

RECENT ADVANCES IN X-RAY ABSORPTION SPECTROSCOPY

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X-ray absorption spectroscopy (XAS) is a well established technique to obtain direct information about local atomic structure and electronic state of the absorbing ions. The elemental specificity and local sensitivity, being largely independent on the aggregation state of the system, make XAS based techniques suited in several research fields ranging from fundamental condensed matter physics, material science, biology, chemistry. Moreover the relative simplicity of the experimental set-up makes XAS particularly suited in studying materials in extreme conditions: high temperature, high pressure, high magnetic fields and ultra-diluted systems. In the recent years enormous progresses have been made in XAS, both in the experimental methods, in theory, in data analysis and interpretation methods.

The absorption spectra are usually distinguished, as a function of the information can be obtained and of the analysis methods, into two main regions: the extended (EXAFS) the near-edge (XANES) regions. At the origin of the ample popularity of EXAFS is the relative simplicity of the theoretical formula, which is well suited for intuitive and accurate experimental data refinement as a function of structural parameters (*i.e.*: coordination numbers, interatomic distances and disorder factors). The high brilliance of 3rd generation synchrotron radiation (SR) sources, coupled with the improved experimental set-up, greatly enhanced the quality of the EXAFS data pushing, for example, the metrical precision down to the *pm* and even *fm* scale. Such a great accuracy on experimental data has permitted to go beyond the simple Gaussian approximation exploiting the cumulant expansion to investigate anharmonic effects in the atomic distribution functions. This approach allowed, for example, to deeply probe the static and dynamic disorder in crystals to shed light on phenomena such as negative thermal expansion in bulk or in nanosized clusters.

From a technical point of view *micro-focus* and *time resolution* are keywords in development of SR facilities. The μ -XAS technique, available on micro focused SR beamlines is providing a unique probe for in-situ chemical analysis probing not only the elemental map in a sample (as X-ray μ -fluorescence) but also the chemical form of the ions; such information being relevant in biology, medicine, environmental science and cultural heritage. Time resolved XAS (TR-XAS) is reaching the *fs* time resolution so probing fast time scale electron transfer processes, transient states and structural dynamics, which are crucial phenomena in chemistry, biology as well in technological devices.

Due to the strong interaction between photoelectrons and atomic potentials, it is not sufficient to restrict the interpretation of the XAS data to single scattering processes; even in the EXAFS region multiple scattering (MS) effects must be taken into account. MS terms probes simultaneously the relative disposition of several ions around the absorber providing topological information through. The sensibility *n*-atoms distribution functions makes the XAS a very special probe in condensed matter complementary, for example, to X-ray and neutron scattering techniques which are intrinsically limited to pair distribution functions. Progresses have been made to quantitatively interpret the *n*-body distributions which are particularly relevant, for example, in amorphous and liquids systems in which the absence of long range order constraints allows structural degree of freedom absent in their crystalline counterparts.

Modelling and interpretation of XANES data is generally complex due to the large amount of structural and electronic information condensed in the near edge region, and to the long computation time usually required for *ab-initio* theoretical calculations. This often limits the XANES analysis to a qualitative or semi-quantitative stage. The recent evolution in XANES analysis improved the theory and developed experimental data refinement techniques. Progress in theoretical calculation include self consistent algorithms and full-potential methods to go beyond the muffin-tin (MT) approximation. Failure of MT approximation, in fact, is specially evident dealing with asymmetric local environment and in the very near edge regions of the spectra, where the low kinetic energy makes the photoelectron sensitive to the details of the electronic structure. The increasing computational velocity on dedicated workstations and/or code parallelization methods have favoured the development of packages addressing the problem of quantitative refinement of XANES data such as the *MXAN* code, for *ab-initio* data refinement as a function of structural and electronic degree of freedom, or *FitIt* which uses a reduced set of *ab-initio* models and a multidimensional interpolation algorithm to reduce the computation time.

Light elements like oxygen, carbon, nitrogen play an essential role in life, chemistry and material science. However, the application of XAS dealing with light absorbers is strongly limited by experimental constraints imposed by the low energies of the K edges involved. X-ray Raman scattering (XRS) offers a valid method to overcome these constraints. The high brilliance available on last generation SR facilities is making XRS set-up routinely available.