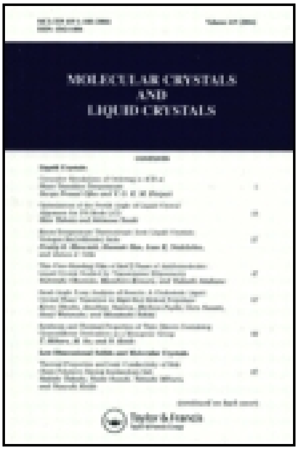

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Structural Characterisation of Condensed Molecular Materials using Polarised NEXAFS Spectroscopy

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Structural Characterisation of Condensed Molecular Materials using Polarised NEXAFS Spectroscopy

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The basic principals underpinning the technique of polarised Near Edge X-ray Absorption Fine Structure (NEXAFS) spectroscopy using synchrotron radiation are described with particular relevance to the technique's application in the structural characterisation of organic surfaces and interfaces. Experimental data, recorded in the ultra-soft spectral region close to the C and N K-edges (ca. 200eV to 500eV) on beamline U1A at the Brookhaven National Synchrotron Light Source (NSLS) is presented including applications to thin films of long chain hydrocarbons, LB films, anti-corrosion coatings and organic single crystals.

Keywords: Polarised NEXAFS spectroscopy, structural characterisation, molecular surfaces and interfaces, soft X-rays from synchrotron radiation

INTRODUCTION

The fundamental structural nature of condensed molecular interfaces underpins our understanding of a wide range of chemical processes including; colloidal systems and formulations, electrochemical systems and corrosion processes, paints and coatings, precipitation and crystallisation, lubrication and tribological systems etc. Many industrial processes rely on the molecular-scale control of interfacial systems for a wide range of processes including materials purification and solid-liquid separation. Despite this, detailed knowledge of the actual surface structure of molecular solids is very limited. This contrasts with inorganic systems such as metals, oxides and semiconductors where our understanding of surface structure is much more developed.

For molecular solids, in particular, the inter-relationship between surface chemistry, growth interfacial ordering and process kinetics remains totally unknown at the present time. Historically, there has been a critical lack of detailed experimental data relating to the atomic-scale surface and sub-surface structure of molecular solids, their mediation by heterogeneous phases and the changes in their surface chemistry associated with the formation, operation and mediation of condensed phases.

Recently, however, highly intense and tuneable photon sources provided from synchrotron storage rings have been applied to this generic area. In this paper the application of X-ray absorption spectroscopy to this research area is presented and highlights recent work applying this technique within the ultra-soft spectral region focusing, in particular, on an examination of Near-Edge X-ray Absorption Fine Structure (NEXAFS) spectroscopy using polarised synchrotron radiation. In this respect this paper complements an earlier review(1) in which application of Extended X-ray Absorption Fine Structure (EXAFS) at higher photon energies was described. For reasons of brevity an overview of the principals of synchrotron radiation, given in the earlier paper, will not be repeated here. Much of the work presented here is part of the doctoral work[2] of one of us (JJ).

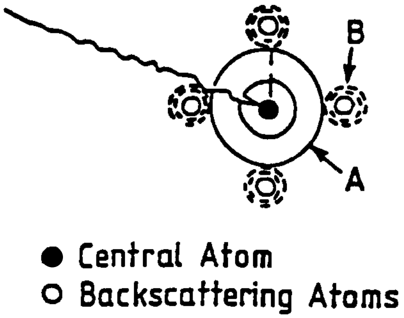

FIGURE 1. Generation of photoelectron waves (A), via excitation of core-shell electrons during absorption process, subsequently backscattered by near neighbouring atoms (B) producing interference dependent upon the distance, number and type of the associated atom-atom correlations.

POLARISED NEXAFS SPECTROSCOPY

Basic Principles

The oscillatory fine structure observed close to the X-ray absorption threshold can be attributed to interactions between photo-electron waves generated via the promotion of core shell electrons into excited states and the same waves following backscattering from near neighbour atoms (see Fig. 1).

Since the mean free path of the scattered electrons is short, the analysis of NEXAFS spectroscopy(3) data spectra provides structural information on the local atomic and molecular structure around the absorbing atom site. In the ultra-soft spectral region adjacent to the C and N K-edges (ca. 200-500eV)

NEXAFS is typically sensitive to molecular π- or σ-orbitals and provides strong resonance features in the experimental spectra when the E-vector of the incident radiation is parallel to a specific molecular orbital. By varying the angle of the incident synchrotron beam (within the plane of the synchrotron source), and hence its polarisation, with respect to the surface, the molecular orientation of a molecule can be determined[3]. Consider Fig. 2 which shows schematically a long-chain hydrocarbon molecule with its chain backbone aligned along the normal to the substrate surface. When this arrangement is examined using NEXAFS in normal incidence geometry (a) the electric field vector is strongly sensitive to the C-H* and less so to the C-C σ* interaction. The situation becomes reversed at glancing angles (b) of incidence where the latter interactions are highlighted and become more prominent. In this way, by examining both the position and intensity of the resonance features resulting from specific inter atomic/molecular interactions, it is possible to discriminate between the same atoms involved in different bonding configurations.

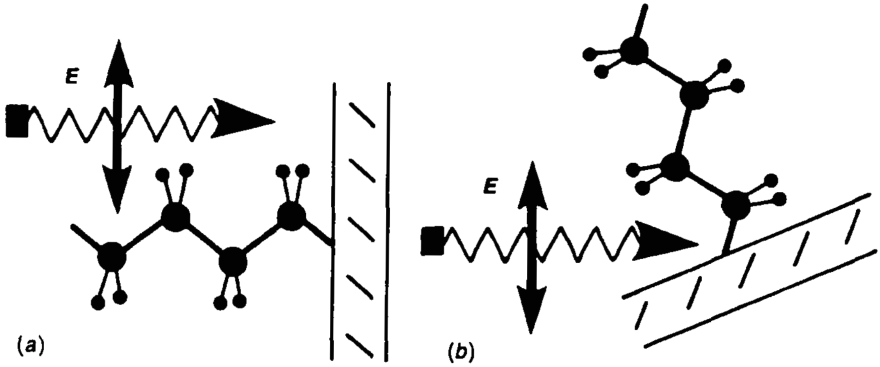

FIGURE 2. Use of polarisation to determine bond orientation with NEXAFS spectroscopy: (a) normal incidence - dominant transition C-H*; (b) glancing angle dominant transition - C-C σ*.

The depth sensitivity of this technique can be varied through the use of different detection methods, electron yield (EY) typically examining the top 5nm layer of the sample whereas fluorescence yield (FY) probes up to 100nm into the surface. Thus, using the two detection systems together we can build up a simultaneous picture of the orientation of the molecules and their intra- and inter-molecular interactions in both the surface and sub-surface regions.

Being a photon-based technique polarised NEXAFS spectroscopy provides the capability, in principle, to probe the structure of interfaces without recourse to ultra high vacuum (UHV) and/or electron beam based analytical tools such as ESCA/SIMS, SEM/EDAX etc. electron microscopy. Also, as NEXAFS does not demand long-range order or ultra-clean surface preparative methods it is an ideal tool for the structural analysis of 'real' chemical systems such as liquids in contact with solid surfaces. In addition, high intensity provided by SR enables interfaces to be examined *in-situ* and structural changes to be probed dynamically.

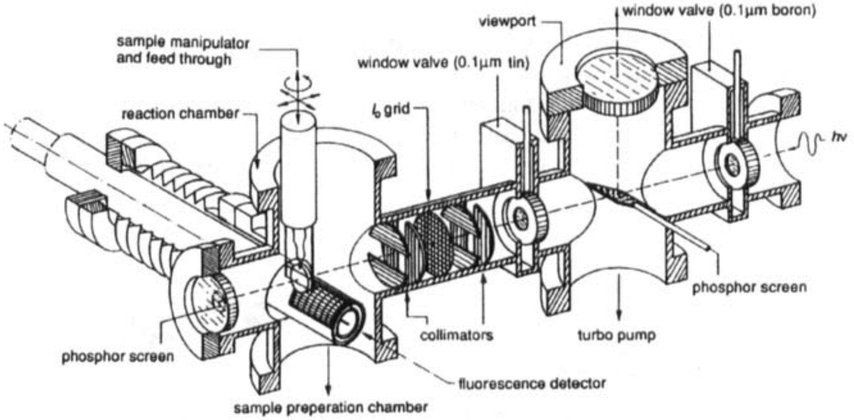

FIGURE 3. Experimental set up[5] on beamline U1A[4]

The NEXAFS Facility on Beamline U1A at the Brookhaven NSLS

The data and results presented here have been carried out on beamline U1A[4] at the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory, in the USA. The experimental chamber, summarised in Fig. 3, provides for measurements to be made in both FY and EY detection modes while the sample is maintained under vacuum conditions. For the former we used a differentially pumped gas-flow proportional counter[5] whilst for the latter a conventional channeltron detector was used. The sample chamber, which is separated from the UHV beamline by a differentially pumped aluminium window (typically 0.1-0.4 μm thick), is maintained at moderate pressures (ca. 1×10^{-6} mbar) and is thus suitable for examination of organic systems. The samples were mounted onto a conducting earthed metal mount which was fixed to a vertically rotating stage.

The spectra were normalised and the orientation of a bonding orbital, as identified from the NEXAFS data, with respect to the substrate determined by employing a method outlined by Stöhr[3].

EXAMPLES OF NEXAFS STUDIES TAKEN FROM RECENT WORK

Full details of the experimental details are given in the primary publications, cited below, and will not be given again here.

Characterisation of Long Chain Hydrocarbons deposited onto Si(111)[6-8]

Understanding the molecular science underpinning the crystallisation of long-chain hydrocarbons is important for a wide-range of industrial products and processes including surfactants, food products, electronic materials, membrane technology and colloid science. Here the utility of NEXAFS spectroscopy to the examination of the supra-molecular organisation adopted by condensed thin films of a number of representative long chain hydrocarbons with varying head groups is demonstrated.

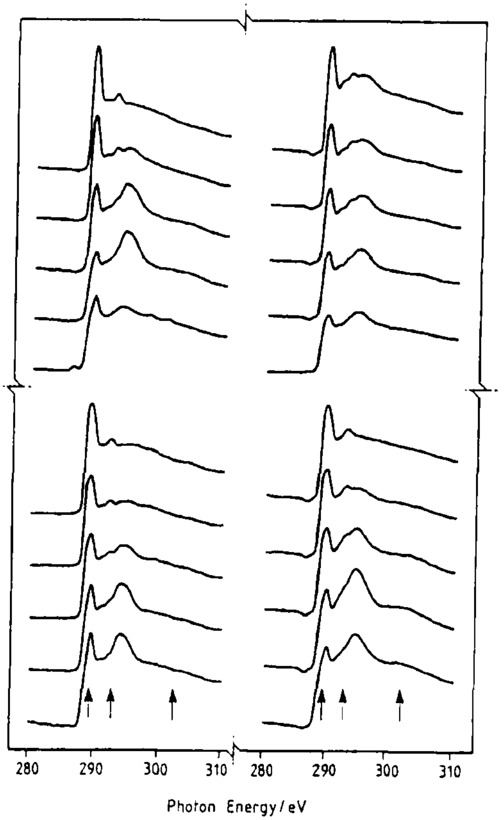

FIGURE 4. NEXAFS (EY) data: hexacosane (top left); eicosanol (top right); araichidic acid (bottom left); sodium stearate (bottom right), incidence angles (top to bottom) 90°, 70°, 50°, 30° and 10°, respectively.

Fig. 4 shows data taken for four representative long chain hydrocarbon systems: an alkane (hexacosane, $C_{26}H_{54}$); an alcohol (eicosanol, $C_{19}H_{39}$-OH); an acid (araichidic acid, $C_{19}H_{39}$-COOH); and a soap (sodium stearate, $C_{17}H_{35}$-COO.Na) as prepared in thin film form via vacuum deposition on to Si (111) substrates. The data reveal the spectra to be dominated by resonance features at 289eV, 293eV and 303eV which are characteristic, respectively, of the C-H*, C-Cσ* and C-Cσ* contributions to the molecular orbitals. From the strong angular dependence of these resonance features it is clear that all the samples show well developed supra-molecular order. The sharpness of the C-H* resonance features in the NEXAFS spectra taken in normal incidence geometry (top) reveals the molecular axis of the long chain backbones to be aligned at low tilt angles (τ) with respect to the substrate surface normal.

For hexacosane (τ=28±2°) comparison with its close homologue tetracosane[9], which has a tilt angle of 17.8°, reveals the thin film of the longer chain molecule to pack with a much larger tilt angle than the shorter homologue. The reverse trend is seen in the case of eicosanol (τ=18°±2) in comparison to the published structure[10] for the shorter alcohol hexadecanol which has a larger tilt angle of 33°.

The NEXAFS data for araichidic acid (τ=30±2°) reveals a good match for close homologue stearic acid although the precision of our measurements is not sufficient to identify whether the film structure is consistent with the β, γ or ε polymorph of stearic acid[11-13] each of which have very similar tilt angles (27.2°, 31.7° and 29.4° respectively). For the anhydrous sodium stearate (τ=30±2°, see Fig. 5) soap, we have only the hydrated form of the shorter chain soap potassium palmitate[14], which has a tilt angle of 38.0°, to compare with. The lower tilt angle for vacuum prepared anhydrous film presumably reflects the more efficient packing of the alkyl chains brought about by the lack of hydration water molecules in the inter-laminae region.

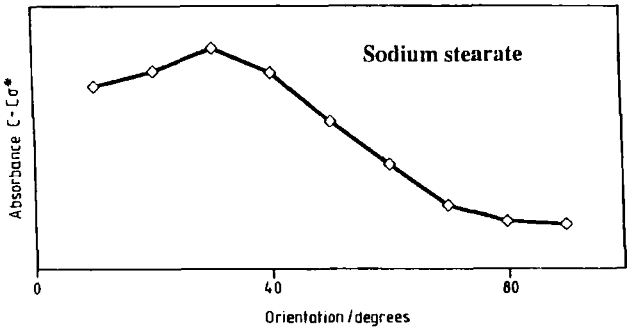

FIGURE 5. Incident angle dependence of C-Cσ* resonance with respect to the normalised C K-edge NEXAFS spectra recorded for the sodium stearate.

Surface Nucleation of Hexatetracontane from the Melt Phase[7,8]

NEXAFS measurements, made as a function of temperature, using simultaneous EY and FY techniques can give a unique insight into the often complex interplay between nucleation, growth interface kinetics and resultant crystal form that underpins a wide range of chemical processes notably purification and separation.

Figure 6 shows NEXAFS spectra of a sample of hexatetracontane ($C_{46}H_{94}$) prepared in a similar manner to those described above which is subjected to temperature cycling through melting and re-crystallisation. The data show that molecular orientational disorder is introduced, in the sub-surface region (FY) as the temperature approaches the melting point whilst the surface (EY) retains its structural order. This effect is marked by a decrease in the relative intensity of the dominant C-H* transition (at 289 eV) when the substrate is at 90° with respect to the incident beam and a decrease of the dominant C-C σ * transition (294 eV) at 20° incident angle. The melting point, at 90°C, is accompanied by a complete breakdown in bulk structure while the surface still remains ordered up to 2°C beyond the melting point.

Upon cooling the surface freezes out at 92°C, above the melting point as before, while the bulk remains fluid-like down to 90°C. At room temperature the system re-orientates and exhibits a structural organisation in the surface and sub-surface regions which is indistinguishable from that observed prior to melting, i.e. the process is reversible. This direct observation of surface nucleation provides a basis for understanding the hetero-nucleation mechanism in n-alkanes which are known to supercool to much higher degrees when surface nucleation is not allowed (see Table 1).

n	Structure	Heterogeneous Taggart et al[15]	Homogeneous Oliver & Calvert[16]
13	Orthorhombic	0.3°C	16.1°C
14	Triclinic	2.9°C	17.0°C
15	Orthorhombic	0.3°C	not measured
16	Triclinic	2.2°C	16.6°C
17	Orthorhombic	0.1°C	13.6°C
18	Triclinic	1.2°C	13.9°C
19	Orthorhombic	0.2°C	13.4°C

TABLE 1. Experimental supercoolings for n-alkanes crystallising with heterogeneous (narrow supercooling) and homogeneous (wide supercooling) nucleation mechanisms. Note the odd/even chain length effect showing bigger supercoolings for the more crystallographically stable triclinic phases.

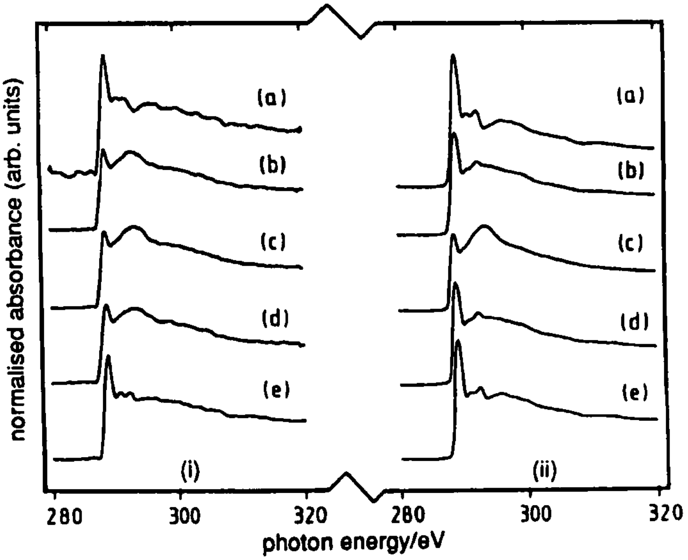

FIGURE 6. Variable temperature normal incidence C K-edge NEXAFS spectra of $C_{46}H_{94}$ ((i) FY - bulk sensitive; EY - surface sensitive): (a) room temperature (27°C), (b) bulk melt (90°C), (c) surface and bulk melting (92°C), (d) surface freezing and bulk melt (90°C) and (e) return to room temperature.

Molecular Organisation in a Cu Phthalocyanine Langmuir-Blodgett Film[17]

Metal phthalocyanines are well established, industrially, due to their structural and thermal stability. They are widely used as dyes[18] and can also be used as simple models for more complex biological molecules chlorophyll and haemoglobin[19]. However, they are also of interest due to their interesting conduction properties which can be engineered by varying the substituent metal atom. Langmuir-Blodgett (LB) films can be made from lightly substituted phthalocyanines, such as tetra-*t*-butyl phthalocyanine (TBP) providing materials which are durable and abrasion resistant.

Cu-TBP has a planar conformation with N=N double bonds associated with π orbitals normal to the ring plane. NEXAFS spectra taken of a 4 monolayer thick Cu-TBP LB film recorded at the N K-edge (Figure 7) reveal clear orientational behaviour associated with a well-defined minima and maxima in the N=N π* resonance feature at 399eV at for glancing and normal incidence conditions respectively. This confirms that the π orbitals of the Cu-TBP molecule are aligned parallel to the substrate. Since these bonds are themselves perpendicular to the plane of the molecule, this therefore shows the plane of the

Cu-TBP molecule to be oriented normal to the substrate in confirmation of previous TEM studies by Fryer et al[20].

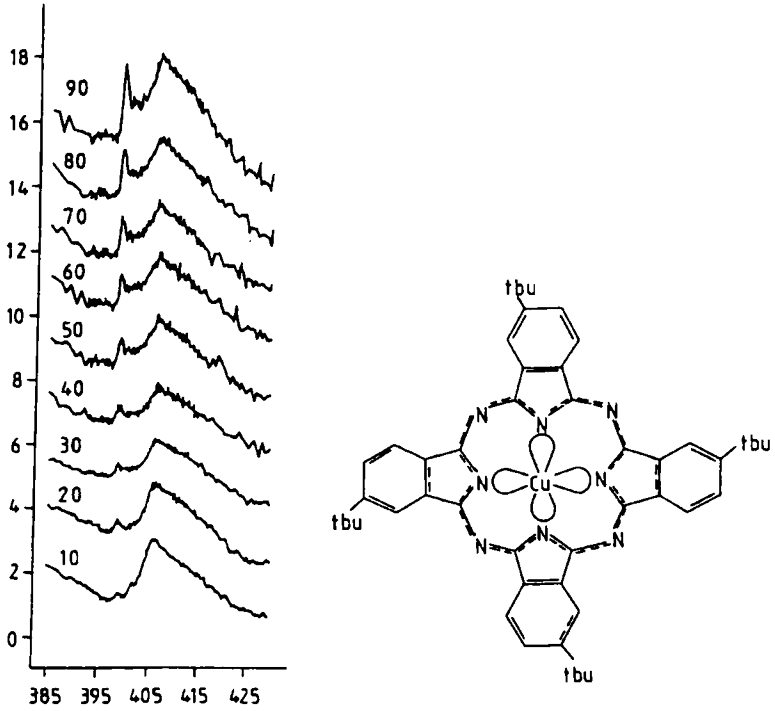

FIGURE 7. Orientation dependent NEXAFS spectra, at the N K-edge, of a 4 monolayer LB film of Cu-TBP

Orientation of Benzotriazole Molecules on Oxidised Cu Surfaces[21]

Benzotriazole (BTA) has, for over 50 years, been established as a corrosion inhibitor of copper and its alloys. However, despite numerous studies, the interfacial chemistry involved in its action has never been satisfactorily established. The binding site of the BTA molecule was resolved by Pizzini et al[22] who used EXAFS spectroscopy at the Cu K-edge to reveal that the BTA molecule binds to the central N2 atom (see model 2 in Fig. 8) in the triazole ring.

Inspection of NEXAFS data taken of BTA films adsorbed onto oxidised Cu thin films reveal the C=C π* transitions to be much stronger for the spectra recorded in normal incidence when compared to those recorded at grazing angles of incidence. Detailed curve fitting confirms this observation revealing the BTA molecules to be tilted at around 29-32° (dependant on substrate thickness) with respect to the substrate normal, except for very thin (< 200Å) Cu films where the tilt angle is much smaller (typically 3°). Detailed surface constrained molecular modelling reveals a BTA molecular arrangement consistent with a classic herringbone inter-molecular packing motif.

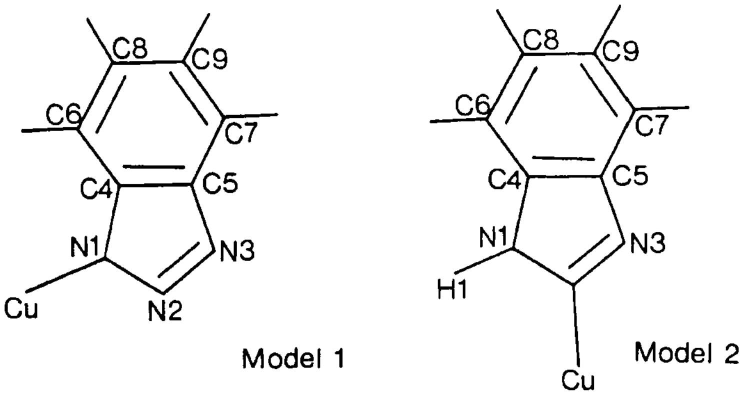

FIGURE 8. Binding sites of the BTA molecule for bonding to metallic substrates.

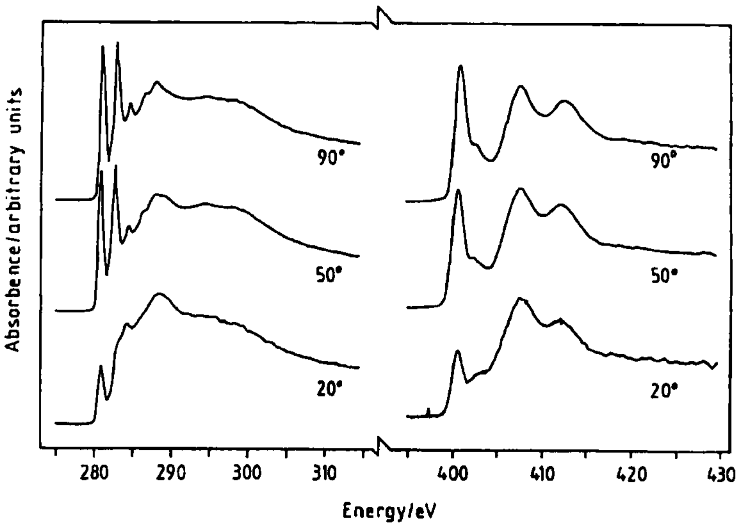

FIGURE 9. NEXAFS data (left, C K-edge; right, N K-edge).for BTA on Ag showing well defined surface orientational behaviour consistent with the ring plane of the BTA molecules being at 25.5° with respect to the substrate normal:

This overall structure is supported via measurements on close BTA molecular analogues and other substrates. For example, benzimidazole, which lacks the central N2 site necessary for binding to the Cu substrate, does not appear to be oriented at all. The fact that this compound is a poor corrosion inhibitor lends support to the importance of defined supra-molecular order in effecting durable anti-corrosion films for Cu substrates. Measurements made on other substrate materials, such as Ag (Fig. 9), appear to result in similar surface configurations as found for Cu-BTA.

Surface Reconstruction on Benzil (0001)[23,24]

The surfaces of simple elemental compounds are known to reconstruct due to the termination of strong primary bonding at the exposed surface thus leading to relaxation of atoms from their bulk positions and hence a reduction of the surface symmetry. Intuitively one would not expect such effects to be as strong in organic solids where the crystal chemistry is dominated by much weaker (mostly van der Waals') forces when compared to those prevalent in elemental solids. However, the conformational flexibility inherent in many complex organic molecules would suggest that some molecular re-arrangement should take place in cases where crystal packing forces induce a change in molecular conformation with respect to that expected for the free molecule[25].

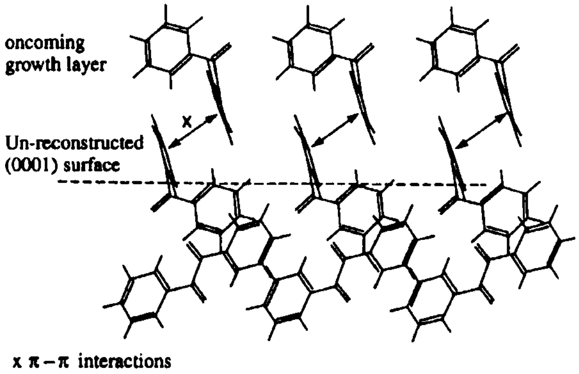

FIGURE 10. Molecular packing along the a-axis showing the interleaving intermolecular packing motif involved in the formation of the benzil (0001) surface.

Benzil $(C_6H_5C{=}O)_2$ comprises two phenyl rings joined together by two *trans* carbonyl groups, with the latter providing a degree of conformational flexibility. It crystallises in a trigonal structure $P3_12$ in a tri-molecular unit cell with a= 8.409 Å and c= 13.672 Å. Comparison between the molecular structure derived from semi-empirical quantum chemistry calculations with that derived from the crystallographic structure[26] reveal a substantial change in molecular conformation associated with the crystallisation process. This change reflects the strong inter-molecular packing forces in the solid-state dominated by strong π-π interactions associated with an interleaved packing motif between benzil molecules from adjacent molecular layers (as shown in Fig. 10) across the basal (0001) plane. It is the strength of these π-π intermolecular interactions (-8.04 kcal/mol) with respect to the overall lattice energy (-25.9 kcal/mol) which maintain the benzil molecules in a conformation away from that expected for a minimum intra-molecular energy.

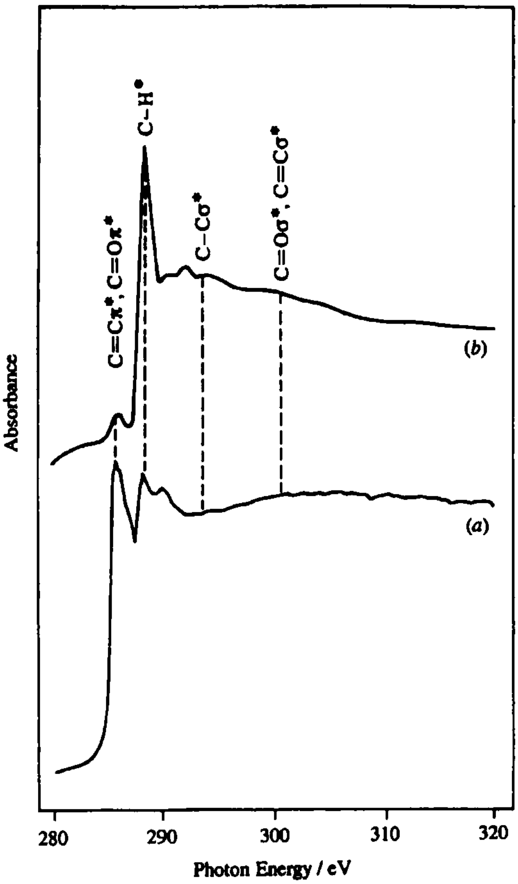

FIGURE 11. Carbon K-edge NEXAFS spectra recording in normal incidence geometry from a Benzil (0001) surface: (a) FY; (b) EY.

It is thus reasonable to suppose that during the growth process the conformation of the benzil molecules on the (0001) surface will relax back towards that expected for the isolated molecular state. This supposition is confirmed by NEXAFS spectroscopy (Fig. 11) which reveal that the exposed surface molecules experience conformational change due to the loss of the inter-molecular π-π interactions which are present in the bulk structure but which are absent on the exposed (0001) surface during growth.

The FY NEXAFS spectra, representative of the bulk crystal structure, reveals (a) well defined C-H* and C=C π* resonance features, together with other, less distinct features. The strong C=C π* resonance reflects the fact that the ring planes of the phenyl groups of the benzil molecules in the bulk structure are aligned normal to the surface. Hence the π orbitals of the molecules are parallel to the electric field vector of the linearly polarised synchrotron beam which for this orientation runs parallel to the sample surface.

In contrast, the C=C π* resonance is substantially reduced in the EY data (b) reflecting significant disordering of the ring orientation in the phenyl rings in direct confirmation of the molecular modelling studies. Thus this work provides direct evidence for a degree of surface reconstruction in the organic solid-state. In the case of benzil (0001) the reconstruction involves conformational changes to the surface molecules, rather than shifts in their relative position, as would be more typical for such effects in elemental compounds.

CLOSURE AND FORWARD LOOK

The past decade has seen the maturing of polarised NEXAFS spectroscopy as an accessible technique beyond its application within the UHV surface science community towards its application within the broader areas of organic solid-state, interface and materials chemistry. The scope and range of studies in the latter area are now being extended so that measurements can be made on a wider range of organic solids, which due to high vapour pressures, have not, as of yet, been examined using this technique. In this respect a new environmental chamber[27] has been built and commissioned on beamline U3C at the NSLS to extend the scope of these experiments providing the capability to be able to carry out NEXAFS studies over a wider range of pressures and temperatures. In addition, the new set-up enables the use of horizontal sample orientation thus permitting the examination of liquid surfaces and liquid/solid interfaces.

We hope that the NEXAFS results obtained from this new chamber together with other theoretical and experimental studies currently being pursued at the Centre for Molecular and Interface Engineering at Heriot-Watt University will, in due course, advance significantly our understanding of the structural chemistry of molecular surfaces and interfaces operating under realistic conditions. This will, we believe, ultimately open the way towards the use of advanced structural techniques in understanding the science underpinning industrial interfaces and processes.

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