PHILOSOPHICAL TRANSACTIONS OF THE ROYAL SOCIETY A
MATHEMATICAL, PHYSICAL & ENGINEERING SCIENCES

Commentary on Progress and Prospects in Surface Science

Ronald Mason

Phil. Trans. R. Soc. Lond. A 1986 **318**, 283-284
doi: 10.1098/rsta.1986.0076

Phil. Trans. R. Soc. Lond. A **318**, 283–284 (1986)   [283]
Printed in Great Britain

Commentary on progress and prospects in surface science

By Sir Ronald Mason, F.R.S.

School of Chemical and Molecular Sciences, University of Sussex,
Lewes Road, Brighton BN1 9QJ, U.K.

This Discussion Meeting marks more than fifteen years of the quantitative application of electron emission or scattering from chemically and geometrically well characterized surfaces of metals and semiconductors. As a result, surface science has matured significantly, particularly in the context of an understanding of clean surfaces and of their physisorption and (non-reactive) chemisorption of simple atoms and molecules. Many of this Meeting's contributions mark the increasing emphasis on surface-structure–reactivity relations.

Professor Pendry rightly emphasizes the advances in surface crystallography that have come from the low-energy electron diffraction experiment, but one can anticipate that, at least for complex surfaces, there will be a need for independent structural information such as the data provided by extended X-ray absorption fine structure. Professor King gives a very useful summary of the s.e.X.a.f.s. of simple adsorbate structures and of the increasing importance of high-flux photon sources (more generally, as Professor Siegbahn, Dr Turner and Dr Venables indicate, the scope of photoelectron spectroscopy and photoelectron microscopy will be extended significantly with high-intensity monochromatic photon sources). Of particular promise is the development that relies on the uniquely high brightness of laser-induced plasmas as X-ray sources; typically, five orders of magnitude brightness of the laser sources at soft X-ray energies makes possible single subnanosecond pulse recording of transient events where a synchroton course would require the superposition of 10^5 pulses. A spectrum has been obtained from a single nanosecond pulse diffracted by a silicon crystal and the dynamics of a laser annealing pulse and concomitant thermal wave in the crystal followed by measuring spectral shifts and the broadening of diffracted X-rays. The scope for following surface transitions and the dynamics of adsorbed layers is considerable. Continuous radiation can be generated also and, with streak camera techniques, a time-resolved e.X.a.f.s. spectrum may be obtained.

Two sets of data discussed at the Meeting are important to an understanding of molecular reactions at simple surfaces. Professor Roberts and his colleagues have established via electron spectroscopy, the involvement of a variety of redox states in the interaction of oxygen with Ni (100) and Ni (210) surfaces; and have convincingly related their results to the theoretical studies by Gallagher *et al.* (1979), who explain the series of overlayer structures for oxygen on the Ni(100) surface in terms of a 'local orbital' made up of the overlap of oxygen 2p orbitals and neighbouring nickel 4s/4p states. These ligand–metal orbitals give rise to Van der Waals attraction at large oxygen–oxygen separations and, obviously, closed-shell repulsions at shorter distances. Redox states such as Ni(II) and Ni(III) only appear when the nickel 3d electrons are involved (as they are during oxidation when nickel–nickel bonds at the surface are broken). Secondly, low-energy electron diffraction and electron energy loss spectroscopy have established unequivocally the dehydrogenation of ethylene to σ-bonded ethylidene on rhodium and other surfaces. The contribution of electron loss spectroscopy to a description of the coordination geometries of ethylene by Professor Sheppard and carbon monoxide by Professor Yates is a remarkable one; Professor Sheppard's classification of the mode of bonding of ethylene at different surfaces of several metals should be rationalizable by reference to metal–metal bond distances and work functions but, more importantly, could firmly establish the precursor states that may sustain oxidative addition to carbon–hydrogen bonds and therefore dehydrogenation reactions.

The extreme surface sensitivity of the spectroscopy provided by de-excitation of metastable noble gas atoms will clearly provide critical data on the chemisorption bond with Professor Ertl and Professor Yates defining experimentally the involvement of the $2\pi^*$ antibonding state of carbon monoxide (clarification of the 'σ' and 'π' metal–ethylene bond classification will follow since the di-σ-adsorbed state (Professor Sheppard's paper) will be distinguished by increased emission from the metal d-ligand $2\pi^*$ orbitals).

De-excitation and energy loss spectroscopy are shown, in several contributions, to provide insight into the mechanisms of promotion or poisoning of surface reactions by simple adatoms such as potassium and sulphur. Professor Ertl, Professor Somorjai and Professor Yates give important observations on the effects of Lewis acids and bases on, *inter alia*, the local coordination geometries of carbon monoxide, on the modified dissociation reactions of carbon monoxide and dinitrogen and on the electronic factors determining the effective 'range' of adatom effects. The observations of the varying reactivity of low, and high, Miller index crystal surfaces must provide data that stand close to the analysis of local structure–reactivity relations on practical catalytic surfaces. One can suppose that diffusion processes, the reactive collisions of adatoms and admolecules at surfaces with steps or kinks, or both, will be studied with increasing precision by surface microscopy and time-resolved diffraction. There is already substantive evidence of the dependence of the activation energy for dissociation reactions of diatomic molecules on surfaces with sites of differing 'coordinative unsaturation', but a quantitative electronic theory for the observations is not available. Professor Somorjai's distinctions between the catalytic reactions sustained over a metal surface, on the surface of an overlayer and on co-adsorbate modified surfaces have most significance in suggesting what studies should be followed in looking for surface sensitivity and surface insensitivity correlations with local site coordination geometries and reactions in homogeneous systems.

Professor Siegbahn's contributions to the development of electron spectroscopy in atomic, molecular and surface chemical physics have been massive ones and this Meeting benefits enormously from his wide ranging and seminal paper. With the progress in techniques that he describes, electron spectroscopy is clearly able to move on to a preoccupation with electronically excited states, with surface alloy structures, with solvation phenomena and with the structure and (perhaps) the dynamics of the very important double-layer surfaces.

The Organizing Committee of this Discussion Meeting is grateful that the 'state of the art' application of electron spectroscopy and scattering to our understanding of simple and more complex surfaces is so well represented by the contributions made here.

REFERENCE

Gallagher, J. M., Haydock, R. & Heine, V. 1979 *J. phys. Chem.* **12**, L13.