

# Chemistry

## in the light

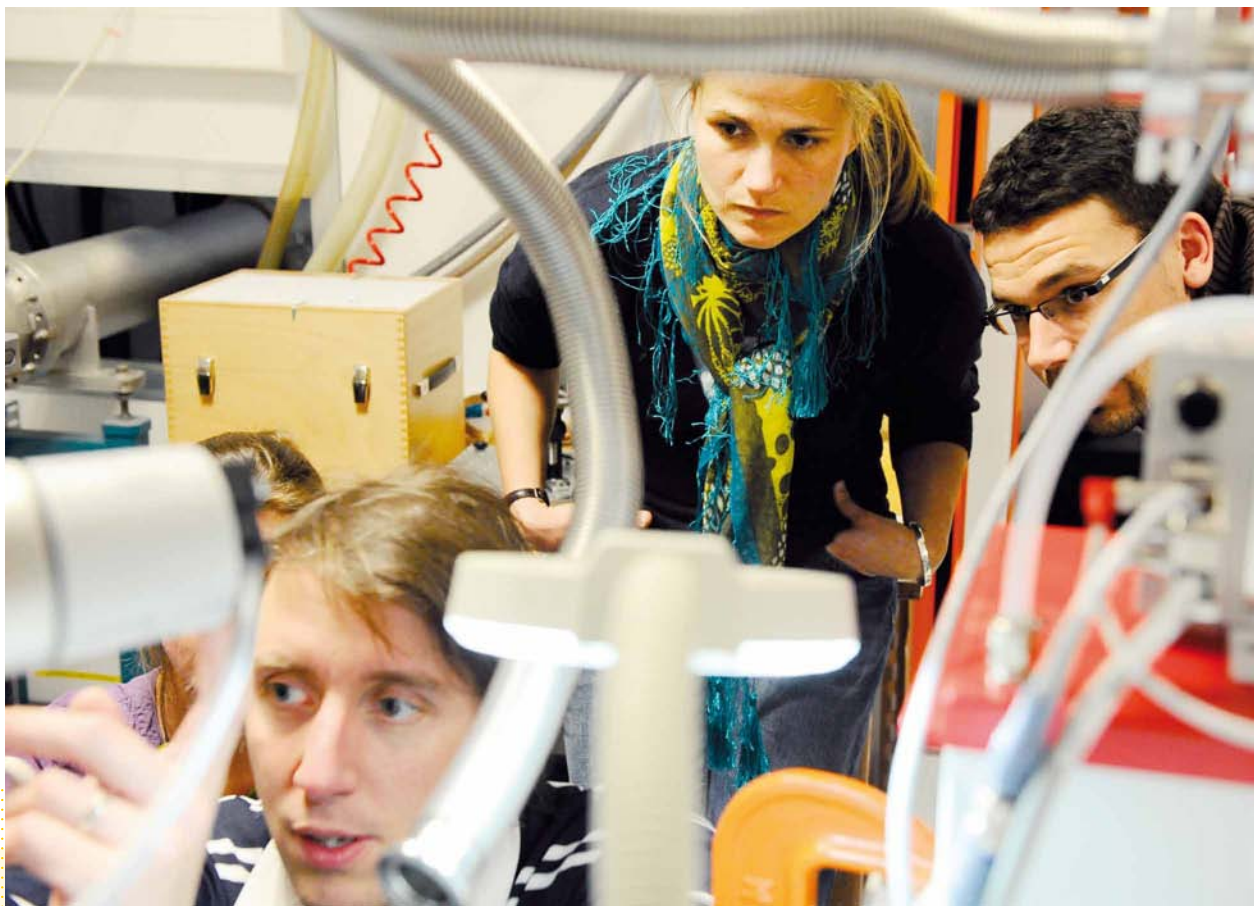


Synchrotron radiation offers unique possibilities for analysis and understanding of basic mechanisms, of reactivity and the properties of assemblies and interfaces. Based on the electronic properties of the elements, these are the basis of chemistry, a fundamental discipline in the natural sciences. Because of its omnipresence in our lives, the importance of chemistry is sometimes forgotten.

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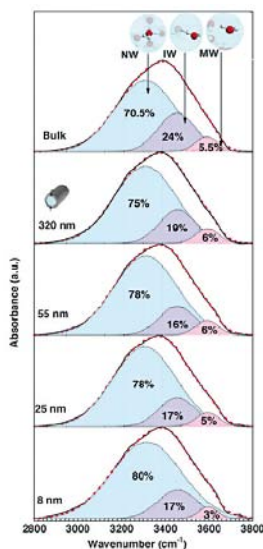
# Chemistry in the light



A part of AILES  
beamline's team

**S**ynchrotron radiation offers unique possibilities for analysis and understanding of basic mechanisms, of reactivity and the properties of assemblies and interfaces. Based on the electronic properties of the elements, these are the basis of chemistry, a fundamental discipline in the natural sciences. Because of its omnipresence in our lives, the importance of chemistry is sometimes forgotten. Current developments, considered revolutionary in terms of scientific and technological innovations, are accompanied daily by new applications that affect us all, whether involving energy, materials, health, transport or communications. These developments create new requirements in terms of fundamental knowledge, and quality control, with major economic and environmental impacts. The interfaces of chemistry with other disciplines are growing and tools for characterization and analysis should make significant contributions. Third generation synchrotrons play a major role. Other sources of very in-

tense and pulsed light will also soon contribute. Third generation synchrotrons, due to the energy range and the properties of the photon beams they deliver, will make it possible to implement all the methods for the study of light-matter interactions with ever growing accuracy, sensitivity and resolution, revealing the properties of matter so far unknown but essential to the requirements mentioned above. To compile this section, we relied on results from a selection of the SOLEIL beamlines whose research topics are most strongly related to chemistry. The articles brought together illustrate applications in diffraction, X-ray or IR absorption by elements, X-ray absorption with polarized beams, and a few applications that exploit the coherence of the X-ray beam. The variety of areas that these methodologies have a strong impact on is remarkable, ranging from biology to molecular self-assembly, CO<sub>2</sub> sequestration batteries, new heritage materials, molecular asymmetry to planetary atmospheres, or even the chemistry of nanoparticles and interfaces to that of complex, heterogeneous



**Infrared spectra in the 2800-4000 cm<sup>-1</sup> spectral range (OH stretching mode) of bulk water and in the case of water confined in 8 nm, 55 nm et 320 nm. The curves have been normalized. The infrared spectra have been measured in the ATR mode and then corrected from the variation in effective path length. The experimental data are the dotted points and the line corresponds to the global fit. The decomposition into the three Gaussian components is presented together with the percentage of their respective contribution.**

## AILES

# Water network in nanoporous material: the role of interfaces

When water is confined in a nanoscale cavity, its structural and dynamical properties are modified with respect to those of bulk water. The properties of water confined in oxides present fundamental interest as well as practical relevance but very little is known about the state of water network in these rigid cavities. Vibrational spectroscopy is a powerful tool to study water as it can provide information about: (i) intramolecular vibrations above 1000 cm<sup>-1</sup>; (ii) librational band spanning from 300 to 1000 cm<sup>-1</sup> and (iii) hindered translational bands in the 30-300 cm<sup>-1</sup> energy range. Up to now, most results have been obtained on water confined in soft matter. Using the AILES beam, we have measured the infrared spectra of water confined in porous silica for various pore sizes using the ATR (attenuated total reflection) technique. We chose silica glasses containing a well-defined network of pores with size ranging from 8 to 320 nm. The infrared spectra of water confined in glasses of various pore sizes are reported for the O-H region together with equivalent spectrum for bulk water (see figure). The three Gaussians correspond respectively to water with fully established H bonds (NW),

Intermediate (IW) and no or few established H bond (MW). The distinct differences compared to the bulk spectrum suggest that even in the large pores, the water network is significantly perturbed. The establishment of network is found to increase when the pore size decreases, indicating that confinement increases the H-bonding between neighboring water molecules. This can be related to some ordering induced by the rigid walls of the pores. Furthermore, the partial filling of pores causes a significant modification to the water network, resembling heating of the trapped liquid thus suggesting a role played by the water/air interface. Indeed, these molecules are expected to present pendant bonds as can be found in water at higher temperature. It would be worth verifying the effect of these poorly connected water molecules on the reactivity.

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For more details: S. Le Caer et al, PCCP, DOI: 10.1039/c1cp21980d

and hierarchical organizations. In terms of methodology, temporal aspects also become important, both to study reaction kinetics ( $\mu\text{s}$  ...  $\text{ms}$ ) or to elucidate ultrafast dynamics ( $\text{ps}$ ...  $\text{fs}$ ) that govern the evolution of a particular system over a longer scale.

## Three additional beamlines

In addition to those beamlines for which the results are presented in this section, three other beamlines will also contribute to the "chemistry" area by 2013. These beamlines will benefit from major technological developments in X-ray optics and in their components, sensors and energy sources themselves. These developments are themselves the result of multidisciplinary research, and their implementation has been possible only by the joint effort of groups with complementary skills. It is now possible to go further and design and build beamlines over 150 meters long, to exploit the coherence of the beam and focus it down to the size of a few nanometers on the same sample, for multimodal studies (see article on page 9).

« SOLEIL REVEALS THE INNER STRUCTURE OF MATERIALS, WHETHER ANCIENT OR RECENTLY DESIGNED BY CHEMISTS. IT IS AN UNPARALLELED TOOL TO PROBE THE ARRANGEMENT OF STRUCTURES ON AN ATOMIC SCALE, OR INVESTIGATE THEIR REACTIVITY OVER VERY SHORT TIMES. »

GILBERT CHAMBAUD, UNIVERSITY PROFESSOR, MARNE-LA-VALLÉE

With such instruments available to scientific communities, SOLEIL synchrotron will provide methods and analytical tools to understand and explore matter on this scale with performances of an order of magnitude higher than the current possibilities. Although spatial and three-dimensional imaging information on a nanoscale is obviously important in all areas of chemistry, temporal information is no less so.

To be continued on page 16...

## DESIRS

# Ion trap - Synchrotron coupling in the VUV: mass spectrometry and photoionization of biopolymers in the gas phase

An original device has just been developed, coupling a commercial ion trap mass spectrometer to the DESIRS beamline at SOLEIL, where synchrotron radiation in the VUV offers a wide tunability of the photon energy (5-40 eV), and a high photon flux ( $10^{12}$  -  $10^{13}$  photons / s / 0.1% BP). Such an important quantity of photons allows obtaining a significant signal

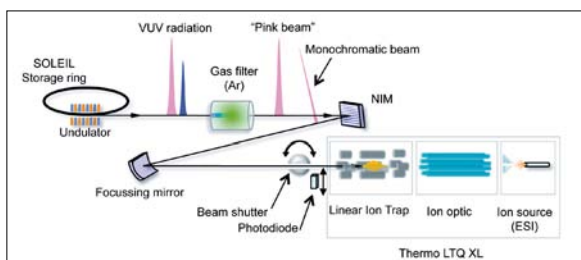
despite the low concentration of the species analyzed, such as positive or negative ions of biopolymers (a few tens of kDa) in the gas phase for which we want to understand the structure and photodynamics. The interaction between the photon beam and the stored ions takes place in a trapping volume of  $1 \times 1 \times 10 \text{ mm}^3$ , requiring a very accurate alignment, better than  $100 \mu\text{m}$ , with respect to the beamline.

Initial results on cytochrome c, a heme protein of 12 kDa, show that the device can ionize the protonated molecule in numerous charged states ( $4+$ ,  $5+$  ...  $15+$ ), previously produced by electrospray and selected in the trap. Measurement of the ions yields for the different species present inside the trap after interaction with synchrotron radiation resulting from photoionization or photodissociation as a function of the photon energy, one obtains action spectra. From those spectra, spectroscopic information, such as ionization energy, may be derived. This energy increases with the charge state: the higher the protein is protonated, the higher the energy required to remove an electron

(photoionization process).

However, in the case of cytochrome c, this increase is quite low. This could be related to the relatively flexible secondary structure of the molecule, free of disulfide bonds, readily adopting different conformations in the gas phase, leading to a decrease in the ionization potential of the protein. Thus, these results already provide indirect information on the tertiary structure of the molecule under study, even without a fragmentation step - which could be implemented later. Analytical and structural chemistry appears to be one of the areas of research for which this device is a promising tool. Being able to analyze large molecules such as proteins in the gas phase can also provide access to intramolecular relaxation mechanisms such as fragmentation, charge transfer or ionization processes. Finally, we can foresee the study of the effects of UV radiation on biological molecules, this time from a medical perspective (VUV phototherapy).

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**Schematic of the coupling of the linear ion trap with the DESIRS beamline.** The VUV radiation produced by the OPHELIE2 (HU640 type) electromagnetic undulator of the beamline is filtered by a gas filter, removing the harmonic content of the source spectrum. The 7% bandwidth so-called "pink beam" may either be used directly for flux-hungry experiments (zero<sup>th</sup> order of the monochromator) or be monochromatized by the Normal Incidence Monochromator (NIM), typical 10 meV bandwidths. A fast beam shutter is used to allow the incoming VUV light inside the trap for controlled duration.

... Continued from page 15

Such information is essential with regard to reactivity, especially in the catalysis and energy fields. SOLEIL will provide these communities with the ROCK beamline dedicated to these studies, which will link the monitoring of catalytic or electrochemical phenomena on the tens of millisecond scale through the almost simultaneous analysis of the state and speciation of several elements, on the formation or transformation of components, reactants and products. Prospects in the field of time-resolved studies at SOLEIL are increasing in the short-term with the development of "slicing" techniques to transfer some energy to the electron bunches with an intense femtosecond laser and thus generate pulses of 100-150 fs X (see "Rayon de SOLEIL" n° 20, p 11). Its major advantage will be to aim for even shorter temporal resolutions.

## Tools suited to a complex science

Chemistry is creative, situated at the interface with all other disciplines and as the basis of a science that is growing in complexity. Its connections with biology have always been strong and are now developing further through "biomimetic" and "bioinspired" innovations. There are major new directions in materials science, while supramolecular chemistry, nano-objects and their applications, organo-mineral hybrids, soft matter and soft chemistry are encouraging new and emerging fields.

This complexity in modern science, a potential for innovation and improvements, requires leading-edge platforms for analysis and characterization, of which the French Synchrotron, SOLEIL, will contribute fully with its developments and performance records.

## SIRIUS

## Semi-fluorinated alkane monolayers

Semi-fluorinated alkanes ( $C_nF_{2n+1}C_mH_{2m+1}$ ) are diblocks made of a hydrogenated, hydrophobic chain and of a fluorinated, hydrophobic and lipophobic\* chain. These molecules have numerous potential applications ranging from pharmacology to emulsions due to these antagonist properties and to the ability of fluorinated chains to act as gas carrier. Their application often depends on their self-assembling properties, which remains poorly understood. In the case of monolayer at the air/water interface (Langmuir monolayer) or transferred on solid substrates, different techniques (Optical microscopies, AFM, grazing incidence x-ray diffraction or x-ray reflectivity) led to contradictory results. Structures have been proposed which range from homogenous monolayer organized where molecules are organized on a hexagonal network to domains formation of a few ten of nanometres size and of various shape (circular, elongated, spirals ...) (ref. 1, 2). We studied this system by grazing incidence x-ray scattering at small and wide angles (GISAXS et GIXD). These techniques enable to determine the organisation of molecules (GIXD) and the supramolecular organisation (domains formation) or density

**GISAXS spectrum of the F8H18 Langmuir monolayer at the bidimensional pressure of  $5 \text{ mNm}^{-1}$ . Diffraction peaks are indexed on an hexagonal lattice of  $40.3 \text{ nm}$  parameter. Inset: AFM Image of a F8H18 monolayer deposited by spin coating on a solid substrate showing the domains organisation evidenced by GISAXS on water substrate.**



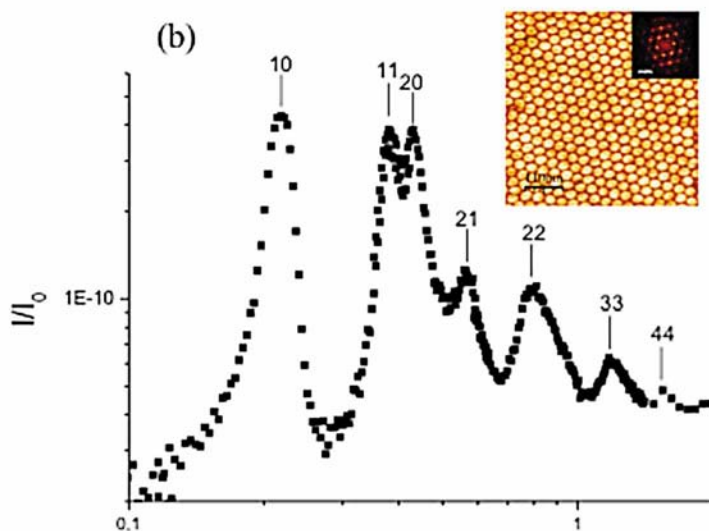
**Langmuir trough installed at the ESRF for GISAXS experiment. The same setup will be available on SIRIUS beamline.**

fluctuations (GISAXS). These experiments evidence the formation of two lattices at two different length scales. Molecules are organized on a hexagonal lattice which parameter corresponds to the fluorinated chain cross section ( $2.7 \text{ nm}^2$ ). However the extent of the order is rather small limited to a few molecules. A second network is observed with a rather larger lattice parameter varying between  $30$  to  $50 \text{ nm}$  depending on the molecular architecture (ref. 3,4,5). This second lattice is compatible with a crystalline organisation of circular domains. The weak correlation length of the molecular network is explained considering that molecules are organized within a domain without any correlation between

molecules of neighbouring domains.

The simultaneous observation of these two networks closes the controversy in the literature concerning the structure of these monolayers not only on the surface of water, but also on solid substrate.

Such simultaneous measurements at small and wide angle will be possible very soon on the same sample on liquid or solid substrate on the SIRIUS beamline at SOLEIL using the diffractometer. It may hosts dedicated sample environment and is equipped with two detector arms. This will enable to use two different detection setups.



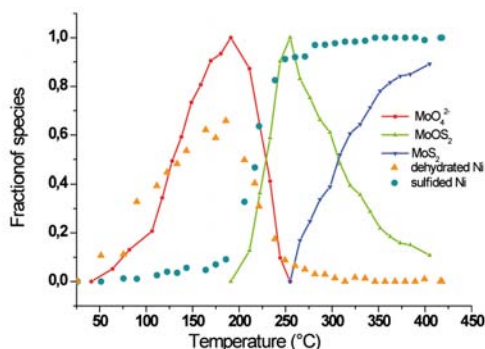
\* Molecules were provided by M.-P. Krafft (ICS, Strasbourg) and E. Filipe (IST, Lisbonne).

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## SAMBA

# Quick-EXAFS and sulfur tracking



**Figure 1 :**  
Proportions of the different phases of molybdenum and nickel present during the sulfidation of the dried NiMo catalyst.



**Figure 2 :**  
Experimental setup.

To meet environmental regulations that have become ever more stringent and obtain "clean" petroleum products, the oil industry needs to improve hydrotreating processes and especially the hydrodesulfurization process (HDS) used to remove most of the compounds producing polluting sulfur molecules after combustion in an engine (SOx). The HDS reaction requires the use of a heterogeneous bimetallic

catalyst generally consisting of a lamellar phase of molybdenum sulfide, MoS<sub>2</sub>, and a promoter (Ni or Co) "decorating" the periphery of the MoS<sub>2</sub> slabs<sup>1</sup>. To form the active species, the catalyst, initially prepared in oxide form, is sulfided under H<sub>2</sub>S gas flow. The activity and selectivity of the catalyst depend on both the good dispersion of the active phase on the support and the good decoration of the slabs by the promoter.

The improved performance of the catalyst thus requires control over the preparation of these active species and the detailed understanding of the reaction mechanisms involved.

With the new equipment on the SAMBA beamline<sup>2</sup> (Quick-EXAFS double monochromator, analysis cell<sup>3</sup>, gas distribution system, etc...) we performed for the first time the simultaneous *in situ* analysis of the K edges of nickel and molybdenum on the same sample under realistic sulfidation conditions.

We were able to determine the catalysts sulfidation processes whose preparation parameters varied. Thus, during sulfidation of the dried catalyst, two intermediate phases were identified by XAS: an isolated molybdate MoO<sub>4</sub><sup>2-</sup> that

turns into an oxysulfide {MoOS<sub>2</sub>} before being converted into MoS<sub>2</sub>. Furthermore, simultaneous characterization of the two elements Ni and Mo showed that sulfidation of the promoter begins before that of molybdenum. The sulfidation of nickel starts in competition with the dehydration of the oxide species. Then the kinetics of molybdenum and nickel sulfidation have the same conversion rate within the same temperature range. These results led us to the conclusion that only in the second stage of sulfidation, does the active MoS<sub>2</sub> phase decorated by the promoter takes place and that about 10% of the promoter forms a non-active NiS<sub>x</sub> sulfide phase.

Thus, from its genesis to its activation and the setting up its reaction conditions, each key stage in the life of the catalyst can now be characterized *in situ* under actual working conditions on the SAMBA beamline.

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## SWING

# Nanocomposite materials with controlled anisotropic reinforcement triggered by magnetic self-assembly

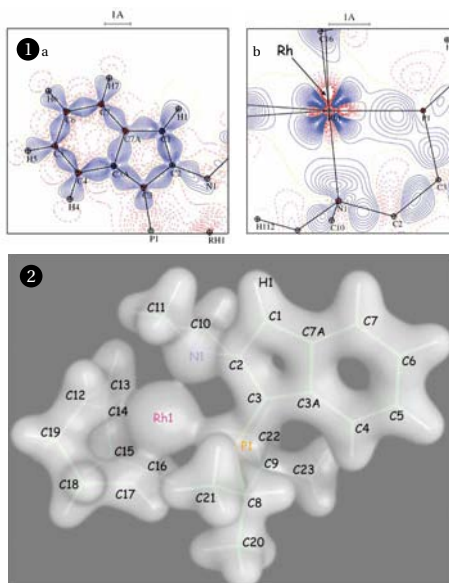
Out of the whole range of polymeric materials, nanocomposites filled with hard colloids are the prolific in industrial use due to their strong reinforcement properties. However, the understanding and description of the local contributions of both fillers and chains on the macroscopic response of the material under deformation remain to be documented. It is well-known that if the size of the reinforcing nanoparticles is decreased down to the nanometer range, the resulting increase of contact surface between fillers and polymer chains strongly enhances the

mechanical properties of the nanocomposites<sup>1</sup>. The originality of our work is to apply a moderate external magnetic field during the processing of the nanocomposites resulting in a thron of anisotropic structures. The spherical magnetic nanoparticles, or fillers, self-organise giving rise to structures ranging from quasi-isotropic to homogeneously dispersed aligned chains of nanoparticles. This was evidenced by a structural study combining Small Angle X-ray Scattering (SAXS) experiments performed on the SWING beamline, and Transmission Electron

Microscopy (TEM) experiments (Figure 1). The resulting anisotropy of the mechanical properties is spectacular. The Young modulus can reach values three times higher when the bulk material is stretched parallel counter to perpendicular to the chains. This correlates quantitatively in a linear way with the anisotropy of the microstructure. Such a quantitative correlation is a new insight into both the processing of nanocomposites and the understanding of the relationship between the local filler nanostructure and the macroscopic properties of

## CRISTAL

# Chemical bonds revealed by high resolution X-ray diffraction



**Figure 1a:** Static deformation density map (electron density remaining after subtracting the contribution of core electrons) in the aromatic rings of a rhodium complex, clearly showing the C-C bonds (contour =  $0.05 \text{ e}^-/\text{\AA}^3$ ).

**Figure 1b:** Static deformation density map around the Rh atom (contour =  $0.05 \text{ e}^-/\text{\AA}^3$ ).

**Figure 2:** Three-dimensional representation of the total (static) electron density in a rhodium complex in its zwitterionic form.

X-ray diffraction is an indispensable technique for determining the atomic structures of materials in the crystalline state. It applies equally to the study of materials containing only a few atoms per unit cell as to compounds containing several thousands (eg, macromolecules such as proteins). The single crystal diffraction technique remains the most effective for the most detailed analysis. In particular, when the crystalline quality of the sample permits, the intensities diffracted by the crystal planes up to the larger angles of incidence (i.e. large scattering vectors) can be measured, making it possible not only to go down to atomic positions and displacements but also to electron distribution on the atomic and molecular scale.

Such experiments require very precise measurement of a large number of structure factors and are usually carried out using laboratory diffractometers and X-ray sources. However, in difficult cases where the sample is very absorbant and / or perfect (extinction phenomena), synchrotron radiation (e.g. the CRISTAL beamline at SOLEIL) remains the last resort (brilliance, wave length tunability and diffraction at short wavelengths) to minimize those effects

that interfere with the accuracy of the measurements.

The contributions of core electrons and valence electrons can then be distinguished (multipolar model of the electron density), allowing modeling of the deformation of electron clouds under the effect of interatomic interactions and the formation of chemical bonds. Thus, these experiments not only give access to the arrangement of atoms in the motif or in the asymmetric unit but especially to interatomic interactions / chemical bonds and thus, more generally, the physicochemical properties of the materials under study.

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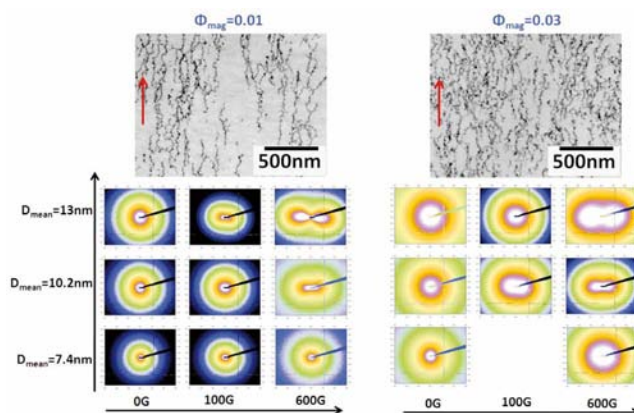
the material. From an applicative point of view, this opens the way for the design of new types of materials with the choice and optimization of the parameters governing the final material's properties (size of nanoparticles, filler content, applied field intensity...). From a fundamental point of view, such a quantitative correlation will allow to improve the understanding of current macroscopic mechanical models, by providing the relevant spatial length scale of such nanostructures.

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For more information:

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**Figure 1 :** Influence of the magnetic field on the nanoparticle's dispersion in two concentrated regimes as a function of the nanoparticle size. 2-D SAXS patterns, in reciprocal space, of the nanostructure of the films for  $\Phi_{\text{mag}}=0.01$  (left) and  $\Phi_{\text{mag}}=0.03$  (right) and for 3 nanoparticle mean diameters (from bottom to top: nanoparticles S ( $D_{\text{mean}}=7.4 \text{ nm}$ ), nanoparticles M

( $D_{\text{mean}}=10.2 \text{ nm}$ ) and nanoparticles L ( $D_{\text{mean}}=13 \text{ nm}$ ) for 3 magnetic fields (from left to right: B=0 Gauss, B=100 Gauss and B=600 Gauss). Corresponding TEM pictures of films for  $\Phi_{\text{mag}}=0.01$  and  $\Phi_{\text{mag}}=0.03$  for nanoparticles L ( $D_{\text{mean}}=13 \text{ nm}$ ) synthesised under a 600 Gauss magnetic field. The red arrow indicates the direction of the applied magnetic field.