expert theoretical groups, are of CO adsorption on Pt(111) [16] and Rh(111) [17], for which calculations predict the preferred adsorption site to the three-fold coordinated hollows rather than the single-coordinated atop sites found experimentally. Whatever the reasons for these failures [18 , 19 , 17] they are further timely reminders of the need for quantitative experimental structural studies.

Of course, it is also important to recognise that DFT (and other theoretical) structure 'determinations' based on total energy calculations suffer from the same trial-and-error limitation of the experimental methods. Even if the methods correctly determine the true lowest-energy structural parameters for a particular structural model, the optimisation algorithms embedded in such computer programs have no ability to search for fundamentally different models (which could, for example, differ in the number of atoms in a unit mesh and the associated stoichiometry). In this regard, therefore, theoretical total energy structure determinations suffer from the same fundamental weakness of experimental methods – that the final solution is only as good as the imagination of the researcher involved. Unfortunately, in too many such studies, the search of different structural models is significantly less exhaustive than is common practice in the application of quantitative experimental methods of surface structure determination.

This article is intended to be a ‘prospective’, yet in truth, much of what I have written above is more of a ‘perspective’ – a personal view of some of the very general important issues and changes that have been taking place in surface science in the last few years. What of the future? Well, one of the general concerns I have expressed above is that excessive reliance on scanning probe microscopy, and of DFT calculations, when used in isolation, fails to exploit the rich range of methods available to surface scientists. As such, it reflects an ‘unlearning’ of the lessons learnt in surface science over the last 40 years or so, namely that one can only gain real understanding of surface problems through the use of several complementary methods, some of which are quantitative. The more positive view of the future, on the other hand, is that both scanning probe microscopy and DFT modelling are incredibly important tools in the surface scientist’ armoury that have come to the fore in the relatively recent past, and that if used in combination with more traditional methods, that can be used to establish the (average) surface composition, long-range order, electronic and vibrational structure, and thermal desorption behaviour, real inroads can be made into newer and more complex surface problems. Such studies are surely taking place now in the best groups (where I define best as those meeting these criteria!), and one may hope that in the future an increasing number of researchers will take advantage of the complementary nature of the traditional and new methods available.

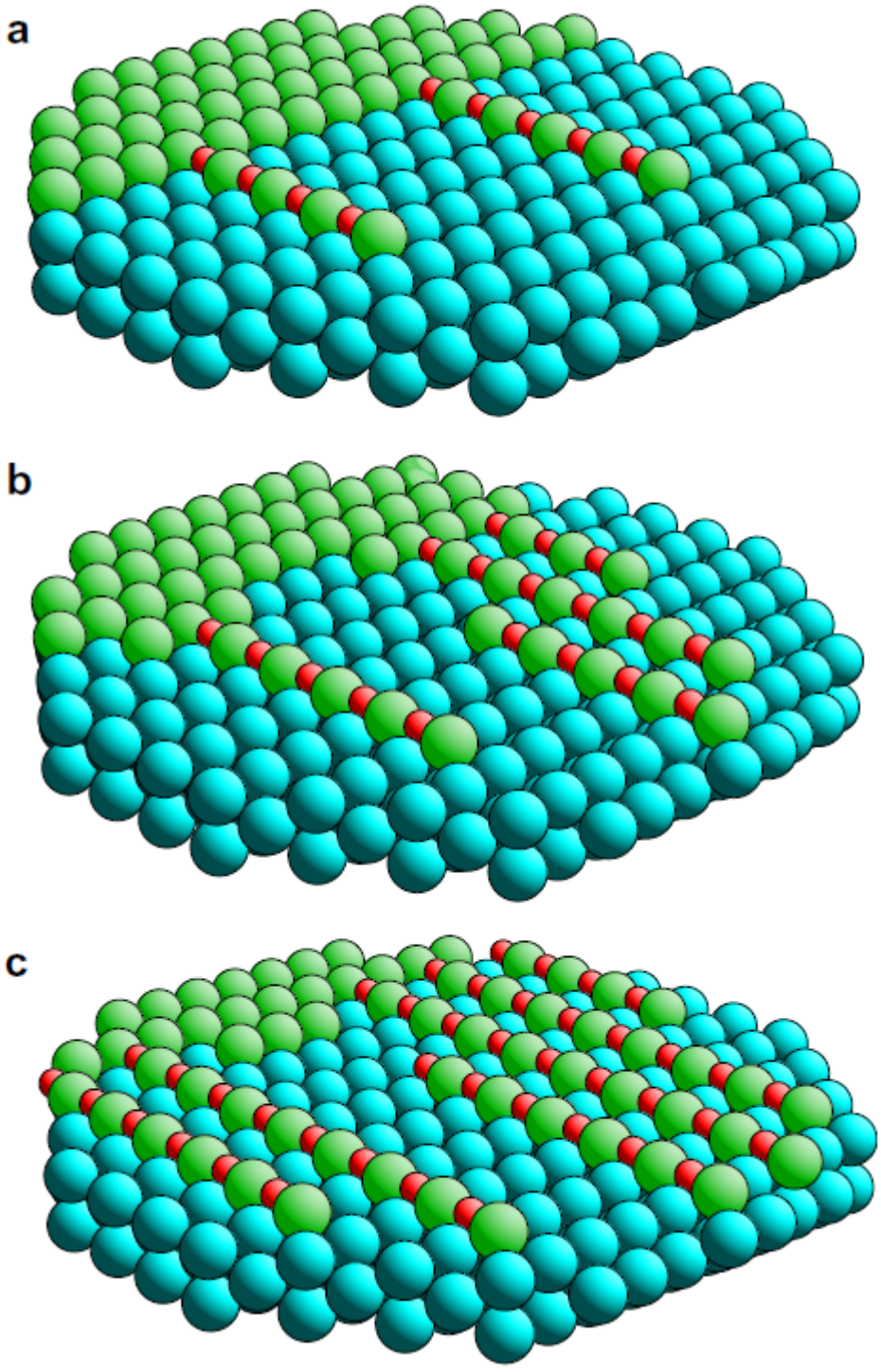

Fig. 1. Schematic atomic ball model of the growth of the (2x1)-O 'added row structure' on Cu(110) in the sequence from (a) to (c), as deduced from dynamic STM imaging studies during the course of oxygen dosing as described in more detail in ref [8]. For clarity the Cu atoms in the upper terrace are shown with a different shading than those of the underlying bulk. Cu-O-Cu- atomic rows grow out on the lower terrace, extracting Cu atoms from the step at the edge of the upper terrace and groups of these rows eventually merge to form the long-range ordered (2x1) structure.

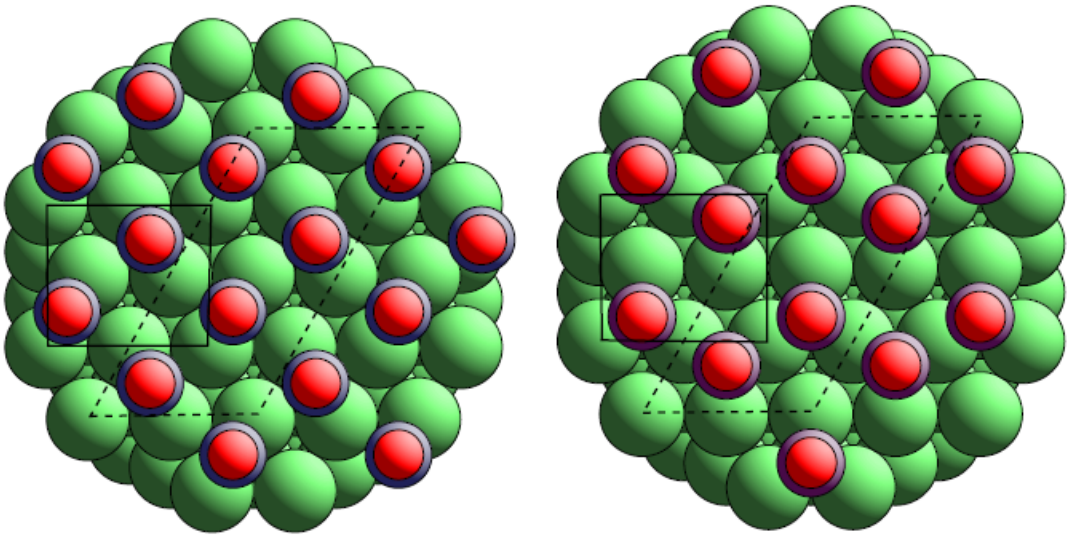

Fig. 2 Schematic plan view of two models of the c(4x2)-CO structure formed on Ni(111) and Pd(111). The dashed lines show the c(4x2) unit mesh, while the full lines show the primitive (2x2√3)rect. unit mesh. On the left is shown the original model, based on assignment of the C-O stretching vibrational frequency to a bridging site, in which the CO molecules lie on a smaller 'c(2x2√3)rect.' sub-mesh, while on the right is shown the true structure as extracted from quantitative structural methods, in which the CO molecules occupy the two inequivalent three-fold coordinated hollow sites.

References

1 Both the slides and a video of the Nobel Lecture provide an elegant example of this strategy and may be found at http://nobelprize.org/nobel_prizes/chemistry/laureates/2007/ertl-lecture.html

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