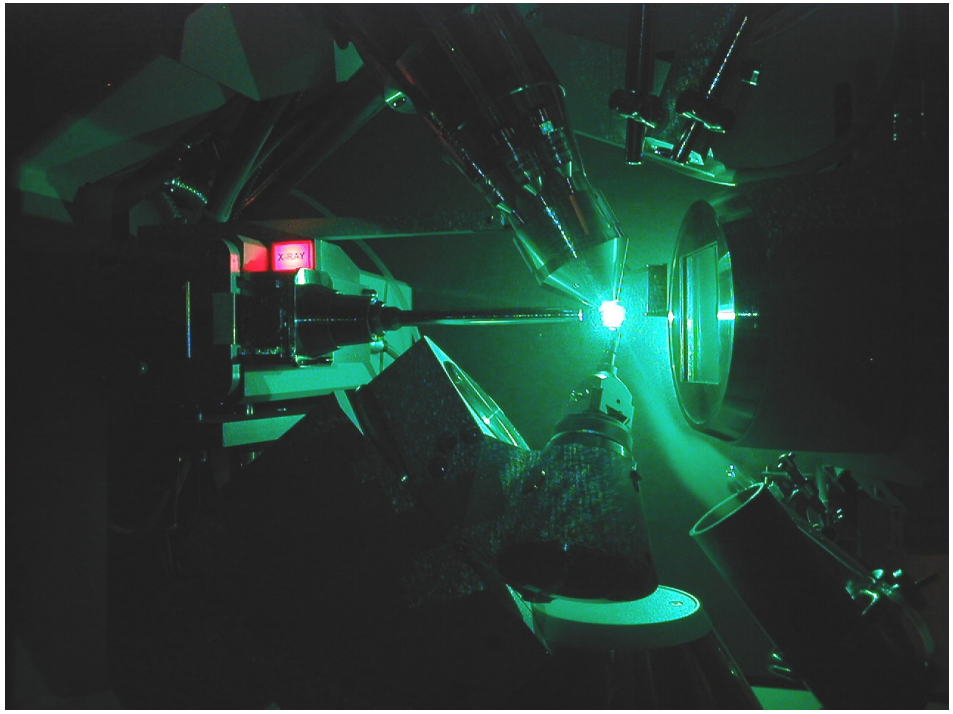
Etudes photo-cristallographiques



Sébastien Pillet
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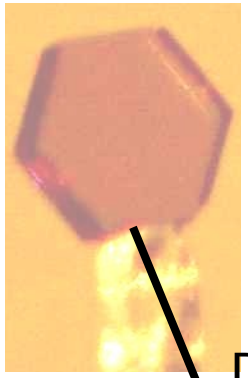
Réunion RECIPROCS 6-7 juillet 2009

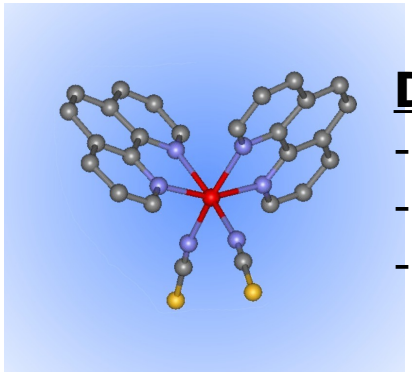
Photo-cristallographie: principe de la technique

état fondamental



DRX

$$\rho_{fond}(r)$$

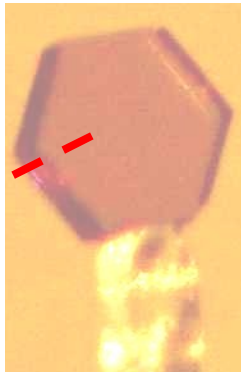


<u>Données cristallographiques :</u>

- structure moléculaire
- structure cristalline
- symétrie

Photo-cristallographie: principe de la technique

état fondamental



état excité

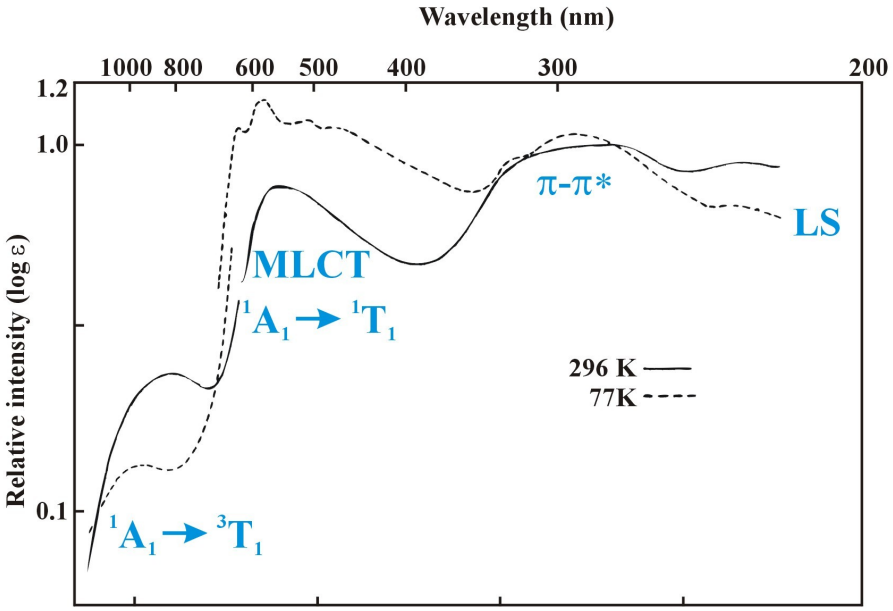
Système photo-chromique

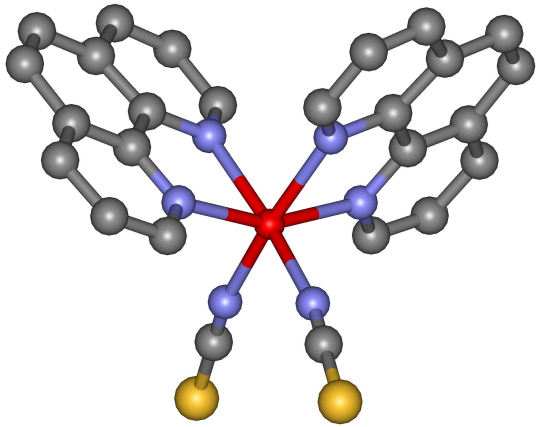
<u>Caractéristiques d'excitation :</u>

- longueur d'onde
- type de source (laser, lampe spectrale)
- durée d'impulsion (continue, ns, fs)
- puissance excitatrice
- taille d'échantillon (profondeur de pénétration)

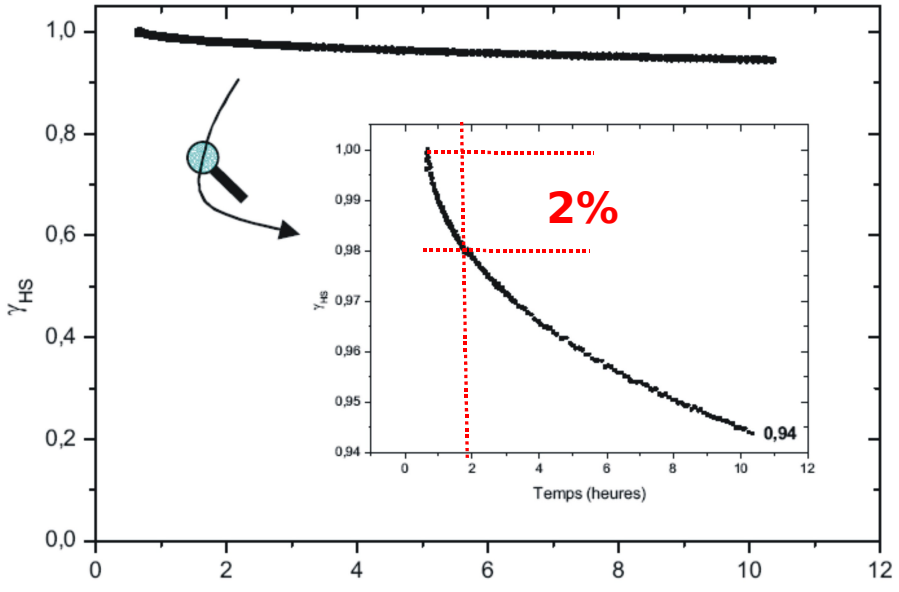
Nécessite des connaissances au préalable, apport d'autres techniques expérimentales (spectro UV-Vis, fluorescence)

Connaissances au préalable: spectro UV-Vis + magnétisme





$Fe(phen)_2(NCS)_2$



Echelles d'énergie d'excitation

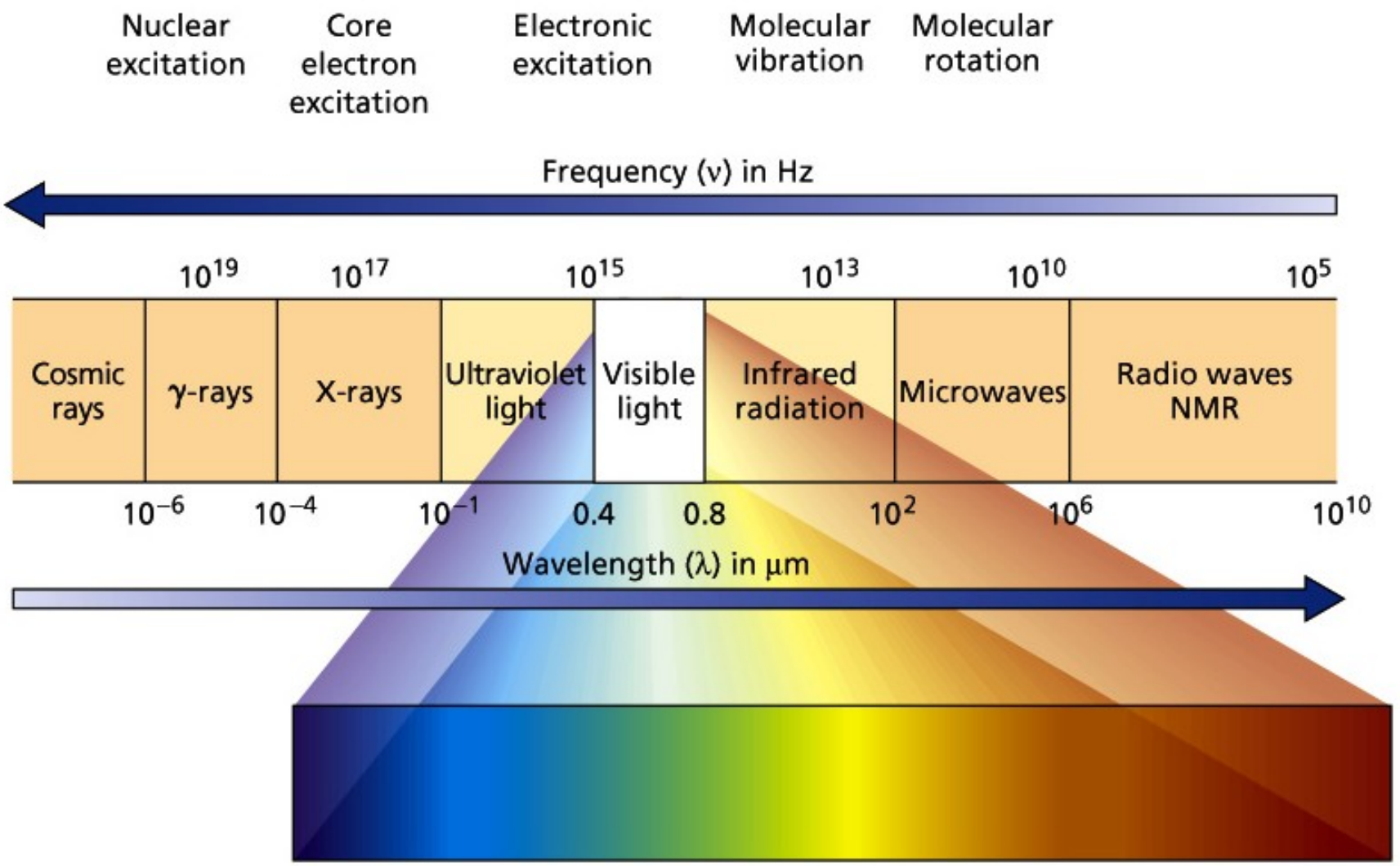
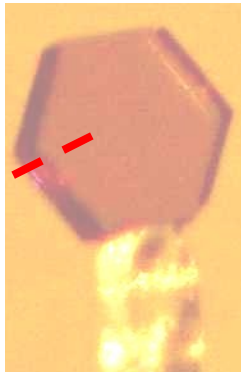
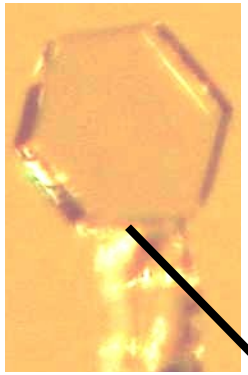


Photo-cristallographie: principe de la technique

état fondamental

état excité

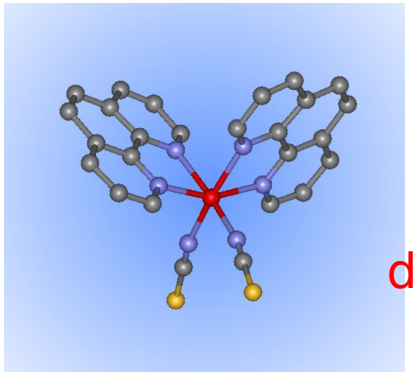




DRX

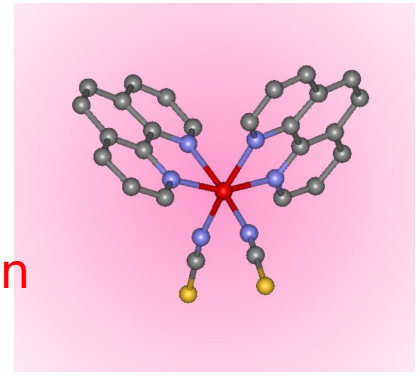
Approche par perturbation

$\rho_{excité}(r)$



modèle

de transformation



Plateformes instrumentales en France

Laboratoire

CRM2, Nancy
- DRX monocristal + DRX poudre
- Soufflette jet He, cryostat bain He
- Laser continue / pulsé , lampe spectrale

IPR, Rennes
- DRX monocristal
- Soufflette jet He

PPF Réseau national de photocristallographie à haute résolution

Synchrotron

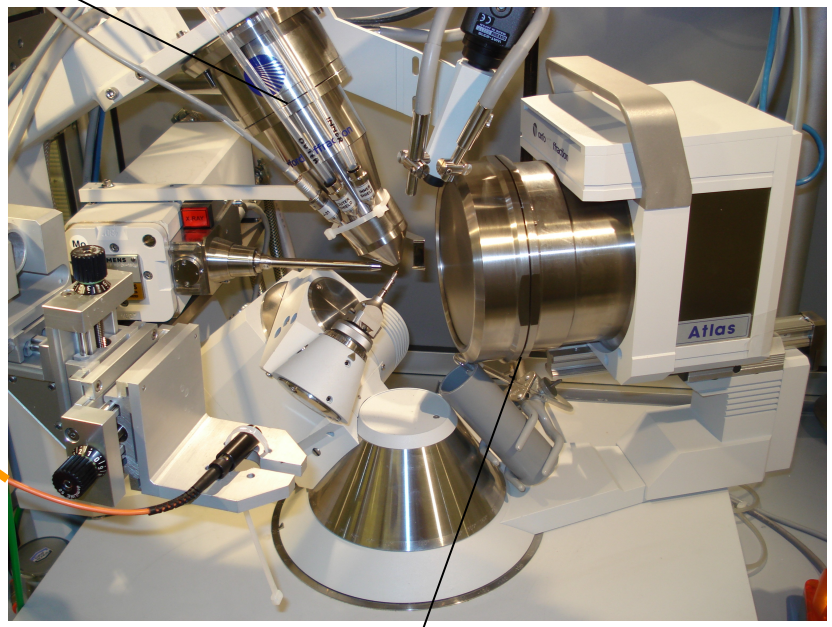
ESRF, SNBL
- DRX monocristal
- soufflette jet He

ESRF, ID09
- DRX monocristal / poudre résolue en temps

SOLEIL, CRISTAL
- DRX monocristal
- Soufflette jet He

CRM2 – diffraction monocristal

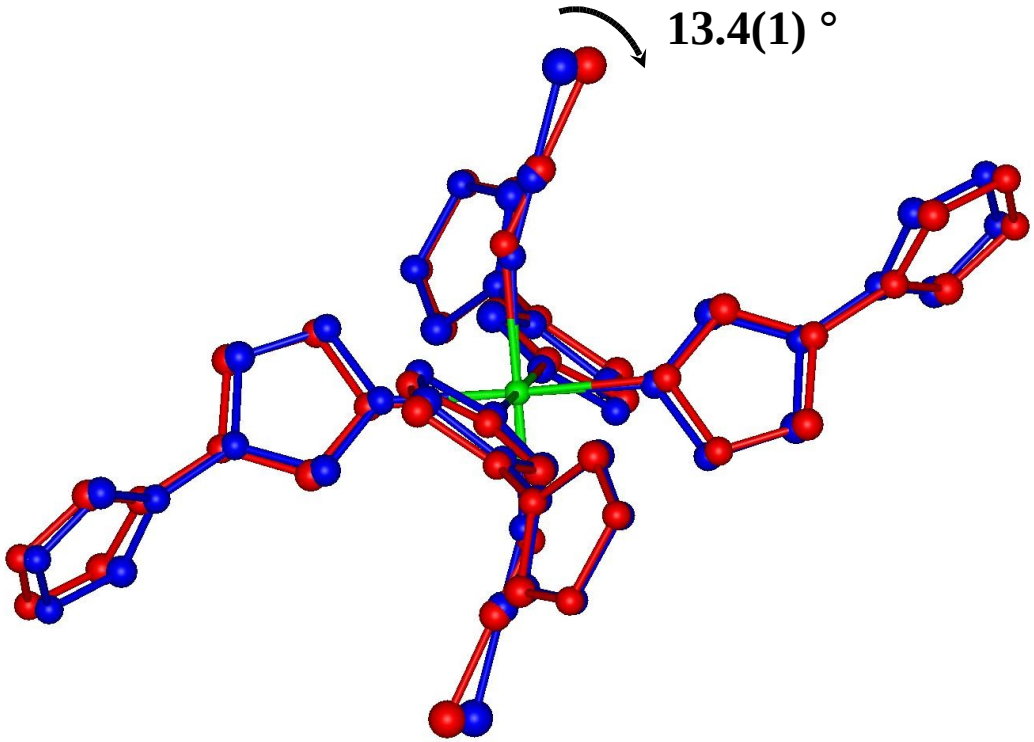
Helijet cryo-system ouvert

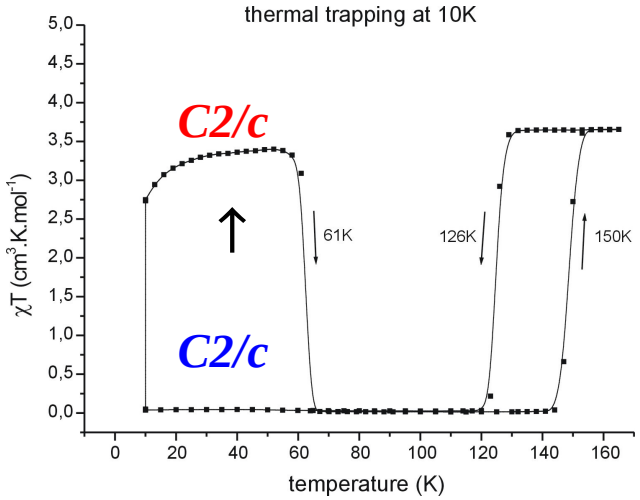


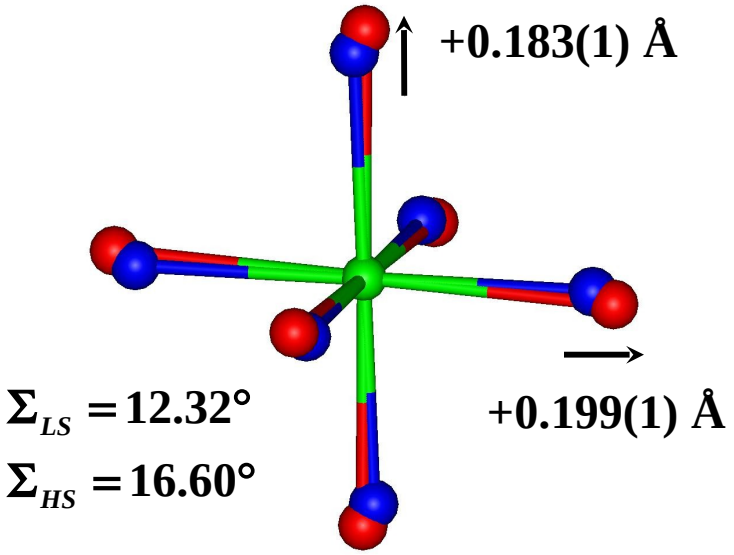
Laser à gaz Ar-Kr

Détecteur ATLAS

$Fe(btr)_2(NCS)_2.H_2O$: Transition photo-induite



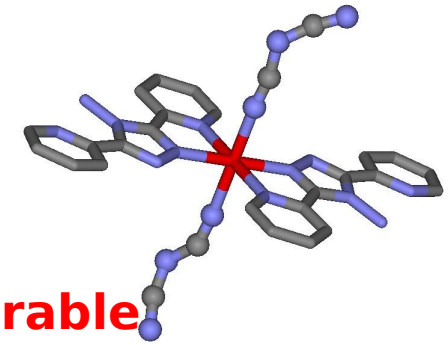




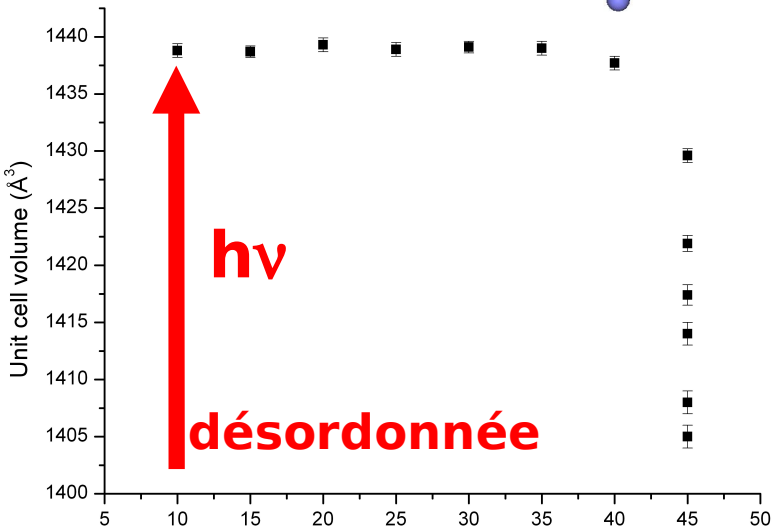
Pillet *et al.*, (2004), *Eur. Phys. J.* **B38**, 541.
Legrand *et al.*, (2007), *Eur. J. Inorg. Chem.* 5693.

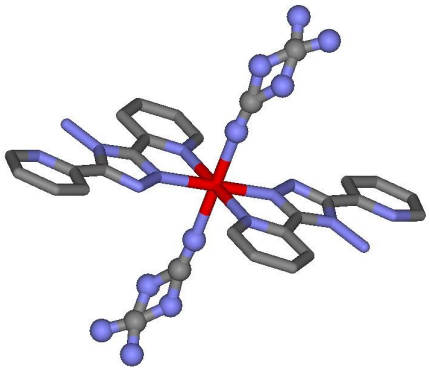
Mise en ordre incommensurable photo-induite

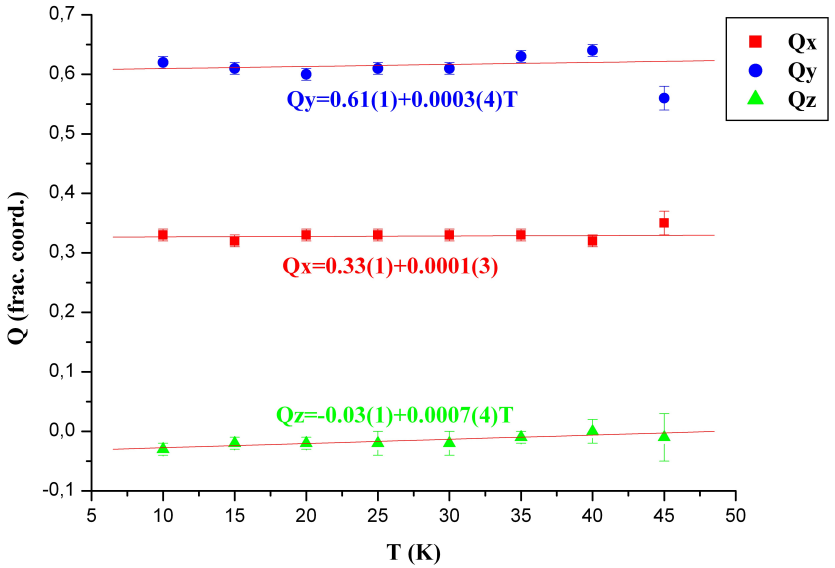
Modulation displacive + occupationnelle

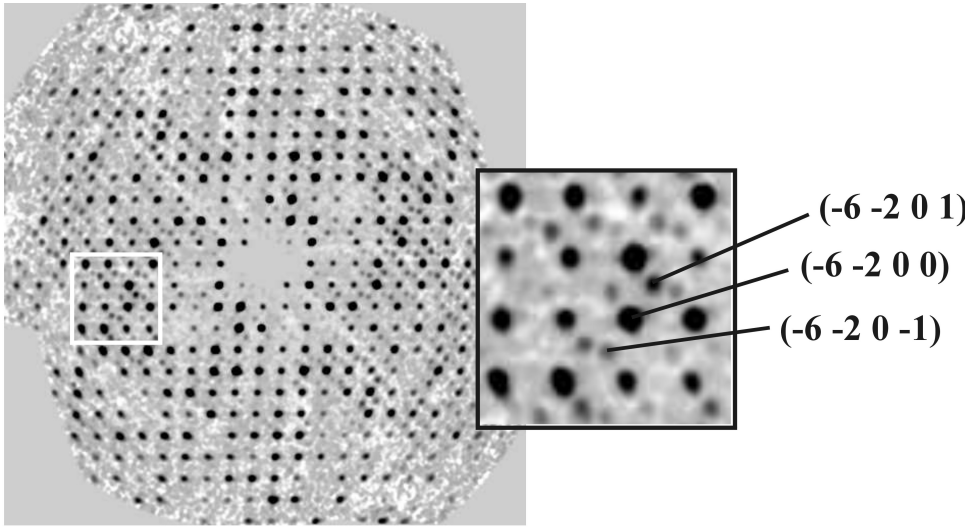


Incommensurable

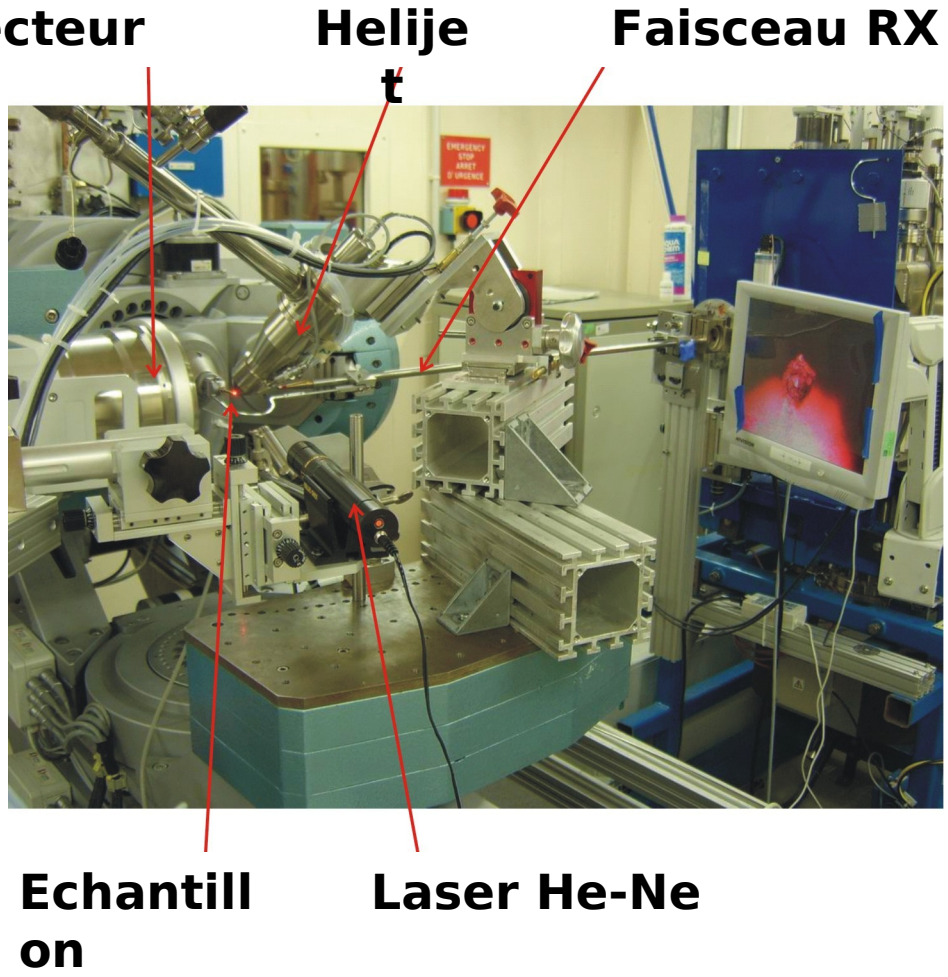


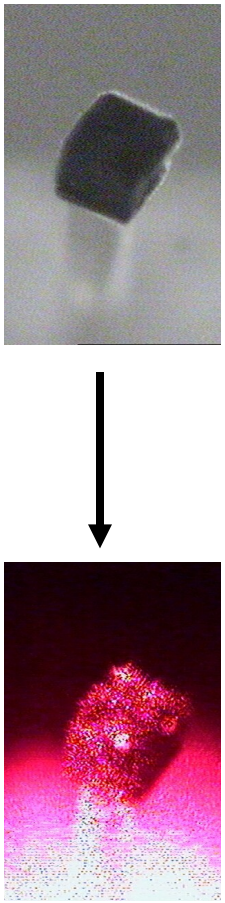






ESRF - SNBL



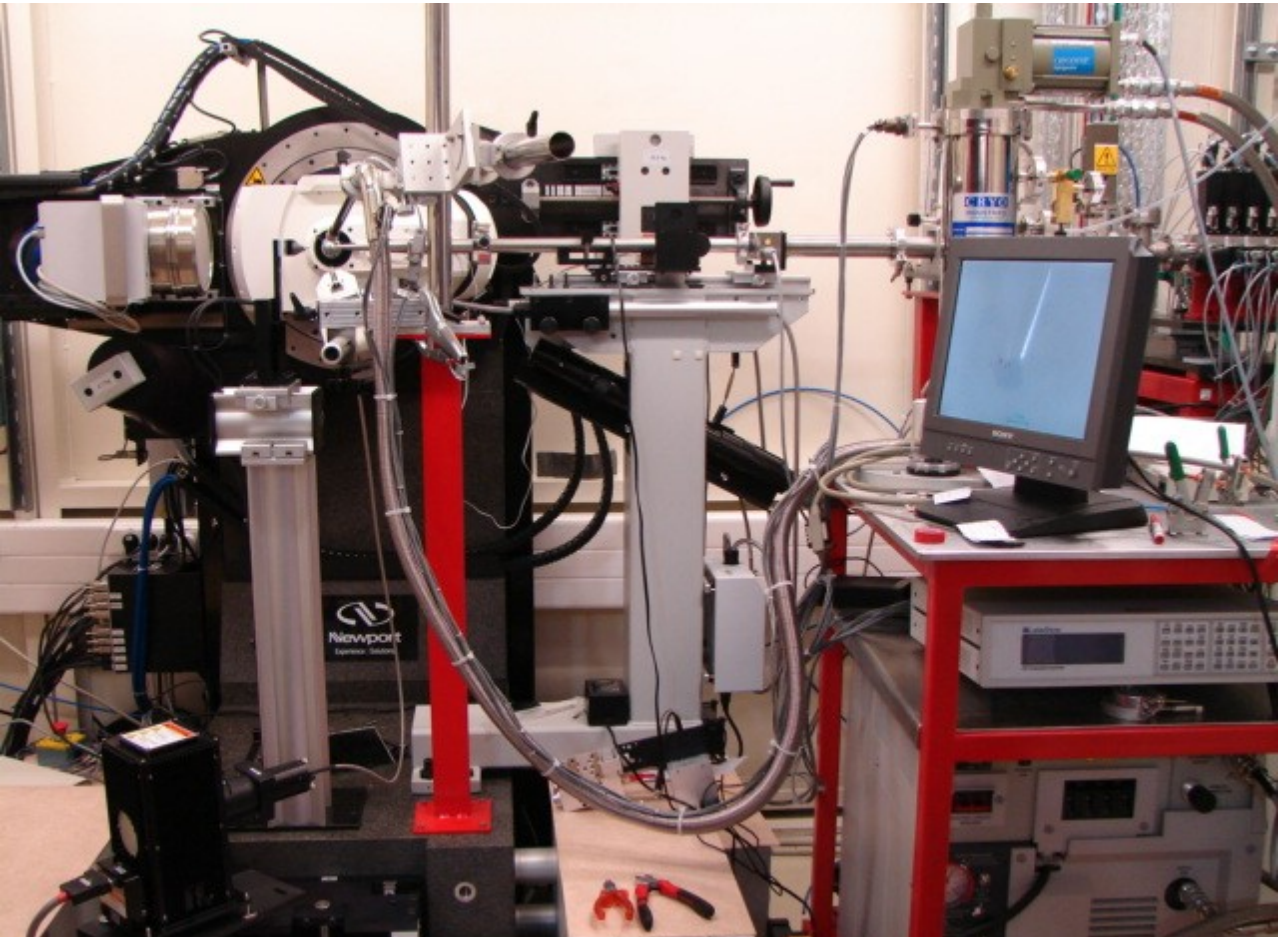


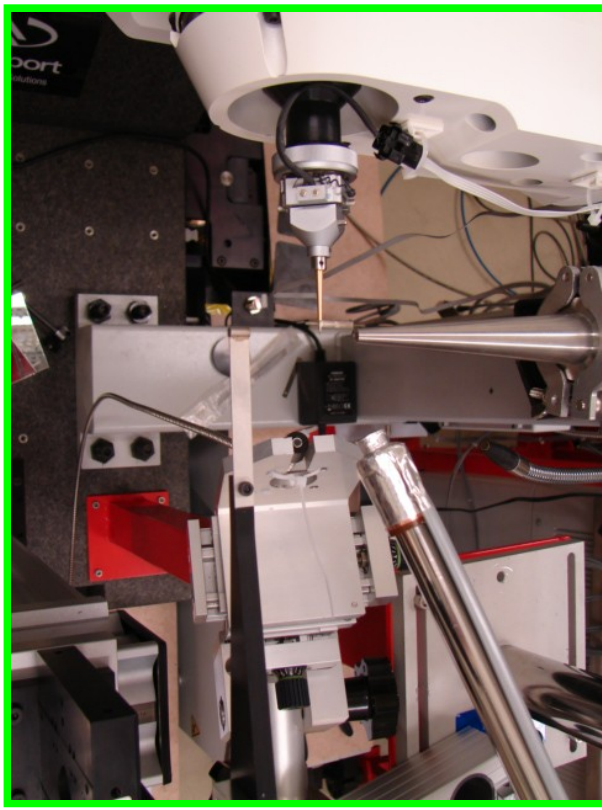
<u>Enorme avantage = flux</u>

- meilleur statistique signal/bruit (contraste faible)
- échantillon de taille réduite = maximiser la profondeur de pénétration,

meilleur homogénéité de photo-transformation

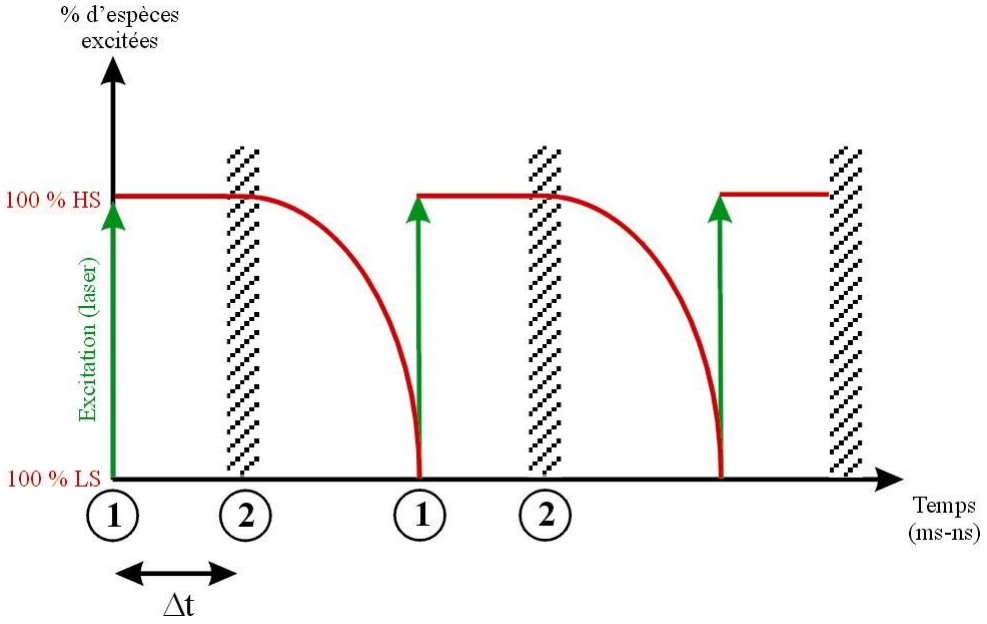
SOLEIL - CRISTAL

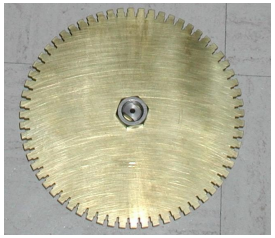


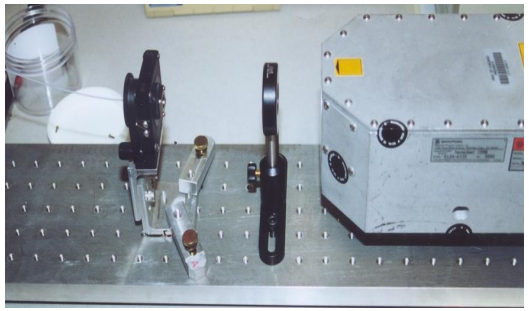


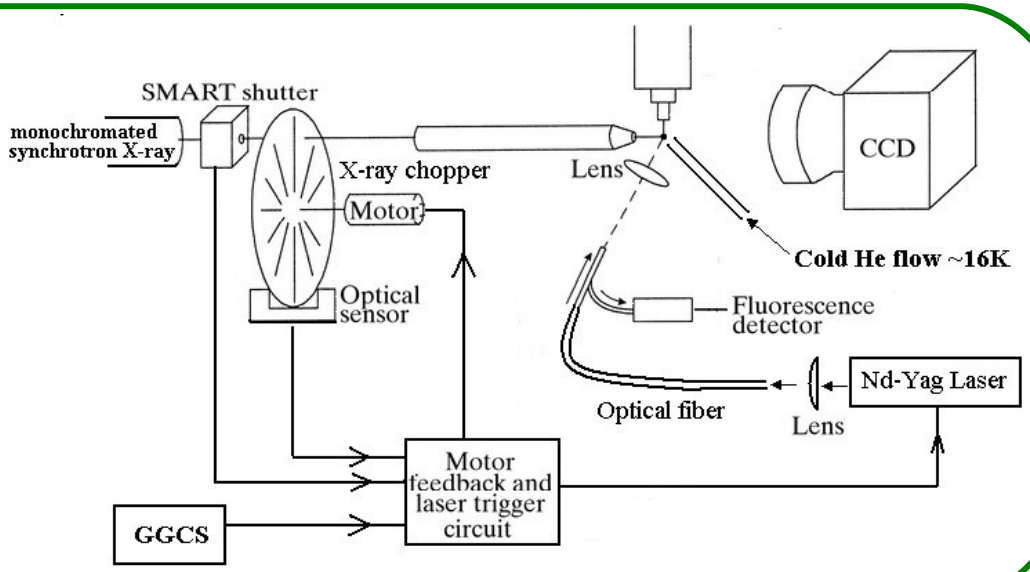
V. Marvaud, L. M. Chamoreau, S. Pillet

Mesures stroboscopiques résolues en temps







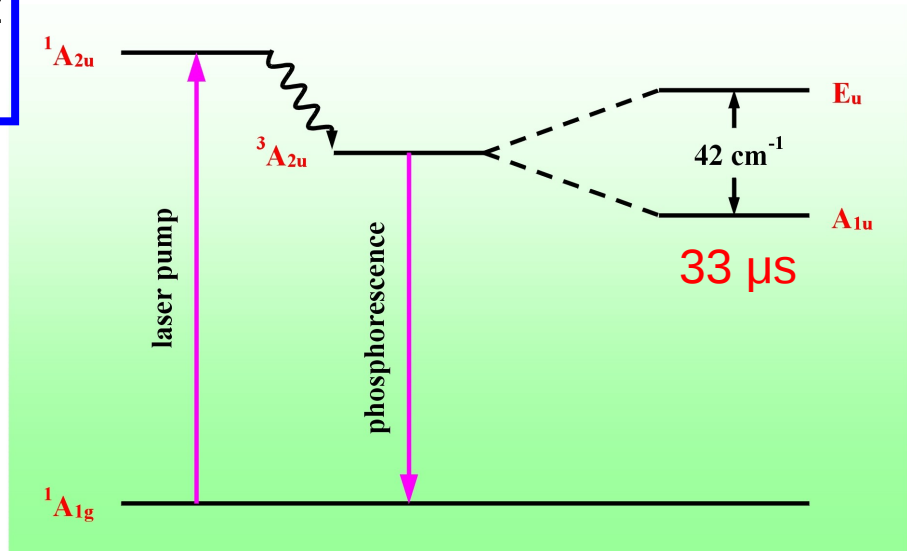


$[Pt_2(H_2P_2O_5)_4]^{4-}$: état excité triplet

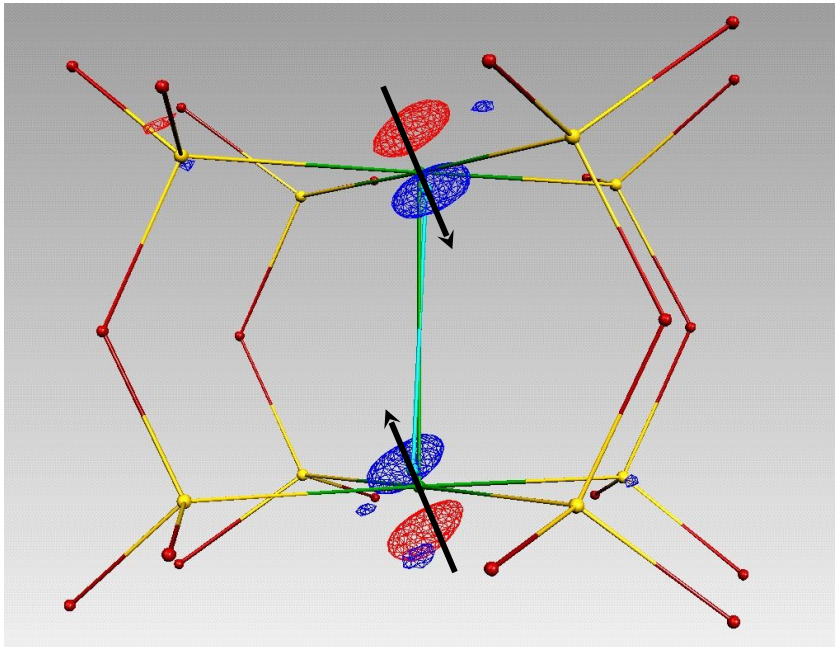
DRX : NSLS **Excitation :**

Température : 17 K Fréquence : 5100 Hz

λ = 0.6361 Å λ = 355 nm



Carte de photo-différence



Δd(Pt-Pt) = -0.28(9)Å

$[\sigma^*(d_{z2})]^2 \rightarrow [\sigma^*(d_{z2})\ \sigma(p_z)]$

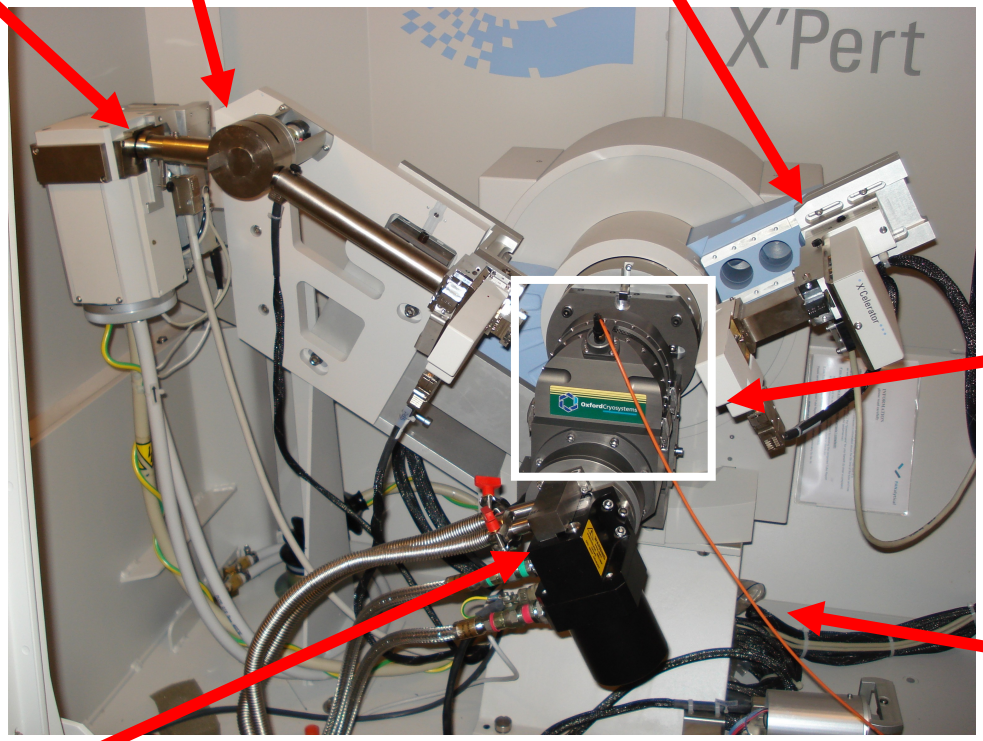
Kim *et al.*, (2002). *Acta Cryst.* **A58**, 133.

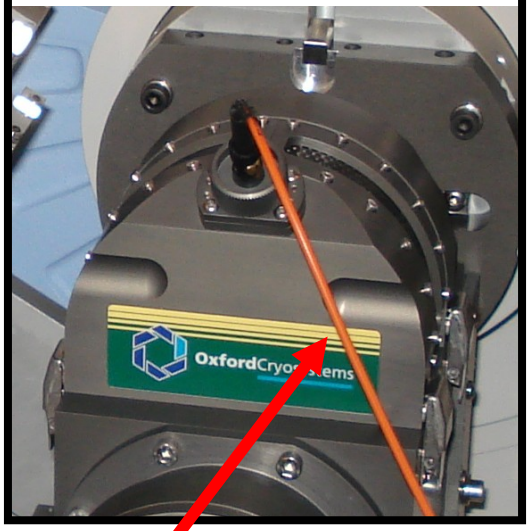
CRM2 – diffraction de poudre

Tube Cu + mono Ge(111)

détecteur X'Celerator

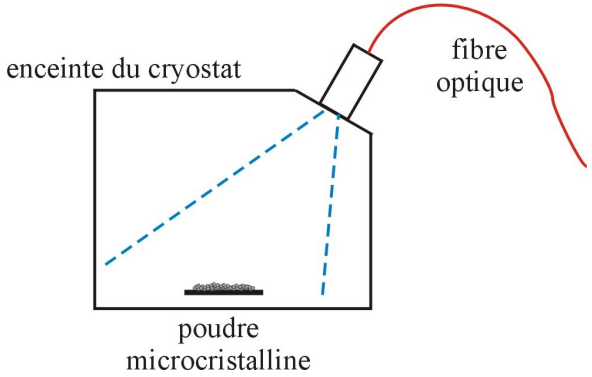
Enceinte du cryostat



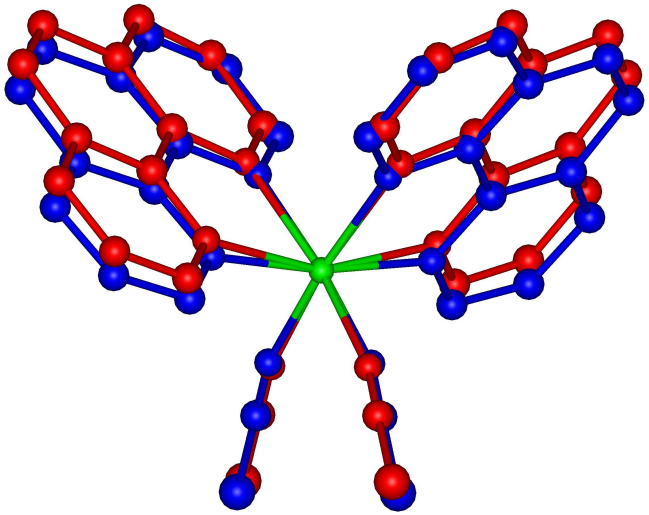


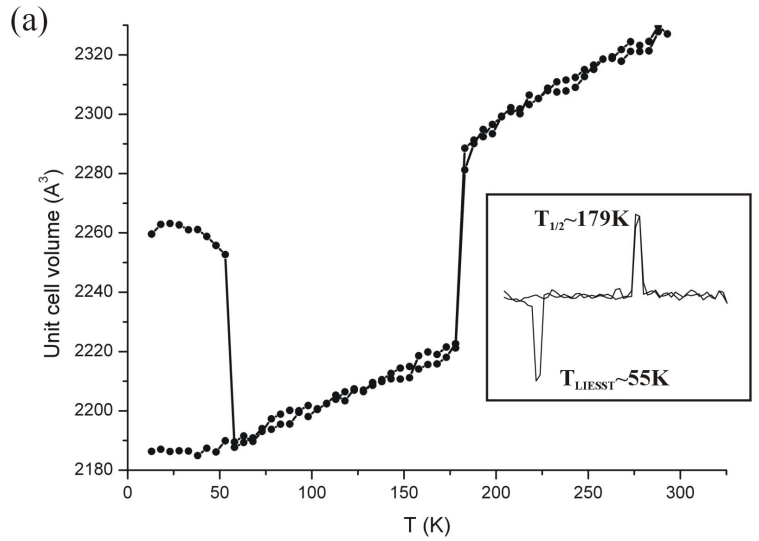
fibre optique

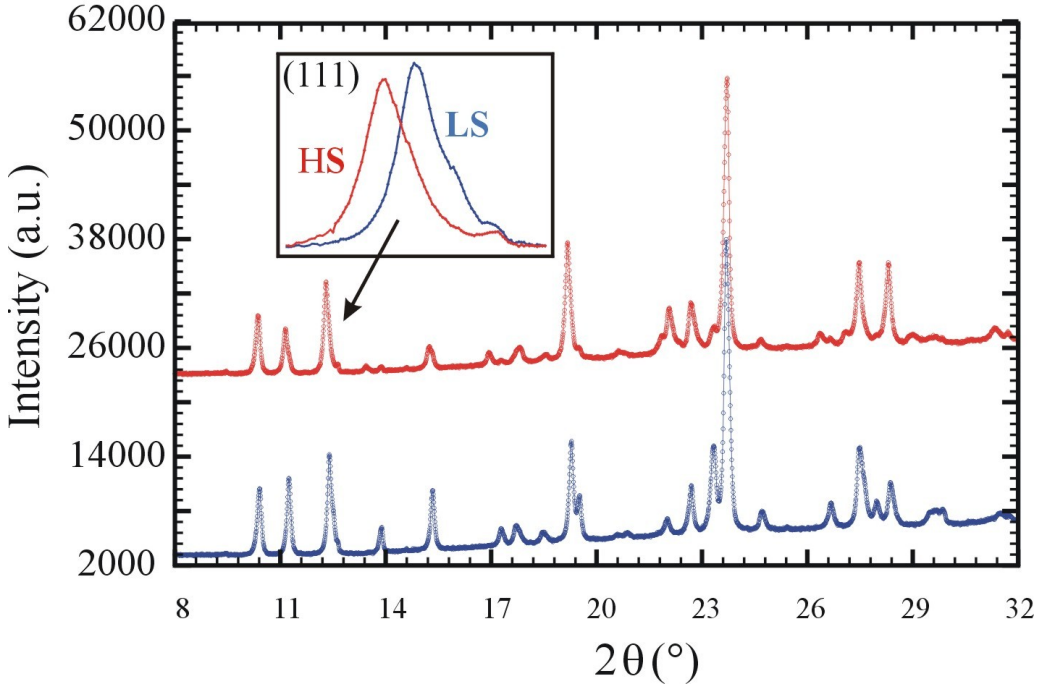
cryostat



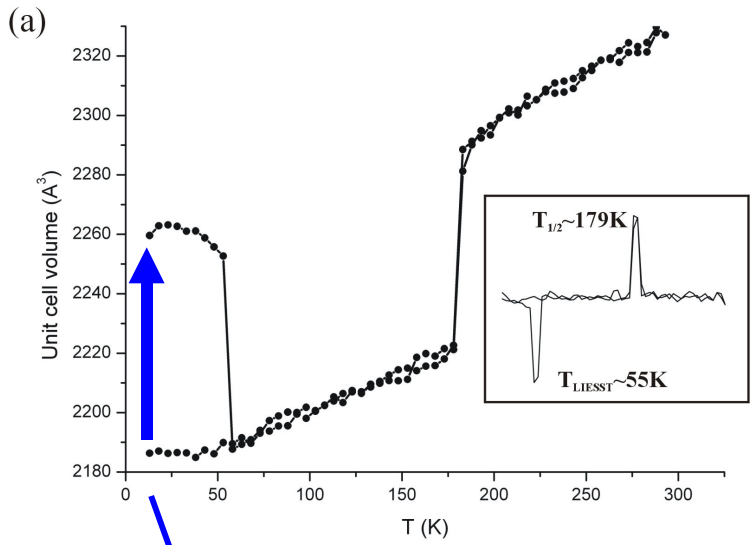
Etude cinétique par diffraction sur poudre

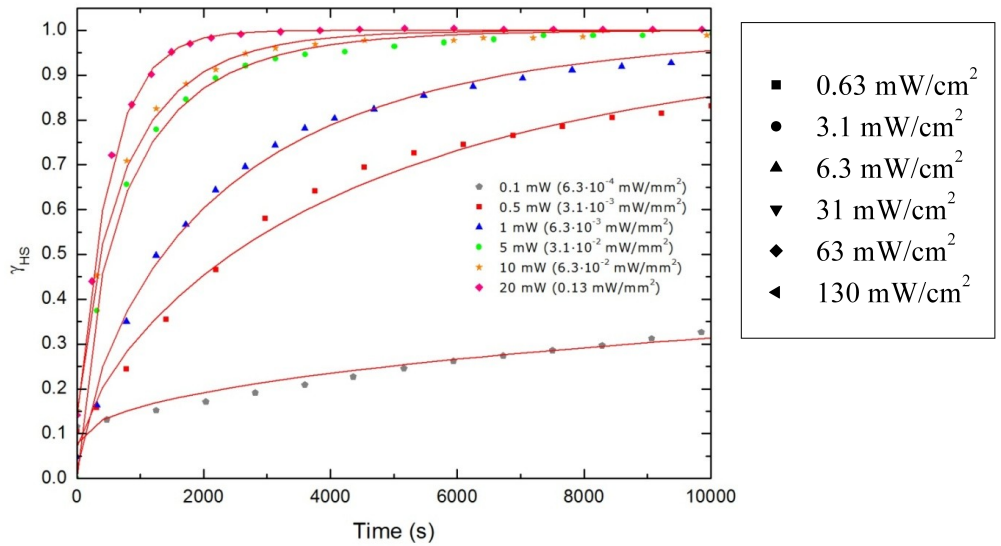




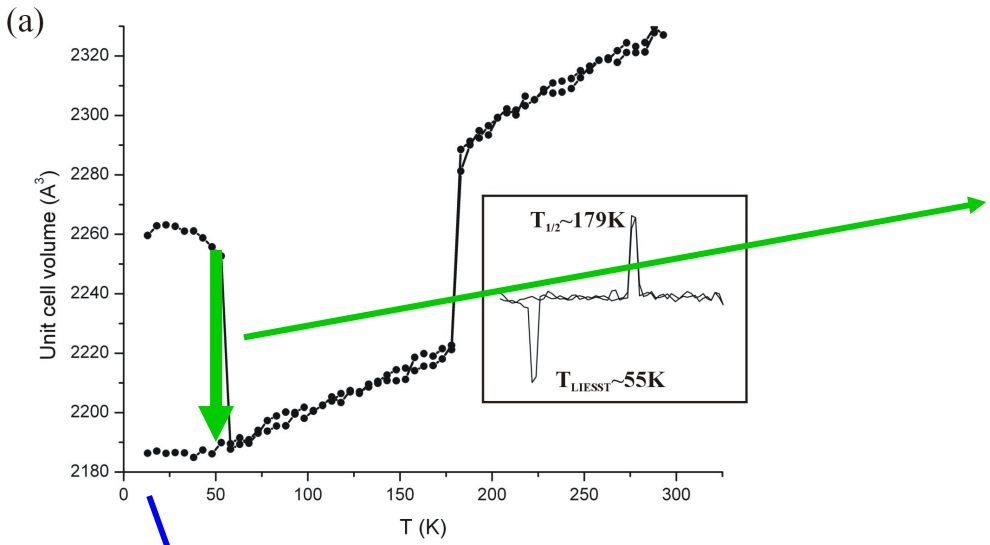


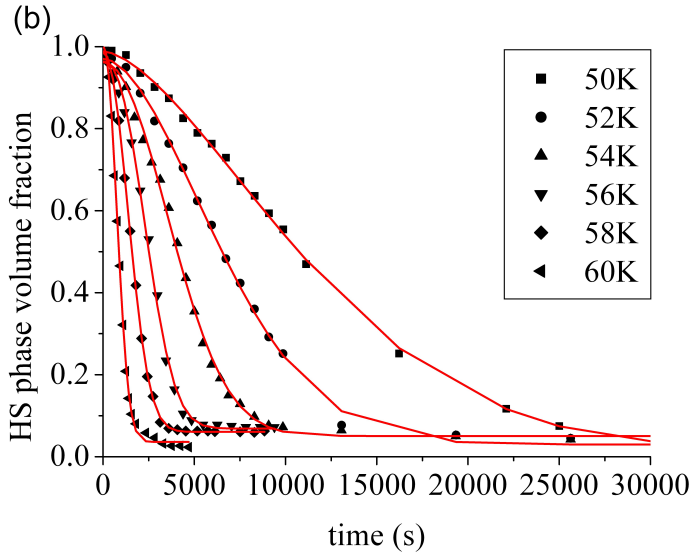
Etude cinétique par diffraction sur poudre

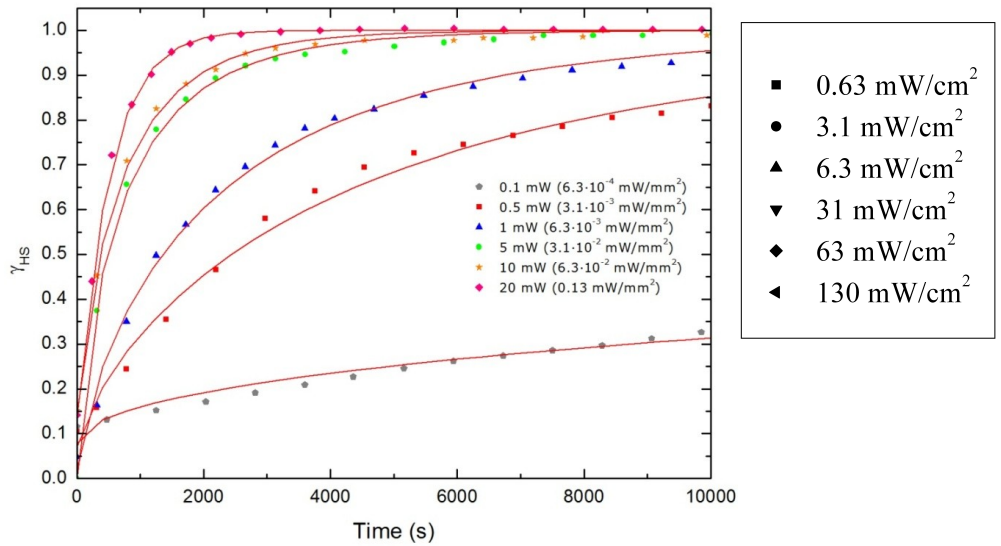


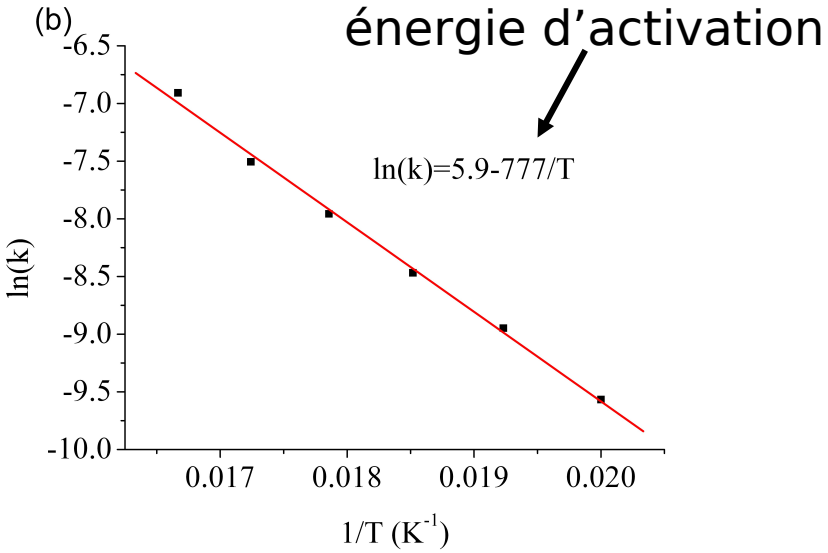


Etude cinétique par diffraction sur poudre

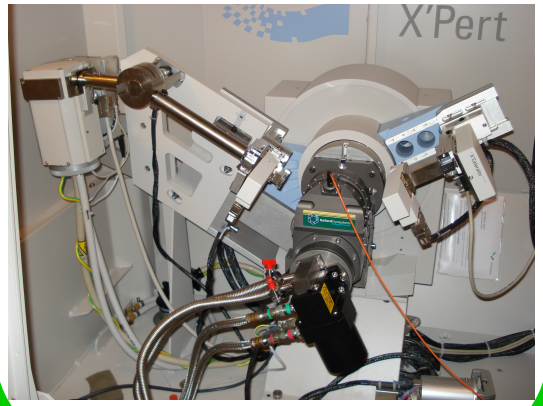




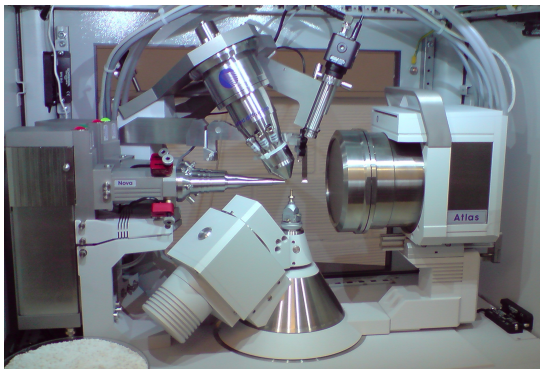




DRX poudre
11K-300K



DRX monoXtal
5K-1000K
µ–source Cu/Mo



PPF Réseau national de photocristallographie à haute résolution

(sebastien.pillet@crm2.uhp-nancy.fr)

Laser continue
330-650nm

830nm
1310nm

Lampe Q-W fibrée

Laser pulsé fibré
1064, 532, 355nm