Near edge X-ray absorption fine structure spectroscopy as a tool to probe electronic and structural properties of thin organic films and liquids

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Synchrotron-based spectroscopic techniques have contributed significantly to a better understanding of the properties of materials on the macroscopic and microscopic scale over the last decades. They can be applied to samples from a diversity of fields, including Biology, Life Sciences, Chemistry and Materials. One of these techniques is Near Edge X-Ray Absorption Fine Structure (NEXAFS) spectroscopy, revealing electronic structure and information on the orientation of adsorbed molecules. The present article describes the basics of the technique and the progress it has made over the last three decades, and summarizes some of its more recent developments and applications. This *tutorial review* article should be accessible for novices to the field from Physics, Chemistry, Biology, Materials, and the Life Sciences, interested in thin organic films and liquid systems.

1. Introduction

Electronic and structural properties are of utmost importance for a fundamental understanding of the macroscopic and microscopic behavior of materials. Surface properties play a particularly important role since they determine the interaction of an object with its environment. Basic knowledge of the structure and electronic characteristics of the surface of a material is therefore crucial for many applications, *e.g.*, in the Life Sciences, in Biology, or where advanced materials are involved. Examples of surface properties that are determined by electronic and structural characteristics are tribological behavior, wetting, and biocompatibility. Fundamental knowledge can also lead to a tailoring and tuning of these properties, which is a challenge in current interfacial science.

Tools and techniques to explore electronic and structural properties have been developed over the last century. One example is synchrotron radiation sources, which were first built in the 1940s, but have been employed as an independent tool to investigate materials since some 40 years ago.[1] Over the last three decades, they have contributed significantly to a better understanding of materials on the molecular and macroscopic scale and opened up entirely new avenues to explore matter. In the past, most synchrotron radiation research was performed in 'parasitic' mode, using the radiation that was produced as a by-product of high-energy physics experiments. In contrast to these first-generation synchrotrons, newer facilities are dedicated solely to generating synchrotron light for use as a probe in science (second and third generation facilities). Today's synchrotron sources are brilliance-optimized, *i.e.* provide a beam with a small beam cross section and a high degree of collimation, using special devices called wigglers and undulators.[1]

Many synchrotron-based techniques have been developed that allow the detailed exploration of the properties of different materials. The technique called near-edge X-ray absorption fine structure spectroscopy (NEXAFS) was devised in the 1980s, mainly in order to resolve the structure of molecules bonded to surfaces. It was particularly intended to be applied to so-called low-*Z* molecules (*Z* is the atomic number), *i.e.* mostly organic molecules that consist of 'light' atoms such as carbon, nitrogen, oxygen and fluorine.[2] Since then it has been applied to many other molecules and materials. It probes transitions from (usually) the K-edge (deepest core shell) of an atomic species into molecular orbitals of bonds to intra-molecular and extra-molecular (surface atoms) neighbors. NEXAFS is a powerful structural tool that provides information on the electronic structure and orientation of molecules or molecular fragments. The present article

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Synchrotron radiation and in particular NEXAFS spectroscopy have played a major role in Dr Hähner's research activities for more than a decade. The technique was mainly applied in connection with ultrathin organic films on a variety of different substrates.

describes the basics of this technique and compares it briefly to other in-house laboratory surface analytical tools revealing similar information. Selected examples of applications are given to demonstrate the breadth and the strength of this particular type of spectroscopy.

2. Experimental section

2.1 Properties of synchrotron radiation

Electric charges that are accelerated, *i.e.* experience a force, generate electromagnetic radiation. This fact is exploited for the generation of synchrotron radiation, where charges—usually electrons—are forced to move on a curved path. Synchrotron radiation facilities concentrate on the production of such radiation. A synchrotron radiation facility consists of a storage ring and a booster, where the charged particles are accelerated close to the speed of light before being injected into the storage ring (Fig. 1). The synchrotron booster is a roughly circular ring of magnets for focusing and bending the electron beam, and straight sections for accelerating the particles. The magnetic field is raised *synchronously* (hence the term synchrotron) with the particle energy to keep the electrons on a circular path with a constant radius. When the electrons have reached the desired relativistic energy, they are transferred to the storage ring, where the magnetic field remains constant. The electrons then orbit in the storage ring, *i.e.* a circular accelerator. Synchrotron radiation is generated in bending magnets keeping the electrons on a closed path, and in wigglers or undulators that are placed into the linear sections.[1] In the bending magnets and insertion devices the electrons are subject to acceleration and therefore emit radiation.

Synchrotron radiation obtained from the storage ring covers a wide range of the electromagnetic spectrum. The detailed frequency characteristics of the radiation depend on parameters such as the number and the energy of the stored electrons, and hence differ for the different synchrotron sources around the world. However, it provides a continuous spectrum over a wide energy range, with the energy of maximum intensity depending on the energy of the electrons.[3] The radiated flux is superior to most conventional sources by orders of magnitude. In combination with the broad spectral range it is, in fact, unmatched by any other source.

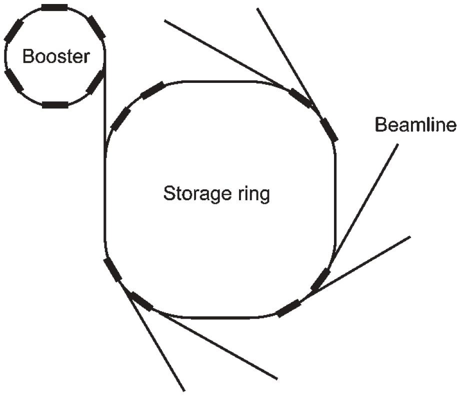

Fig. 1 Schematic of a synchrotron facility. Electrons are injected into an electron synchrotron (Booster) at a relatively low energy ($\sim$100 MeV) and accelerated to $\sim$GeV before being transferred to the storage ring.

The light is conveyed to experimental chambers through beamlines. A monochromator in the beamline helps to select a single wavelength thus providing a high-brilliance, tunable, monochromatic X-ray source for the experimentalists. In addition to its high brilliance the synchrotron light is polarized. It is (almost) linearly polarized in the plane of the storage ring for bending magnets and undulators.[3] The degree of polarization is determined by the X-ray energy and the beamline optics.

When the radiation enters the user's experimental chamber it has two properties which distinguish it from conventional X-rays created by in-house laboratory X-ray sources, and which are exploited in NEXAFS: Firstly, it is a tunable monochromatic source of X-rays and secondly, the radiation has a high degree of polarization. Depending on the machine settings circularly or linearly polarized light can be obtained.

While historically the application of synchrotron radiation is confined to samples in a vacuum, more recently techniques have been developed that also allow its application to samples in high pressure and liquid environments. This makes it a very attractive technique for the Life Sciences and biological applications.

2.2 The NEXAFS technique

Compared to other types of X-ray absorption spectroscopy, NEXAFS is a relatively young technique. It probes the absorption of electromagnetic radiation by excitation of core electrons into unoccupied bound or continuum states. The near edge X-ray absorption fine structure exhibits strong and distinctive features in the energy region just below and up to about 50 eV above the absorption edge (*e.g.* K-edge).

2.2.1 Electron- and fluorescence yield NEXAFS. During a measurement the sample is irradiated with monochromatic X-rays. The energy of the X-rays is varied around an ionization edge. The dominant process in the soft X-ray energy range (<2000 eV) is (by orders of magnitude) photoabsorption. The absorption process results in a photoelectron and a core hole. The hole is subsequently filled by an electron either radiatively by the emission of a fluorescent photon, or non-radiatively by the emission of an Auger electron (see Fig. 2). Both channels are a direct measure of the existence of a core hole created by the X-ray absorption and are therefore a measure of the absorption cross section. In

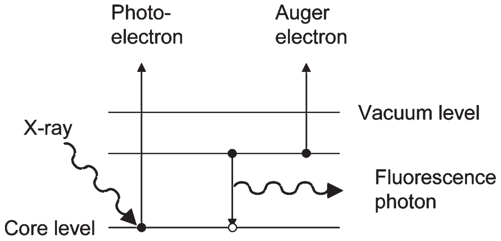

Fig. 2 Energy diagram of the photoabsorption process and the subsequent filling of the core hole by emission of a photon or an Auger electron.

principle, either channel can be detected. For electrons, a channeltron or an energy analyzer can be employed, while measuring radiative emission requires a fluorescence detector. However, the Auger electron yield is much higher than the fluorescence yield for low-Z molecules (composed of atoms such as carbon, nitrogen or oxygen).[4] In addition, electron detection provides the higher surface sensitivity and in the majority of studies published in the literature this detection scheme has been employed.

The reason for the higher surface sensitivity is the relatively low kinetic energy of the electrons and the corresponding mean free path in matter, which is typically less than 1 nm for energies between 250 eV and 600 eV.[5] Although the X-ray photons penetrate many microns deep into the sample, the electrons generated at that depth do not emerge from the sample. The inelastic scattering process leads to an electron cascade, of which only those electrons with sufficient energy to overcome the work function of the material will escape the surface. The resulting effective escape depth—and therefore the information depth of electron yield NEXAFS—has been estimated to be in the range of 5 nm for metals and semiconductors, and slightly larger for insulators due to the reduced electron–electron scattering mechanism.[2] The surface sensitivity can be further enhanced by applying a retarding voltage before the electrons enter the channeltron. By suppressing lower kinetic energy electrons, only those electrons that emerge from the outermost surface region ($\approx$3 nm) are detected. For the investigation of adsorbates on surfaces, this so-called partial electron yield (PEY) detection has a better signal-to-background ratio than total electron yield (TEY) detection, where all electrons that emerge from the surface are detected. A further option is Auger electron yield (AEY) detection, where only *elastically* scattered Auger electrons are recorded. The AEY mode requires an electron energy analyzer but provides the best surface sensitivity of the three detection techniques.

In the case of fluorescence detection, an appropriate detector has to be employed. As mentioned before, the effect for low-Z molecules is lower compared to the electron yield. As a general rule PEY, AEY and fluorescence yield (FY) all exhibit a sufficiently large signal-to-background ratio for most thin film samples.[2] The detection technique best suited to a particular sample depends on the type of sample and the optimum signal-to-noise ratio. Note that FY detection is the method of choice for studies of samples in liquid environments due to the limited mean free path of the electrons, and in the energy range below 1000 eV in gaseous environments. Its power in connection with such environments has recently been demonstrated (see 3.3 below).

2.2.2 Origin of NEXAFS spectra—information on electronic structure. An understanding of the various features observed in NEXAFS spectra is a prerequisite for the use of NEXAFS as a tool to investigate electronic structures and molecular orientations. In the following, a brief phenomenological description of these features and their origin is given.

A NEXAFS spectrum reflects the dependence of the photoabsorption cross section on the photon energy for values from just below the ionization threshold up to around 50 eV above it. In general, the energy dependence of the atomic photoabsorption cross section resembles a step function. At high energies, E, it is identical with the ionization cross section, *i.e.* proportional to $E^{-7/2}$.[6] The absorption step results from the excitation of the core electron to a continuum or quasi-continuum of final states. It is almost always obscured by transitions into Rydberg states. The origin of NEXAFS features is schematically illustrated in Fig. 3. The effective potential and corresponding K-shell spectrum for a diatomic unit are shown. Around the ionization threshold, resonant transitions are superimposed on the step-like shape. Such transitions occur if the energy of the incoming photons matches exactly the energy difference between the initial state and an unoccupied (molecular) state. Unfilled molecular orbitals are labeled as π*- or σ*-orbitals according to their symmetry.

The lowest unoccupied molecular orbital of a π-bonded diatomic subunit of a molecule is usually a π*-orbital, while σ*-orbitals are found at higher energies. The latter are most often found above the vacuum level for the neutral molecule. However, the π*-state is pulled below the ionization potential by the electron–hole Coulomb interaction.[2] Of course, a 1s → π*-transition or π*-resonance can only be observed for

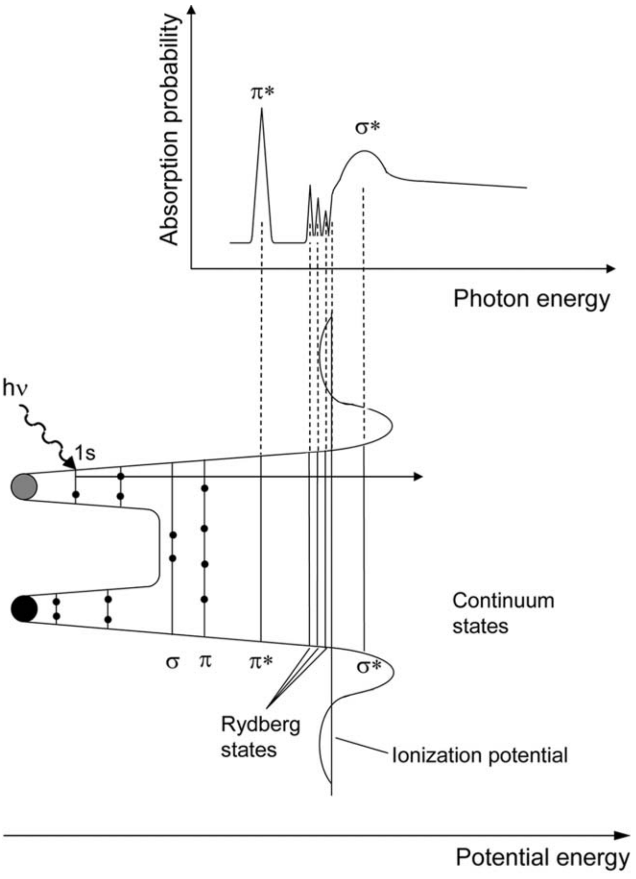

Fig. 3 Schematic potential (bottom) and corresponding NEXAFS K-shell spectrum (top) of a diatomic molecular (sub)group. In addition to Rydberg states and a continuum of empty states similar to those expected for atoms, unfilled molecular orbitals are present, which is reflected in the absorption spectrum.

molecules with π-bonding, *i.e.* double and triple bonds or aromatic systems, but not for single bonds.

The measured width of a resonance is determined by the resolution of the instrument (resulting in a Gaussian lineshape), the lifetime of the excited state (resulting in a Lorentzian lineshape), and the vibrational motion of the molecule leading to an unsymmetrical broadening. Broadening due to the lifetime of a π*-resonance is generally very small, because the final state lifetime is determined by the de-excitation of the excited electron, *i.e.* the decay of the core hole. Broader resonances that arise from transitions to orbitals of σ-symmetry can usually be found at higher energies above the threshold. Because of the large overlap of these states with the continuum, the decay probability of the electron to continuum states increases. As a rule of thumb, the higher the resonance lies in the continuum the larger is its linewidth. If the resolution is high enough the vibronic broadening can be observed.[2] The asymmetric lineshape of σ*- resonances is therefore a consequence of a combination of lifetime broadening and molecular vibration along the bond direction.

In some cases, the energy positions of σ*-resonances depend sensitively on the length of the corresponding bond. This has been exploited to estimate bond lengths from NEXAFS spectra (the so-called "bond length with a ruler" concept).[2]

Rydberg orbitals give rise to sharp but weak resonances. They are generally located between the π*-resonance and the ionization potential. In the condensed phase or for strongly chemisorbed molecules, pure Rydberg resonances are quenched because of the large spatial extent of the orbitals, which have most of their orbital density at the periphery of the molecule. In the presence of bonds to hydrogen atoms, mixing of Rydberg orbitals with hydrogen-derived antibonding orbitals of the same symmetry increases the intensity of the corresponding resonance. In particular, the C K-edge spectra of hydrocarbons and other molecules with C–H bonds show pronounced features that are best described as mixed Rydberg/valence resonances.[7,8]

Finally, NEXAFS spectra can also exhibit multi-electron features, such as so-called shake-up structures (analogous to those observed with X-ray photoelectron spectroscopy). For a more detailed discussion see ref. 2.

2.2.3 Angular dependence of the spectra—information on the molecular orientation.

In addition to the information on the electronic structure of molecules or molecular fragments, NEXAFS can also reveal information about their orientation. For this purpose, the polarization characteristics of synchrotron radiation are exploited. By taking NEXAFS measurements at two or more angles of incidence of the X-rays, the spatial orientation of an orbital can be extracted. Synchrotron radiation from a bending magnet is almost linearly polarized in the plane of the storage ring. For the sake of simplicity, we will assume that the radiation is linearly polarized in the following. The quantum mechanical description of the excitation process for a single electron in the dipole approximation leads to an equation relating the initial state, Ψ_i, and the final state, Ψ_f, to the absorption cross section, σ_x (Fermi's Golden Rule):

$$\sigma_x \propto |\langle \Psi_f | \mathbf{e}\cdot\mathbf{p} | \Psi_i \rangle|^2 \rho_f(E) \qquad (1)$$

with **e** being the unit electric field vector, **p** the dipole transition operator, and $\rho_f(\mathrm{E})$ the density of final states.[2]

Bonds and the associated molecular orbitals are highly directional and the spatial orientation of an orbital, *i.e.* the direction of maximum orbital amplitude on the excited atom, determines the angular dependence of the K-shell spectra. Therefore, the transition intensities depend on the orientation of the electric field vector relative to the orientation of the molecule. Note that σ*-orbitals have a maximum orbital amplitude along the bond axis while π*-orbitals have maximum amplitude normal to the bond direction.

In the case of linearly polarized light, the angular dependence of the matrix element of interest $|\langle \Psi_f | \mathbf{e}\cdot\mathbf{p} | \Psi_i \rangle|^2 = |\mathbf{e}\langle \Psi_f | \mathbf{p} | \Psi_i \rangle|^2$ assumes a simple form. For a 1s initial state and a directional final state orbital the matrix element $\langle \Psi_f | \mathbf{p} | \Psi_{1s} \rangle$ points in the direction of the final state orbital ***O*** and the transition intensity becomes

$$I \propto |\mathbf{e}\langle \Psi_f | \mathbf{p} | \Psi_{1s} \rangle|^2 \propto |\mathbf{eO}|^2 \propto \cos^2\delta \qquad (2)$$

with δ being the angle between the electric field vector, ***E***, and the direction of the final state orbital, ***O***. Therefore, the intensity of a resonance is largest when the electric field vector **E** lies along the direction of the final state molecular orbital (as schematically shown in Fig. 4), and vanishes when ***E*** is perpendicular to it.

Recently, techniques have been developed that allow eqn (1) to be solved numerically with high precision. These theoretical calculations reveal subtle details in NEXAFS spectra and lead to a deeper understanding of the underlying processes. The approach is based on multiple-scattering theory. The NEXAFS spectra are thought to result from the multiple-scattering of the electrons involved. Readers interested in the details are referred to the literature, *e.g.* ref. 9,10.

2.2.4 Data analysis.

To extract quantitative information on the orientation of bonds, spectra recorded at different angles of incidence have to be normalized to the flux of the incoming photons and to the step height.[2] To express the intensity of a specific resonance in terms of the angle of incidence of the

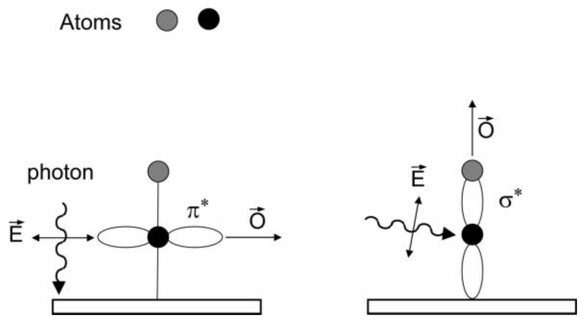

Fig. 4 Schematic representation of the origin of the angular dependence of NEXAFS resonances for a π-bonded diatomic molecule adsorbed with its molecular axis normal to the surface. As a result of the different overlap between the electric field vector, **E**, and the direction of the final state orbitals, **O**, the π*-resonance is maximized at normal incidence (left), while the σ*-resonance is maximized at grazing incidence (right).

incoming X-rays, all dipole transition moments contributing to the resonance must be taken into account. In principle, the tilt angle of a molecular orbital can then be found by determining the intensity of the corresponding resonance as a function of the angle of incidence of the photons, θ. This requires a decomposition of the angle-dependent spectra into their components by fitting the ionization step(s) and the various transitions. In the case of molecules with π-bonds, the large π^*-resonance is most suitable for a quantitative evaluation of the angular dependence because of its clear separation from the ionization step and the absence of any interfering background. In this case, the height of the resonance or its area can be analyzed as a function of the angle, θ, yielding the average tilt angle, α, of the corresponding bond (see 3.2 below).

Note that the spatial resolution of NEXAFS is determined by the spot size of the X-rays on the surface and the acceptance area of the analyzer, and is usually macroscopic, *i.e.* the information obtained on the electronic structure and the molecular orientation will normally be an average value from a macroscopic region.

2.3 Brief comparison to other techniques revealing electronic and/or structural properties

Compared to other techniques that are used to analyze the electronic and structural properties in ultrathin molecular layers, such as infrared (IR) or electron spectroscopy, NEXAFS has far less stringent requirements regarding substrates (*e.g.* IR transparency or electrical conductivity), and is also highly sensitive even to small adsorbate coverages.

Both X-ray photoelectron spectroscopy (XPS) and ultraviolet photoelectron spectroscopy (UPS) probe *occupied* states in the core region and the valence region, respectively. Electrons are detected with an electron analyzer. The spectra consist of peaks corresponding to directly excited elastically scattered electrons, and a background caused by secondary and inelastically scattered electrons.[5] In contrast, NEXAFS probes *unoccupied* states and is thus complementary to XPS and UPS. One clear advantage is that is has a very high sensitivity toward chemical changes and the chemical environment of an atom. For example, with XPS the C 1s electrons of a hydrocarbon and an aromatic compound such as benzene differ by a shift of $\sim$0.1 eV in the XPS spectrum, which is often below the resolution of the analyzer. Consequently, both signals appear in one peak, which has to be deconvoluted. Fig. 5 shows the XPS and the NEXAFS C 1s spectra for grazing and normal incidence of a benzene monolayer adsorbed on Ag(110). In contrast to the XPS spectrum, the NEXAFS spectrum of the C 1s edge shows distinct peaks (separated by several eV), which may be assigned to transitions to σ^*- and π^*-orbitals. The presence of double bonds is usually easily recognized.

This confers a very high chemical sensitivity on the technique. Note, however, that, in contrast to XPS, NEXAFS is generally not quantitative, because electrons are integrally collected, *i.e.* both primary and secondary electrons are contributing to a resonant peak.

IR and its derivatives can be employed as in-house techniques to determine the chemical composition and, in some cases, molecular conformation. IR probes the vibrational properties of molecules. The energy of the observed bands is characteristic of the bonds. While IR spectroscopy has been successfully employed to study many systems, it has certain selection rules. In order for a vibrational mode to be IR active there must be a change in the dipole moment when the molecule vibrates. It can also be difficult to obtain spectra from monomolecular or sub-monolayer films due to a poor signal-to-noise ratio. When a molecule is adsorbed on a conducting surface, only the mode components normal to the

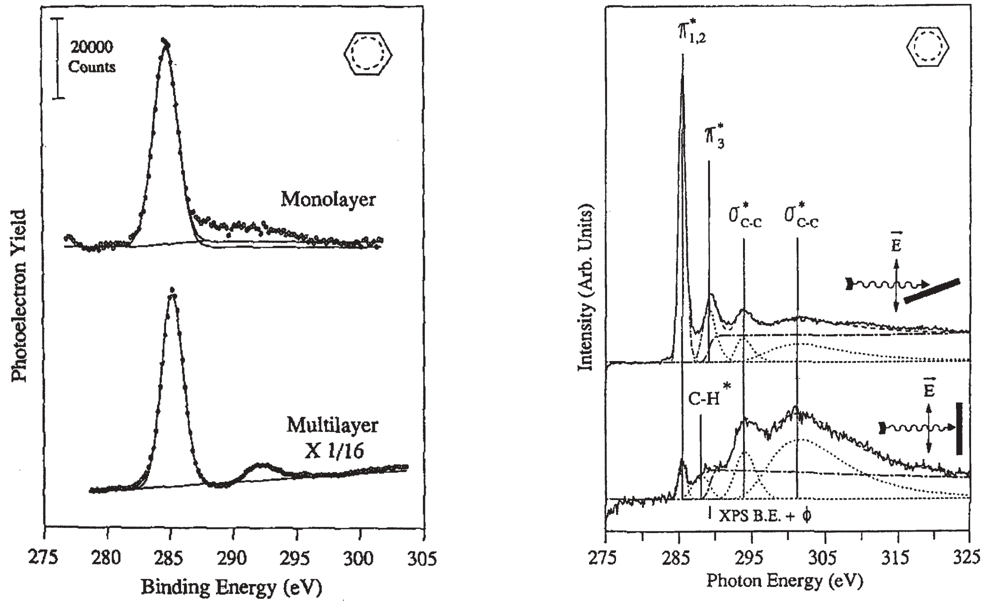

Fig. 5 XPS (left) and NEXAFS spectra (right) of a benzene monolayer adsorbed on Ag(110) recorded at the C 1s edge. The presence of double bonds is easily recognized from the NEXAFS spectrum in contrast to the XPS spectrum. (Reprinted with permission from ref. 11. Copyright (1991) Elsevier.)

surface are probed. This fact can be exploited to determine the orientation of a molecule. Though possible in principle, this is not straightforward and requires some effort.[12] In order to extract information on the molecular orientation with NEXAFS, the measurement of two spectra is required, which can usually be done within minutes. There are no selection rules and the technique has very successfully been applied to determine the molecular orientation of many different systems. The sensitivity to specific moieties and functional groups, however, is, in many cases, exceeded by IR.

3. Applications

3.1 Application to 'small' molecules

The technique was first applied to 'small' molecules such as CO and NO adsorbed on single crystal metal surfaces in the 1980s,[13] and has since then been used successfully to determine the electronic structure and molecular orientation of many different molecules on the surfaces of many different substrates.

As an example, some of the early results obtained for CO and NO on Ni(100) are shown below to demonstrate the practical aspects of the technique, *i.e.* how electronic structure information and molecular orientation can be obtained from the spectra. Fig. 6 shows the polarization dependence of spectra recorded at the C 1s and N 1s edge, respectively. The number of resonances is small and they can easily be identified. The sharp feature observable at lower energies is the π^*-resonance (A), while the σ^*-resonance (B) is much broader and appears at a higher energy. Of course, similar information can be obtained by measuring the O K-edge.

There is a clear angular dependence of the resonance intensities, which can be used to determine the orientation of the molecule relative to the surface. The π^*-resonance is strongest for normal incidence and disappears for grazing incidence while the σ^*-resonance behaves in the opposite way. This indicates that both CO and NO are standing upright on the surface. Exact determination of the resonance intensities allows a more rigorous quantitative determination of the molecular tilt angles.

Similarly, several other small molecules have been investigated on a variety of surfaces, including N_2, O_2, ethylene, benzene and several of its derivatives.[2]

3.2 Application to larger molecules and polymers

3.2.1 Larger molecules. NEXAFS spectra can reveal information about the electronic structure of molecules or adsorbates and the orientation of molecular orbitals. In the discussion of resonances presented so far, the effect of delocalization or conjugation has not been taken into account. Systems with significant bond–bond interactions experience a

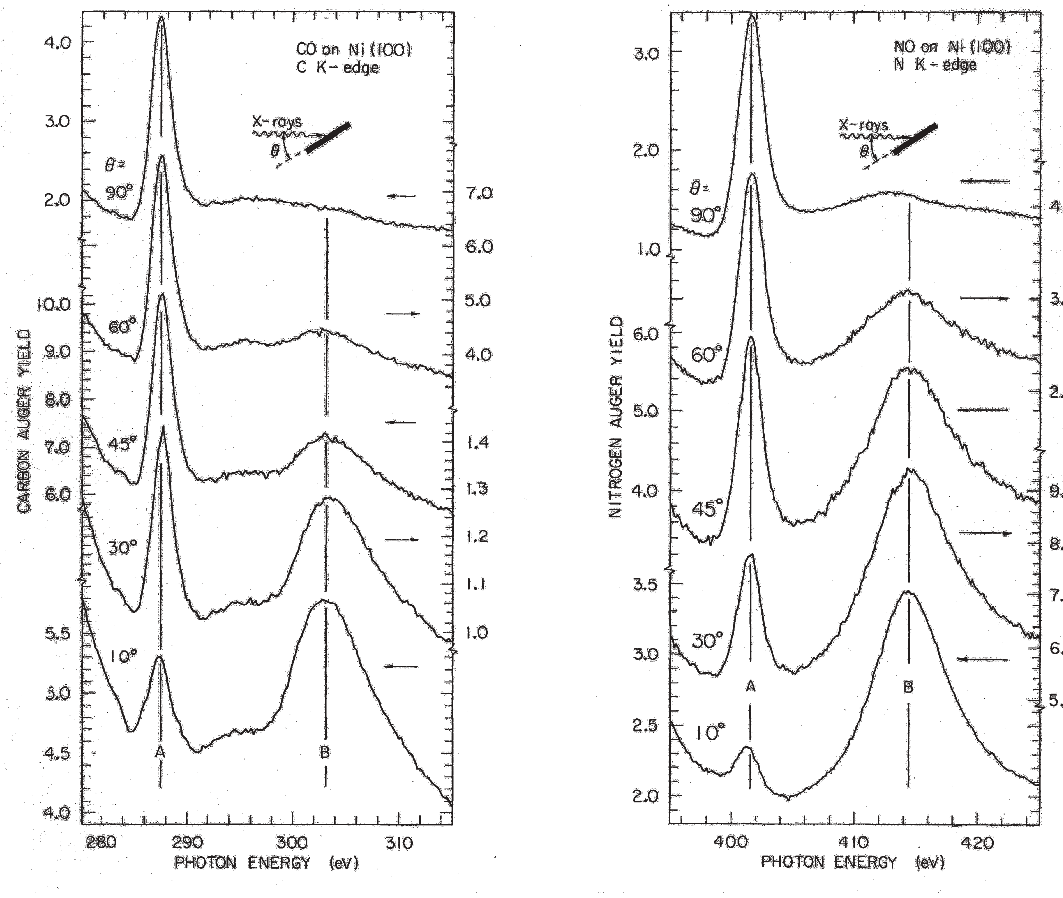

Fig. 6 Angle dependent C and N K-edge NEXAFS spectra of CO and NO adsorbed on a Ni(100) surface. (Reprinted with permission from ref. 13. Copyright (1981) American Physical Society.)

splitting of the corresponding energy levels and hence display a higher number of resonances. In addition to this final state effect, the number of resonances can also increase because of an initial state effect. Different chemical environments of the various excited atoms in a larger molecule can lead to energy shifts of the resonances.

The number of resonances increases with the number of atoms of the same element in chemically different environments in the molecule, making the assignment and evaluation for larger molecules more challenging. In general, the assignment of resonances in the NEXAFS spectra of larger molecules can be difficult.

In cases where the observed resonances arise from states that are localized in space within the molecules, the spectra can be decomposed into building blocks of diatomic subunits or ring-like structures (so-called 'building block scheme'[2]). This approach is valid if the wave function of an orbital has significant amplitude only in certain parts of the molecule, *i.e.* is localized. The entire spectrum is then considered to be a superposition of the spectra of the building blocks. Accordingly, the spectra of many molecules can be decomposed into contributions stemming from 'local' bonds. This is caused by the localized nature of the NEXAFS excitations, which probe the valence orbital final states near the core of the excited electron. Note however that there are limitations to this simple scheme, *e.g.* in molecules with a delocalized π-system.[2]

As a starting point the observed resonance positions obtained for larger molecules are compared with those of the appropriate building blocks. For molecules containing aromatic moieties, for instance, the NEXAFS spectra of benzene may serve as a clue. In a second step, interactions between antibonding orbitals have to be taken into account. The angular variation of the resonances can aid their assignment. An exact identification is in many cases prevented by the fact that resonances may overlap with each other and with the absorption step(s).

Orientation of larger molecules. The determination of the orientation of larger molecules can be challenging due to the increasing number of possible conformations. An example where a π*-resonance can be used to determine the orientation of larger conjugated molecules is the application of NEXAFS to dyes, such as methylene blue, adsorbed on mica (see Fig. 7).[14] Dyes are employed to determine the specific surface areas of layered silicates. It is usually assumed that the adsorbed molecules are lying flat on the surface. The NEXAFS results revealed, however, that the orientation is significantly different from the presumed flat lying geometry, having some implication for the determination of specific surface areas with dye molecules. Note that high quality spectra in PEY mode were obtained on a highly insulating substrate.

Films of hydrocarbons up to a chain length of around 25 methylene units are another example of larger molecules that have been successfully studied with NEXAFS. They contain a small number of different atoms and building blocks, and can be treated similarly to small molecules. Alkane chain based molecules have been studied to some extent and in some detail both experimentally and theoretically because of their fundamental importance in many biological and technical systems. Fig. 8 (left) shows the spectra of a long-chain hydrocarbon (octadecylphosphoric acid ester) adsorbed on a metal oxide (TiO_2) surface. The electronic transitions of hydrocarbons can be easily identified. The exact assignment of the molecular orbitals involved, however, has been discussed in the literature,[2,7,8] and the applicability of the building block scheme in connection with long chain hydrocarbons has been questioned. Note that the energetic positions of all resonances (C–H and C–C related) are above the ionization edge. In consequence, to determine the molecular orientation an exact knowledge of the step shape is required to extract the intensity of the resonances. A direct determination of the orientation of the chains is difficult for two reasons. Firstly, the analysis is extremely sensitive to the exact energy position of the ionization step, since the intensity associated with the transition into the C–H-orbitals is strongly influenced by this value. Secondly, an angle independent (isotropic) background has to be assumed in the fitting procedure.[2]

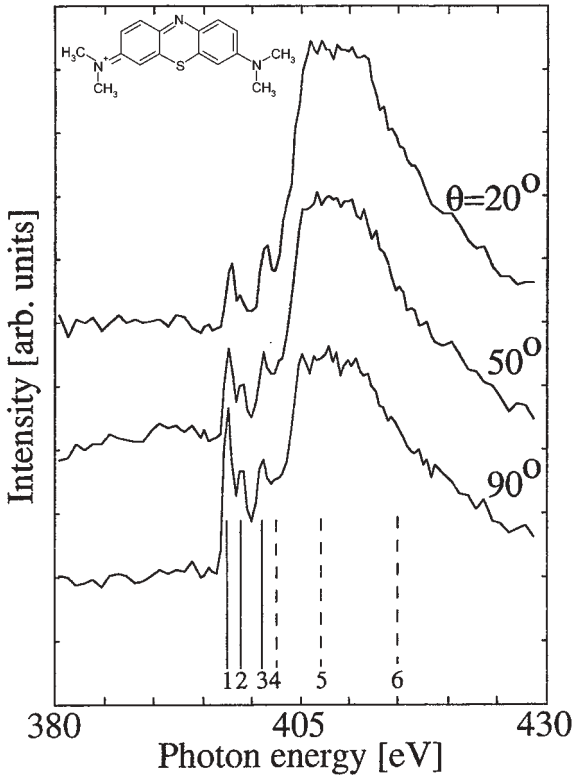

Fig. 7 Angle dependent N 1s spectra of methylene blue adsorbed on mica. The π*-resonances labeled 1 and 2 indicate a tilt angle of 70° of the molecular plane relative to the surface. (Reprinted with permission from ref. 14. Copyright (1996) American Institute of Physics.)

An alternative to this evaluation scheme of the spectra exists if the orientation of a chemically similar system is known (Fig. 8, right). Then the orientation can be obtained by comparison of the angle dependent spectra with those of the known reference system. This procedure makes use of difference spectra.[2] It does not require exact knowledge of the step function, the isotropic background, and instrumental factors. It has successfully been applied to hydrocarbon based

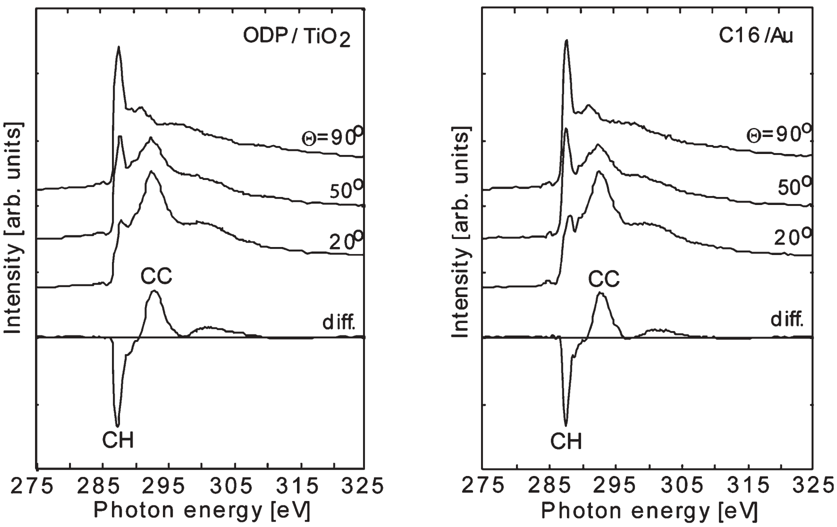

Fig. 8 C 1s spectra of an alkanephosphate film adsorbed on a metal oxide (left) and spectra of a hexadecane thiol film on gold of known orientation, serving as the reference system (right). (Reprinted with permission from ref. 15. Copyright (2002) American Chemical Society.)

species on metal oxide surfaces, *e.g.* ref. 15, as well as on insulating substrates, such as mica, *e.g.* ref. 16.

In many cases NEXAFS is employed together with other surface analytical techniques to reveal a comprehensive picture of a system under investigation. A recent example is the investigation of the interaction of water with organic surfaces, which plays an important role in many fields, for example for biosensors, medical implants, or drug-release systems. Despite their crucial significance, the molecular mechanisms underlying the wettability of hydrophilic organic surfaces are still far from being completely understood. Zubavichus and coworkers have studied the adsorption of water on self-assembled monolayers (SAMs) of 4-(4-mercaptophenyl)pyridine on gold at low temperatures under ultrahigh vacuum conditions by synchrotron radiation, X-ray photoelectron and absorption spectroscopy.[17] NEXAFS revealed that water adsorption induces a strong modification of the chemical state of the pyridine N atoms at the SAM/ice interface, indicative of strong H-bonding and partial proton transfer between water molecules and pyridine moieties. Additionally, the authors report that the initial molecular orientation within the SAM changed upon formation of an adsorbed water multilayer.

A further example is reported in ref. 18. Nelson *et al.* employed NEXAFS (amongst other techniques) to investigate the self-assembly of streptavidin onto biotinylated alkylthiolate monolayers on gold. This system has served as an important model system for protein immobilization at surfaces. They report a detailed study of the surface composition and structure of mixed SAMs containing biotinylated and diluent alkylthiolates and their use to specifically immobilize streptavidin. Films produced on gold from a range of binary mixtures of a biotinylated alkylthiol (BAT) and either a methyl-terminated thiol (mercaptohexadecane, MHD) or a C-11-oligo(ethylene glycol)-terminated (OEG) thiol in ethanol were investigated. NEXAFS characterization demonstrated that pure OEG and mixed BAT/OEG SAMs do not show significant anisotropy in C–C bond orientation. In contrast, the aliphatic segments of MHD and mixed BAT/MHD SAMs exhibit pseudo-crystalline packing. Adsorption measurements with streptavidin indicated that it binds both specifically and nonspecifically to the BAT/MHD SAMs, but purely specifically to BAT/OEG SAMs. The results obtained contribute to the clarification of the relationship between the specificity of streptavidin recognition and the surface architecture and properties of the mixed SAMs.

3.2.2 Polymers.

Polymers play an important role in many areas of modern technology. The difficulty in determining the electronic structure and orientation of polymers on a surface increases with the size of the molecule. The average orientation of the polymer will often be random due to the huge number of contributing components and their many different orientations relative to the surface. NEXAFS spectra can nevertheless be extremely useful. They can help to establish a fundamental understanding of the electronic structure, and allow, in some cases, a quantitative compositional analysis of the polymer. Huge collections of spectra recorded for many different polymers have been compiled, see *e.g.* ref. 19,20. In ref. 20 the authors report a set of NEXAFS spectra from 24 common polymers that represent a range of chemical functionalities. This enabled the creation of a database of calibrated polymer NEXAFS spectra to be used for compositional analysis. These spectra are used to demonstrate the sensitivity of NEXAFS spectroscopy to the polymer composition, illustrating the potential of NEXAFS for chemical analysis.

Chemical sensitivity of NEXAFS. A detailed understanding of the electronic structure of large molecules is often lacking. Ade and Urquhart have recently reviewed the use of NEXAFS to polymer systems.[21] They state, as a rule of thumb, that a resolution of 50 meV at the C 1s edge often reveals many subtleties in the NEXAFS spectra of polymers such as splitting of π^*-resonances and vibronic features.

Theoretical calculations can also contribute to a deeper understanding of the details of electronic spectra, but they are becoming more difficult with increasing number of atoms and can be quite challenging. A recent example of how calculations can shed some light on the details of NEXAFS spectra is given in ref. 22. It was shown that subtle differences in the resonance shape of poly(ethylene) may be attributed to intermolecular interactions and are not caused by intramolecular interactions, as had been discussed for some time.

The applicability of the building block scheme can in certain cases be extended to so-called 'fingerprint spectra' in the case of polymers. Such spectra are based on larger subunits and -groups, for example ring units or small molecular units. Molecular subgroups often show a typical fingerprint spectrum. These spectra can be useful for the identification of similar groups and local bonding environments in macromolecules. They can also help to establish the orientation of particular molecular segments. Fingerprint spectra are reported in the literature, *e.g.* ref. 19,20, and can be used as a starting point to study macromolecules. Ade and Urquhart discuss, in some detail, the usefulness of the building block scheme for polymers in their review.[21]

An example of the applicability of the fingerprint spectra was conducted with biological molecules, the aim being to predict spectra for biopolymers such as peptides and proteins from amino acids as building blocks.[23] For this purpose, the carbon spectra of several amino acid monomers were measured. It was estimated that the formation of bonds has a relatively weak influence on the NEXAFS spectra of the macromolecules so that the weighted sum of the monomer spectra should closely resemble the spectrum of the peptide.[24] It opens up the possibility to predict the NEXAFS spectra of proteins based on the constituting amino acids. Fingerprint spectra may also serve to identify regions of high concentrations of certain proteins on a surface, *i.e.* to map their spatial distribution, provided the spatial resolution of the beam is high enough.

Similarly, the C, N, and O K-edge NEXAFS spectra of the 22 most common proteinogenic α-amino acids in the zwitterionic form collected from solvent-free polycrystalline powder films in the partial electron yield mode are reported in ref. 25. Spectral features common to all amino acids, as well as distinctive fingerprints of specific subgroups of these compounds, are presented and discussed.

Polyurethanes have been at the center of interest in a review published by Urquhart *et al.*[26] X-ray spectromicroscopy was successfully applied to study the chemical composition of the polymer and a detailed quantitative analysis is presented. Results are reported outlining a methodology for quantitative speciation of polyurethane polymers. The goal was to understand the spectroscopic basis for chemical analysis of polyurethanes. To reach this goal the authors employed C 1s excitation spectra of a series of molecular and polymeric model compounds. The model species used contained the aromatic urea, aromatic urethane (carbamate), and aliphatic ether functionalities that are the main constituents of polyurethane polymers. The spectral assignments are supported by additional *ab initio* calculations of several of the model molecular compounds. The calculations also give some insight into the origin and relative intensities of characteristic spectral features. The model polymer spectra were then employed as reference standards for qualitative identification and quantitative analysis of polyurethane polymers. The chemical compositions of three polyurethane test polymers with systematic variation in urea/urethane content were measured using the spectra of model toluene diisocyanate (TDI) urea, TDI-carbamate, and poly(propylene oxide) polymers as reference standards.

More examples in which the chemical sensitivity of NEXAFS was used to characterize the electronic and/or geometric structure of polymeric materials can be found in the review by Ade and Urquhart.[21]

Orientational sensitivity of NEXAFS. With increasing molecular size, the number of molecular segments and hence their tendency to show a random (average) orientation increases dramatically. One prominent example of oriented polymer chains in a thin coating is poly(tetrafluoroethylene), which—depending on the preparation conditions—can establish a very high degree of orientational order.[27]

In general, the orientation of polymer chains containing π-bonds and conjugated structures can be determined more easily than those mainly containing σ-bonds, such as aliphatic chains. This is due to the separation of the π^*-resonances from the ionization threshold as described above. Similar to smaller molecules, π^*- and σ^*-resonances of unsaturated polymers can often be easily distinguished.

Another example of the application of NEXAFS to polymers to extract orientational information is the determination of a change in the orientation of polymer chains depending on the depth, *i.e.* surface *versus* bulk orientation. Depth sensitivity can be achieved by applying different retarding voltages in PEY mode or by comparing TEY *versus* PEY *versus* Auger yield. Again, examples for this can be found in ref.21.

3.3 Application to liquids and to molecules in liquid environments

Although wet environments play a crucial role for many biological and chemical processes, much less is known about the electronic structure of liquids and dissolved species in comparison to solids and gases. In consequence, significant efforts have been spent recently on applying the technique to the liquid state and to molecules in a liquid environment.

Electron yield is not the method of choice for samples in liquid environments because the mean free path of the electrons in a liquid is small. In contrast, photons are much less affected by the presence of the liquid. Fluorescence yield is one way to explore molecules in liquids or under high pressure conditions. In the study reported in ref. 28 a UHV compatible liquid cell sealed from the UHV components of the synchrotron was employed. X-rays can pass through the cell without significant loss of intensity and the resulting fluorescence yield can then be detected. The authors studied aqueous solutions of $K_4Fe(CN)_6$ and $K_3Fe(CN)_6$, NaCl, and haemchloride to explore the local electronic structure and, in particular, the oxidation state of the solute, namely Fe and Na. The Fe L-edge for both $K_4Fe(CN)_6$ and $K_3Fe(CN)_6$ was measured at 1 M concentration revealing differences in the electronic structure of the Fe ion. In the case of NaCl, the signal at the Na K-edge was recorded at different concentrations. The experimental setup gave reasonable signals for concentrations down to 100 mM.

The liquid itself has also been the focus of interest in recent experiments. Water, as the most prominent example, was studied in view of its hydrogen bonding properties.[29] X-ray absorption was employed to elucidate the structure in the first coordination shell of liquid water. A detailed description of the hydrogen bond network in liquid water is considered to be the key to understanding its unusual properties. X-ray absorption spectroscopy at the oxygen K-edge is sensitive to distortions of H-bonds on the H-sides (donor H-bonds) of the molecules in the condensed phases of water. The time scale for excitation is much faster than the molecular (vibrational) motions in the liquid. Therefore, this technique probes the electronic structure of a distribution of instantaneous configurations and thus allows decomposition in terms of specific H-bond situations. In ref. 29, NEXAFS data for bulk and surface ice and liquid water are presented. The results are discussed in terms of double donor, single donor, and no donor configurations corresponding to two intact donor H-bonds, one intact and one broken donor H-bond, and two broken donor H-bonds, respectively. The authors emphasize that their findings are consistent with neutron and X-ray diffraction data. A combination of the results sets a limit for possible local structure distributions in liquid water. They conclude that water, on the sub-femtosecond time scale being probed, consists mainly of structures with two strong H-bonds, one donating and one accepting, However, the results obtained show discrepancies with structures based on molecular dynamics simulations.

The technique was also employed to study the energetics of hydrogen network rearrangements in liquid water.[30] It was claimed that the temperature dependence of the oxygen K-edge fine structure can be used to determine an energy value for the rearrangement of fully coordinated (ice like) and distorted (broken donor) local hydrogen bonding configurations. The authors observed a strong temperature dependence of oxygen K-edge X-ray absorption fine structure features for super-cooled and normal liquid water droplets prepared from the break-up of a liquid microjet. Data was analysed over the temperature range from -22 °C to +15 °C. This yielded a value of 1.5 ± 0.5 kilocalories per mole for the average thermal energy required to effect an observable rearrangement between the fully coordinated ("ice-like") and distorted ("broken-donor") local hydrogen-bonding configurations. The latter were assigned to the pre-edge and post-edge features in the measured XAS spectra, respectively. The conclusions, however, led to some controversy,[31] because they contradict some of the results reported in ref. 29.

Nilsson *et al.* have very recently published a further study reiterating that X-ray absorption spectroscopy can be used as a very sensitive probe of the local bonding of water.[32] Realizing that their recent results, which indicated that the hydrogen bond network in liquid water consists mainly of water molecules with only two strong hydrogen bonds, are controversial they compared X-ray absorption spectra of liquid water recorded with five very different techniques sensitive to the local environment of the absorbing molecule, including AEY, PEY and FY. They conclude that X-ray absorption spectroscopy can be applied reliably to study the local bonding of the water molecule and thus to reveal the nature of hydrogen bonding in bulk water.

3.4 Microscopy

With synchrotron sources of ever higher brilliance being developed, the intensity obtained from small spots on the surface upon radiation can be sufficient to acquire a reasonable signal. In consequence, a mapping of electronic and structural properties with high lateral resolution has become possible.

NEXAFS microscopy can be performed in transmission (requiring a very thin sample) or in reflection mode. Since thin films on substrates are generally not transparent only the latter will be described here. For a description of experiments carried out in transmission, the reader is referred to the literature, *e.g.* ref. 33, which also describes some of the technical aspects involved with high resolution mapping, such as instrumentation and acquisition protocols.

NEXAFS microscopy is increasingly employed for the analysis of heterogeneous natural and synthetic polymeric systems, such as engineered polymers, multilayers, latexes, and bio-polymers. This is because of its ability to probe the chemical complexity of the constituents at a relevant spatial scale. Some of the problems in polymer science which require detailed chemical analysis at a submicron scale are phase segregation, determination of the morphology and interface chemistry of blends and co-polymer systems, nano-patterned structures, and self-assembly.

Spatial resolution can be achieved by focusing the X-ray beam to a small spot in connection with scanning, or by using a detector with high resolution. In the latter case, focusing of X-rays is unnecessary. Spatial resolution in the electron yield modes can be achieved by employing a photoemission electron microscope (PEEM) as detector.[34] In this case, the PEEM acts as a low-pass energy filter with a few eV bandwidth. In connection with synchrotron radiation, the technique is often abbreviated as X-PEEM. The technique uses parallel image acquisition and has the potential to reach 1 nm spatial resolution.[34] Because parallel data acquisition is employed, the method is inherently fast and allows the study of processes at video rates. Note that contrast in X-PEEM is caused by several factors, including topography and illumination, in addition to the chemical composition of the material.

A recent example of a successful application of the technique is the mapping of the molecular orientation of pentacene on a patterned surface.[35] The orientation of pentacene films on a surface patterned with SAMs of differently terminated thiols (carboxyl, methyl, aromatic) was studied. The surfactants were used to control the orientation of the pentacene, which was thermally deposited on top of them. NEXAFS spectroscopy, in connection with high resolution imaging, revealed that the different thiols induced a perpendicular alignment of the pentacene, in contrast to the bare Au surface where a parallel alignment was observed.

A further example is the investigation of the selective adsorption of proteins on polymer surfaces.[36] The authors employed X-PEEM in the C 1s, N 1s and O 1s regions to characterize a phase-segregated polystyrene/polymethylmethacrylate (PS/PMMA) polymer thin film, and mapped the adsorption of fibrinogen on the surface from buffered and unbuffered aqueous solutions at different protein concentrations (Fig. 9).

At low concentrations (<0.1 mg ml^{-1}) of the buffered solution, adsorption of fibrinogen occurred with strong preference for PS domains. In contrast, adsorption from similar concentrations of unbuffered solution showed a strong preference for the interface of the PS and PMMA domains. Increasing the solution concentration up to 1 mg ml^{-1} of both buffered and unbuffered solutions led progressively to a full surface coverage (close-packed monolayer).

The authors emphasize that the results obtained clearly demonstrate that X-PEEM with tunable soft X-rays has the sensitivity to locate and detect adsorbed proteins at the submonolayer level. Simultaneously, the spatial distribution of phases, and protein distribution relative to the phases, can be detected at the surface of an underlying microphase-separated polymer substrate.

The power of NEXAFS microscopy in comparison to other microscopies with chemical information, such as IR, NMR or Raman, is based on its ability to exceed the spatial resolution of these other techniques. Microscopy with a resolution better than 50 nm has been achieved and a resolution down to 1 nm appears realistic. In general, sensitivity to specific species or functional groups is higher using other techniques such as IR, NMR or Raman. However, if a surface is chemically heterogeneous and this heterogeneity is to be imaged, X-PEEM is, in many cases, the best method.

4. Outlook

The present article can only cover a fraction of all the work published on the topic. It is intended to give a flavor of the strength and breadth of the technique and should inspire the reader to study the literature for more detailed information on specific topics.

The technique has developed significantly since it was first established at the beginning of the 1980s. NEXAFS is particularly strong in extracting orientational information in parallel with information on electronic structure. The most recent developments—namely the application of the technique to liquids and to molecules in liquid environments, as well as the imaging of electronic and structural properties with high spatial resolution—will play a key role in future applications. The Life Sciences, Biology, and Materials Sciences will clearly benefit enormously from these developments. Concentrations of species in liquids below 1 mM appear realistic to give sufficient signal in the near future, a concentration range relevant for many biological processes. With synchrotron sources of ever higher brilliance, a mapping of the electronic and structural properties with a lateral resolution of a few nm is possible. The number of studies dealing with X-PEEM applied to thin organic films is still low. Organic samples can be quite challenging due to charging and their susceptibility to degrade when irradiated (radiation damage). Nevertheless the technique bears a great potential for applications in the Life Sciences, Medicine and Biology, and certainly has a bright future lying ahead of it. The combination of high chemical sensitivity and spatial resolution assure this type of spectroscopy an important place in the analytical tool box of the surface scientist.

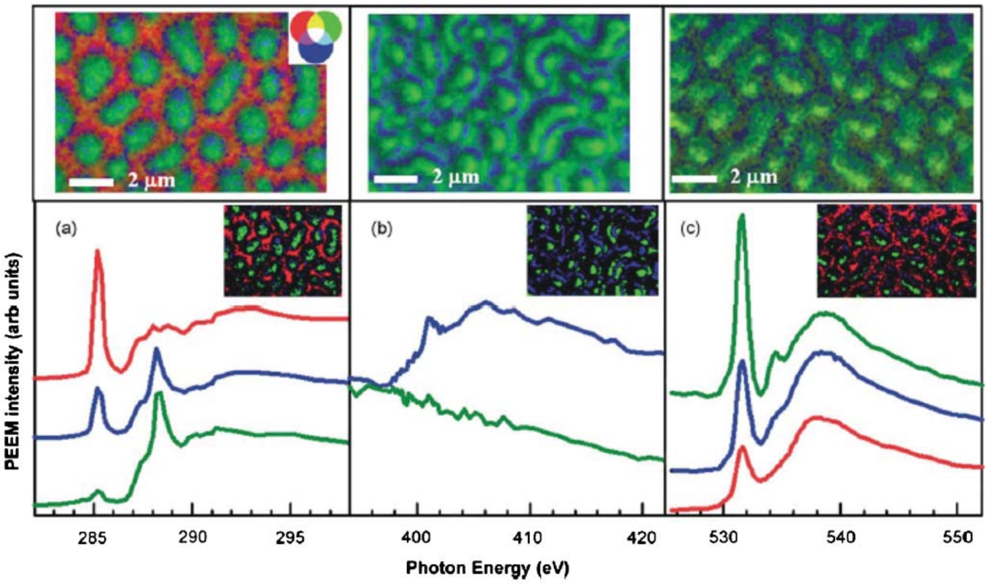

Fig. 9 (a) Color composite map (top) (red: PS; green: PMMA; blue: Fibrinogen (Fg)) and high-PS, high-PMMA and high-Fg spectra derived from a C 1s image sequence recorded for 0.05 mg ml^{-1} Fg(water) (bottom). The inset map in the spectral plot indicates the region from which the spectrum was extracted, identified by threshold masking the component maps. (b) Same for N 1s image sequence. In this case, only a two-component fit was carried out (green: PS and PMMA; blue: Fg). (c) Same for O 1s image sequence. The image sequences were collected over three different regions of the sample which is why the domain patterns differ for each core edge study. (Reprinted with permission from ref. 36. Copyright (2004) Elsevier).

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References

1 http://xdb.lbl.gov/Section2/Sec_2-2.html.

2 J. Stöhr, *NEXAFS Spectroscopy*, Springer, Berlin, 1992.

3 http://xdb.lbl.gov/Section2/Sec_2-1.html.

4 H. Winick, in *Synchrotron Radiation Research*, ed. H Winick and S Doniach, Plenum Press, New York, 1980.

5 G. Ertl and J. Küppers, *Low Energy Electrons and Surface Chemistry*, VCH, Weinheim, 1985.

6 A. S. Dawydow, *Quantenmechanik*, VEB Deutscher Verlag der Wissenschaften, Berlin, 6th edn,1981, p. 422.

7 K. Weiss, P. S. Bagus and C. Wöll, 'Rydberg transitions in X-ray absorption spectroscopy of alkanes: The importance of matrix effects', *J. Chem. Phys.*, 1999, **111**(15), 6834–6845.

8 S. G. Urquhart and R. Gillies, 'Rydberg-Valence mixing in the carbon 1s near-edge X-ray absorption fine structure spectra of gaseous alkanes', *J. Phys. Chem. A*, 2005, **109**(10), 2151–2159.

9 J. J. Rehr and R. C. Albers, 'Theoretical approaches to X-ray absorption fine structure', *Rev. Mod. Phys.*, 2000, **73**(3), 621–654.

10 B. Ravel, 'A practical introduction to multiple scattering theory', *J. lloys Compd.*, 2005, **401**, 118–126.

11 J. L. Solomon, R. J. Madix and J. Stöhr, 'Orientation and absolute coverage of benzene, aniline, and phenol on Ag(110) determined by NEXAFS and XPS', *Surf. Sci.*, 1991, **255**, 12–30.

12 D. L. Allara and R. G. Nuzzo, 'Spontaneously Organized Molecular Assemblies. 2. Quantitative Infrared Spectroscopic Determination of Equilibrium Structures of Solution-Adsorbed n-Alkanoic Acids on an Oxidized Aluminum Surface', *Langmuir*, 1985, **1**, 52–66.

13 J. Stöhr, K. Baberschke, R. Jaeger, R. Treichler and S. Brennan, 'Orientation of chemisorbed molecules from surface-absorption fine-structure measurements – CO and NO on Ni(100)', *Phys. Rev. Lett.*, 1981, **47**(5), 381–384.

14 G. Hähner, A. Marti, W. R. Caseri and N. D. Spencer, 'Orientation and Electronic Structure of Methylene Blue on Mica: A Near Edge X-Ray Absorption Fine Structure Spectroscopy Study', *J. Chem. Phys.*, 1996, **104**(19), 7749–7757.

15 G. Hähner, R. Hofer and I. Klingenfuss, 'Order and Orientation in Self-Assembled Long Chain Alkanephosphate Monolayers Adsorbed on Metal Oxide Substrates', *Langmuir*, 2001, **17**, 7047–7052.

16 G. Hähner, M. Zwahlen and W. Caseri, 'Chain Length Dependence of the Conformational Order in Self-Assembled Dialkylammonium Monolayers on Mica Studied by Soft X-Ray Absorption', *Langmuir*, 2005, **21**, 1424–1427.

17 Y. Zubavichus, M. Zharnikov, Y. J. Yang, O. Fuchs, E. Umbach, C. Heske, A. Ulman and M. Grunze, 'X-ray photoelectron spectroscopy and near-edge X-ray absorption fine structure study of water adsorption on pyridine-terminated thiolate self-assembled monolayers', *Langmuir*, 2004, **20**(25), 11022–11029.

18 K. E. Nelson, L. Gamble, L. S. Jung, M. S. Boeckl, E. Naeemi, S. L. Golledge, T. Sasaki, D. G. Castner, C. T. Campbell and P. S. Stayton, 'Surface characterization of mixed self-assembled monolayers designed for streptavidin immobilization', *Langmuir*, 2001, **17**(9), 2807–2816.

19 http://www.physics.ncsu.edu/stxm/polymerspectro/.

20 O. Dhez, H. Ade and S. G. Urquhart, 'Calibrated NEXAFS spectra of some common polymers', *J. Electron Spectrosc. Relat. Phenom.*, 2003, **128**(1), 85–96.

21 H. Ade and S. G. Urquhart, 'NEXAFS spectroscopy and microscopy of natural and synthetic polymers', in: *Chemical Applications of Synchrotron Radiation*, ed. T. K. Sham, World Scientific Publishing, Singapore, 2002.

22 A. Schöll, R. Fink, E. Umbach, G. E. Mitchell, S. G. Urquhart and H. Ade, 'Towards a detailed understanding of the NEXAFS spectra of bulk polyethylene copolymers and related alkanes', *Chem. Phys. Lett.*, 2003, **370**, 834–841.

23 J. Boese, A. Osanna, C. Jacobson and J. Kirz, 'Carbon edge XANES spectroscopy of amino acids and peptides', *J. Electron Spectrosc. Relat. Phenom.*, 1997, **85**, 9–15.

24 C. Carravetta, O. Plashkevych and H. Agren, 'A theoretical study of the near-edge X-ray absorption spectra of some larger amino acids', *J. Chem. Phys.*, 1998, **109**(4), 1456–1464.

25 Y. Zubavichus, A. Shaporenko, M. Grunze and M. Zharnikov, 'Innershell absorption spectroscopy of amino acids at all relevant absorption edges', *J. Phys. Chem. A*, 2005, **109**(32), 6998–7000.

26 S. G. Urquhart, A. P. Hitchcock, A. P. Smith, H. W. Ade, W. Lidy, E. G. Rightor and G. E. Mitchell, 'NEXAFS spectromicroscopy of polymers: overview and quantitative analysis of polyurethane polymers', *J. Electron Spectrosc. Relat. Phenom.*, 1999, **100**, 119–135Sp. Iss. SI.

27 L. J. Gamble, B. Ravel, D. A. Fischer and D. G. Castner, 'Surface structure and orientation of PTFE films determined by experimental and FEFF8-calculated NEXAFS spectra', *Langmuir*, 2002, **18**(6), 2183–2189.

28 M. Freiwald, S. Cramm, W. Eberhardt and S. Eisebitt, 'Soft X-ray absorption spectroscopy in liquid environments', *J. Electron Spectrosc. Relat. Phenom.*, 2004, **137–140**, 413–416.

29 P. Wernet, D. Nordlund, U. Bergmann, M. Cavalleri, M. Odelius, H. Ogasawara, L. Å. Näslund, T. K. Hirsch, L. Ojamäe, P. Glatzel, L. G. M. Pettersson and A. Nilsson, 'The Structure of the First Coordination Shell in Liquid Water', *Science*, 2004, **304**, 995–999.

30 J. D. Smith, C. D. Cappa, K. R. Wilson, B. M. Messer, R. C. Cohen and R. J. Saykally, 'Energetics of Hydrogen Bond Network Rearrangements in Liquid Water', *Science*, 2004, **306**, 851–853.

31 A. Nilsson, P. Wernet, D. Nordlund, U. Bergmann, M. Cavalleri, M. Odelius, H. Ogasawara, L. A. Näslund, T. K. Hirsch, P. Glatzel and L. G. M. Pettersson, Comment on 'Energetics of hydrogen bond network: Rearrangements in liquid water', *Science*, 2005, **308**, 5723; J. D. Smith, C. D. Cappa, B. M. Messer, R. C. Cohen and R. J. Saykally, Response to Comment on 'Energetics of hydrogen bond network Rearrangements in liquid water', *Science*, 2005, **308**, 5723.

32 L. A. Näslund, J. Luning, Y. Ufuktepe, H. Ogasawara, P. Wernet, U. Bergmann, L. G. M. Pettersson and A. Nilsson, 'X-ray absorption spectroscopy measurements of liquid water', *J. Phys. Chem. B*, 2005, **109**(28), 13835–13839.

33 A. P. Hitchcock, C. Morin, X. R. Zhang, T. Araki, J. Dynes, H. Stover, J. Brash, J. R. Lawrence and G. G. Leppard, 'Soft X-ray spectromicroscopy of biological and synthetic polymer systems', *J. Electron Spectrosc. Relat. Phenom.*, 2005, **144**, 259–269Sp. Iss. SI.

34 E. Bauer, 'Photoelectron microscopy', *J. Phys.: Condens. Matter*, 2001, **13**, 11391–11404.

35 Y. J. Hsu, W. S. Hu, D. H. Wei, Y. S. Wu and Y. T. Yao, 'Mapping molecular orientation of pentacene on patterned Au surface', *J. Electron Spectrosc. Relat. Phenom.*, 2005, **144**, 401–404Sp. Iss. SI.

36 C. Morin, A. P. Hitchcock, R. M. Cornelius, J. L. Brash, S. G. Urquhart, A. Scholl and A. Doran, 'Selective adsorption of protein on polymer surfaces studied by soft X-ray photoemission electron microscopy', *J. Electron Spectrosc. Relat. Phenom.*, 2004, **137–140**, 785–794Sp. Iss. SI.