

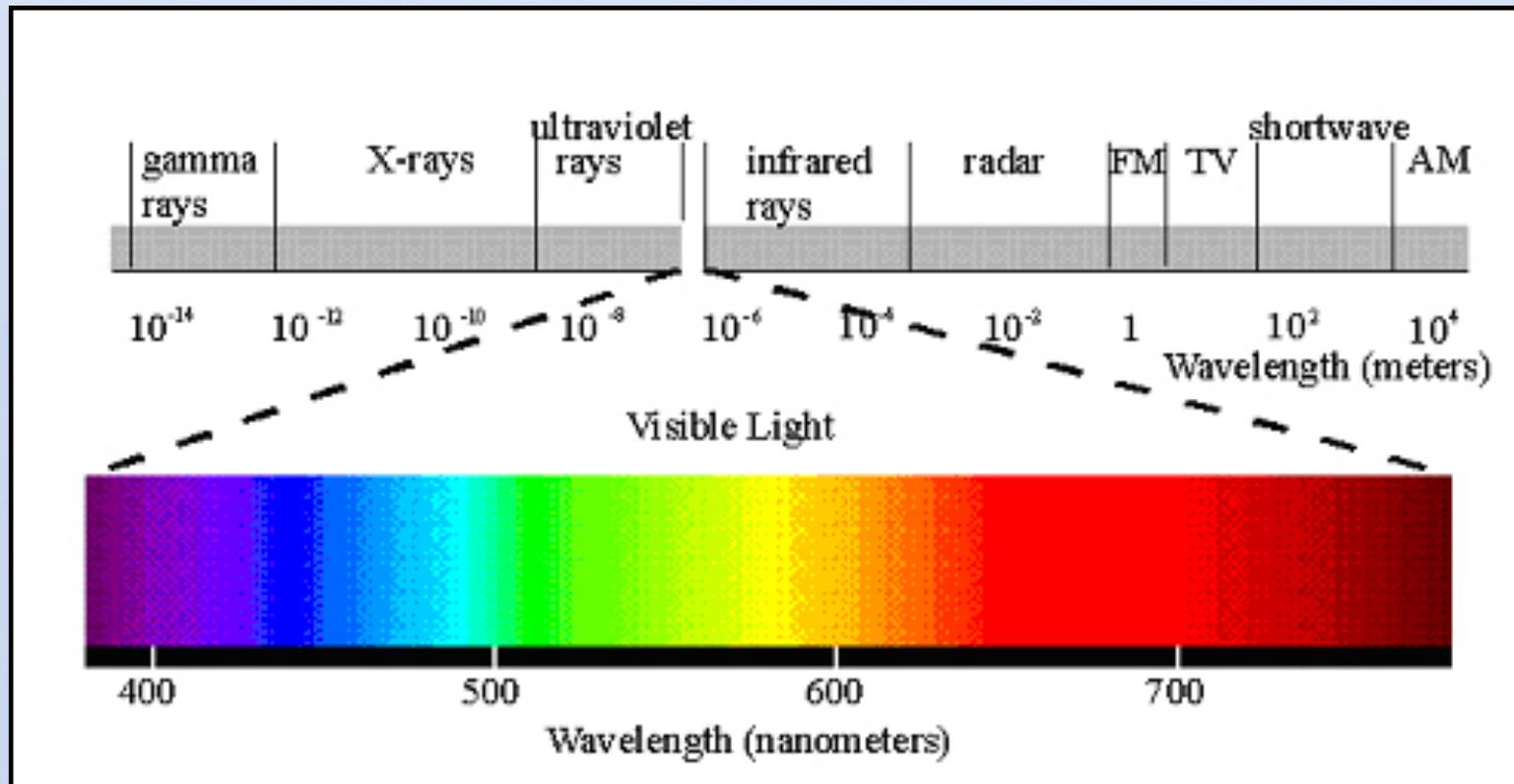
PDS - V 2012:
POWDER DIFFRACTION SCHOOL VILLIGEN
Structure and Microstructure

27-29 November 2012 *Paul Scherrer Institut*

Combined spectroscopy and powder diffraction

Phil Pattison, EPFL & SNBL

Combined **spectroscopy** and **powder diffraction**



Combined **spectroscopy** and powder diffraction

- **Visible / UV spectroscopy**

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- **X-ray absorption spectroscopy (EXAFS & XANES)**

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- **Visible / UV spectroscopy**
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- **Raman spectroscopy**

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- **IR spectroscopy**
- **Raman spectroscopy**
- **NMR spectroscopy**

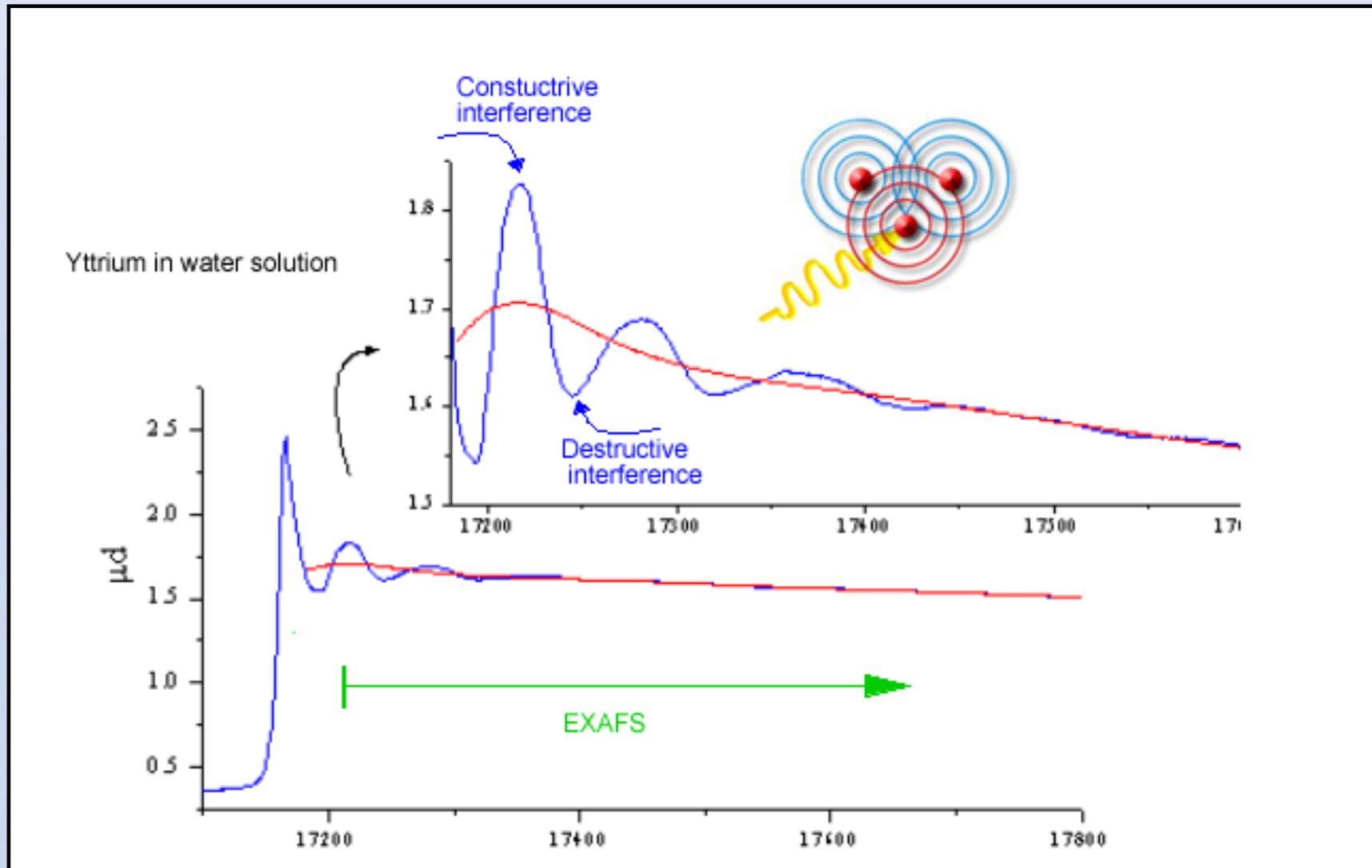
Combined **spectroscopy** and powder diffraction

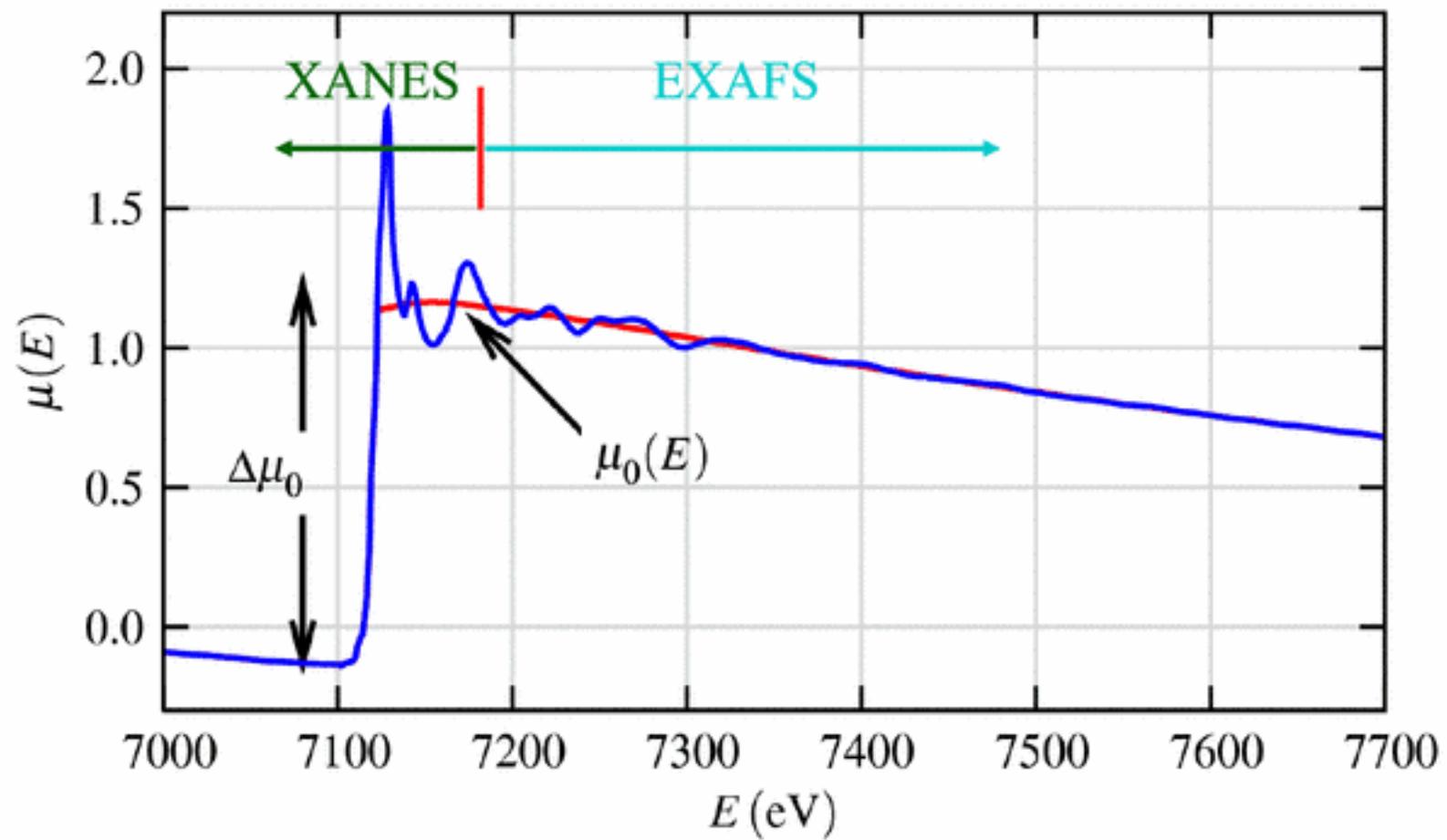
- **Visible / UV spectroscopy**
- **X-ray absorption spectroscopy (EXAFS & XANES)**
- **IR spectroscopy**
- **Raman spectroscopy**
- **NMR spectroscopy**
- **Neutron spectroscopy**

Combined **spectroscopy** and powder diffraction

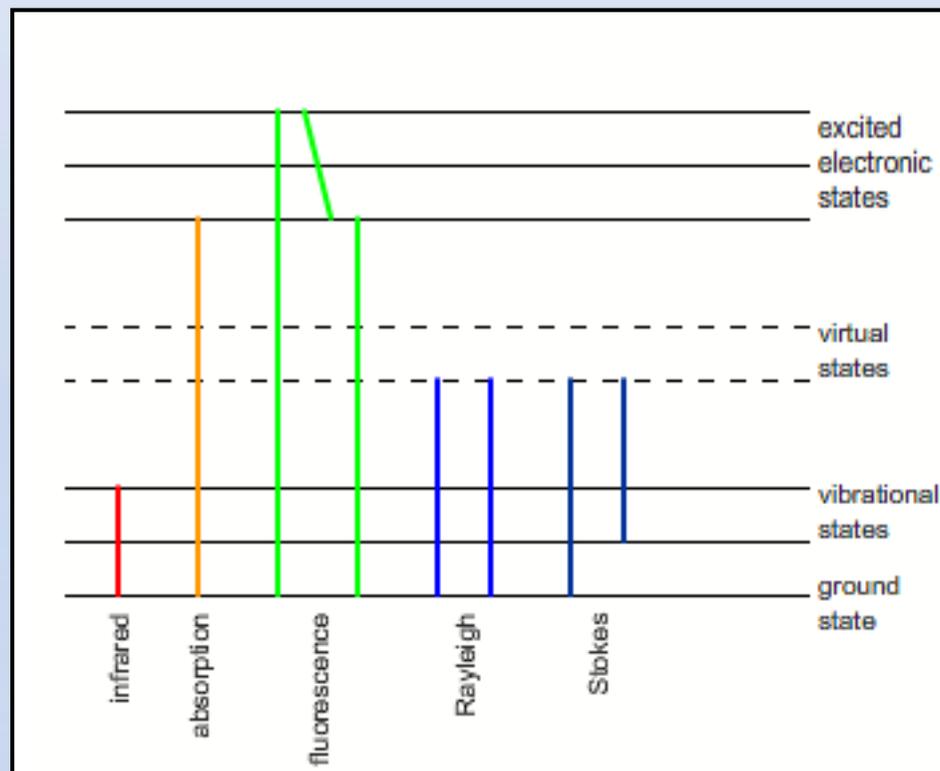
- **Visible / UV spectroscopy**
- **X-ray absorption spectroscopy (EXAFS & XANES)**
- **IR spectroscopy**
- **Raman spectroscopy**
- **NMR spectroscopy**
- **Neutron spectroscopy**
- **Mass spectroscopy**

EXAFS – Extended X-ray Absorption Fine Structure

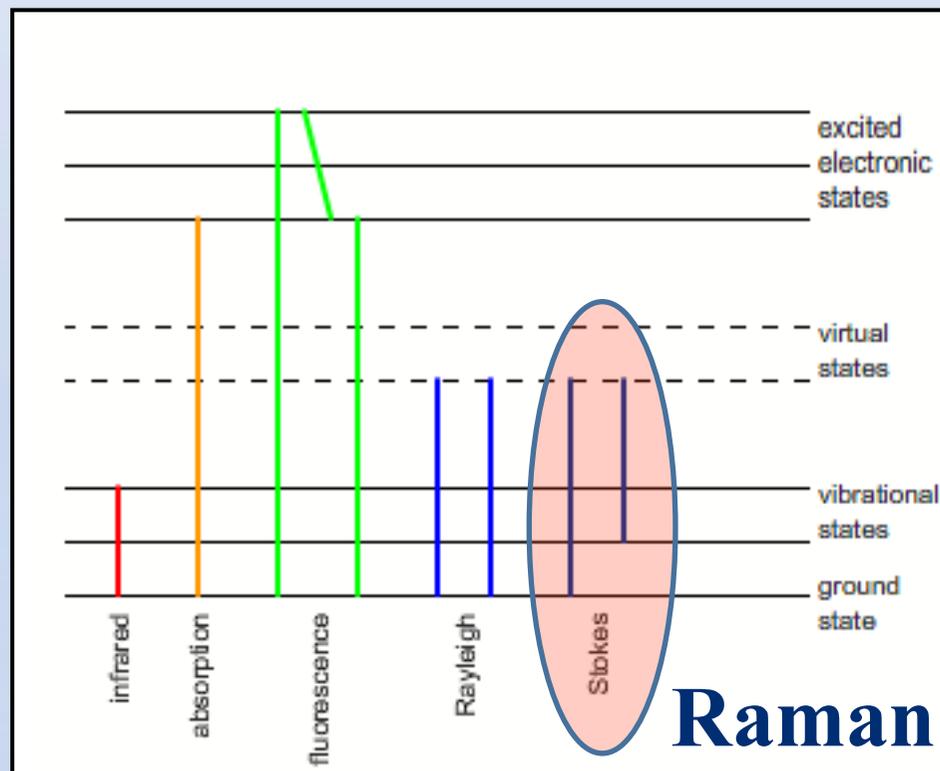


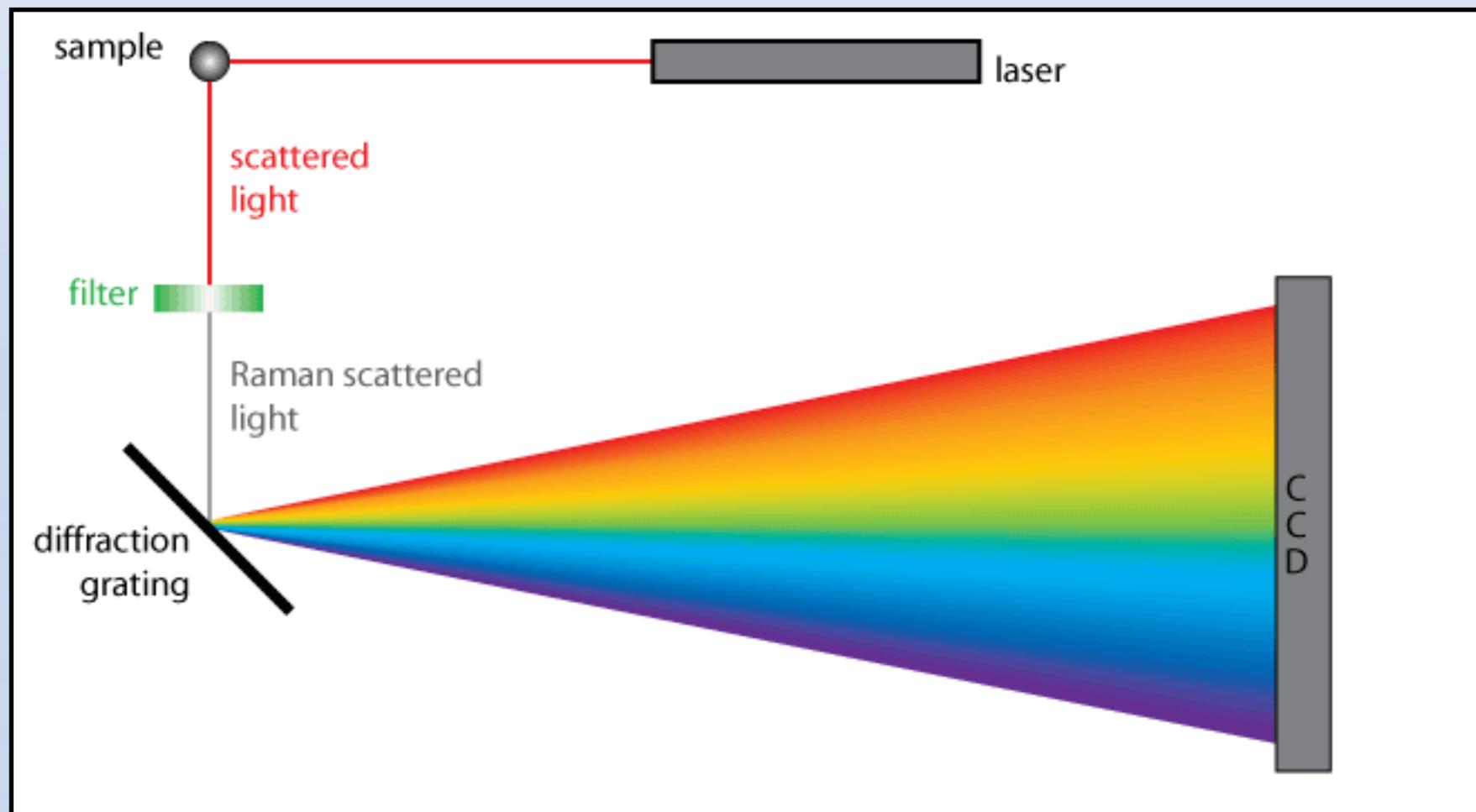


Spectroscopic techniques



Spectroscopic techniques





Raman Spectroscopy: Summary

1. Raman is a vibrational spectroscopy akin to IR
 - Good for fingerprinting, probing molecular symmetry
2. Scattering-based, not transmission/reflection/absorption
 - No need for fancy sample preparation...gas, liquid, or solid
3. You need to pick excitation energy (laser line)
 - 785 nm: Fluorescence less probable; Lower Raman signal
 - 514 nm: Fluorescence more probable;
Resonance more likely; Higher signal

Journal of Pharmaceutical and Biomedical Analysis 49 (2009) 18–25



ELSEVIER

Contents lists available at ScienceDirect

Journal of Pharmaceutical and Biomedical Analysis

journal homepage: www.elsevier.com/locate/jpba

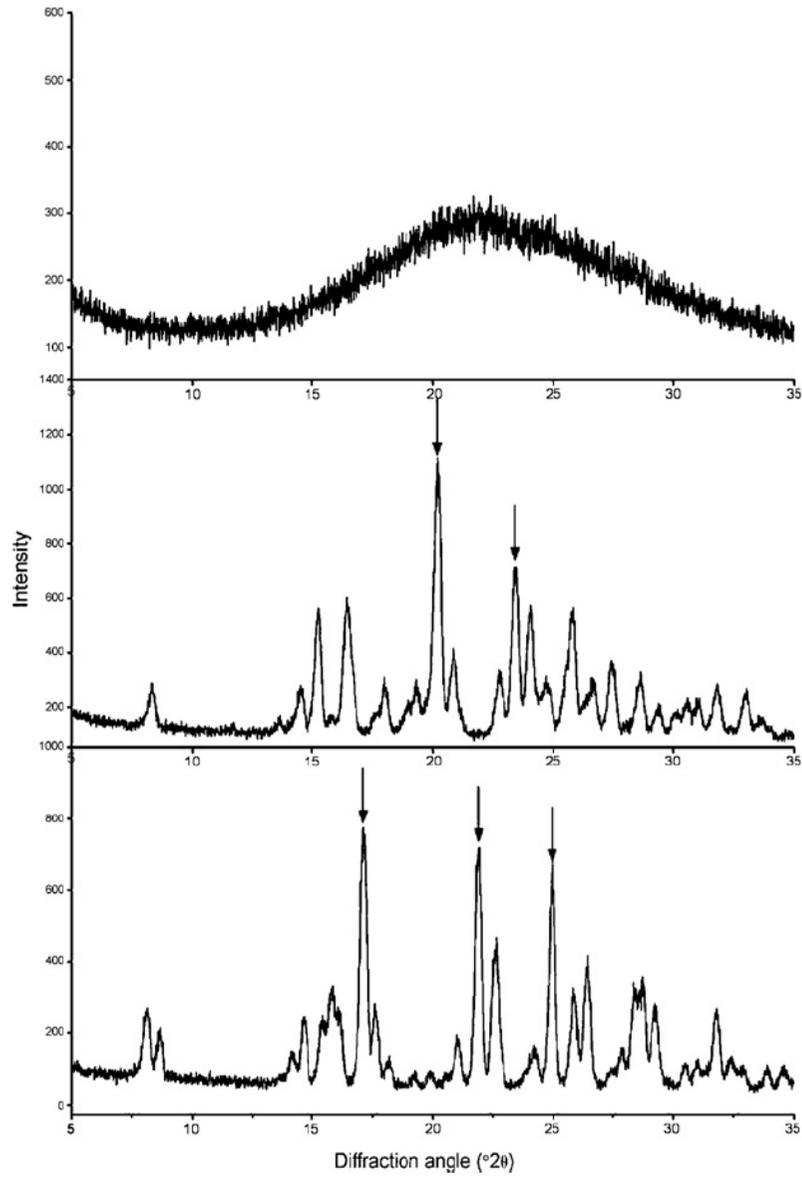


Quantitative solid-state analysis of three solid forms of ranitidine hydrochloride in ternary mixtures using Raman spectroscopy and X-ray powder diffraction

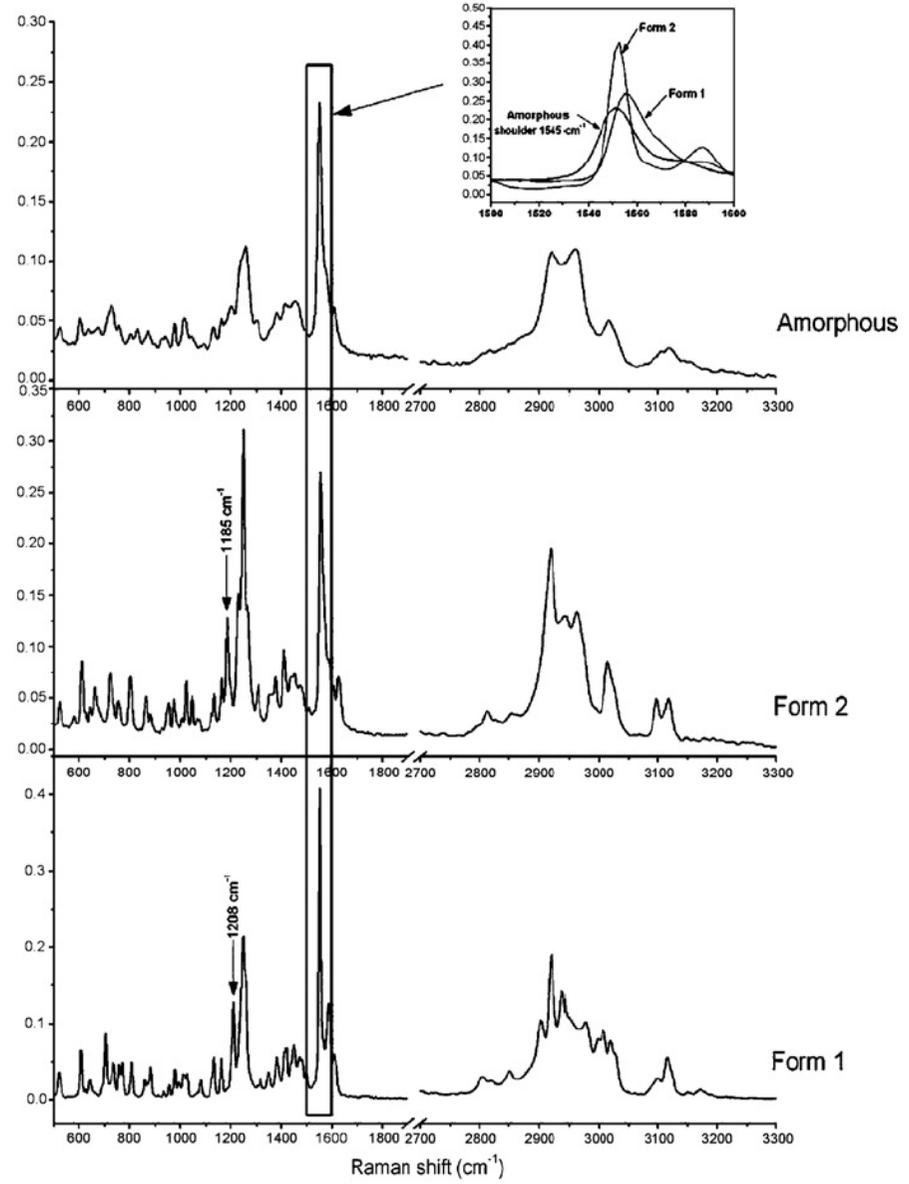
Norman Chieng, Sönke Rehder, Dorothy Saville, Thomas Rades, Jaakko Aaltonen*

School of Pharmacy, University of Otago, Dunedin, New Zealand

XRPD



Raman spectra



XRPD provides information about the crystal packing and is known as the 'gold standard' technique used in the study of polymorphism. However, although providing mostly intramolecular information, Raman spectroscopy may have advantages over XRPD due to its better accuracy and precision, ability to perform on-line monitoring, higher throughput and a lower cost.

Anal. Chem. 2009, 81, 6096–6106

Combined X-ray Diffraction and Raman Identification of Synthetic Organic Pigments in Works of Art: From Powder Samples to Artists' Paints

L. B. Brostoff,^{*,†,||} S. A. Centeno,^{*,‡} P. Ropret,^{§,||} P. Bythrow,^{||} and F. Pottier^{||}

Preservation Research and Testing Division, Preservation Directorate, The Library of Congress, 101 Independence Avenue SE, Washington, D.C. 20540, The Metropolitan Museum of Art, 1000 Fifth Avenue, New York, New York 10028, Institute for the Protection of the Cultural Heritage of Slovenia, Restoration Center, Poljanska 40, 1000 Ljubljana, Slovenia, and Museum Conservation Institute, Smithsonian Institution, 4210 Silver Hill Road, Suitland, Maryland 20746

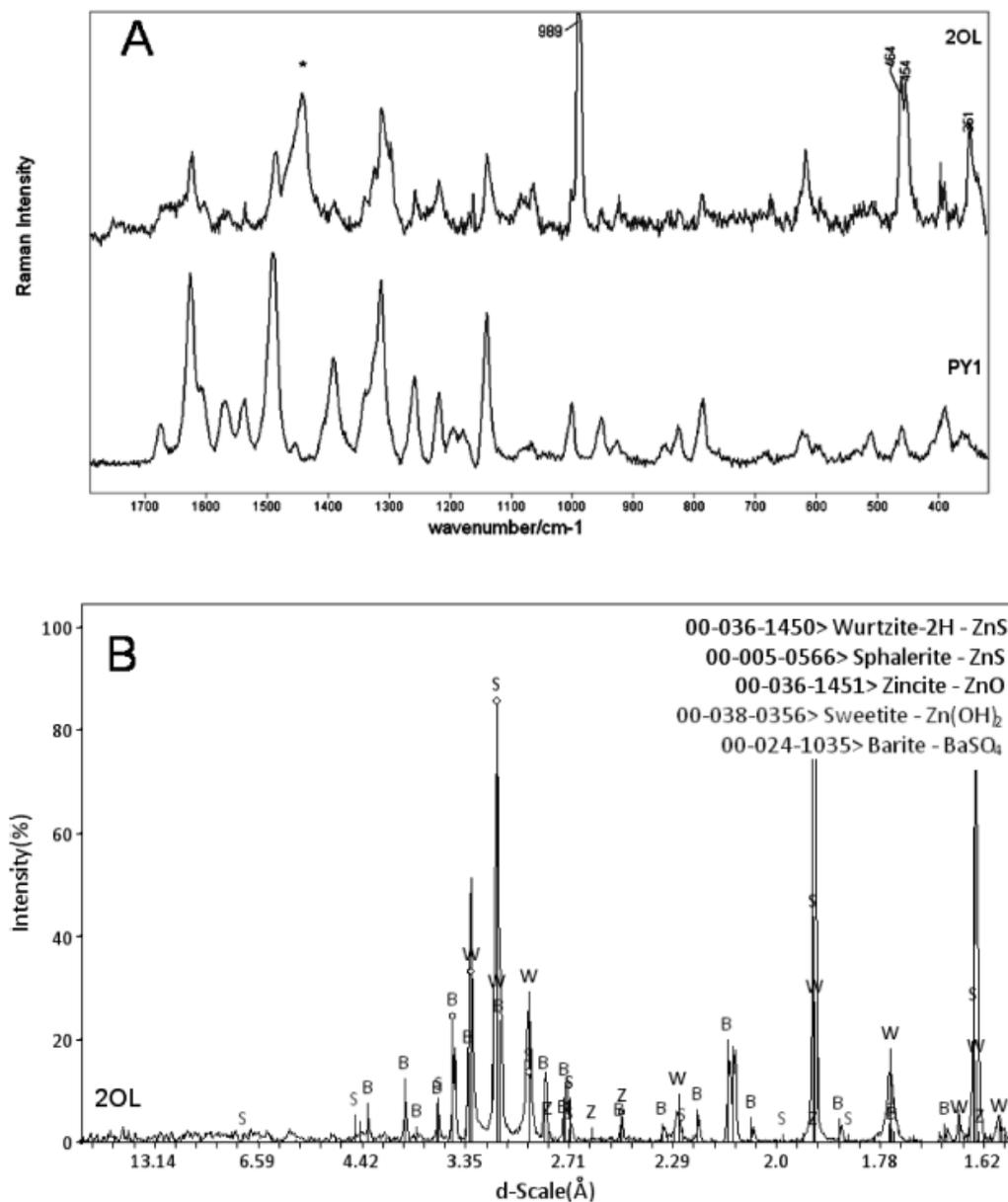


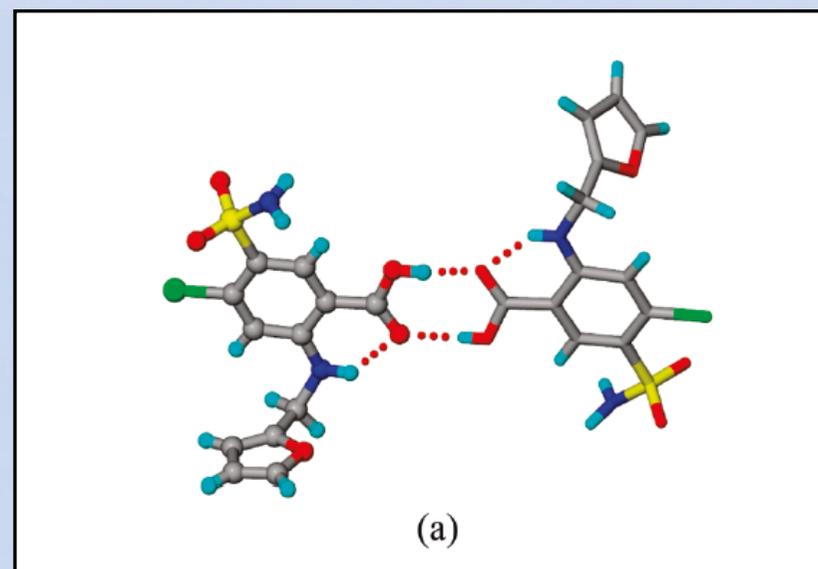
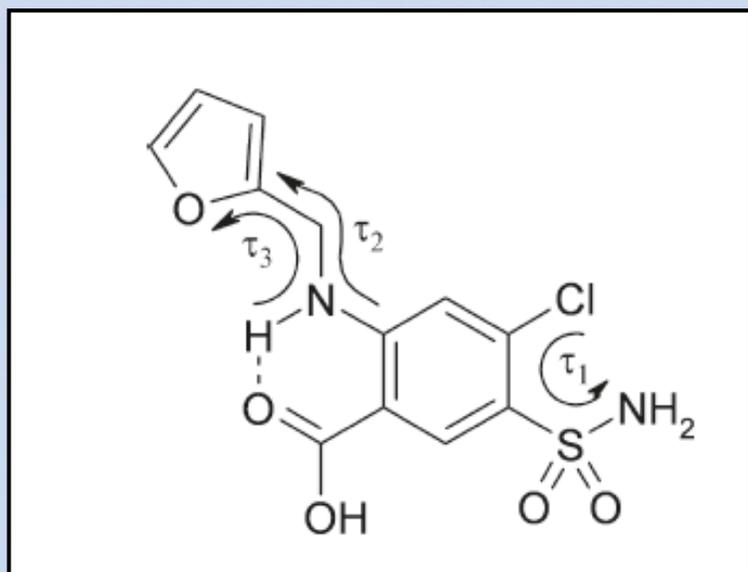
Figure 4. (A) Raman spectra of the oil bound sample 2OL (Lukas (Studio) Brillantgelb hell, top) and of a PY 1 reference sample (SunChemicals, bottom). Main bands are due to the extenders BaSO₄ (ca. 989 cm⁻¹, shown out of range, 464 and 454 cm⁻¹) and ZnS (ca. 351 cm⁻¹) indicated. The band at ca. 1440 cm⁻¹, marked by an asterisk, may arise from CH₂ deformations of the oil binder; λ₀ = 785 nm. (B) μXRD pattern detail (Cr Kα radiation) of paint sample 2OL, after background subtraction, with ICDD pattern matches shown in vertical bars (barite peaks marked with "B"; zincite peaks marked with "Z"; sweetite peaks marked with "S"; wurtzite peaks marked with "W"; sphalerite peaks marked with "S").

DOI: 10.1021/cg100098z

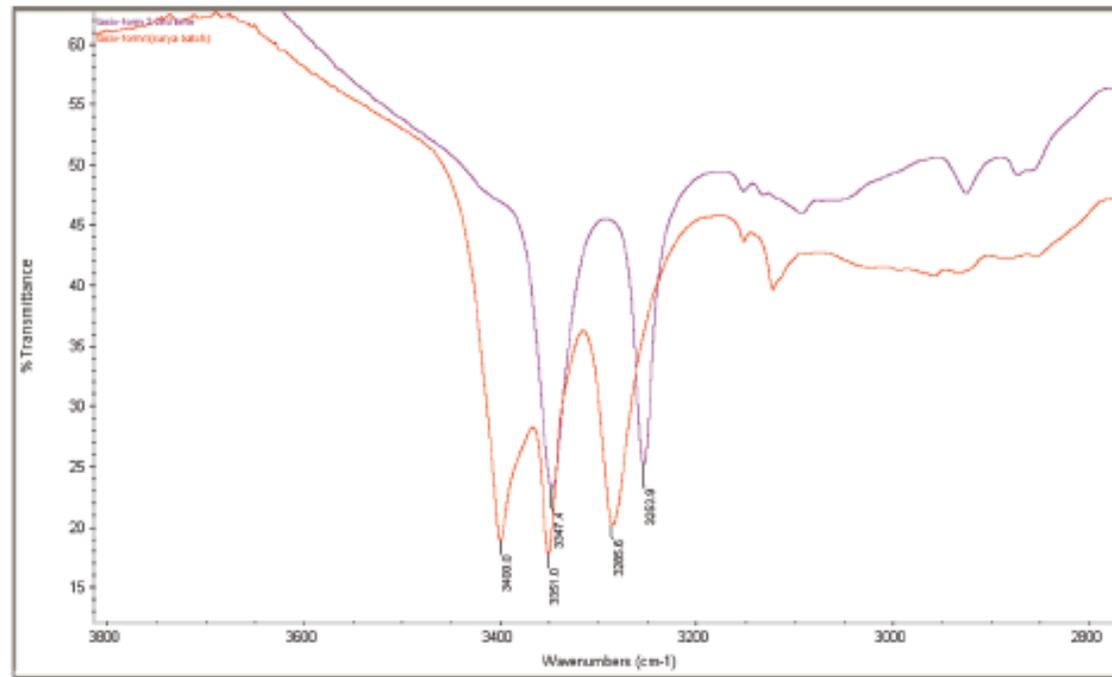
Conformational and Synthron Polymorphism in Furosemide (Lasix)

N. Jagadeesh Babu, Suryanarayan Cherukuvada, Ranjit Thakuria, and Ashwini Nangia*

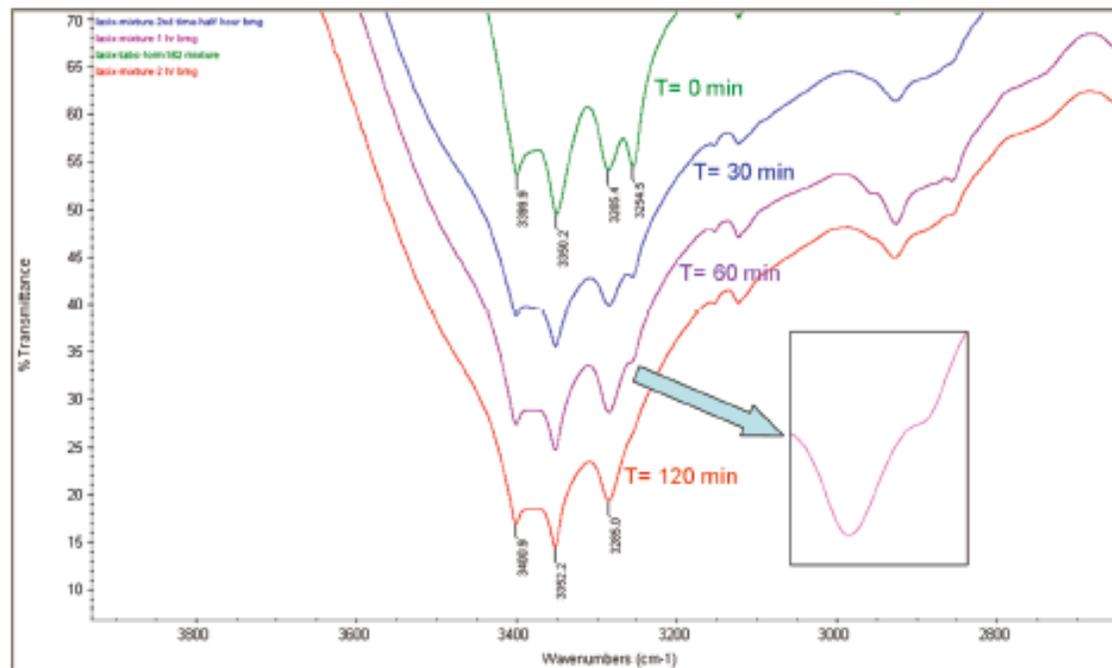
*School of Chemistry, University of Hyderabad, Prof. C. R. Rao Road, Gachibowli, Central University
P.O., Hyderabad 500 046, India*



Phase changes were characterized by X-ray powder diffraction, IR, and Raman spectroscopy. Mechanical grinding of pure furosemide forms 1 or 2 in separate experiments showed no phase conversion. However, when a polymorphic mixture of forms was subjected to grinding in a mortar-pestle phase conversion occurred readily to give form 1 within 1 h.

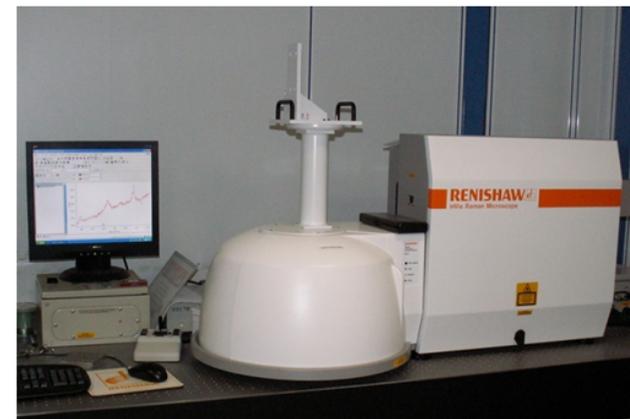
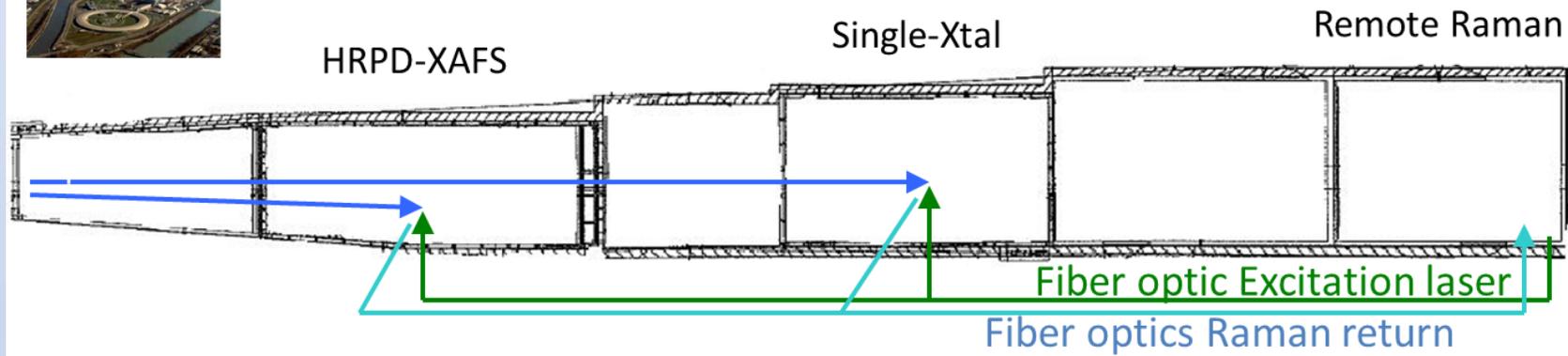


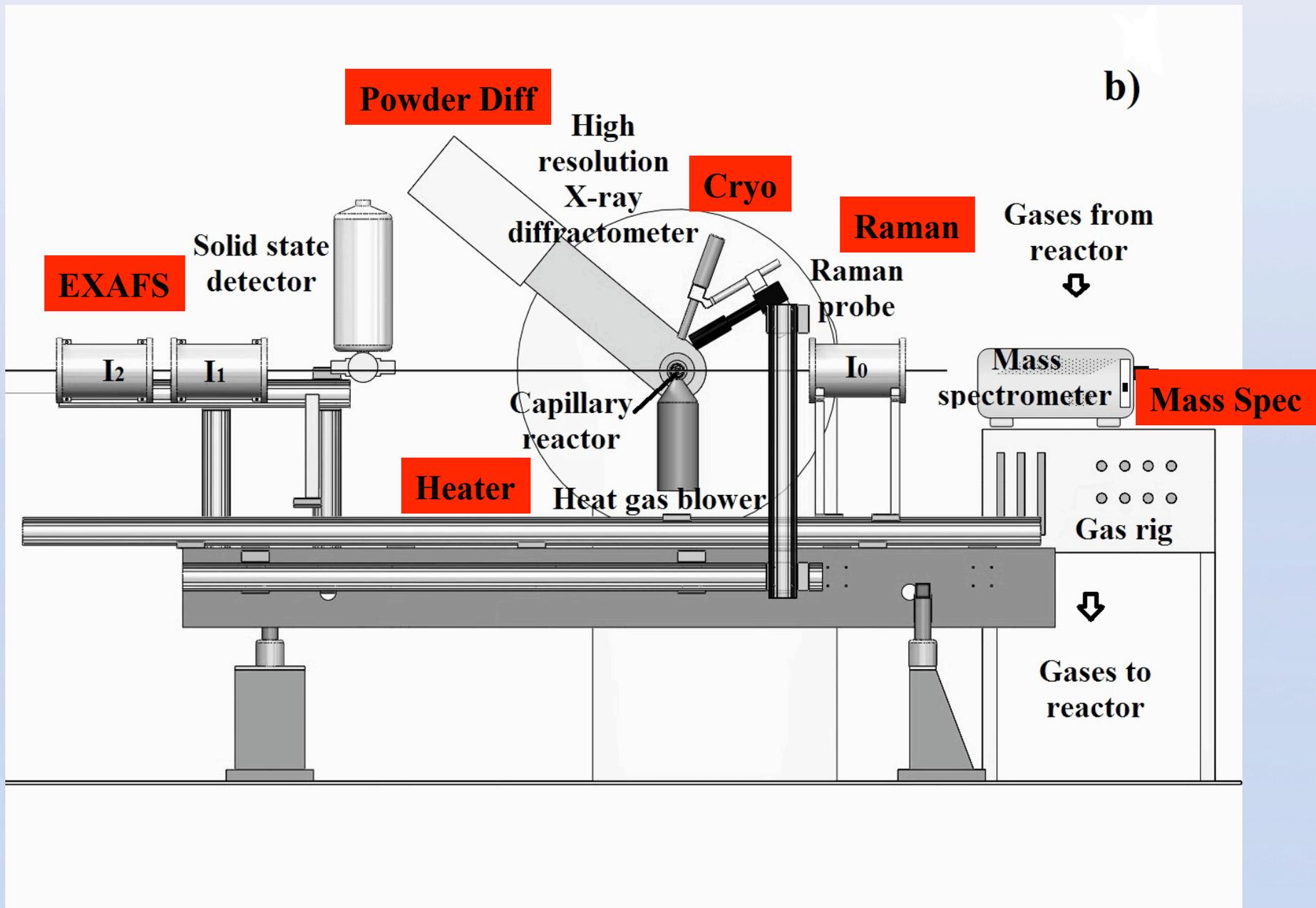
(a)

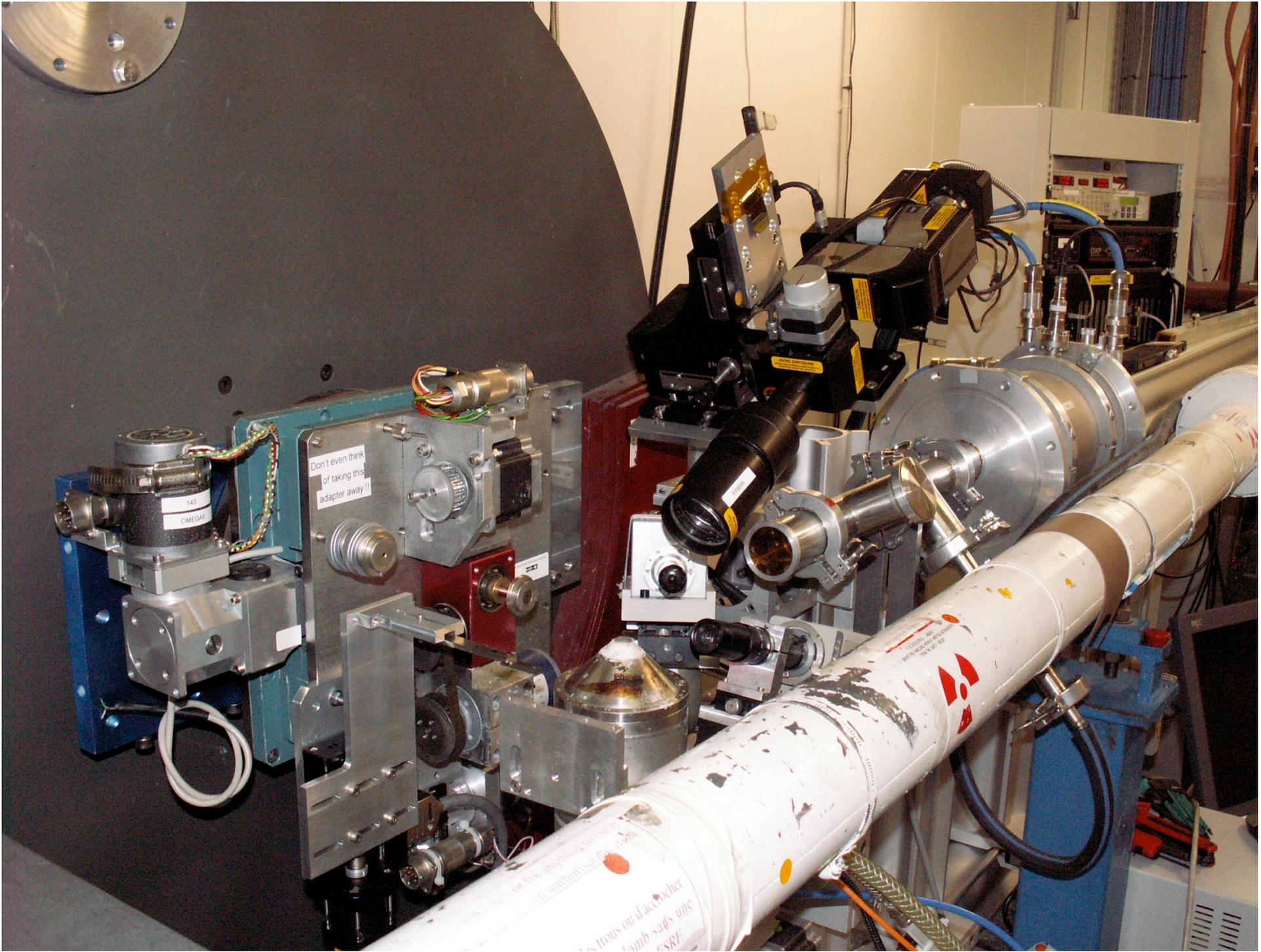


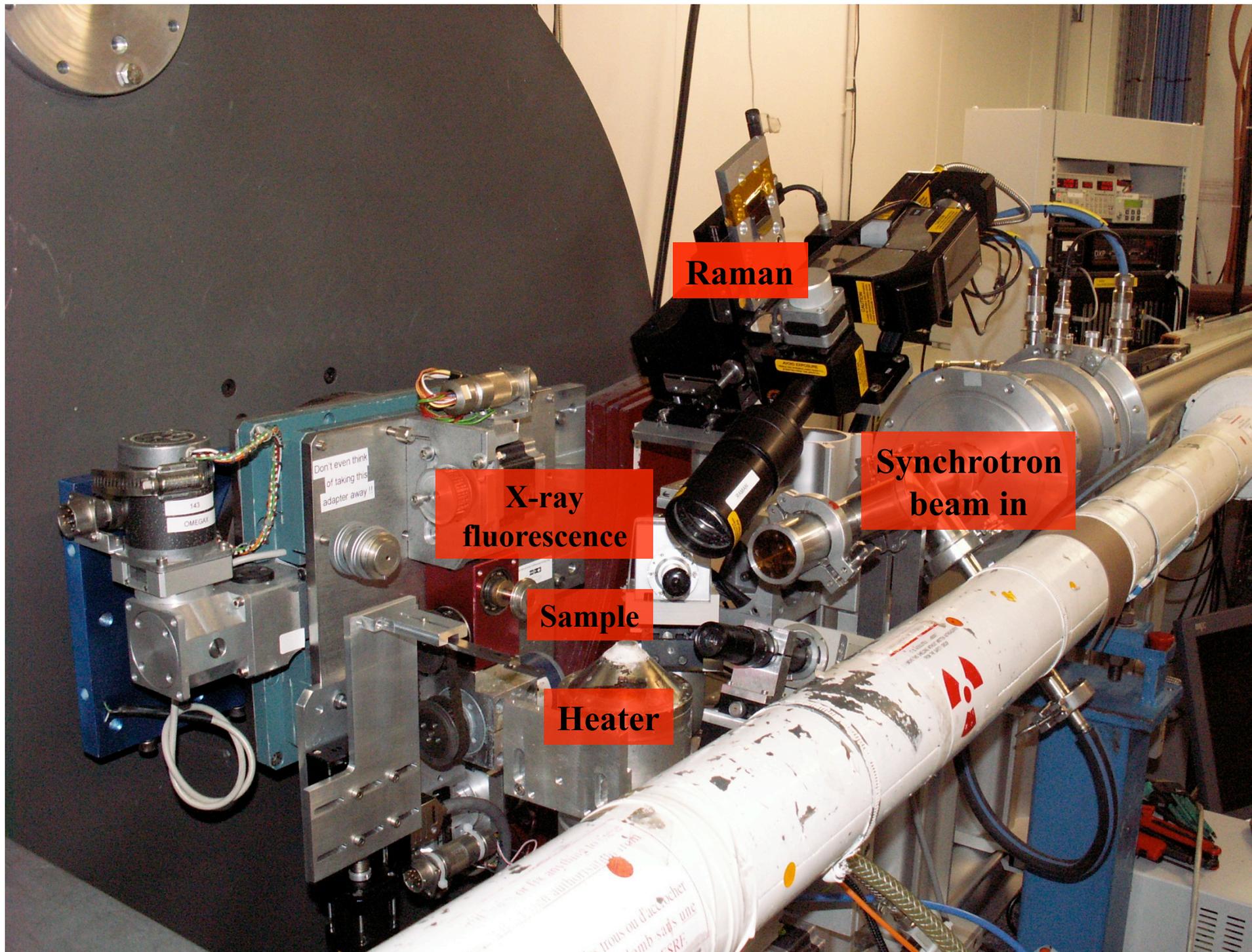


SNBL bending magnet BL layout









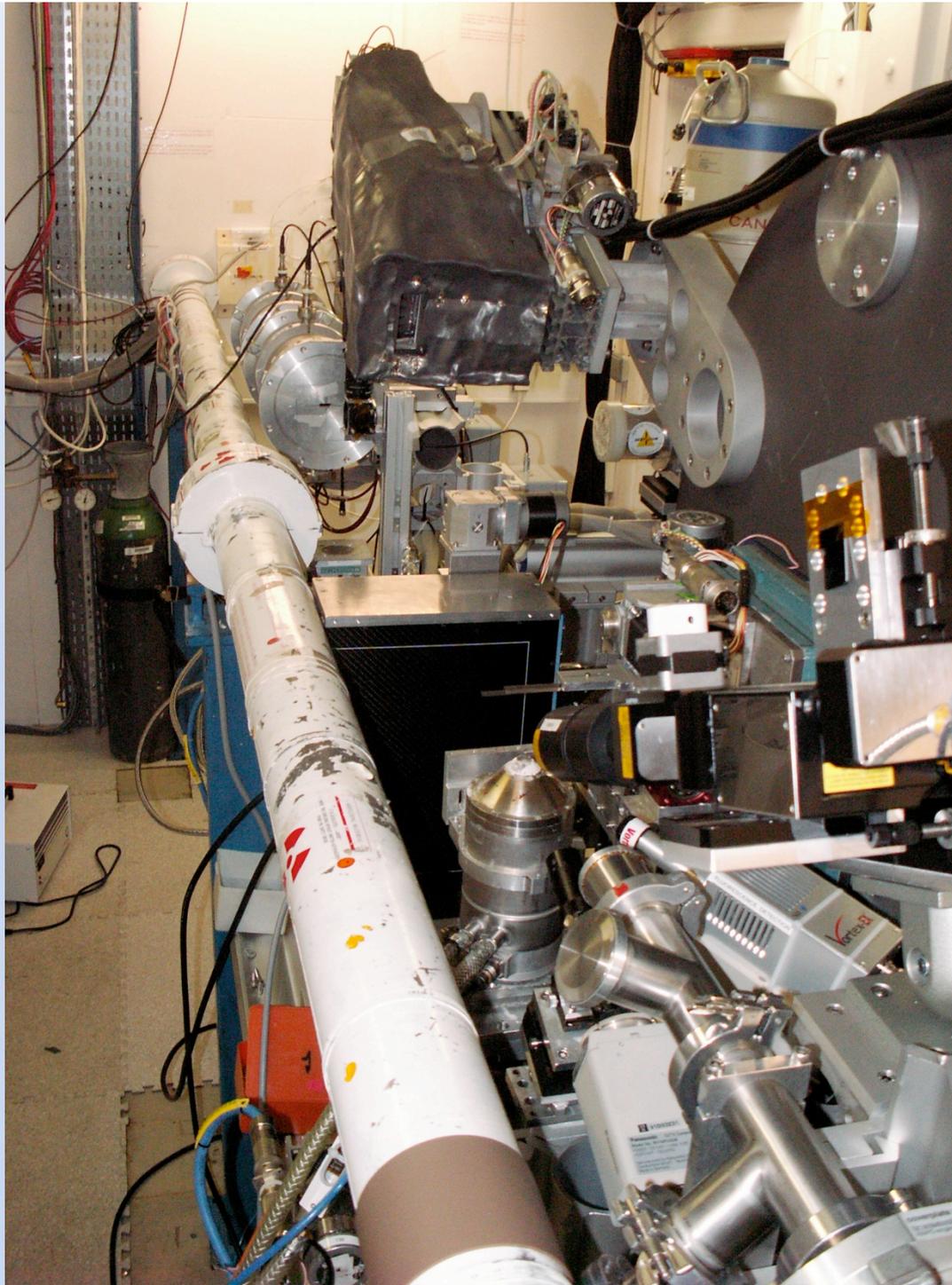
Raman

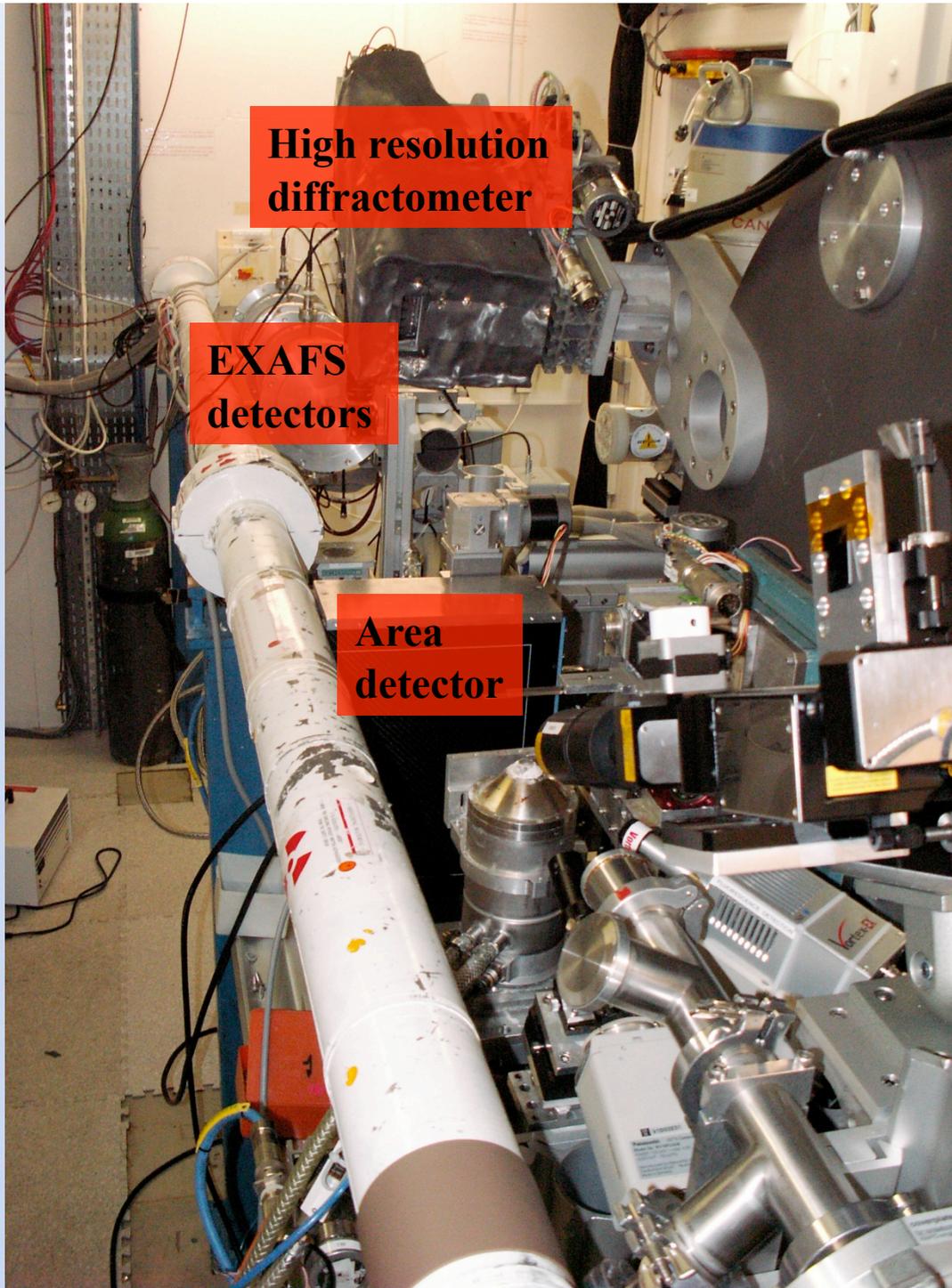
**X-ray
fluorescence**

**Synchrotron
beam in**

Sample

Heater





**High resolution
diffractometer**

**EXAFS
detectors**

**Area
detector**

Article

A Comprehensive Scenario of the Crystal Growth of #- Bi₂MoO₆ Catalyst during Hydrothermal Synthesis

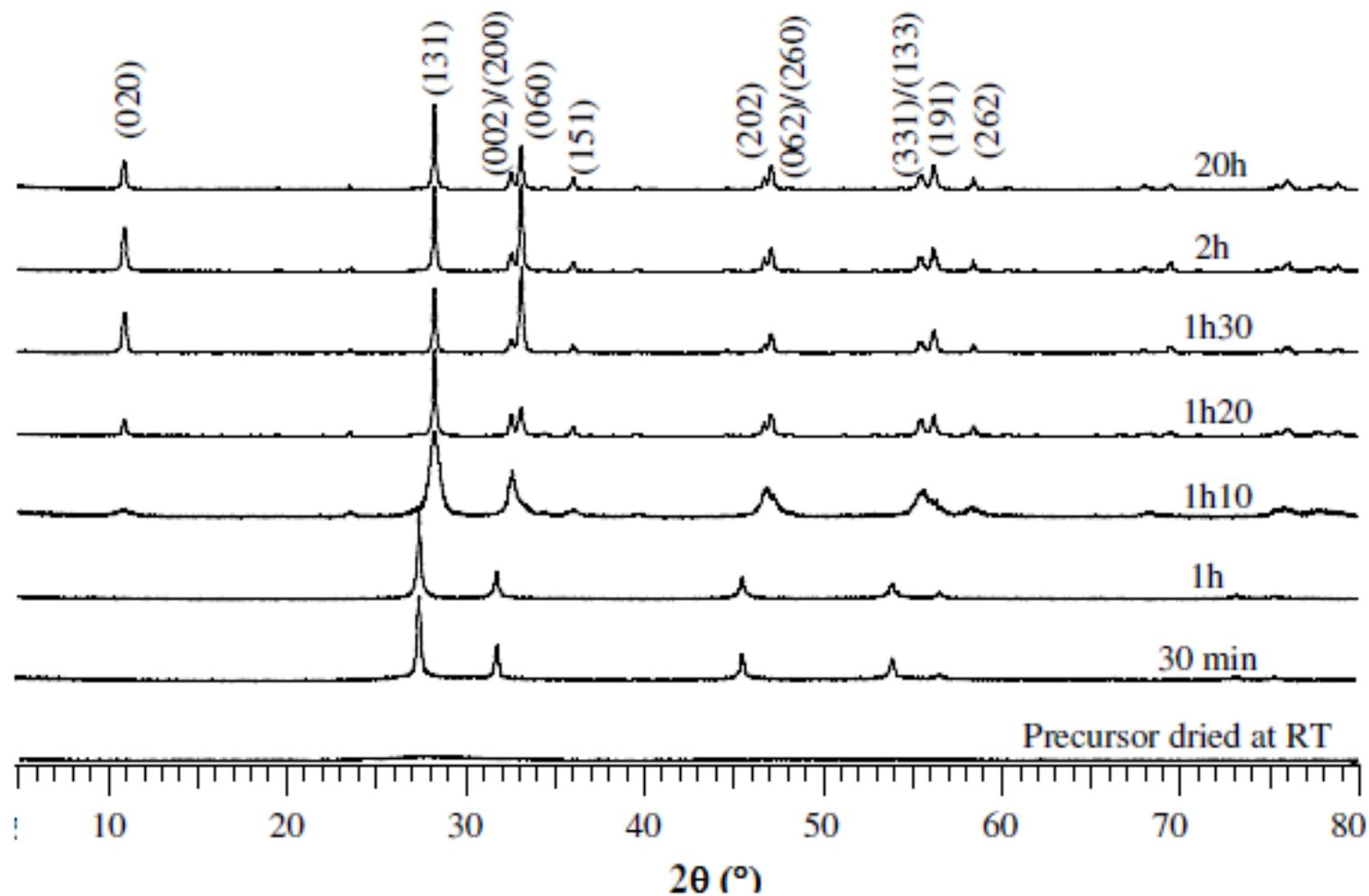
Chanapa Kongmark, Rachel Coulter, Sylvain Cristol, Annick RUBBENS, Caroline Pirovano, Axel Lofberg, Gopinathan Sankar, Wouter Franciscus van Beek, Elisabeth Bordes-Richard, and Rose-Noëlle VANNIER

Cryst. Growth Des., **Just Accepted Manuscript** • Publication Date (Web): 02 Nov 2012

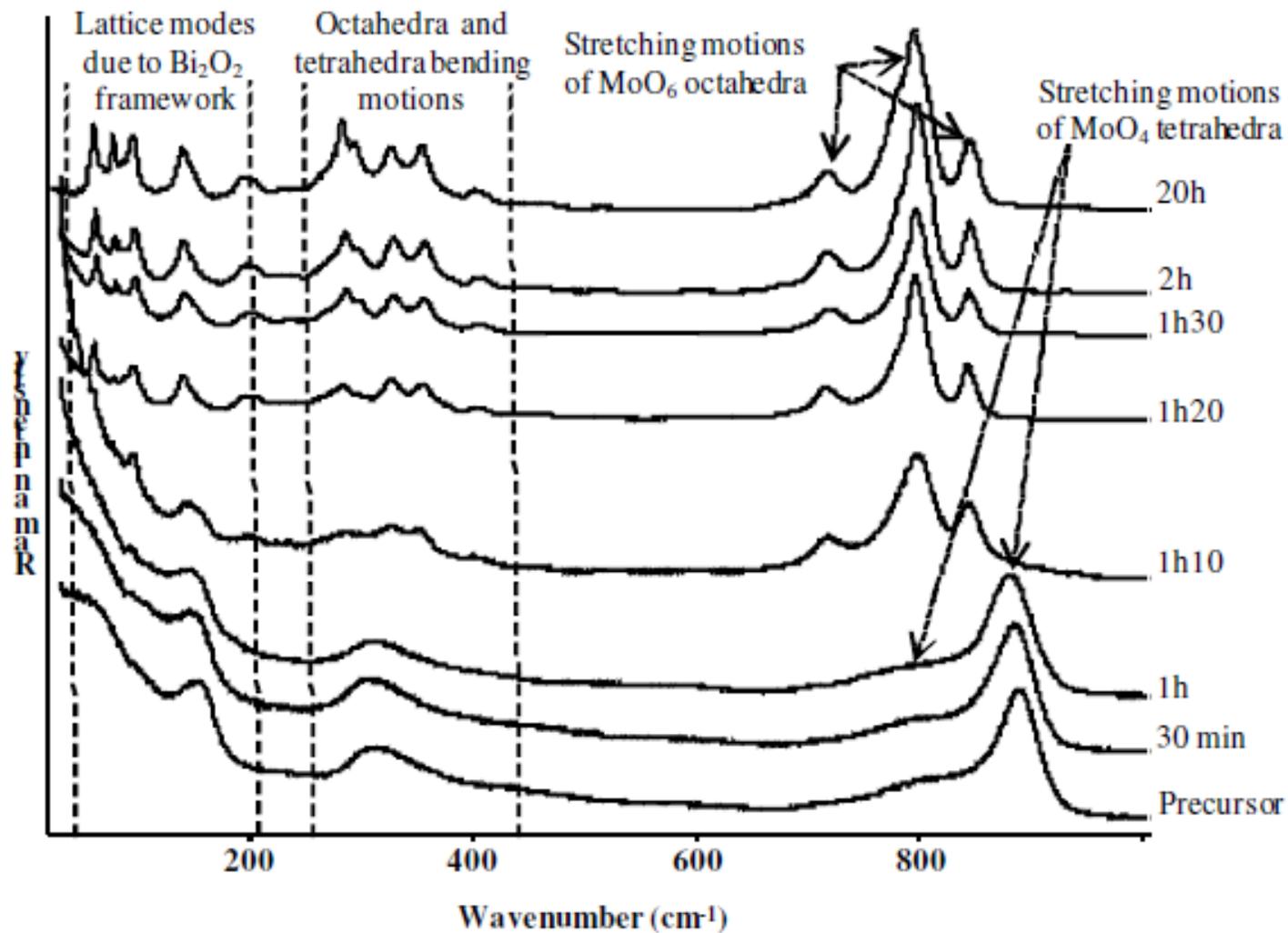
Downloaded from <http://pubs.acs.org> on November 12, 2012

The precursor resulting from mixing **Bi₂O₃ and Mo salt** was amorphous. An intermediate crystalline phase formed after 30 min. Its XRD pattern was refined in the cubic Bi₂O₃ fluorite structure. A good fit was obtained for a cubic cell with $a = 5.638(4)\text{\AA}$. Bismuth only was introduced in the cation site, although the presence of molybdenum could not be excluded (see hereafter). After 1 h 10, the Bragg peaks of this phase disappeared while those of $\gamma\text{-Bi}_2\text{MoO}_6$ started to grow.

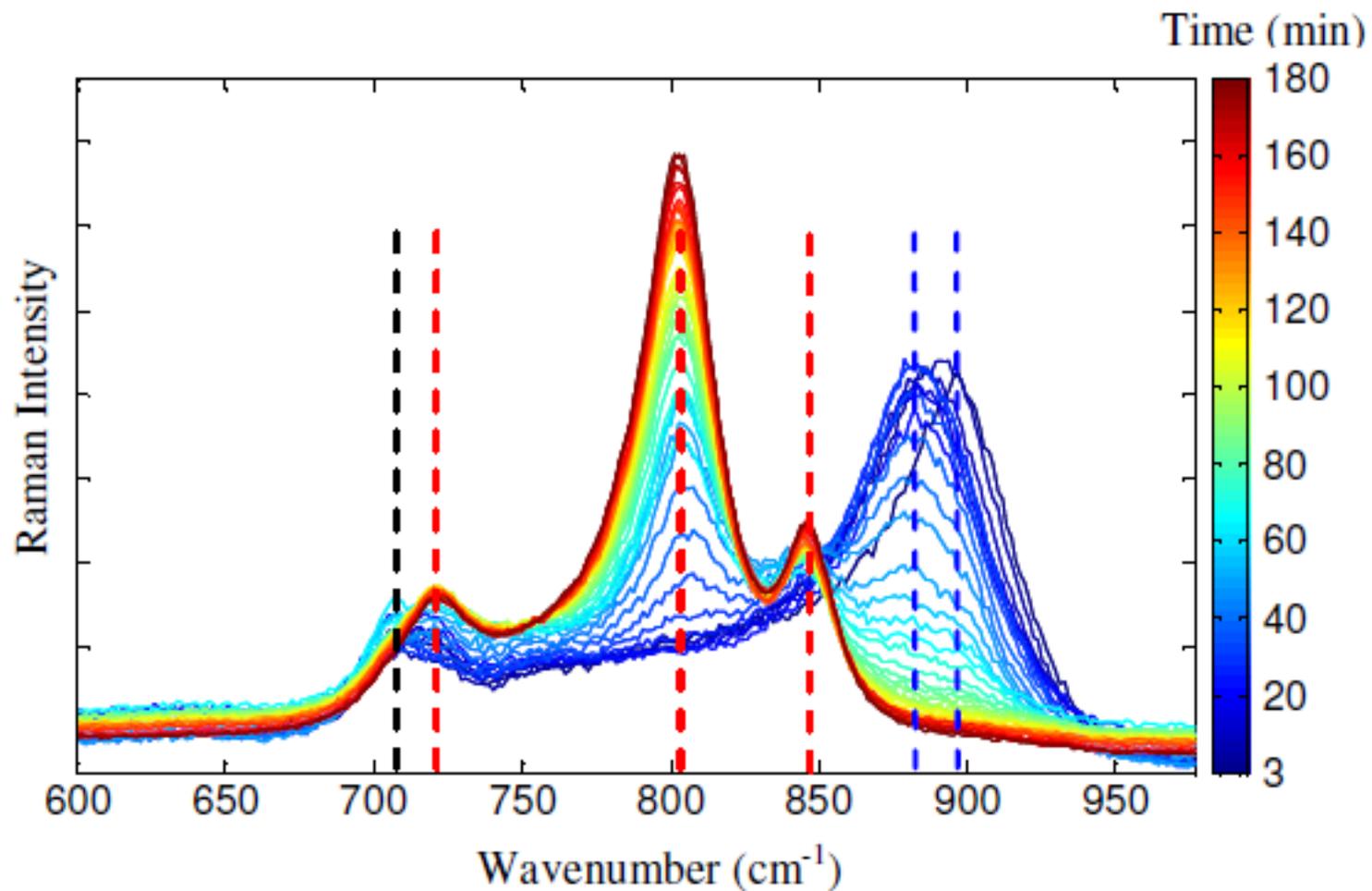
Pure crystalline $\gamma\text{-Bi}_2\text{MoO}_6$ (PDF Cards 76-2388) was successfully obtained as the final product.



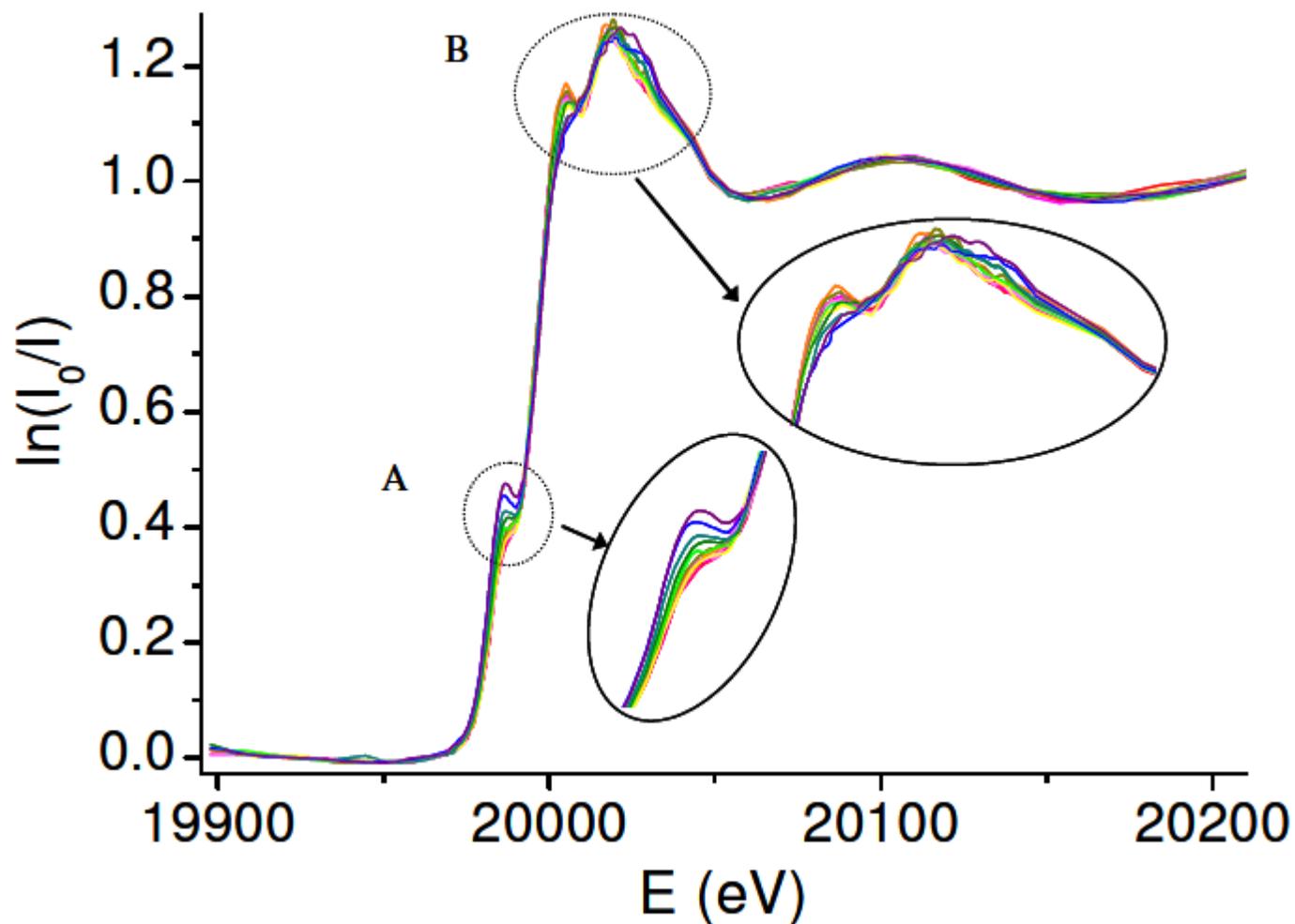
XRD powder patterns of the precursor and of samples prepared by hydrothermal method at 180°C for various reaction times. In brackets, (hkl) of γ -Bi₂MoO₆ lines.



Raman spectra of the precursor and of samples prepared by hydrothermal method at 180°C for various reaction times.

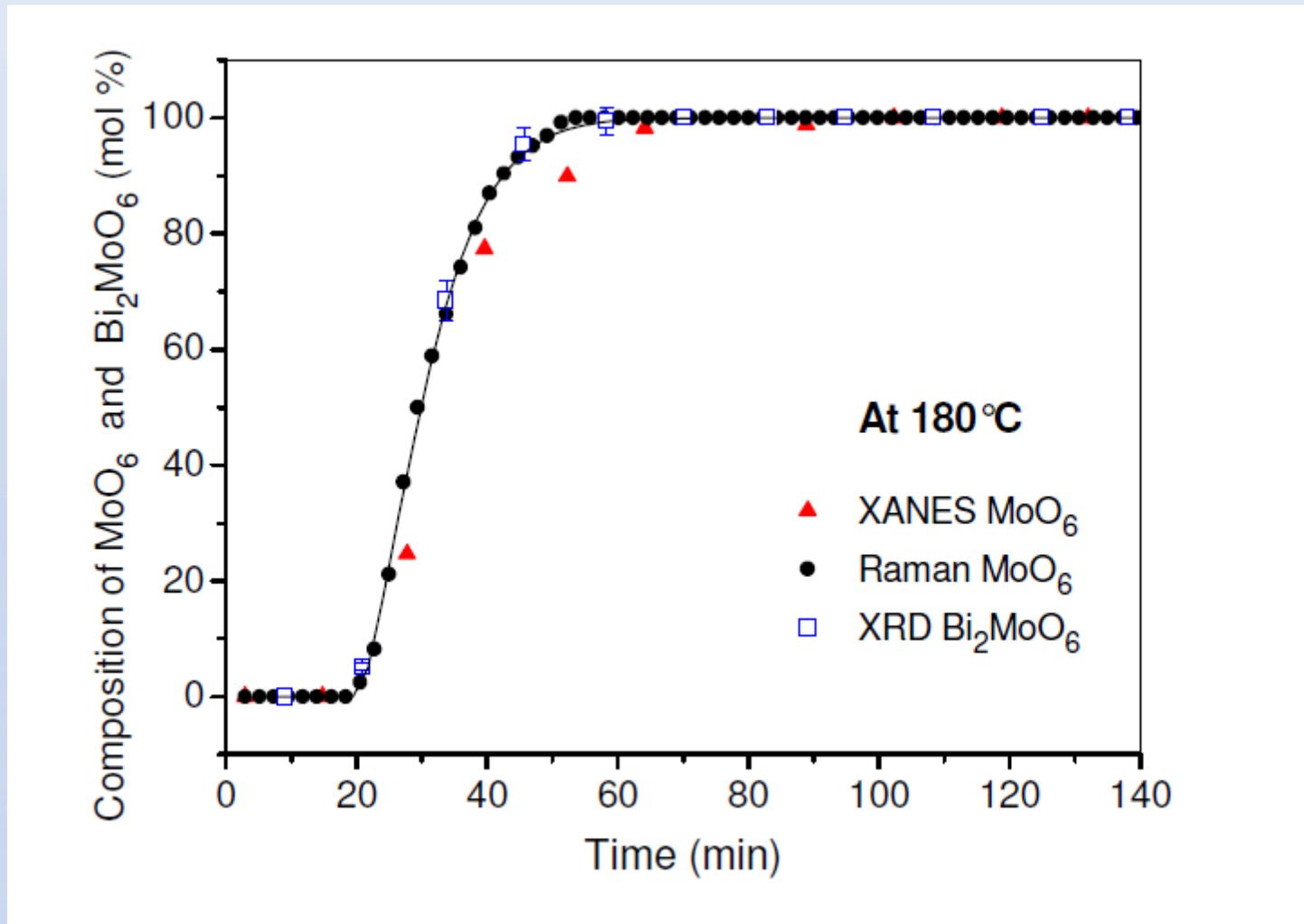


Raman spectra in the range of 600 - 975 cm⁻¹, showing the transformation from [MoO₄] (characteristic band in dotted blue lines) to [MoO₆] in γ -Bi₂MoO₆ (characteristic bands in dotted red lines).

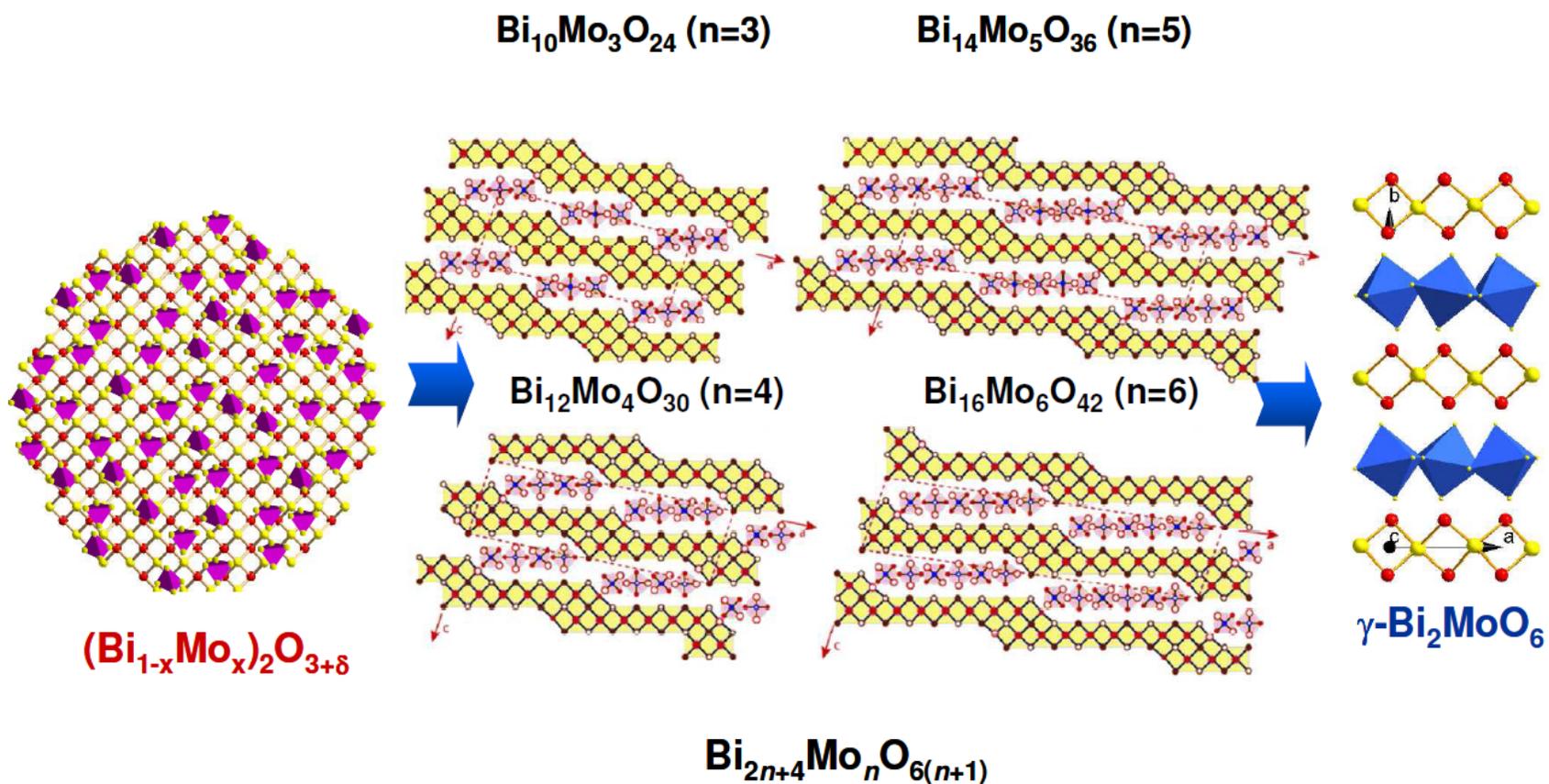


Mo K-edge XANES spectra collected at 160°C showing isobestic points (*in situ* experiments). The features marked A and B are characteristic of Mo(VI) in tetrahedral and octahedral environment, respectively.

Kinetics



***In situ* analyses during the hydrothermal synthesis of γ -Bi₂MoO₆ at 180 °C. Evolution of MoO₆ content (XANES: ▲; Raman: ●), and of Bi₂MoO₆ content obtained from XRD (□).**



Schematics of the successive transformations during the formation of $\gamma\text{-Bi}_2\text{MoO}_6$.

The message

- 1) There are lots of spectroscopic techniques which can help to clarify complex behavior in solids – USE THEM**
- 2) Sometimes powder diffraction is just not good enough, and without long-range order it is not very useful at all.**
- 3) Spectroscopy is complementary, since it depends primarily on short range order. OK for liquids, solids, glasses, mud...**