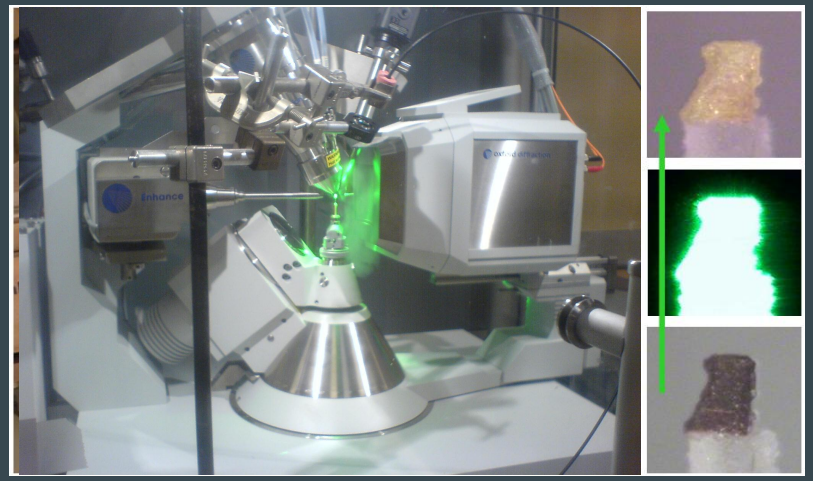
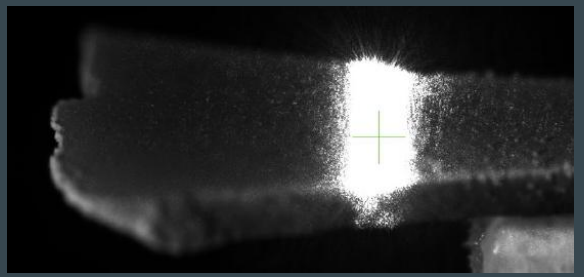
DIFFRACTION
UNDER LASER IRRADIATION





ANF RECIPROCS– 2018
C. Mariette

Photo-excitation mecanisms:
from photo-chemistry to out of equilibrium physics

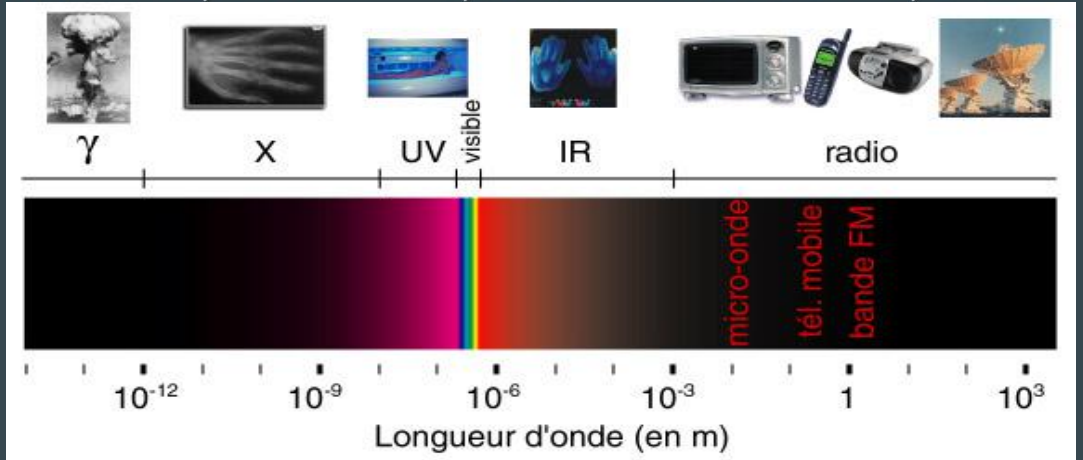
What can you do with a laser on Matter?

Heating : although that is not what you want, keep in mind this will happen in any case !!!...

Shock Waves: high power laser pulse

e- polarisation switching : strong THz field

Electronic transitions: from localized to delocalized electronic states - energy scales : 400 nm = 3eV = 25000 cm-1, 800nm = 1,55 eV = 12500 cm-1, 3 um = 0,4 eV = 3300 cm-1
in or out of resonnance process



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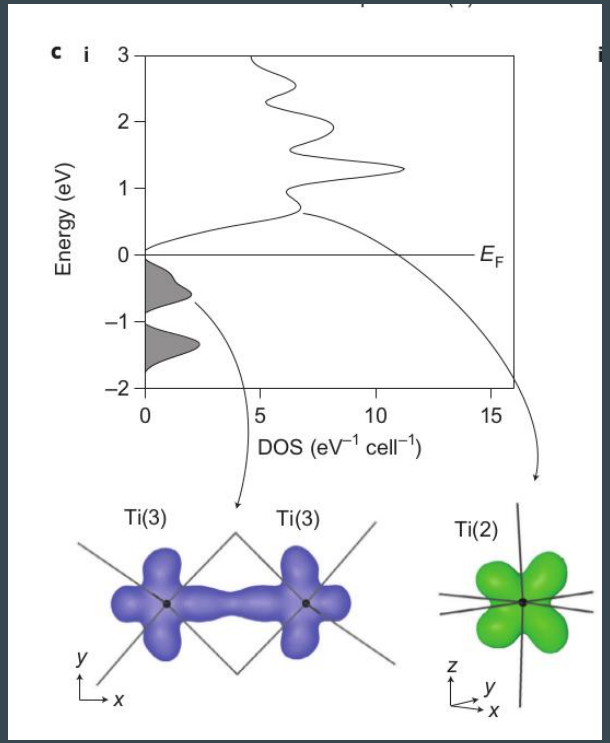
in or out of resonnance process

Possible photo-excitations can be deduced from DOS:

1) DFT calculations of electronic states
2) photo-emission spectra



Okhoshi et al., Nat. Chem.(2010)
Calculated DOS of photo-switchable Ti_3O_5

What can you do with a laser on Matter?

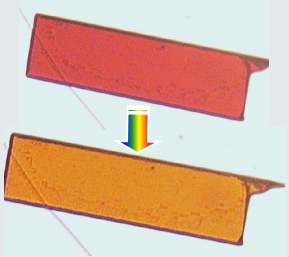
Electronic transitions can couple with other degrees of freedom
-> switching of macroscopic properties

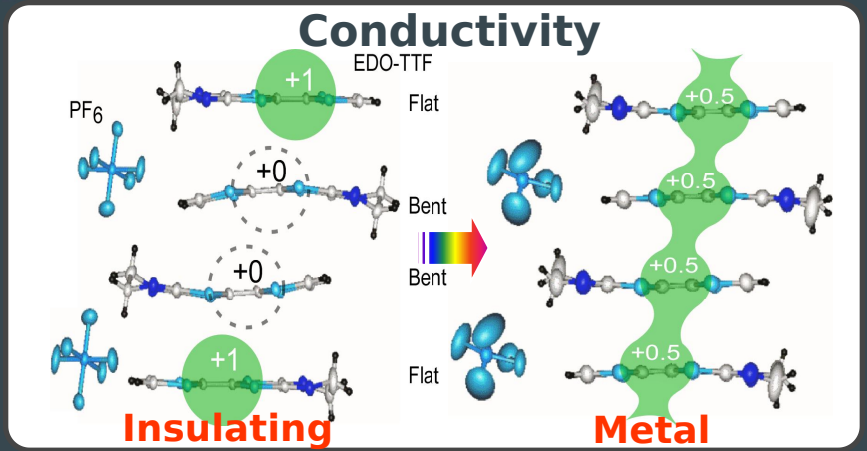
correlated material : e-/phonon/spin coupling -> resistive/magnetic switching ...

isolated molecules: photodissociation, change in magnetic state, coordination....

molecular materials: many coupled degrees of freedom / multifunctionality
-> photochromism, ferroelectricity, magnetism...

Photochromism





A CRYSTAL IS NOT A SUM OF (WELL ORGANIZED) MOLECULES

This also stands true for laser excitation processes …

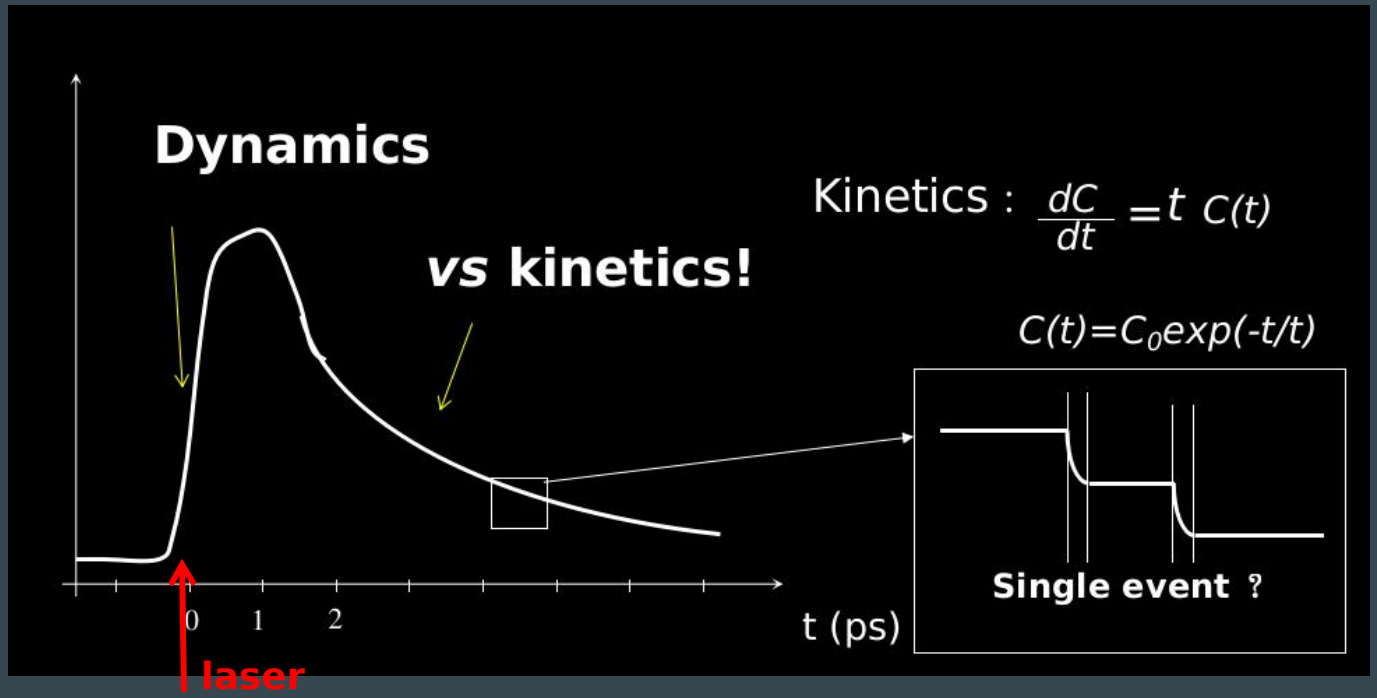
In crystals, N photons can do more than switching N molecules:

- one photon can switch several molecules : non-linear molecular switching
- long range lattice deformations: volume expansion/contraction
- photo-induced phase transition: long range ordered atomic reorganisation
- symmetry breakings
- photo-induced coherent dynamics (selective phonon activation)

-> New long range order can be probed by diffraction measurements

A photo-excitation process is intrisically an out-of-equilibrium process

After laser excitation, the system will evolve in time to reach a metastable
It will finally relax to the stable equilibrium state.



A photo-excitation process is intrisically an out-of-equilibrium process

Under continuous excitation, competition between transition probability and excited state life time can lead to photostationary states

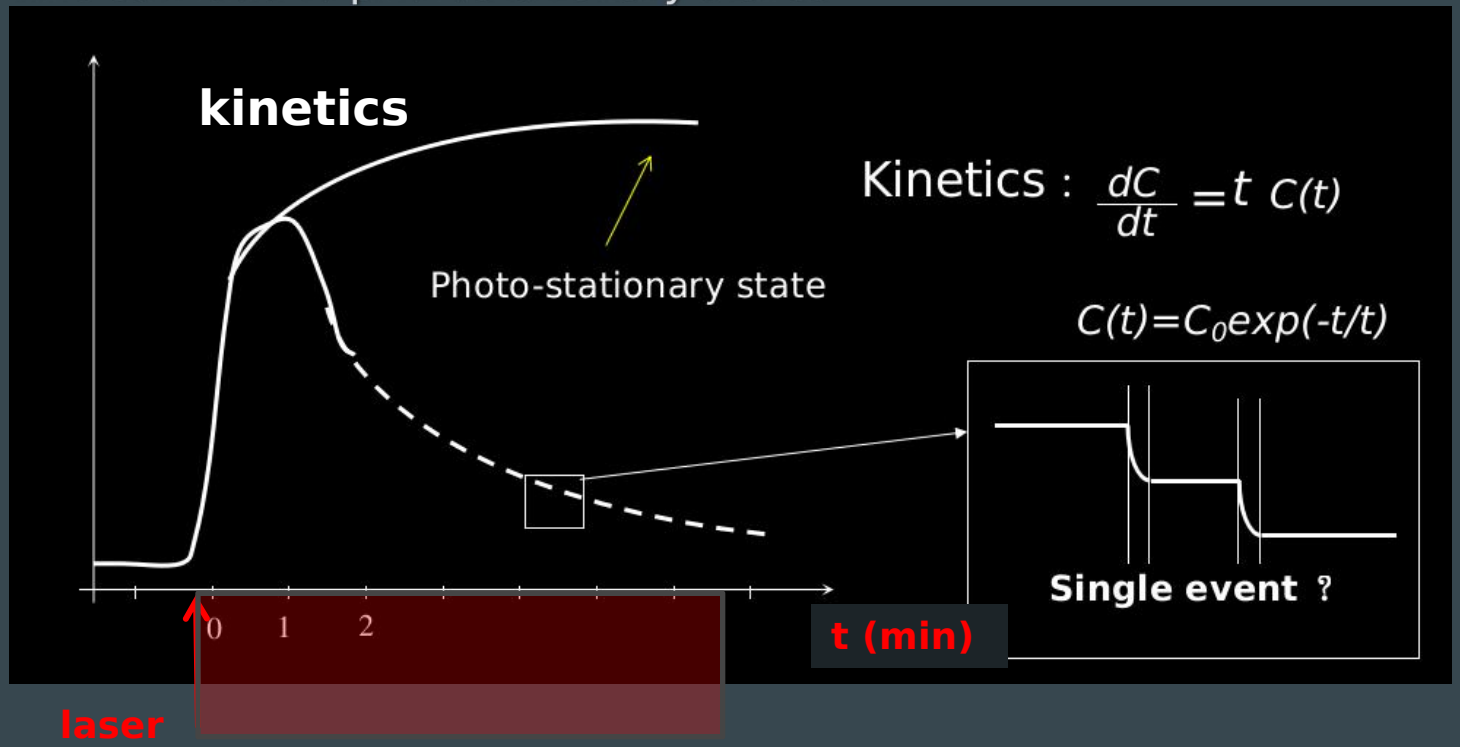


PHOTO-INDUCED PROCESS AND OUT-OF-EQUILIBRIUM PHYSICS

A photo-excitation process is intrisically an out-of-equilibrium process

Conclusion: Time matters !!!

WATCHING LASER DRIVEN PROCESS IN REAL TIME

Your measurement has to be faster than the dynamics / kinetics you want to probe

Typical laboratory measurement:

from few minutes (short cell parameters measurements, small number of Bragg peak analysis) ...

... to hours (complete data collection for structure solutio

Typical synchrotron diffraction measurement
can be faster (few minutes for complete acquisition)

but

What are the relevant time scales?

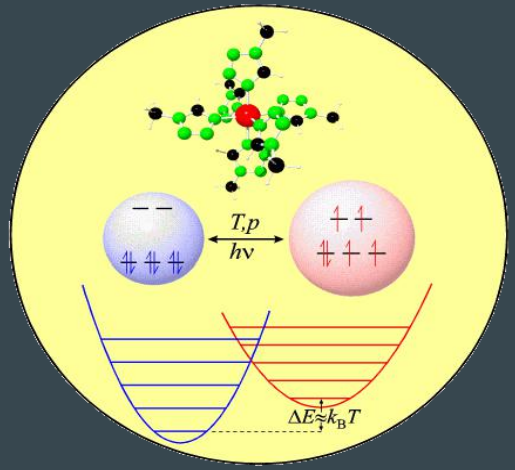
Slow kinetic inhouse measurement

PHOTO-INDUCED MOLECULAR SPIN STATE SWITCHING

LIESST and reverse LIESST Effect :

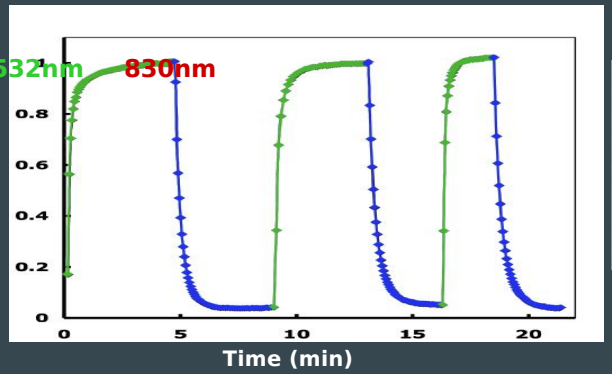
P Gütlich, A Hauser, H Spiering
Angewandte Chemie (1994)
S. Decurtins et al
Chem. Phys. Lett. (1984).

Low Spin S=0



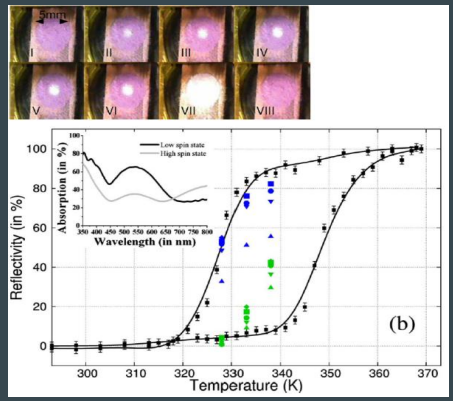
High Spin S=2

Reversible photomagnetic and photochromic pulsed-driven switching



M. Duriska et al, Angew Chem (2009)

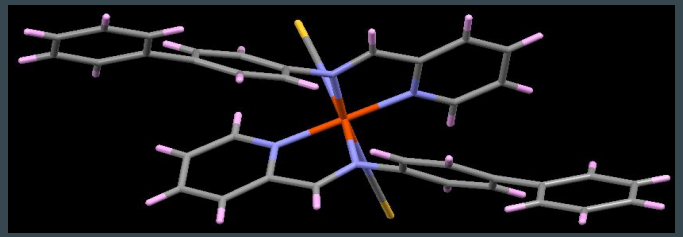
N. Brefuel et al Chem Eur J. (2010)

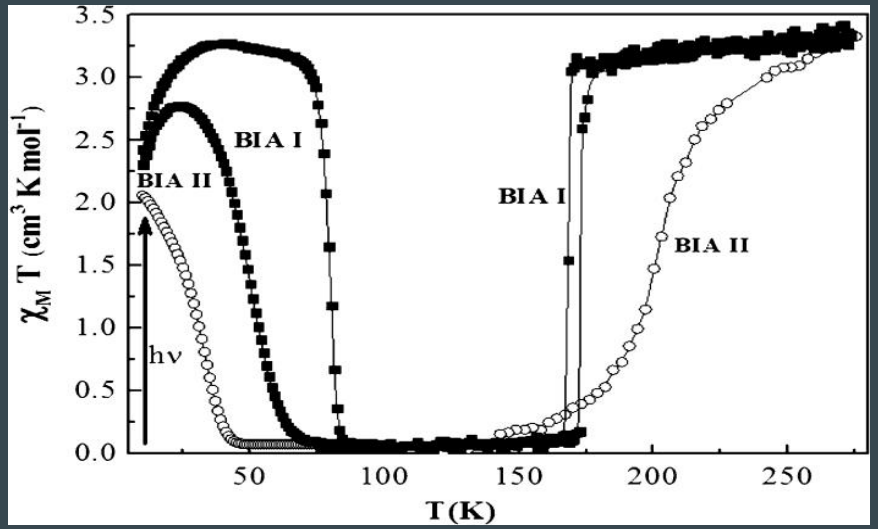


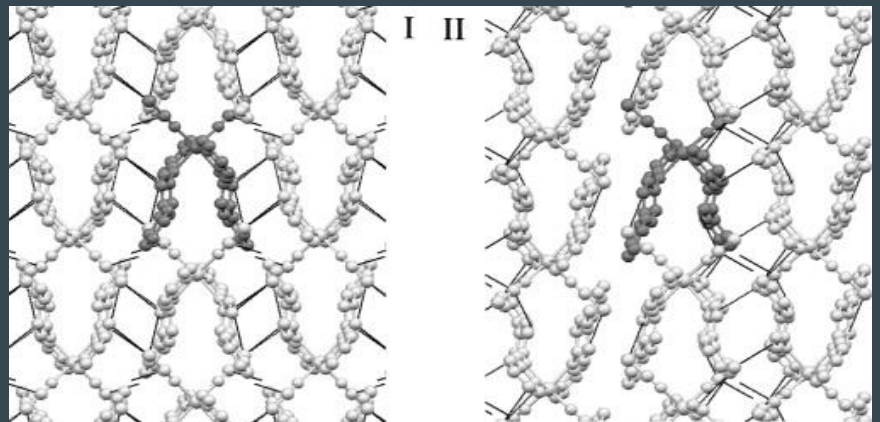
G Gallé et al, Appl. Phys. Lett. (2010)

ELECTRONIC REOGANIZATION VS MOLECULAR STRUCTURE

Change of the molecular structure between LS and HS states: polymorphism



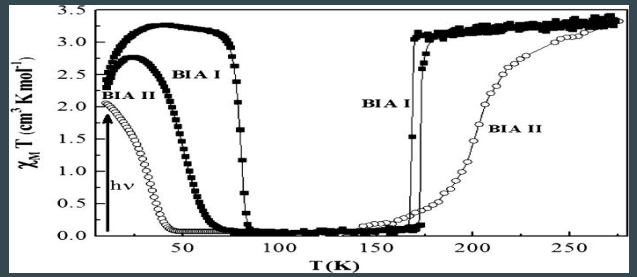




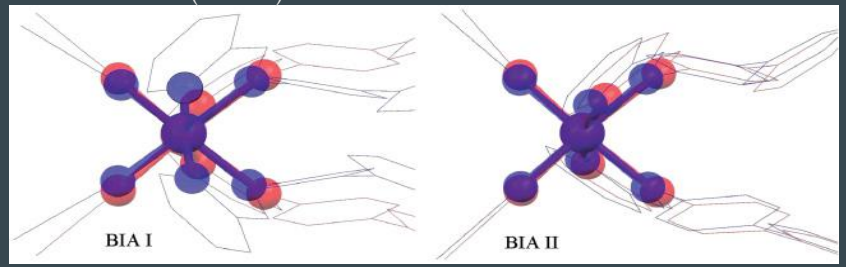
Buron M. et al. Phys. Rev. B 69, 020101(R) (2012)

Molecular reorganization

Change of the molecular structure between LS and HS states:
Polymorphism: role of the deformation in the stabilization of HS state



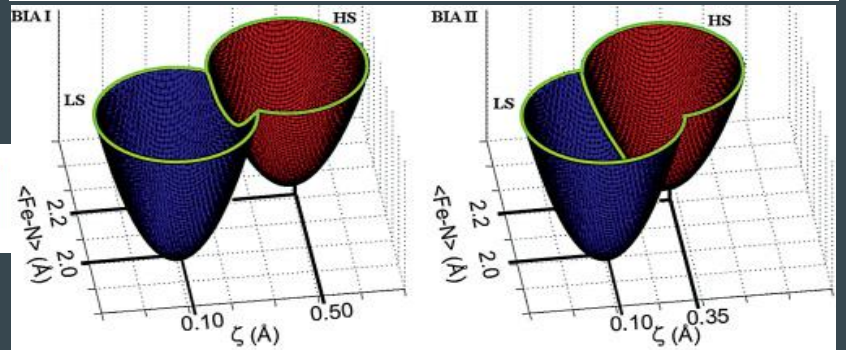
Buron M. et al. Phys. Rev. B 69, 020101(R) (2012)
2 mode description introduced by
A. Hauser et al, Coord. Chem. Rev. 250 (2006).



Order parameters :

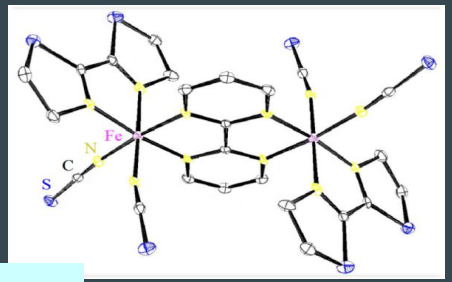
$$\sum = \sum_{i=1}^{12} |90 - \phi_i|$$

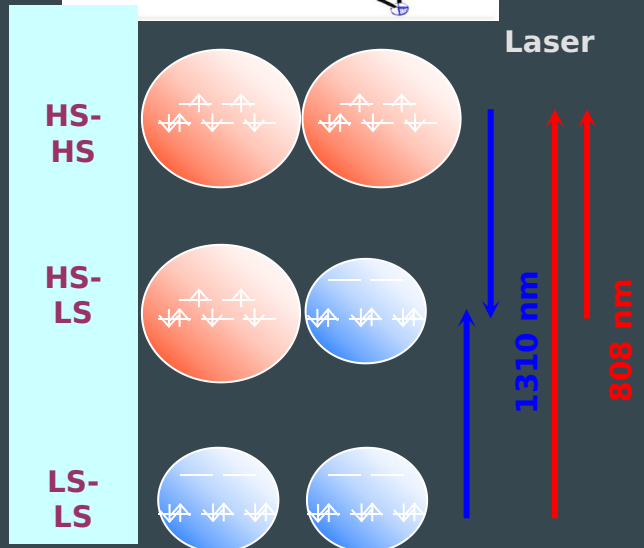
$$\zeta = \sum_{i=1}^{6} |(\text{Fe-N}_i) - \langle \text{Fe-N} \rangle|$$

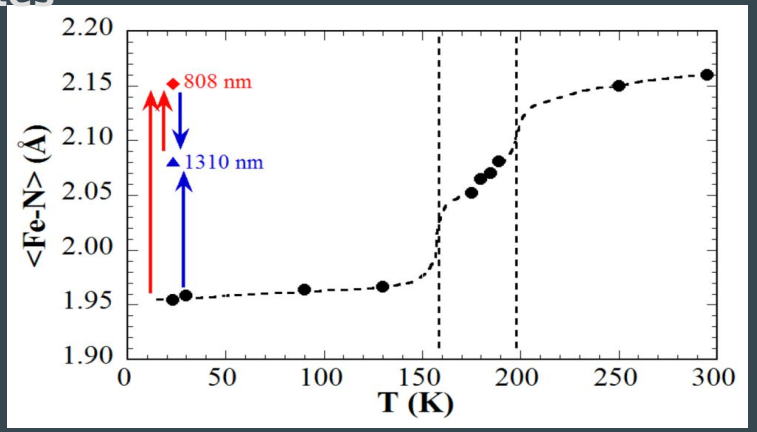


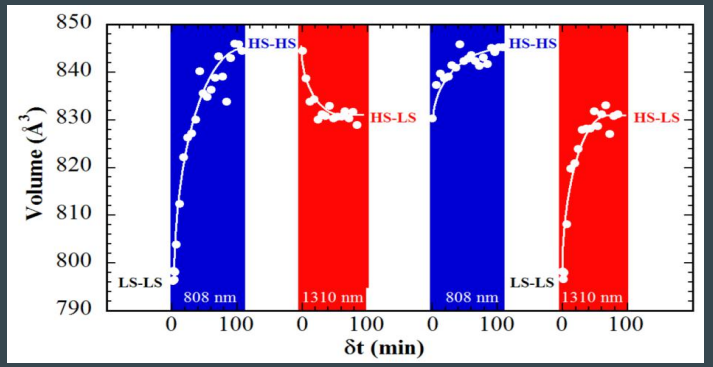
REACHING NEW PHASES BY LIGHT

Transition between excited states





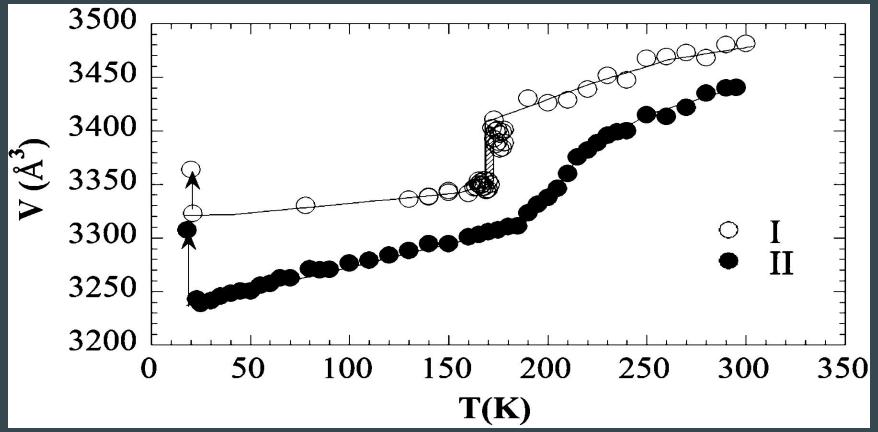




E. Trzop et al, J. App. Cryst (2007)
N. Ould Moussa et al, Phys Rev B (2007)

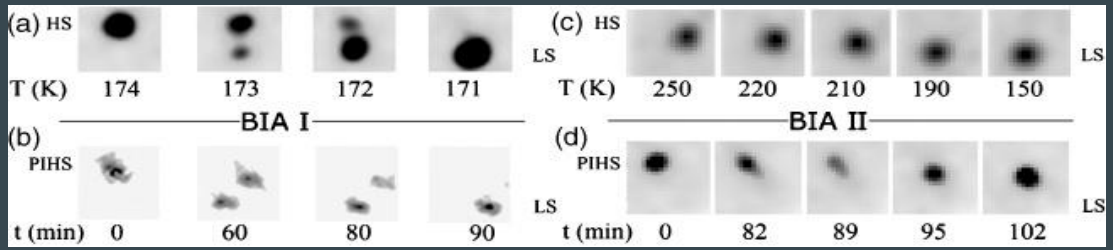
MACROSCOPIC STRUCTURAL CHANGES

Buron M. et al. Phys. Rev. B 69, 020101(R) (2012)



Temperature dependence of the unit cell volume around the spin transition.

Phase separation vs homogeneous crossover



Mechanisms of photo-excitations: Intriseque time scales

Which type of dynamics drives the photo–switching?

How do the different types of degrees of freedom evolve in time?

INTRISIC TIME SCALES

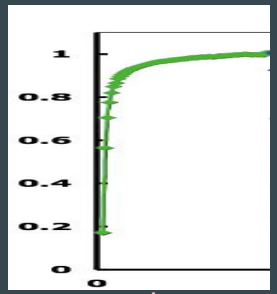
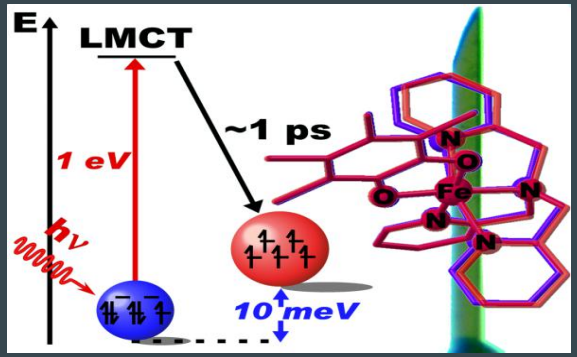
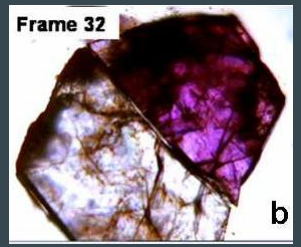
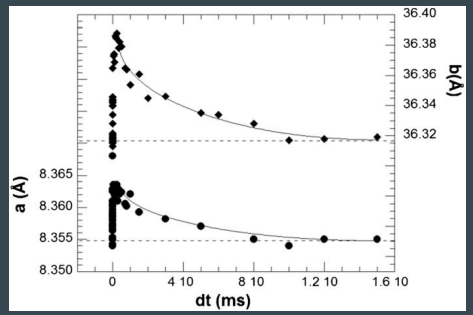


Photo-switching driven by cw laser:
within **few minutes**
Local process: <1ps
14 orders of magnitude difference

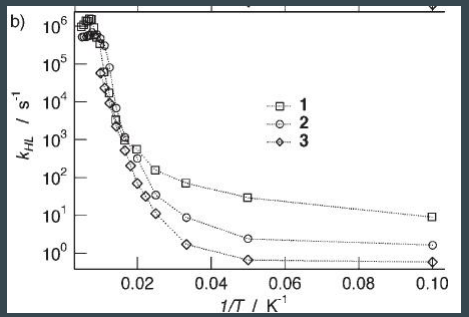




Domain growing : **few µm/s**!
Speed of sound = **few 1000s m/s**!
9 orders of magnitude of difference



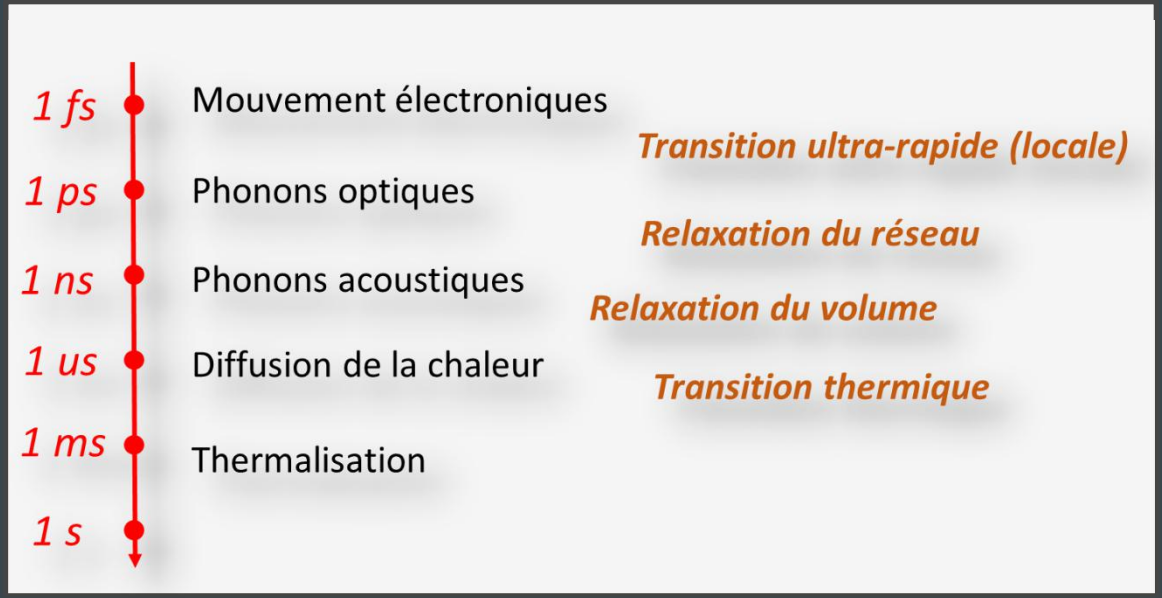
Relaxation from photoinduced :
relaxation rate observed limited by heat transfer (**from us to ms**)



Elementary dynamics <ps are hidden in a statistical average

Intrisic time scales

Multi-scale dynamics and relevant time scales



-> we need fs time resolution

Time resolution

Time resolution is limited by:

- Excitation duration.
- Xray exposure time.
- Detector counting time
- Synchronisation jitters

Ultrafast Xray diffraction

Time resolution

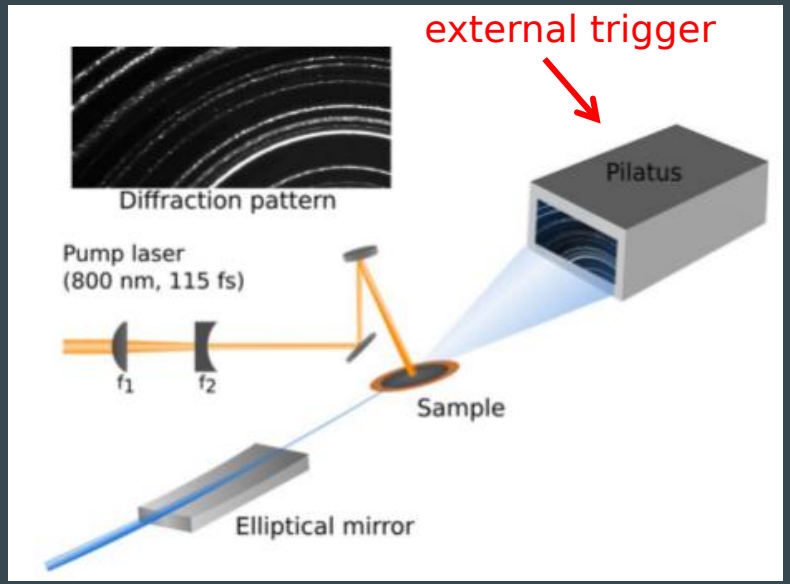
Time resolution is limited by:

- Excitation duration. -> from CW to pulsed laser (up to few fs pulses)
- Xray exposure time.
- Detector counting time
- Synchronisation jitters

Time resolution

Time resolution is limited by:

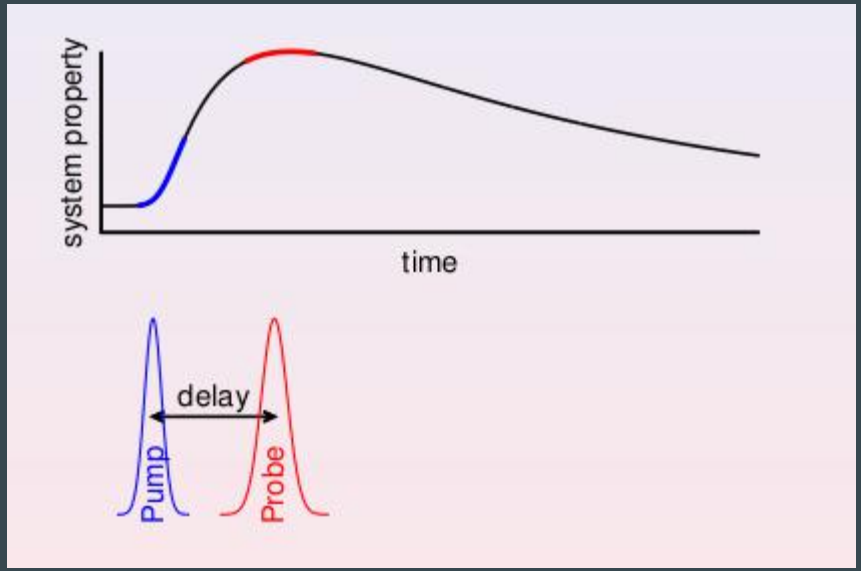
- Excitation duration. -> from CW to pulsed laser (up to few fs pulses)
- Xray exposure time.
- Detector counting time -> detector gating (us exposure)
- Synchronisation jitters



PUMP - PROBE MEASUREMENTS

Pump : synchronized start - ultrashort laser pulse (or E field, ...)

Probe: Ultrashort Xray pulse (or laser, or e^- ...)



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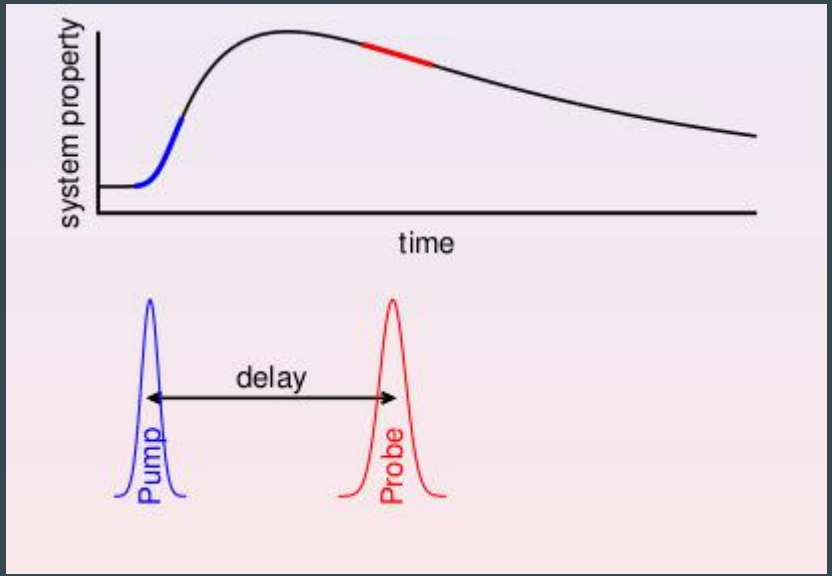

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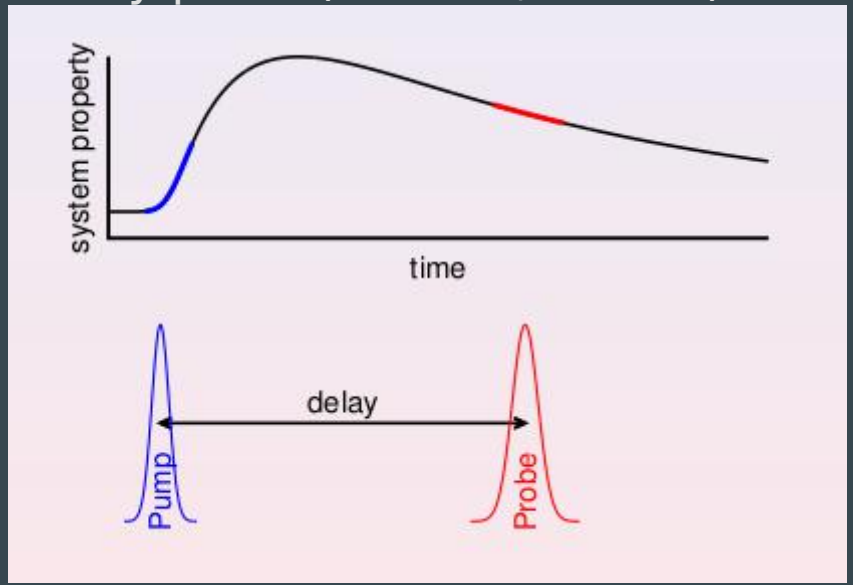

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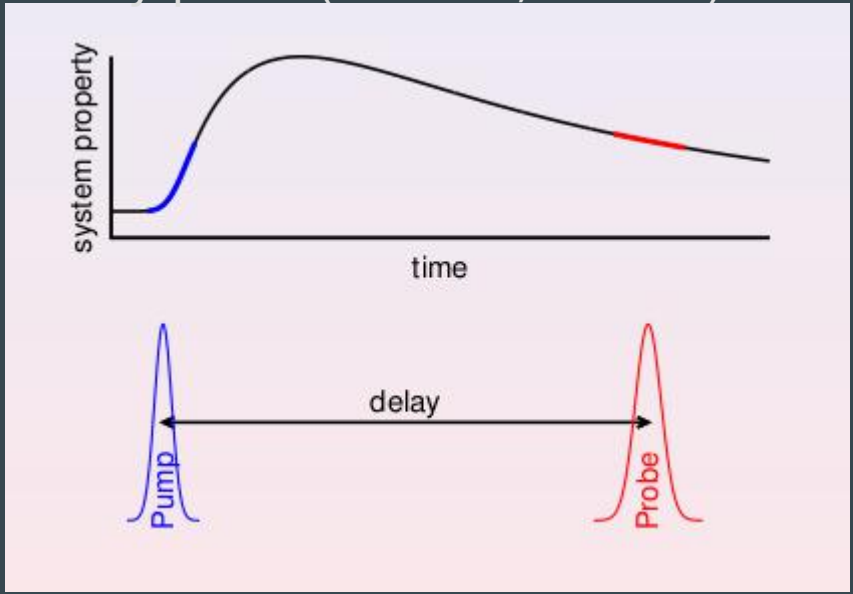


Stroboscopic measurement:

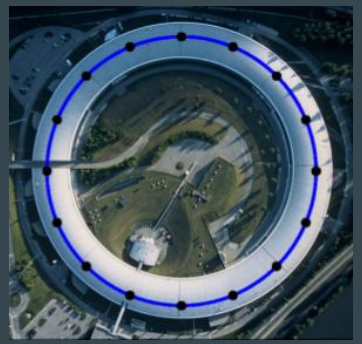
- Time resolution is independant of detector resolution
- depends on pump and probe duration
- depends on pump and probe synchronisation (jitter)

Pulsed Xray generation

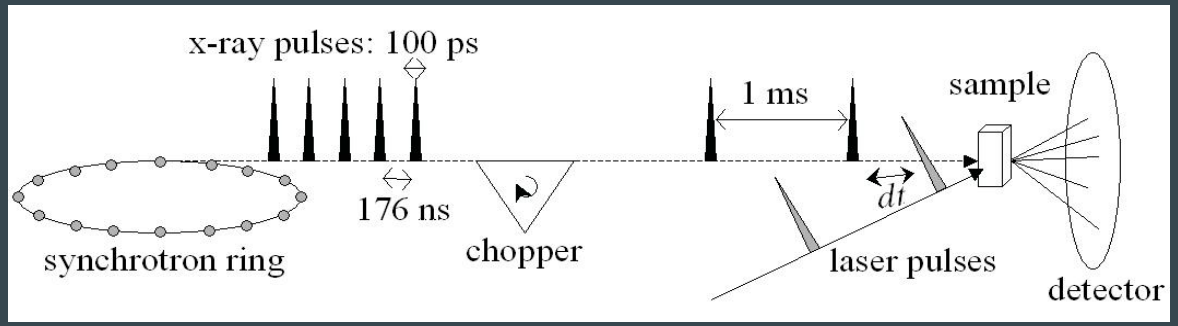
Pulsed Xray sources

Synchrotron "chopped" pulses (id09@ESRF, ID14C - BIOCARS@APS - KEK) -

Time resolution is limited by xray pulse duration **~ 100ps**



Time structure of synchrotron radiation

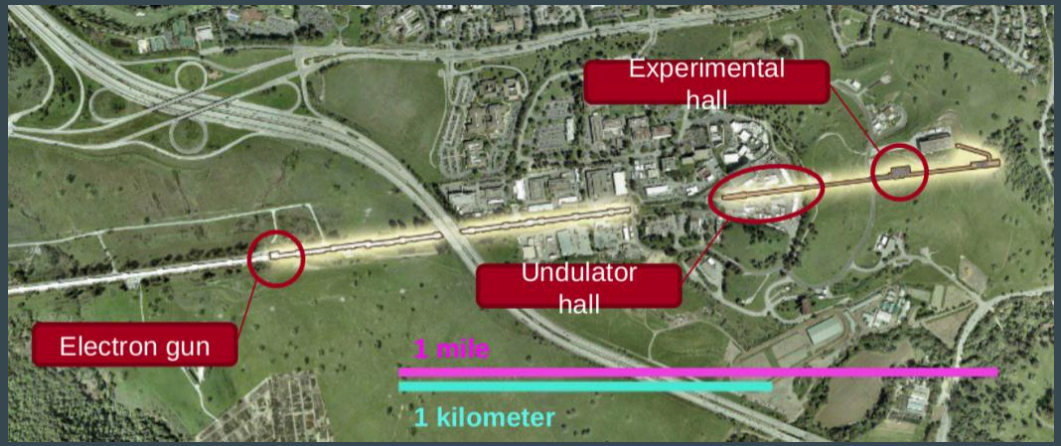


Pulse duration: 100ps
Repetition rate: from 1 KHz to few Hz
Xray energy : from 8 keV to 25 keV / monochromatique or pink beam (1% band width)

Pulsed Xray sources

Free Electron Laser (Xfel)- SLAC (Standford), SPRING8 (Japan),
2017: Swissfel (PSI), European Xfel (Hamburg)

Time resolution is limited by jitters **: up to 10 fs**

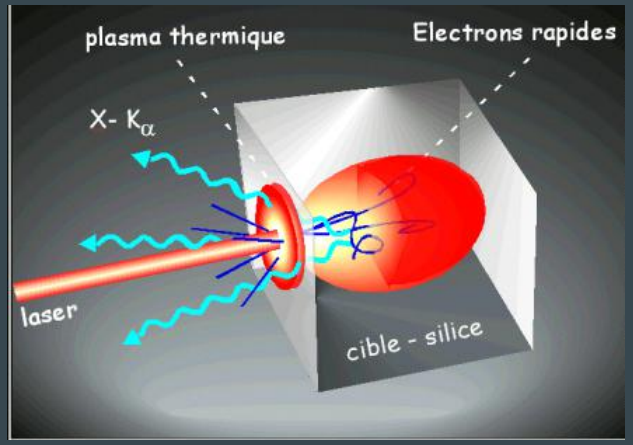


- Pulse duration: 10 fs
- Photon per pulse > 10^3 than synchrotron
- Xray energy : up to 7-10 keV / monochromatic
- BUT xray/laser jitter / energy drift, jitter -> requires complex timing/diagnostic tools and post-processing

PULSED XRAY SOURCES

Alternative fs xray sources:

Plasma (lab) source:



A. Rousse et al, Nature *(2001)*
T. Elseasser et al, Acta Cryst A *66 (2010)*

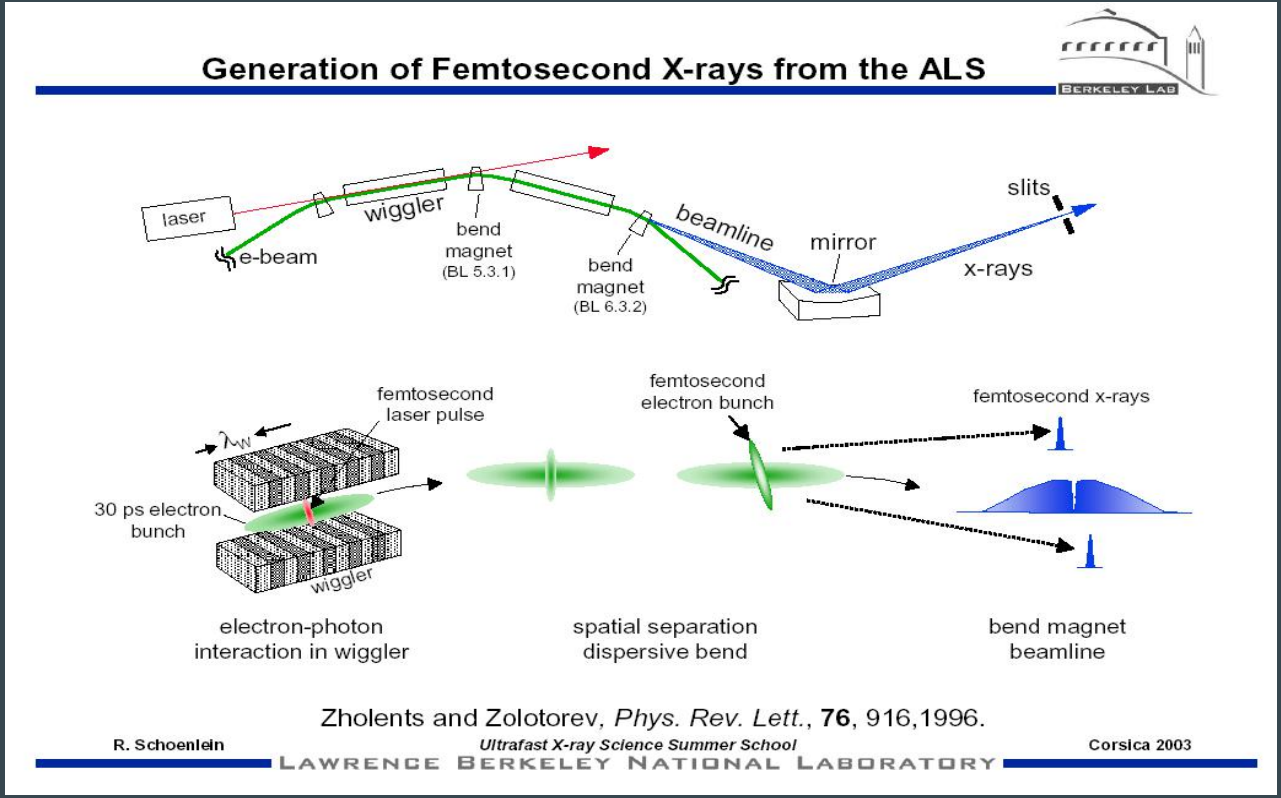
Time resolution ~ **100fs** but small number of photons /pulses

PULSED XRAY SOURCES

Alternative fs xray sources:

Xray slicing @ synchrotron (SLS (PSI), Soleil) :

Time resolution ~ **100fs**



S. Johnson et al,
***Acta** 66 **Cryst A.** 2010)*

Time-resolved Xray diffraction under photo-irradiation: Quantitative analysis

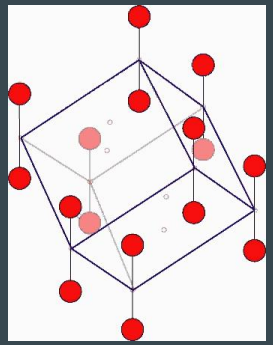
DIFFRACTION ANALYSIS : OPPORTUNITIES AND MAJOR ISSUES

What information you can get (in theory):

- **Volume changes**: peak shifts.
- **Changes of atomic position** ("structure"): changes in peaks relative intensities
- symmetry changes : new Bragg peaks
- Unit cell **strain**: peak broadening
- **Thermal displacement** increase (decrease of the intensity at high q)

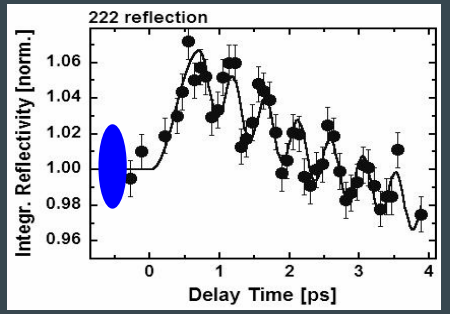
The textbook example: Coherent atomic motion in Bismuth thin film

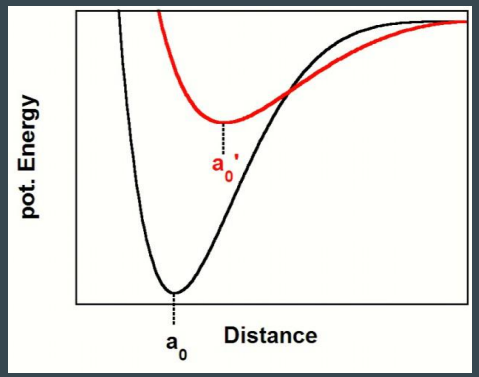
Electronic redistribution after fs excitation:
change of interatomic potential

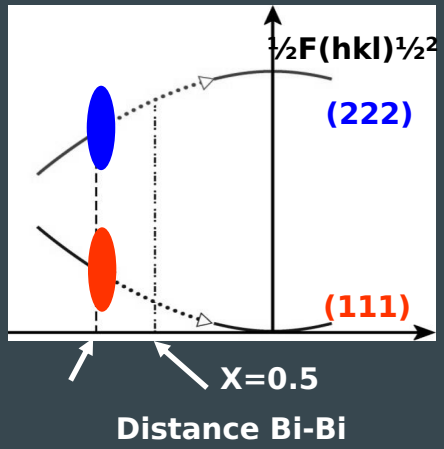


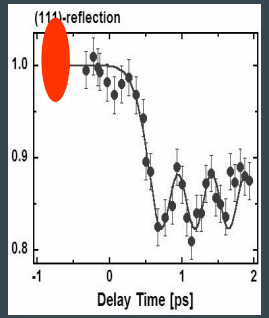
$$F = 2f_{Bi} \cos [p (h + k + l) x]$$
$$X=x_0 cos(wt)$$

Coherence: F_{hkl} (t)
Real time evolution of the structure factor









K. Sokolowski et al., Nature (2003)
D. Fritz et al, Science (2007)
Beaud et al, Phys. Rev. Lett. (2007)

DIFFRACTION ANALYSIS : OPPORTUNITIES AND MAJOR ISSUES

In practice, quantitative analysis is still challenging:

- **Normalisation between different delays is challenging:** strong intensity variation between xray/laser pulses .
- **Sample might be sensitive to both xray and laser pulse ->** macroscopic degradation/microscopic defaults / (displacement)
- **Laser penetration depth is usually small** : surface excitation vs volume probe (xray)
- **Statistic is usually poor (few photons per pulse):** need to average a lot for each image
- High frequency stroboscopic measurements can lead to **residual heating**

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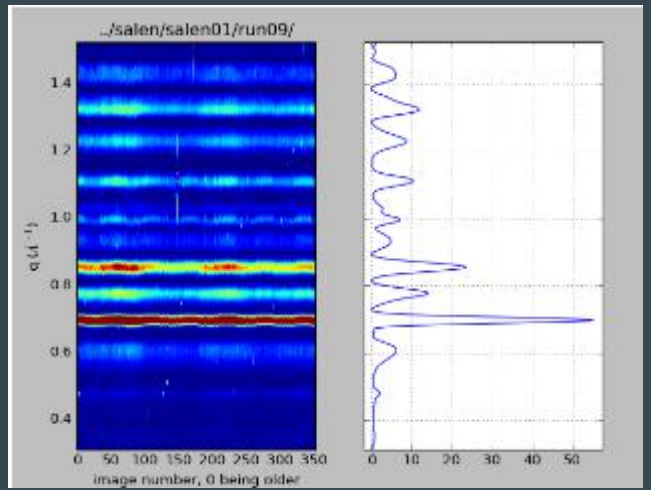
GOLDEN RULES

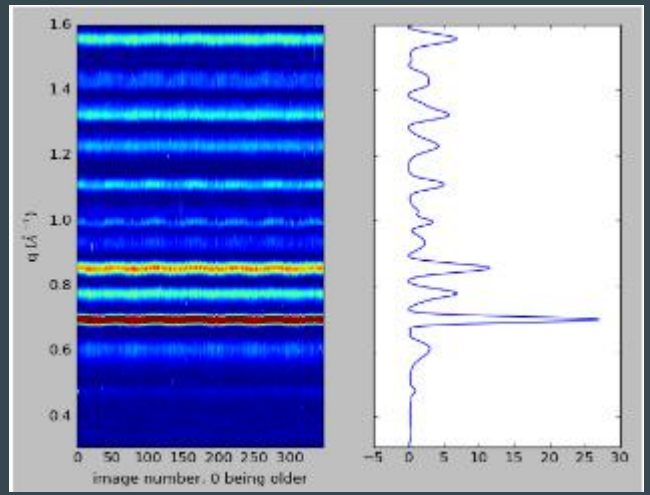
1) simulaneous measurement are always better:

- Laue measurements
- Powder
- large area detectors

2) take as much references as you can:
measure "offs" spectra regularly and check stability

without normalization





normalized

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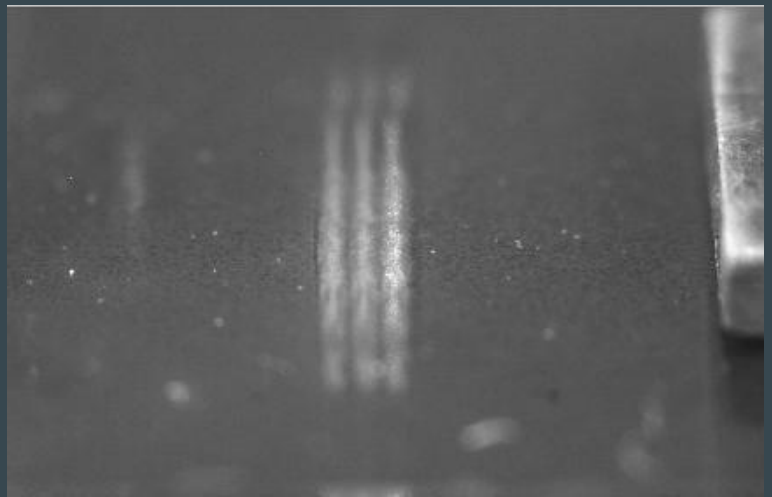
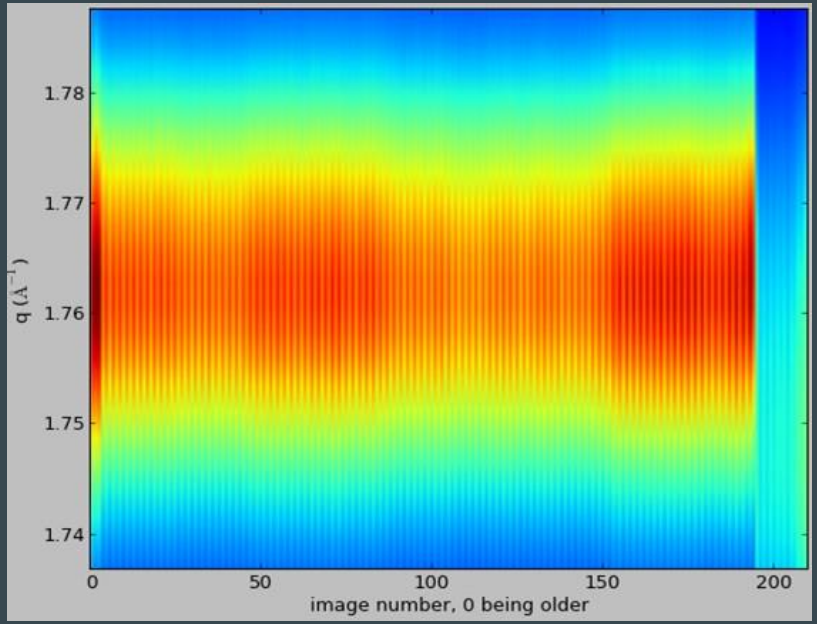
Sample surface after one hour laser exposure



Golden rules

3) check negative time delays to track artefacts/residual effects

4) repetition rate should be as high as possible for better statistics, but not higher!...



Alternating -5ns/offs measurements showing clear residual effect

(id09@ESRF, powder diffraction)

DIFFRACTION ANALYSIS : OPPORTUNITIES AND MAJOR ISSUES

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Laser penetration issue

Laser penetration can be calculated from real/imaginary refractive index measured:

- by specular reflectivity measurement
- by ellipsometry

usually few 100 nm (or less...) !!

Hard xray will penetrate over microns ....

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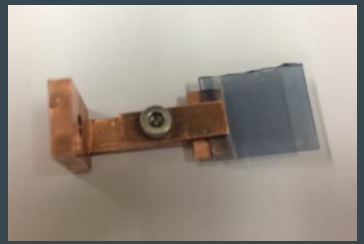
Hard xray will penetrate over microns ....

Strategie 1: Working with thin samples

- very small / thin single crystals
- epitaxial thin films
- polycrystalline thin film



Laser penetration issue

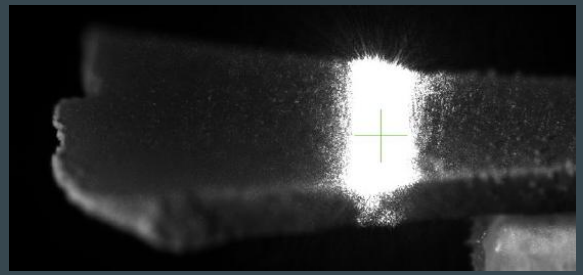
Strategie 2: Limiting xray penetrations

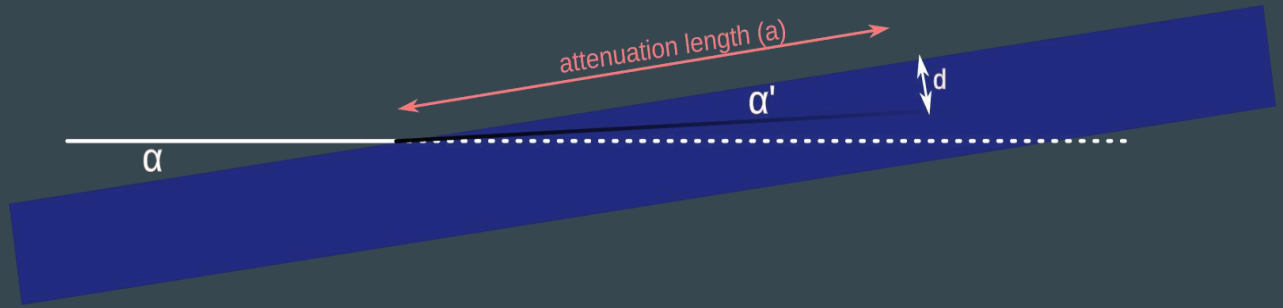
- working with small energy and/or very small incident angle

Drawbacks:

1) no oscillation -> Laue/powder measurement

2) requires larges surface or very small beam
(footprint of 20 um beam at 0.5 deg incidence
is few millimeters)





Living with differentials signals

However hard you work,

- photo-induced signal will usually by small
- excitation will not be homogeneous

You will have to think in the world of differentials signals

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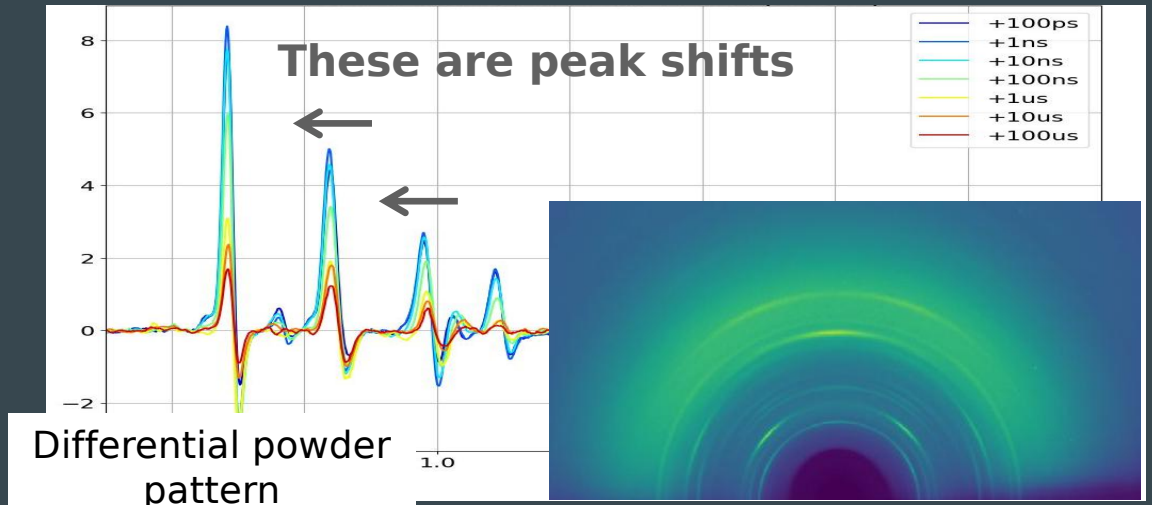

Differential powder pattern

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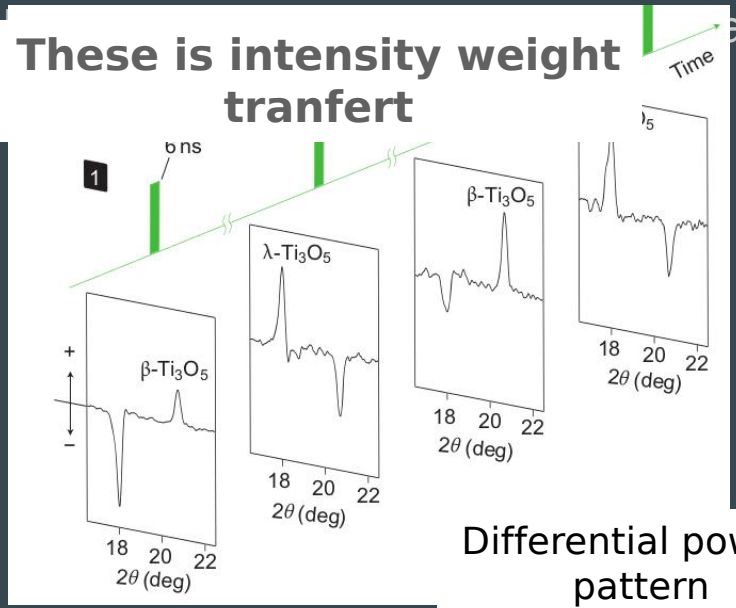


Differential powder pattern

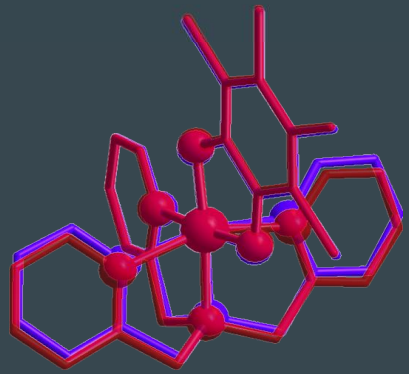
Living with differentials signals : structure refinement

Ex: spin state conversion

Average molecular structure following fs laser excitation

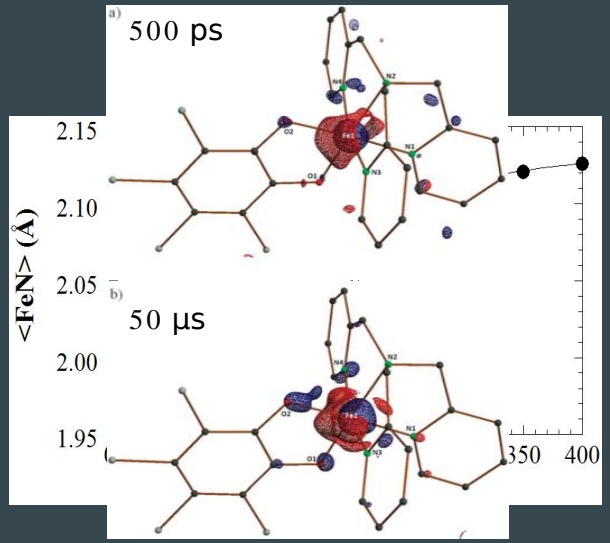
$$\langle F(hkl,t)\rangle = X_{HS}(t)\, F_{HS}(hkl) + (1-X_{HS}(t))\, F_{LS}(hkl)$$

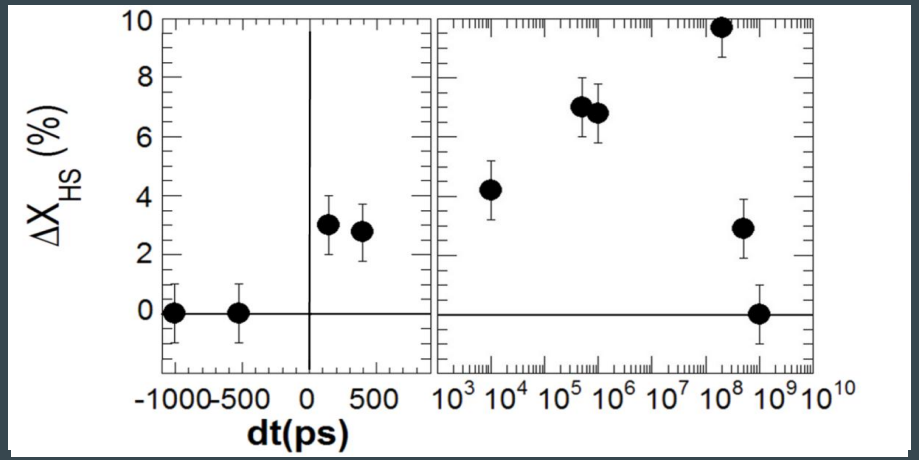
Gives an average <Fe-N>



Order parameter <Fe-N >can be refined:

$$\langle Fe\text{-}N\rangle = X_{HS}(t)\, \langle Fe\text{-}N\rangle_{HS} + (1-X_{HS}(t))\, \langle Fe\text{-}N\rangle_{LS}$$





E. Collet, Phys. Chem. Chem. Phys. **14** 6192 (2012)

Cailleau H. et al, Acta Cryst **A 66** (2010)

Living with differentials signals : structure refinement

Refinement against differentials: the LASER program (*Coppens, J. Appl. Cryst. 2010*)

Based on the **RATIO** method : refinement against $\mathbf{I_{on}/I_{off}}$ **:**

- Equilibrium ("laser off") structure is known (and fixed)
- Out-of-equilibrium (laser "on") structure is refined **with relevant degrees of freedom : fixed geometry, rigid body ...**

Living with differentials signals : structure refinement

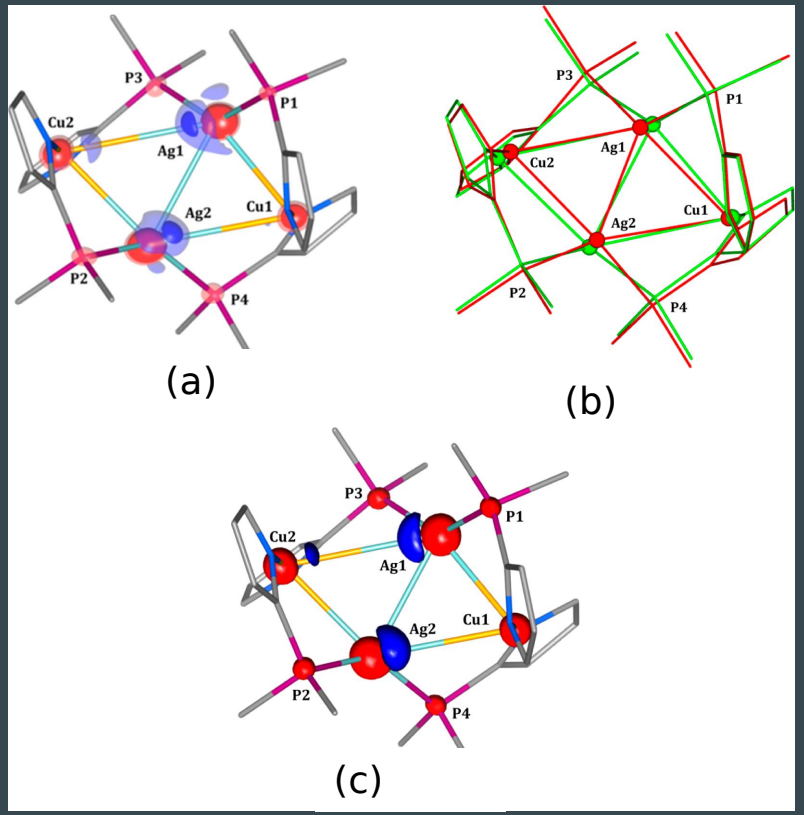
Refinement against differentials: the LASER program (*Coppens, J. Appl. Cryst. 2010*)

Structure determination at 100 ps time delay after ultrashort laser excitation

(a) photodifference map calculated from $<F_{on}-F_{off}>$

(b) refined excited state geometry

(c) deformation map based on the refined model parameters

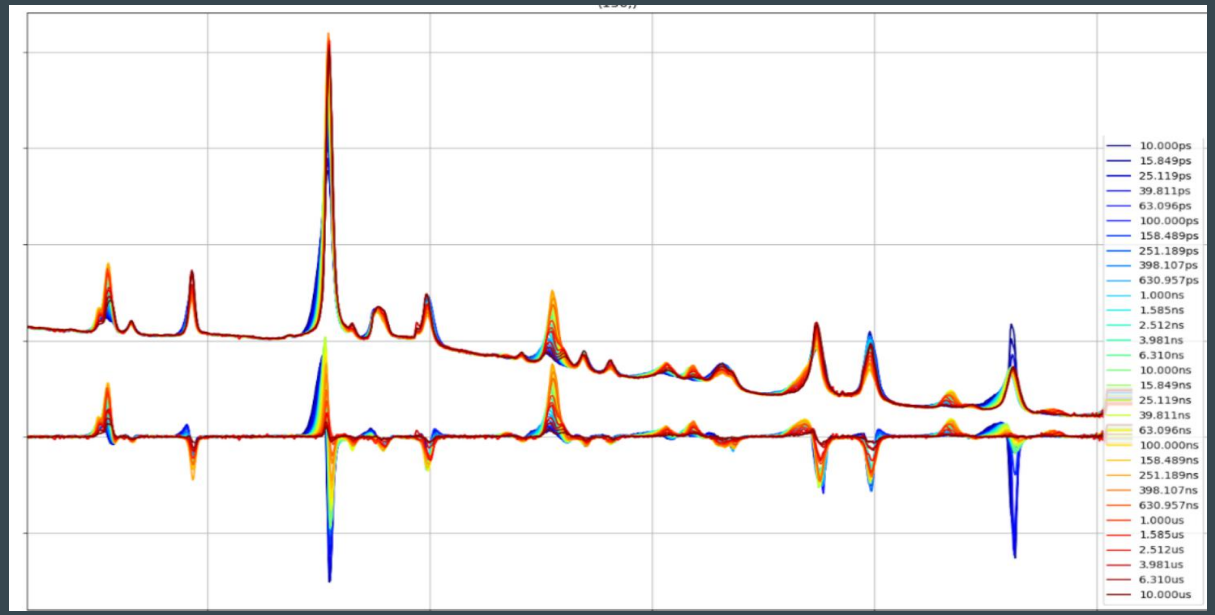


Jarzembska et al., Inorganic chemistry 2014

Time scale matter

Good measurements allow quantitative analysis but:
you cannot refine everything!

Post-processed Xfel powder diffraction pattern
bernina@Swissfel (pilot experiment, dec. 2017, Cammarata, Lemke, Mariette et al.)



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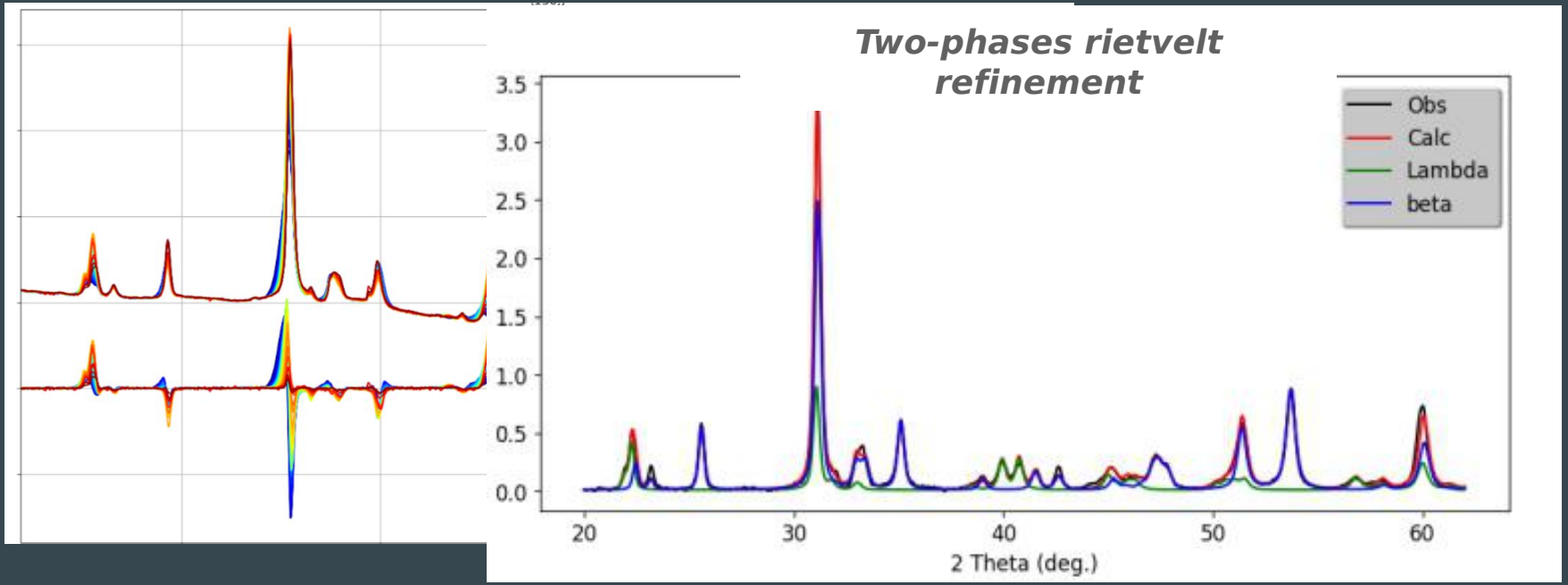

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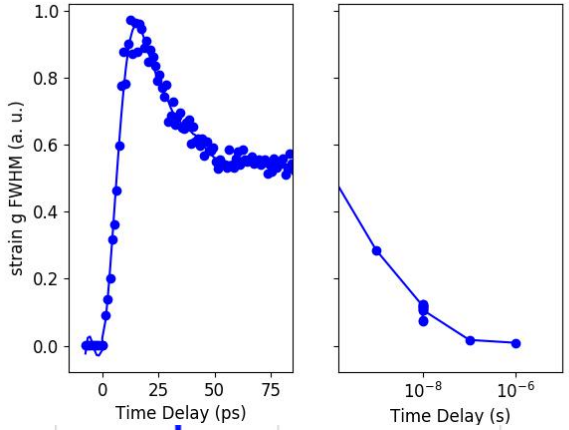
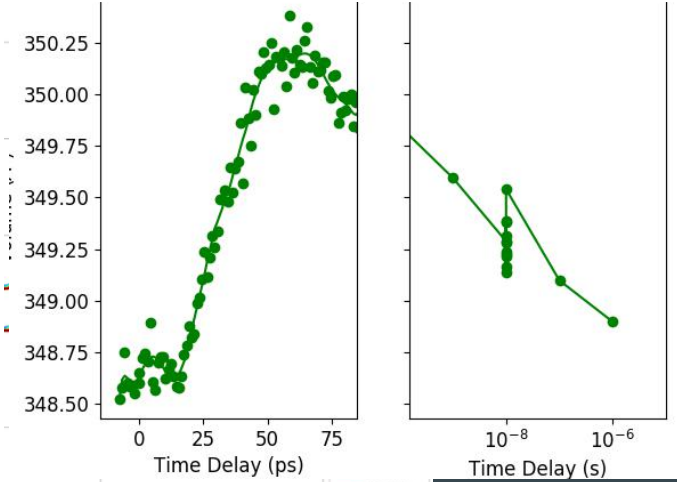
different degrees of freedom have their own time scales:

1) strain appears first



2) volume cannot change before few ps



THE END ...