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An in situ simultaneous Raman-Synchrotron X-ray diffraction study at non ambient conditions: experimental setup and applications

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Raman spectroscopy can often help to overcome the well-known limitations of X-ray powder diffraction (XRPD) alone by providing additional information on samples containing light elements and/or disordered moieties and/or amorphous or liquid-like phases. The synergy between these two methodologies was exploited in many scientific studies, where the Raman and XRPD techniques have been performed *ex situ* and separately. We designed and carried out a simultaneous Raman-XRPD *in situ* experiment to fully exploit the complementarities of the techniques in investigating the kinetics of a transformation occurring in the solid state at non-ambient conditions. The experimental setup was tested on three solid-state to solid-state transformation; *i*) a phase transition of the octakis (isobutyl)octasilsesquioxane (IBUPOSS), occurring at 330K; *ii*) the solid state reaction of fluorene and tetracyanoquinodimethane (TCNQ) to form the molecular complex Fluorene:TCNQ; *iii*) the thermally-induced transformation and degradation of lamellar sterate-hydrotalcite. Monitoring the solid state transition simultaneously using the Raman and XRPD techniques allowed a full structural characterization of the initial and final phases. The complementarities of the two techniques was fully exploited since XRPD gave information on the bulk structural properties and Raman on liquid-like phases, on surface reactivity and disordered moieties. The invaluable added value of the simultaneous RAMAN/XRPD experiment is that the signals of the two coupled techniques (Raman and XRPD) are perfectly correlated in time with the reaction coordinate of the investigated transformation. This condition is almost impossible to achieve when the experiments are performed *ex situ* or in the "in situ but separately" regimes.

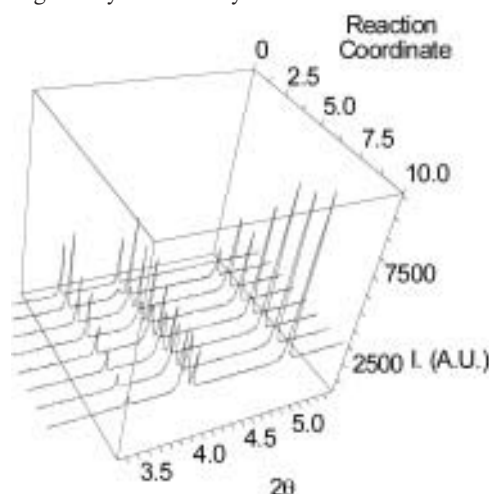
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Ab initio structure solution of powder samples by anomalous dispersion techniques

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We are developing a new method of ab initio structure solution from powder diffraction data, using f' difference Fourier techniques akin to the so-called 'MAD method'. A first paper of concept with a test sample (nickel sulphate hexahydrate) has been published recently using data from SRS 2.3[1]. By collection of data close to the absorption edge, and at a wavelength away from the absorption edge, and after appropriate scaling, it proved possible to compute precise enough differences in intensity arising from the difference of the $Ni f'$ alone. Structure solution then involved the determination of the site of this Ni atom by conventional structure solving methods, namely the Patterson method, with location of the remaining atoms by difference Fourier techniques. Most recently we have (i) recorded MAD data from powder samples of bromine-containing small molecules on SRS 9.1; data evaluation is in progress and looks promising with the structure factors having been extracted and (ii) conducted SIR phasing based on $\Delta f'$ signals with experimental MAD data from a single crystal data of a brominated oligonucleotide which are also encouraging. Overall, we will explore extension to larger organic and inorganic structures than our test cases where we believe that the scope of ab initio structure solution from powder diffraction data can be considerably extended with our approach. Moreover, our approach can be extended to proteins containing metal atoms, selenomethionine or perhaps even sulfur, and where one data set can harness the benefits of softer X-rays i.e. thus spreading out the pattern but also increasing the sample scattering efficiency, which varies as λ^2 . Especially exciting would be extending to those smallest crystal samples of proteins, ie which would otherwise be outside the range of X-ray data collection from a protein single microcrystal. In effect, in the protein powder case the sample volume is not restricted. The various experimental avenues and optimizations are quite numerous and will be investigated systematically.



[1] JR Helliwell, M Helliwell & R H Jones, *Acta Cryst.* (2005). A61, 568-574.