

DFT modelling of X-ray Raman Spectroscopy: applications to lithium model compounds

Emmanuelle de Clermont Gallerande¹, Guillaume Radtke¹, Gérald Lelong¹, Christoph Sahle²,
Delphine Cabaret¹

¹*Sorbonne Université, IMPMC, UMR 7590, Campus Pierre et Marie Curie, 4 place Jussieu, 75005 Paris, France*

²*ESRF, 71 avenue des Martyrs, 38000 Grenoble, France*

Email: emmanuelle.de_clermont_gallerande@upmc.fr

X-ray Raman Spectroscopy (XRS), is a powerful technique to study the electronic structure of compounds containing low-Z elements such as Li, B, C and O. Based on a non-resonant inelastic scattering process, it is an alternative technique for X-ray Absorption Spectroscopy (XAS) in the soft X-ray range. In addition, depending on the magnitude of the photon momentum transfer (q), non-dipole transitions can be easily induced.

We have implemented the calculation of the XRS dynamic structure factor within the module X Spectra of the suite of codes Quantum ESPRESSO. X Spectra is based on density functional theory (DFT) in a plane-wave pseudopotential reciprocal space formalism, reconstructs the all-electron wave function of the final state using the PAW method, and builds Lanczos basis set to compute the spectrum as a continued fraction.

The XRS K -edges spectra of all the elements of four lithium model compounds (LiF, Li₂O, LiBO₂, Li₂CO₃) are calculated at various value of q . The calculations are performed on supercells in the presence of an absorbing atom obtained by removing one 1s core electron from its electronic configuration. Different approaches are used to model the excited electron and the core-hole depending of the absorbing atom, such as the Full-Core Hole approach or the eXcited Core-Hole approach.

The K -edge spectra present different shapes depending on the nature and the environment of the absorbing atom and of the value of the momentum transfer. The q -dependence of the monopole, dipole and quadrupole transitions can be pointed out. By comparison between experimental and calculated spectra, the appropriate approach to solve the core-hole issue is determined and trends can be identified.

The good agreement between theoretical and experimental spectra obtained in lithium model compounds validates the single-particle approximation used for modelling K edge X-ray Raman spectra. DFT thus opens exciting opportunities to study large systems, in particular glasses or crystals with numerous inequivalent crystallographic positions, such as those found in alkaline silicates.