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Diffraction from physisorbed layers

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ABSTRACT

Diffraction techniques used to study the structures of atoms and molecules physically adsorbed onto a variety of solid surfaces are reviewed. This is part of an important topic that includes the thermodynamics, dynamics and simulations/calculations of physisorption. We identify that there has been an interesting recent expansion in the variety of surfaces and molecular adsorbates that have been studied, extending previous mono-component studies to studies of binary mixtures with particular focus on novel intermolecular interactions. Technically, improvements in access to large centralised facilities with appropriate diffraction instrumentation have the potential to allow previously unfeasible measurements to be made and the beginnings of work in this area is summarised. There have also been significant advances in related techniques, such as scanning tunnelling microscopy and atomic force microscopy, that provide important and complementary structural information.

1. Introduction

The physical adsorption of species at solid interfaces is of fundamental importance to a very wide range of important phenomena including oil recovery, detergency and floatation. The presence of the adsorbed material, although representing a very small amount of the total material present, can dominate the behaviour. For example, by changing the nature of the surface from water to oil wet. Physisorption, where the enthalpy of adsorption is rather small and similar to the enthalpy of vaporisation of the adsorbate, can occur from both the vapour and condensed phases. The study of both of these interfaces represent particular experimental challenges, however, it is probably fair to say that the study of adsorption from liquids represents a particular challenge, given that the adsorbed layer is more inaccessible, encompassed by condensed phases on both sides. However, in recent years a combination of theory, simulation and experimental techniques have been developed to probe the structure, dynamics, thermodynamics and electronic properties of physisorbed layers under a variety of conditions. This combination of approaches now gives significantly more insight into these adsorbed layers and their behaviour, both as pure materials and as mixtures.

In this short review we must limit our focus to developments over the last 5–10 years particularly in the use of diffraction techniques to to study the structures of physically adsorbed pure materials and mixtures from the vapour and liquids onto solid substrates. It is important though, not to forget that structural studies are usually done to facilitate a better understanding of physical phenomena. As such this review is just a subset of the studies of physical adsorption and as such the reader may also wish to consult a number of reviews on related material including those by Bruch et al. [••1], Clarke [2] and Inaba [3]. There have also been several reviews of Scanning Tunnelling Microscopy (STM) of organic layers [4,5] and there continues to be significant effort in this area. We have not included chemisorbed systems or other important topics such as self-assembled monolayers (SAM's) on metal surfaces [6,7].

Initially we will review the principle advances in the techniques relevant to this area. We will then consider the different experimental systems that have been addressed in the recent literature. We will consider each adsorbate on different substrates as this provides a convenient grouping to present and compare the topics.

2. Experimental approaches

There are now a fairly large number of experimental methods for the study of physisorbed layers. It is convenient to consider them in two broad classes. The first are surface specific techniques that provide detailed, atomic resolution, information about the adsorbed species and its position relative to a well characterised (often) single

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crystal substrate. The second is to use high-specific-surface-area powdered substrates, which mean that the very small contribution from a monolayer is large enough to be detected by experimental techniques that are not surface-specific.

In the first category, although beam-damage has historically been a problem, Low Energy Electron Diffraction (LEED) has seen some recent developments which improve the measurement of beam-sensitive layers. For example fibre-optic LEED [8] and delay-line-detector LEED [9]. These techniques both allow high sensitivity diffraction patterns with a low-flux electron beam. This is particularly important for physisorbed layers since absorption of high-energy electrons can result in desorption of the monolayer.

Helium atom scattering (HAS) is a rather unusual and potentially powerful experimental approach that can both provide structural and dynamic information on a monolayer simultaneously. There are some recent studies of dynamics of physisorbed layers (e.g. benzene on graphite using both helium and neutron spin-echo spectroscopy [10]), but to our knowledge helium atom diffraction has not recently seen much use in the area of physisorbed layers.

Synchrotron grazing incidence X-ray diffraction (GIXD) is increasingly attractive, partly with the availability of new third generation facilities but also for the rich in-plane structural information that can be obtained. This technique was developed in ultra-high vacuum (UHV) but has increasingly been used to study non-UHV systems. Using this, the related methods of X-ray reflectivity and grazing incidence small angle X-ray scattering (GISAXS), it is possible to obtain detailed structures of thin films adsorbed on a range of surfaces from solid–solid to liquid interfaces over a range of length scales, including polymers [11] and lipids [12]. Technical advances in this area should mean that detailed structural and dynamic studies of these types of complex system will become increasingly viable in the future.

A particularly interesting example in which GIXD has been used is Xenon physisorbed on Ag(111) [••13]. In this study scans of the Xe(10) Bragg rod were able to confirm the structure of a Xenon monolayer with higher resolution than LEED. Further, the out-of plane structure during film growth was also investigated: Scans along the Xe $(0\,1\,l)$ rod were able to show the stacking sequence of the film, and the (0 0 3/2) anti-Bragg position were able to show layer-by-layer film growth. The specular reflectivity scans were able to precisely measure the film thickness during growth. This study clearly demonstrates the level of detailed structural information that is potentially available using this method, and the technique has since been applied to some other systems. However, similar studies have been rare, perhaps due to the difficulties associated with this approach. A small UHV chamber was required with in-situ sputtering, LEED and Auger capability together with sample cooling to 30 K. In general, near-UHV conditions must be considered with some care, as they can lead to desorption of physisorbed species. A common way to address this issue was used in this study; the samples were prepared using a dynamic approach in which the surface is continually dosed to compensate for losses due to continual pumping. This results in a "quasi-equilibrium", in which the local conditions at the sample are nominally equivalent to the presence of a 3D gas. Alternatively, experiments can be performed at temperatures for which the vapour pressure is very small so that desorption is negligible. However, both of these approaches mean that there is some question over thermodynamic equilibrium.

Some other new techniques for studies of surfaces in near-UHV conditions have been developed recently. These include Very High Resolution Ellipsometry (VHRE) [••14] which can quickly and accurately measure the thickness of an adsorbed film and provides a useful addition to the complementary techniques of X-ray and neutron reflectometry. Additionally Environmental Scanning Electron Microscopy (ESEM) has also been used with physisorbed systems [15]. Although the electron gun and most of the beam path are in UHV, the sample can be maintained at a modest vapour pressure preventing desorption.

Measurements with powdered substrates can be made under equilibrium conditions in the presence liquid or vapour, and therefore offers some advantages. When collecting powder diffraction from adsorbed monolayers it is preferable if one uses powders that have just one crystal-facet available for adsorption, historically Graphite and Boron Nitride (which are 'lamella' in nature with an exposed basal plane), and 3D crystals such as Magnesium Oxide which don't show significant faceting. Careful subtraction of patterns obtained from samples with and without adsorbate is used to obtain the scattering pattern of monolayers with peaks which have a distinctive "saw-tooth" line shape that is characteristic of a two-dimensional lattice, which can be used to confirm that an adsorbate is present as a monolayer and not as 3D crystallites. Fig. 1 shows examples of recent synchrotron and neutron measurements that illustrate the high quality of data that can be obtained. These diffraction patterns can be solved using analogous approaches to 3D. However, in most cases the diffraction patterns do not have many peaks and so structural determinations are limited in their complexity and can only be fitted by highly constrained models. Confidence in structural assignments can be improved with additional information in the form of combined X-ray and neutron measurements or by comparing the structures of homologous series of adsorbates where there is a systematic variation of alky chain length (for example). This approach does not directly measure registry with the substrate, but a comparison of the unit cell parameters can be used to infer whether a monolayer structure is commensurate.

It is important to note that these techniques are best used in combination with other supporting techniques. As well as thermodynamic measurements (calorimetry and adsorption isotherms in particular) other techniques such as inelastic and quasi-elastic neutron or helium

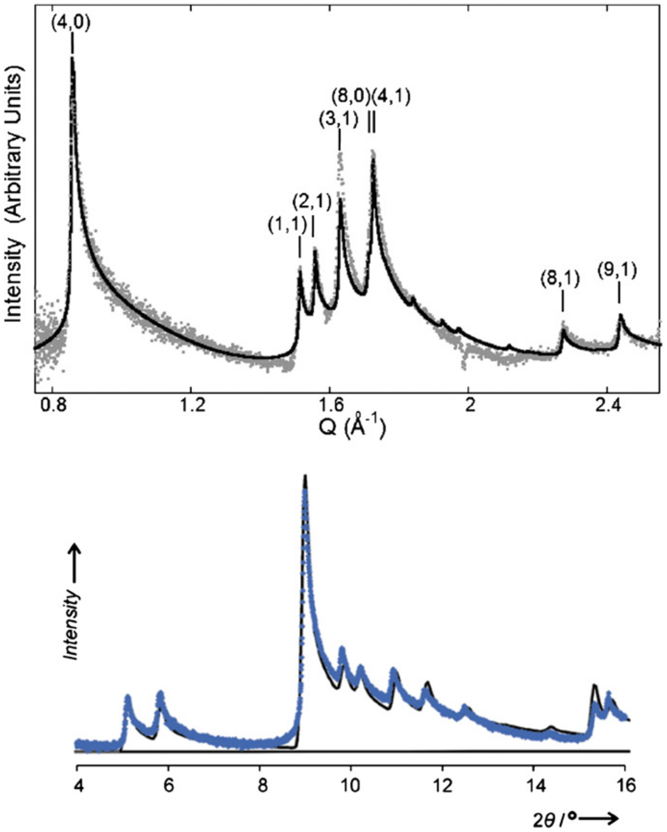

Fig. 1. Two examples of high quality diffraction data due to improved X-ray and neutron instrumentation. Top) Butane on MgO measured at OSIRIS at the ISIS neutron source. Reprinted from [••64] Copyright 2006, American Physical Society. Bottom) A halogen bonded binary mixture on graphite measured on I11 at Diamond Light Source. From [•84] — reproduced by permission of The Royal Society of Chemistry.