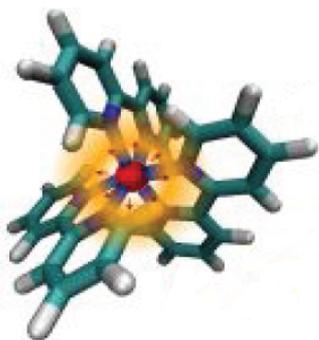
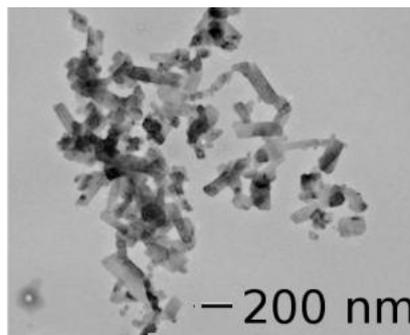




# From molecular switching to material transformation: revisiting the spin crossover with ultrafast lasers and Xrays



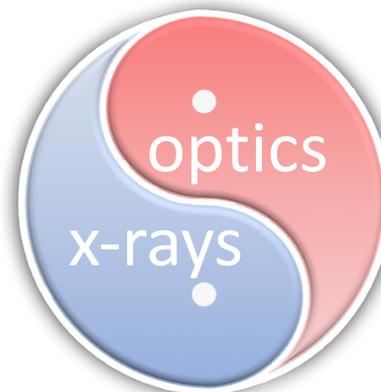
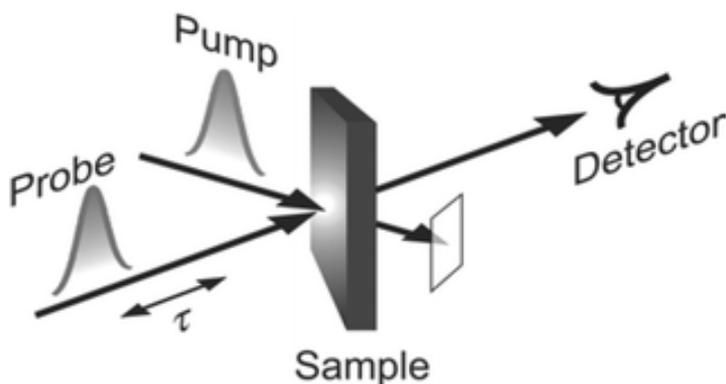
single-molecule

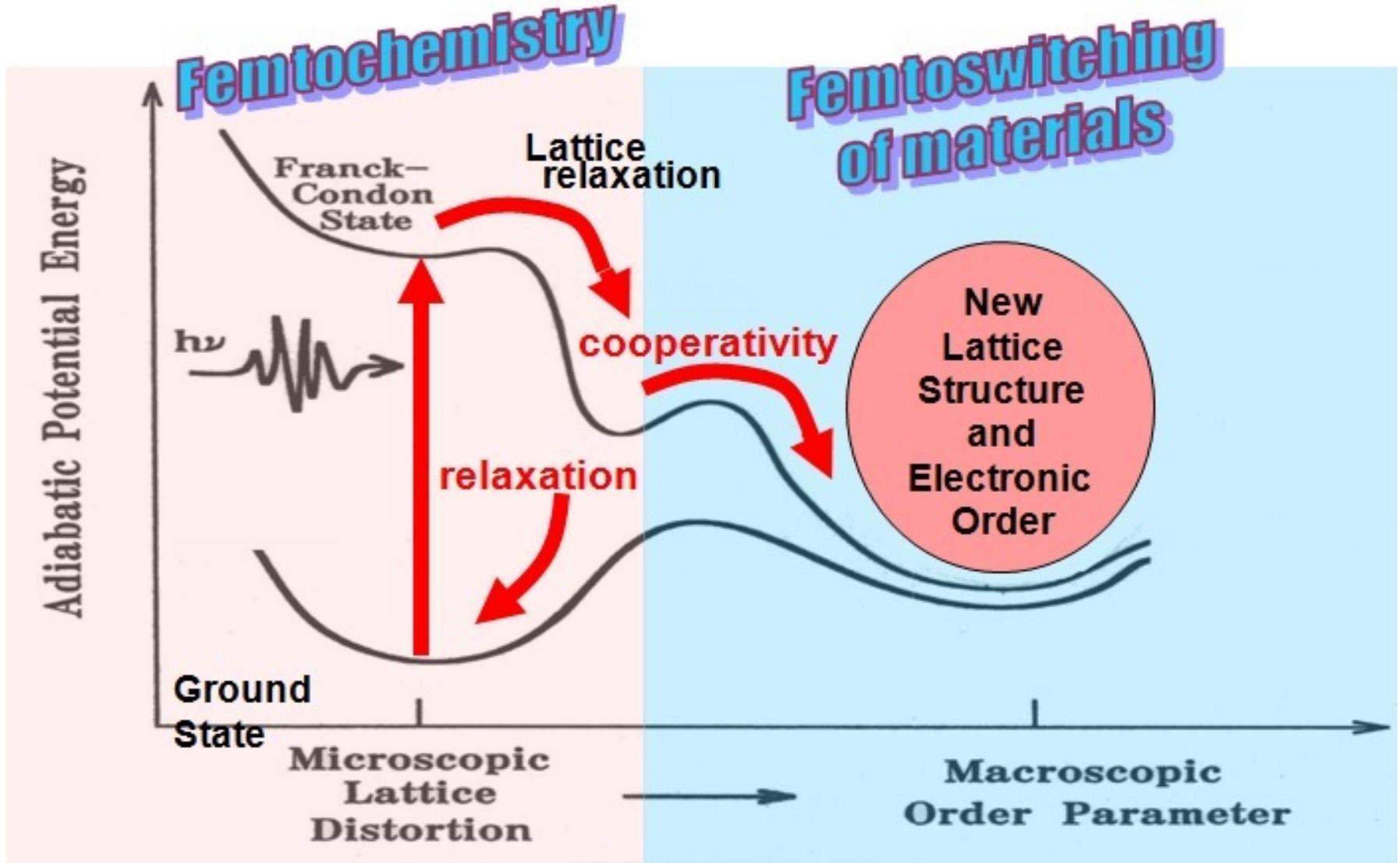


nano-crystal



single-crystal





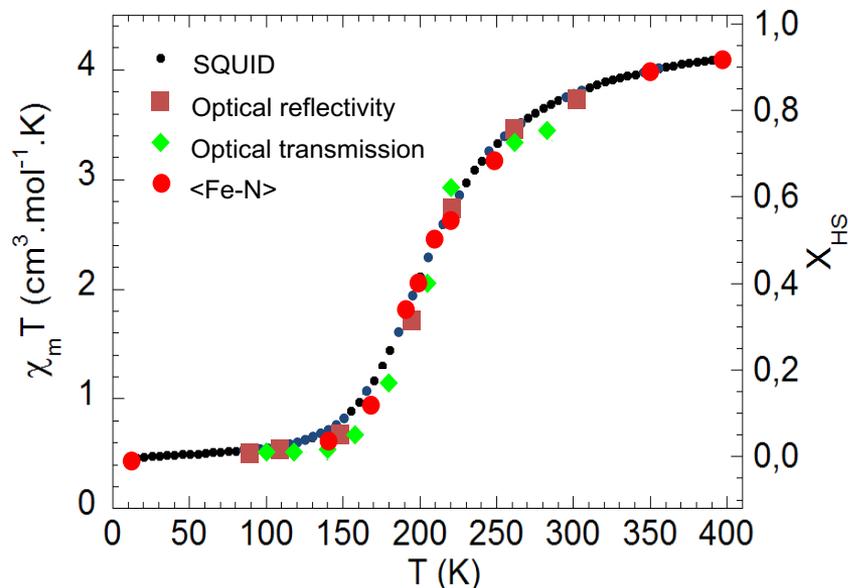
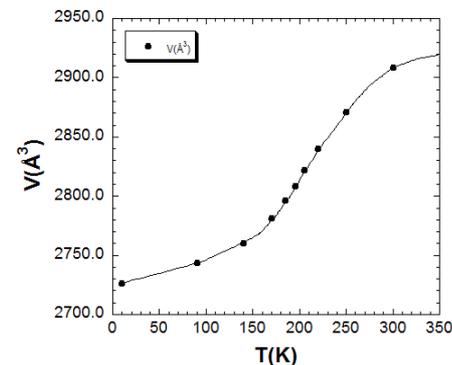
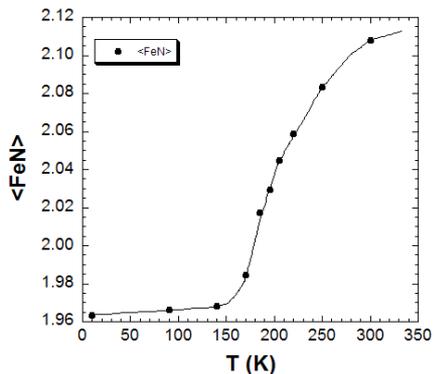
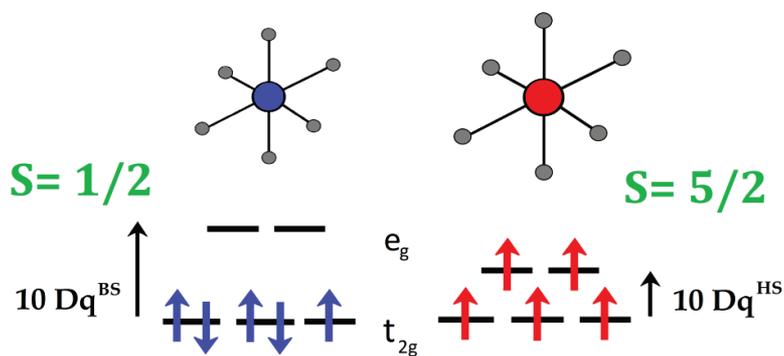
“Spin Crossover in Transition Metal Compounds I-III”, Ed P. Gülich & H.A. Goodwin  
(Springer, 2004)

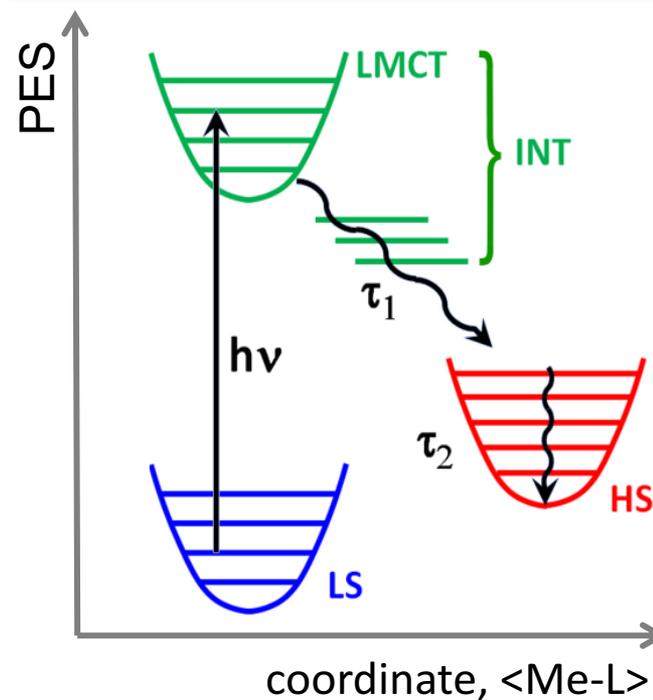
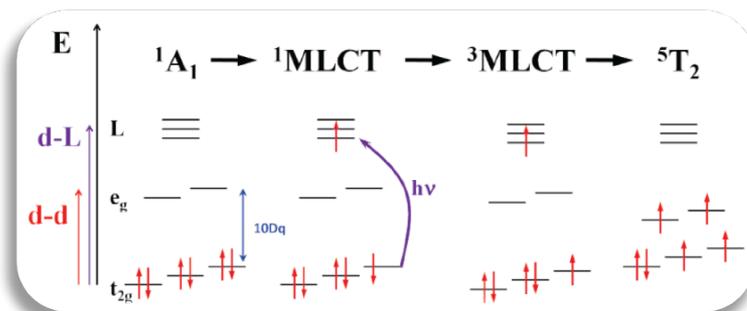
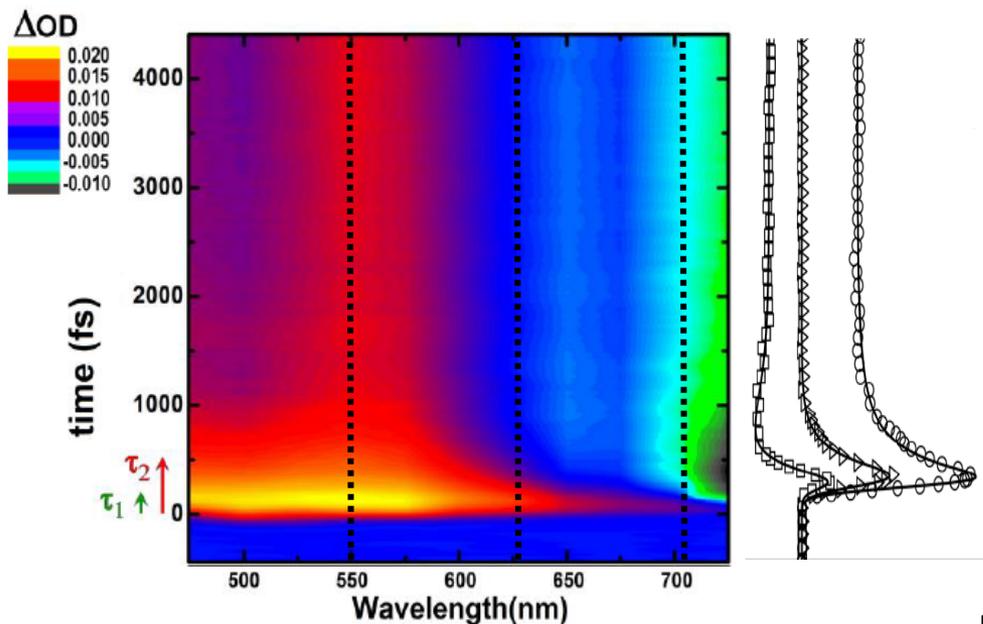
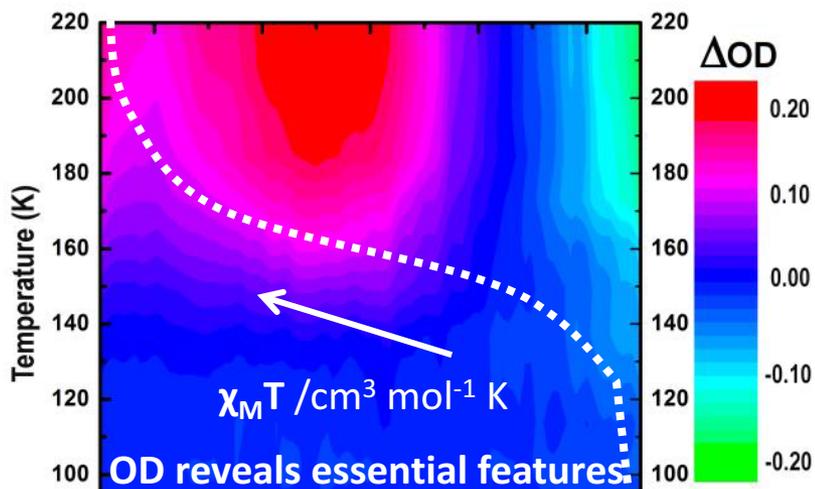
Spin-crossover in molecular crystal

Control parameters :

equilibrium (T, p,...)

out of equilibrium (hv)

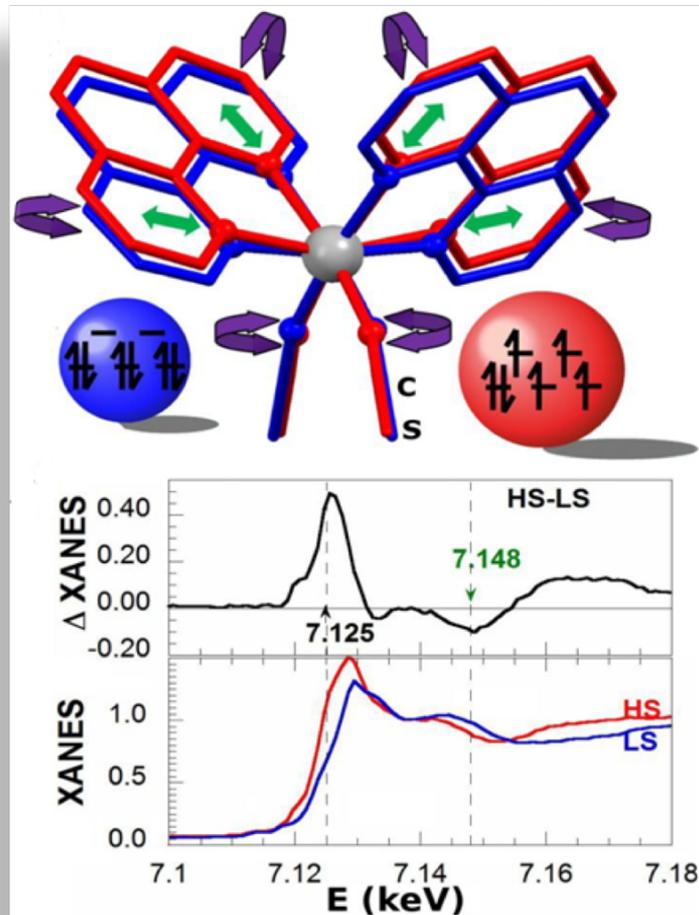
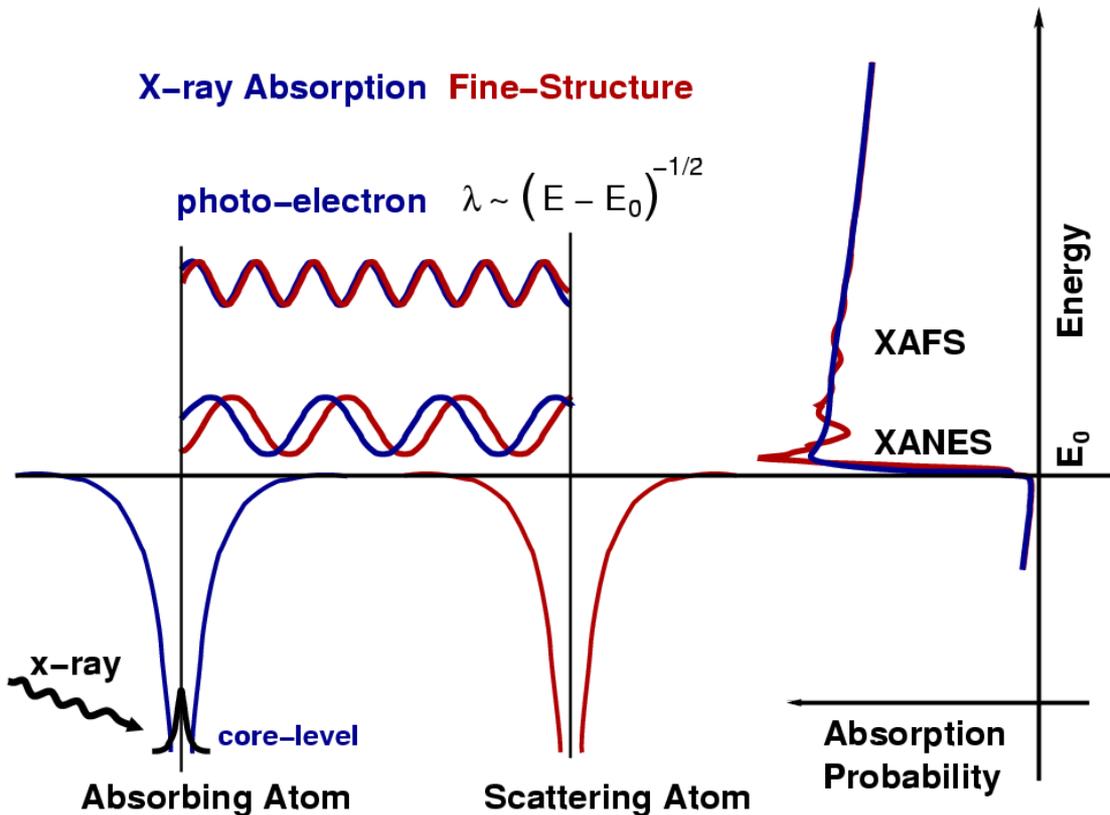




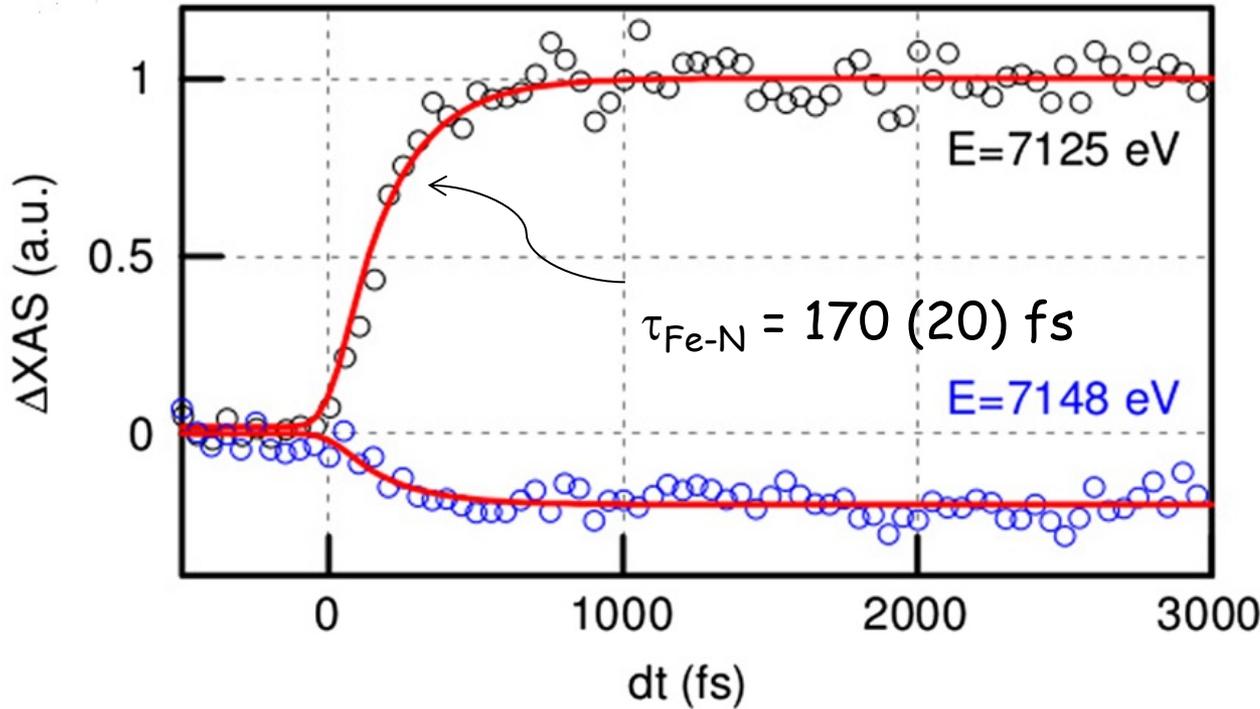
Bertoni *et al.*, *Angew. Chem. Int. Ed.* **51** (2012)

## X-ray Absorption Fine-Structure

photo-electron  $\lambda \sim (E - E_0)^{-1/2}$

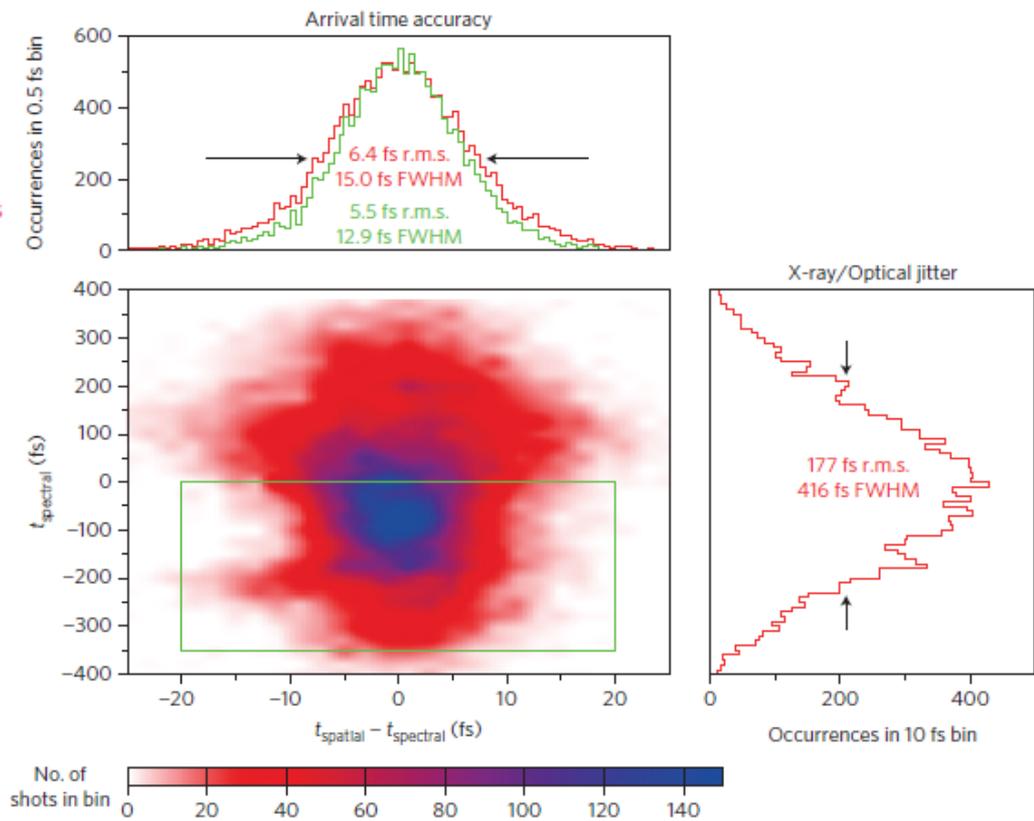
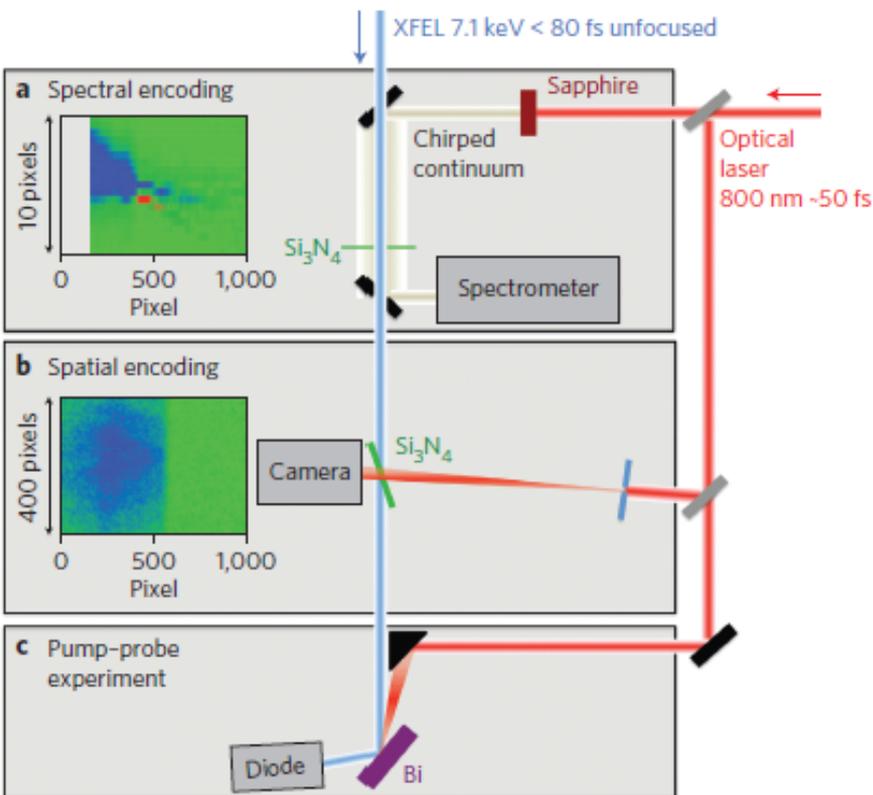


Cammarata *et al.*, Phys. Rev. Lett. 113 (2014)



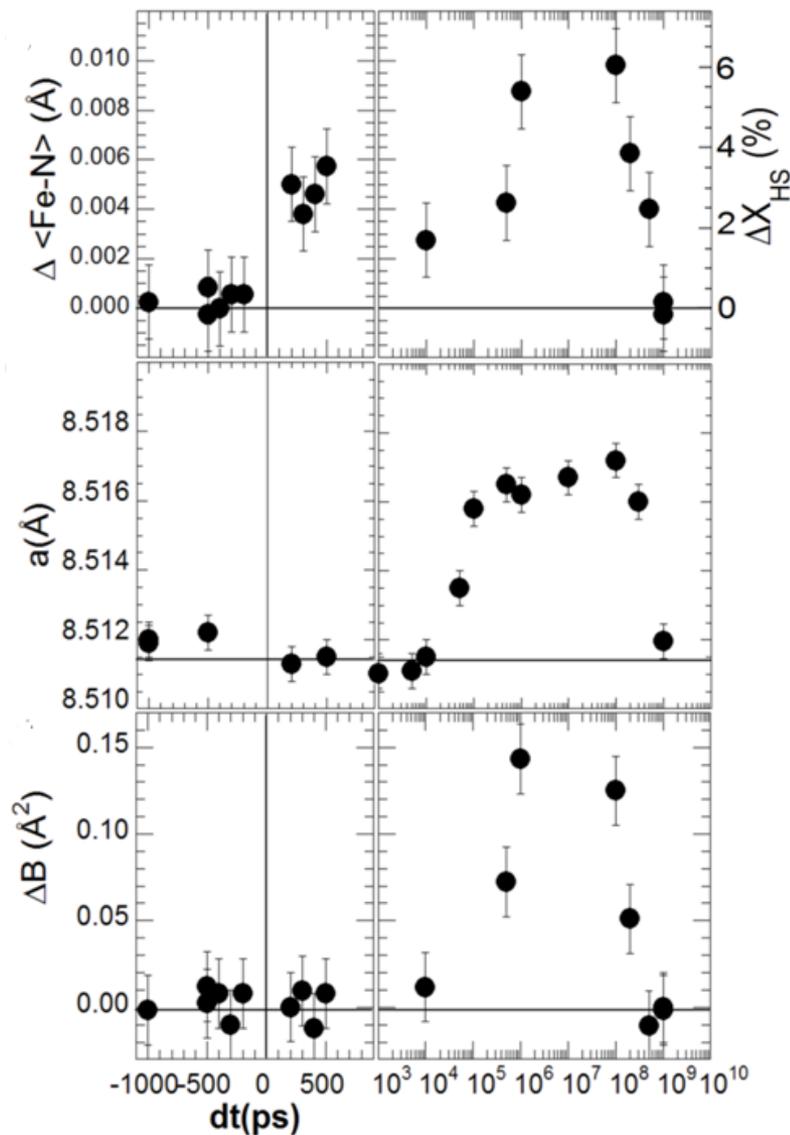
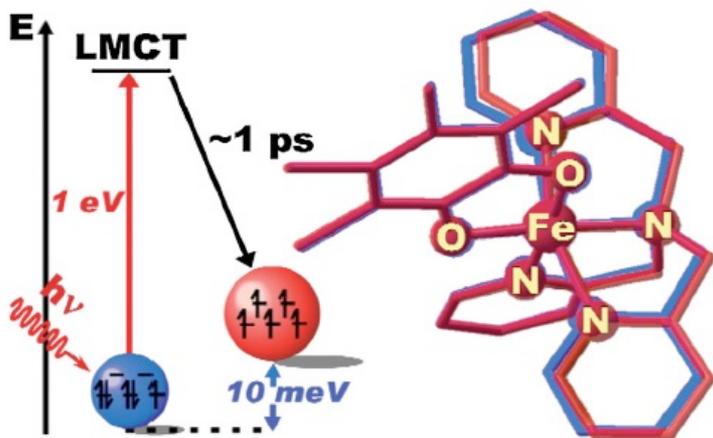
XFEL : 10 - 100 fs, limited by jitter and overcome with timing-tool → LCLS

## Spectral and Spatial Time Encoders @XFEL



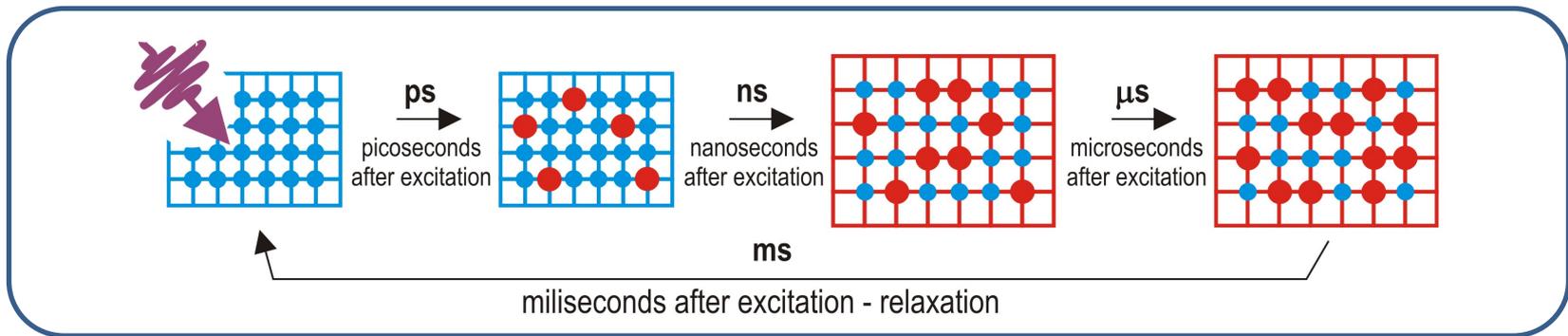
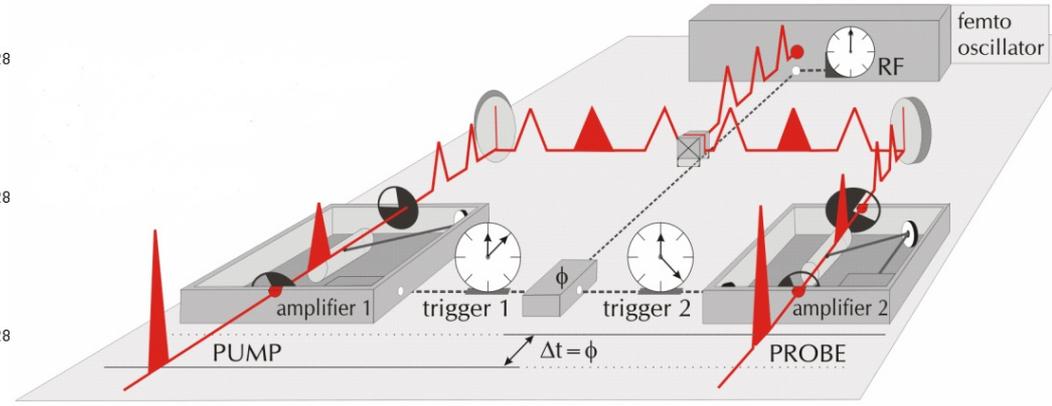
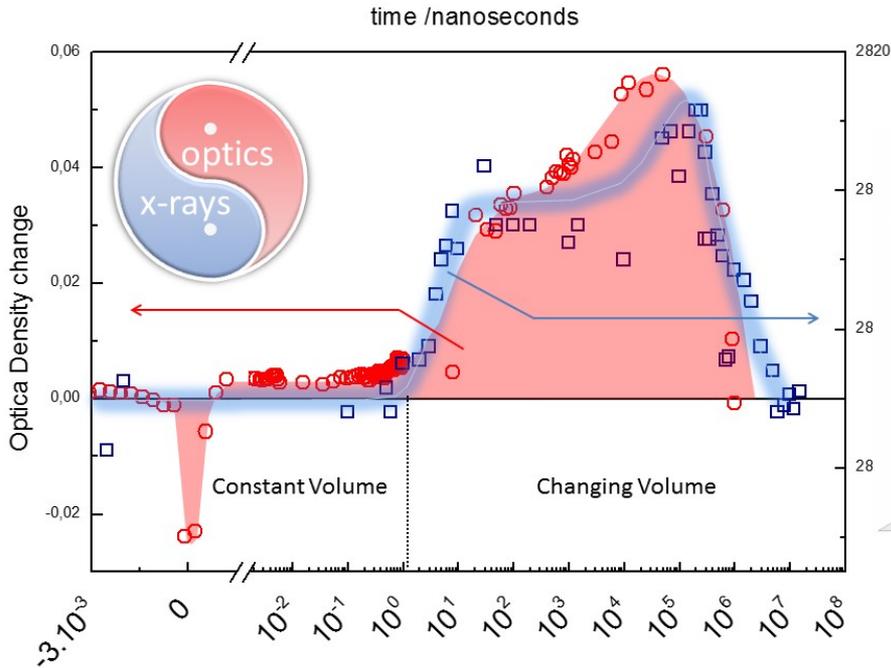
M. Harmand, Nature Photonics 7 (2013)

ESRF (ID09B), Grenoble  
 APS (BioCARS), Argonne USA  
 KEK (NW 14), Tsukuba, Japan  
 SOLEIL (CRISTAL), France

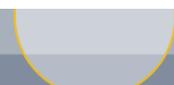


Lorenc *et al.*, Phys. Rev. Lett. **103** (2009)

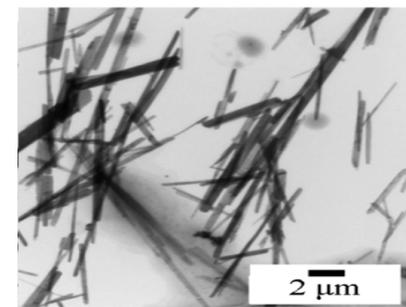
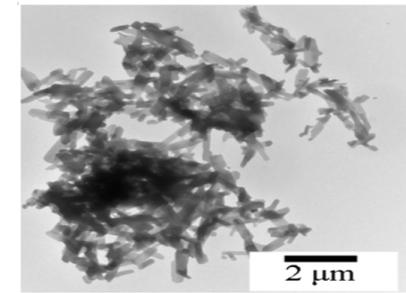
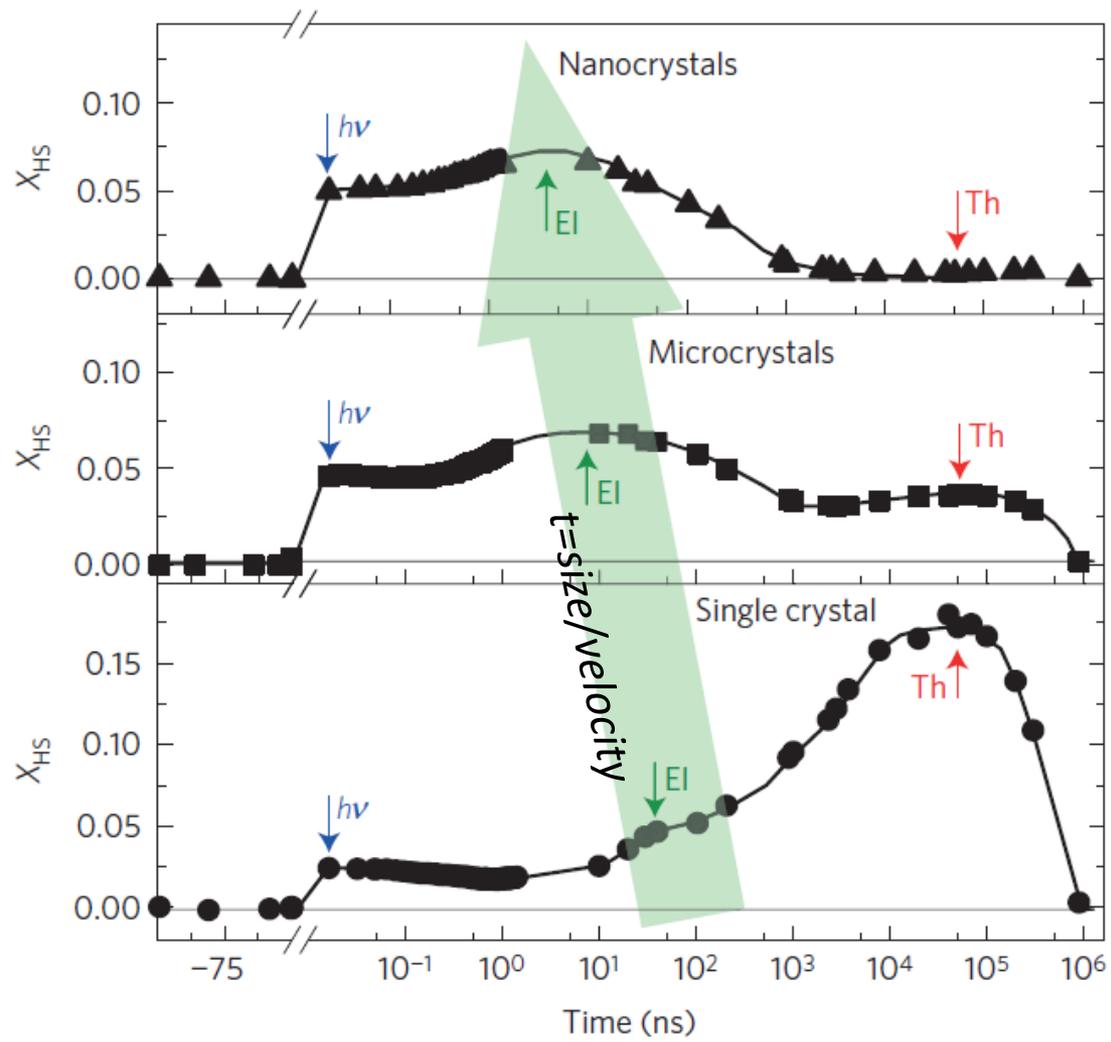
# Multistep dynamics

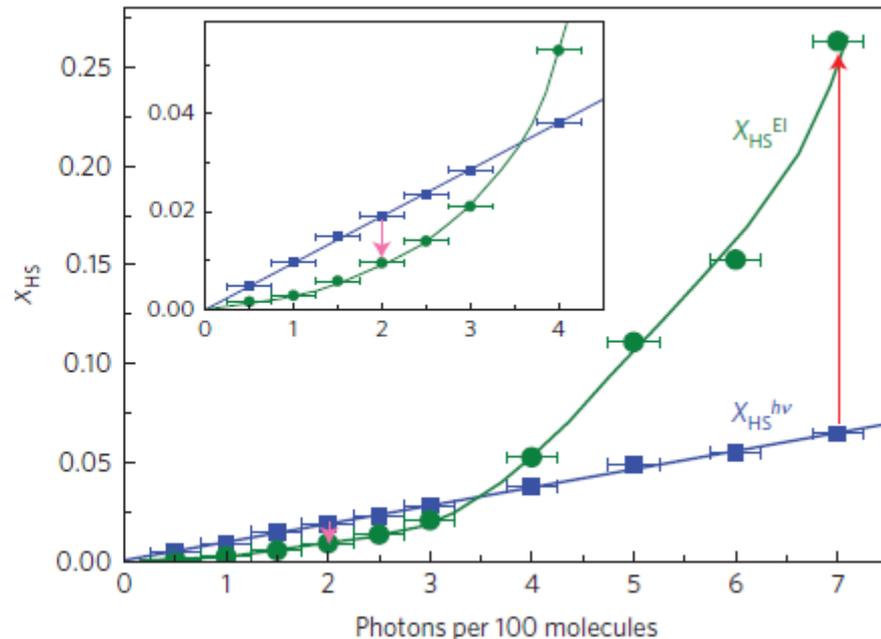
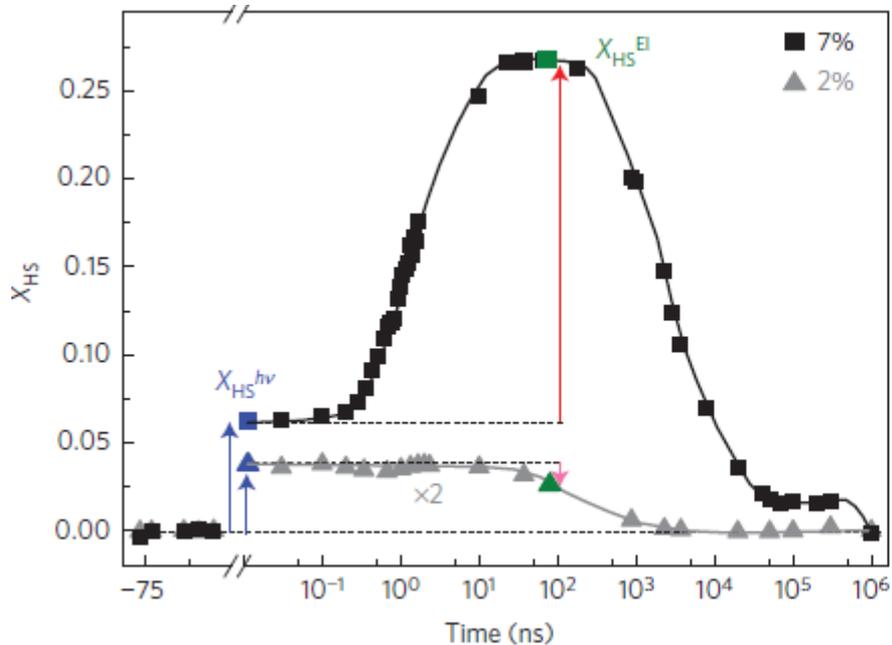


Lorenc *et al.*, Phys. Rev. B **85** (2012); Cailleau *et al.*, Acta Cryst. A **66** (2010)



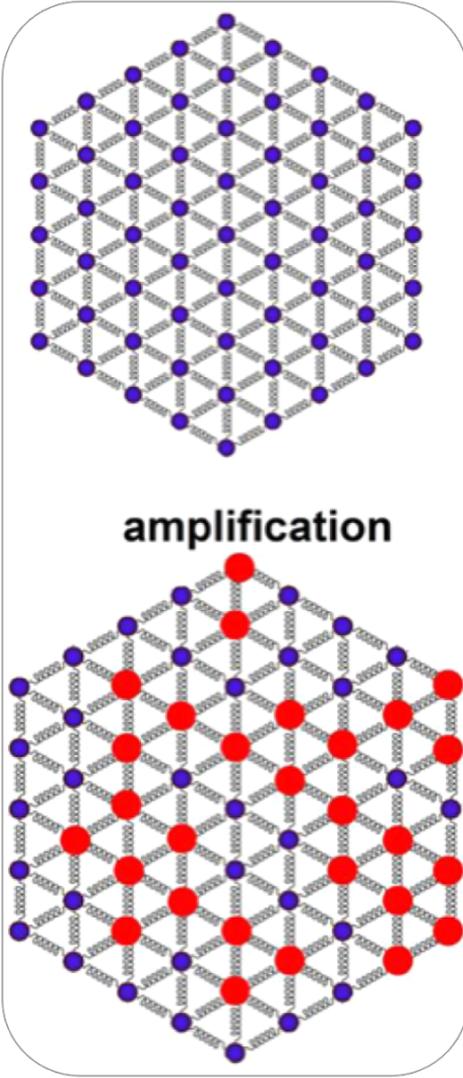
# Size matters





nature materials **LETTERS**  
 PUBLISHED ONLINE: 28 MARCH 2016 | DOI: 10.1038/NMAT4606

## Elastically driven cooperative response of a molecular material impacted by a laser pulse



## Monte Carlo simulation

$$P_{HS \rightarrow LS}^i = \frac{1}{\tau} \exp\left(-\frac{E_A - \kappa p_i}{k_B T}\right)$$

$$P_{LS \rightarrow HS}^i = \frac{1}{\tau} \exp\left(-\frac{D - k_B T \ln g}{k_B T}\right) \exp\left(-\frac{E_A + \kappa p_i}{k_B T}\right)$$

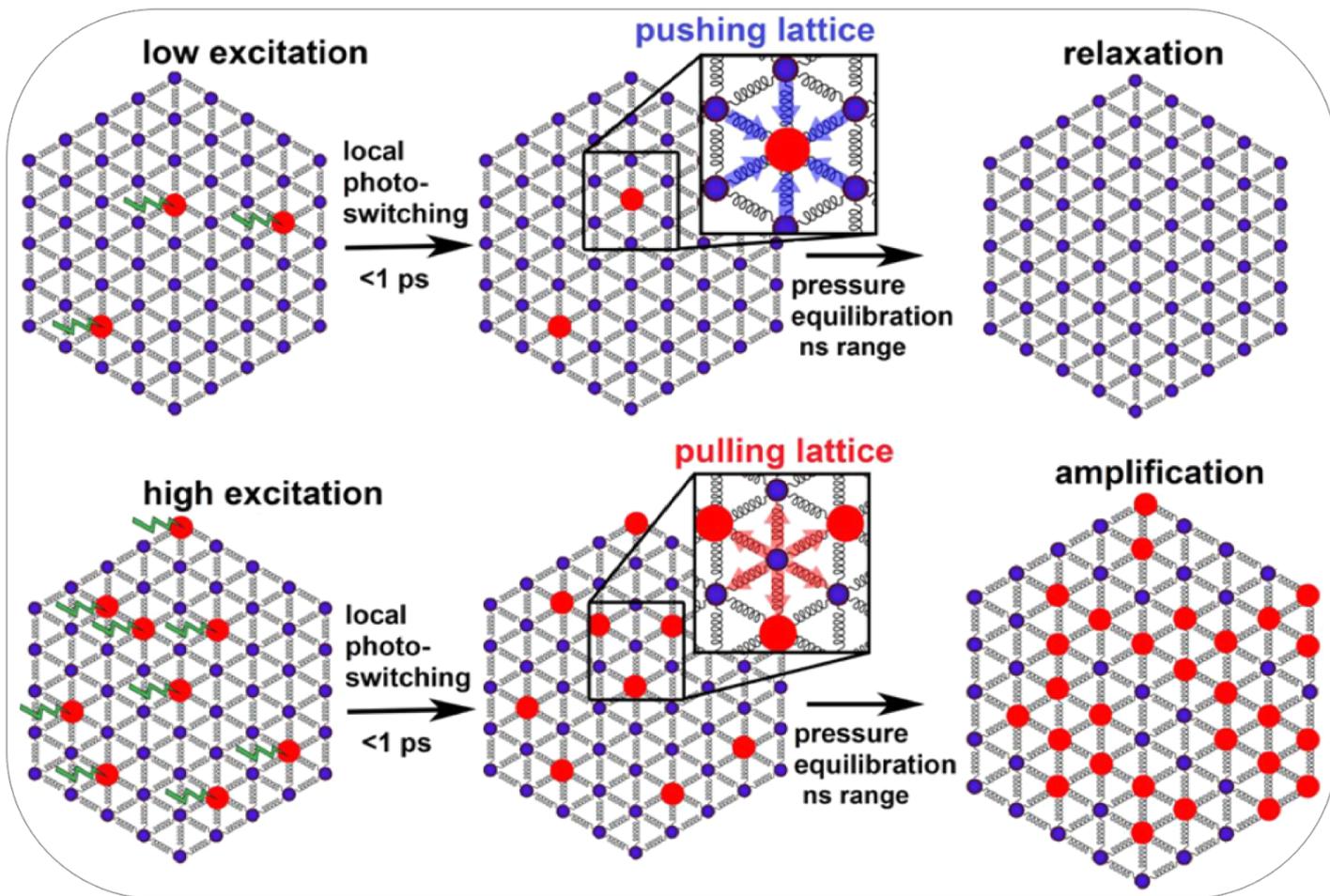


$$\begin{cases} m \frac{d^2 x_i}{dt^2} = F_{xi} - \mu \frac{dx_i}{dt} \\ m \frac{d^2 y_i}{dt^2} = F_{yi} - \mu \frac{dy_i}{dt} \end{cases}$$

$$F_{i,x} = \sum_{\text{neighbor springs}} k \delta r_{ij,x}$$

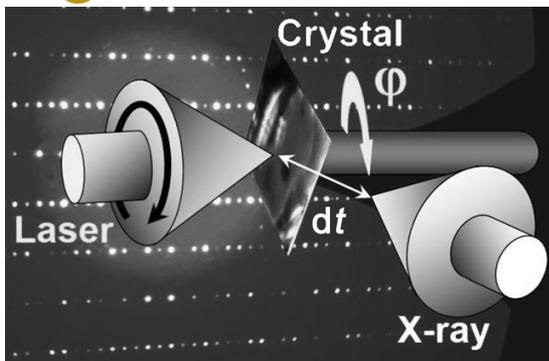
$$F_{i,y} = \sum_{\text{neighbor springs}} k \delta r_{ij,y}$$

# Mechano-elastic model

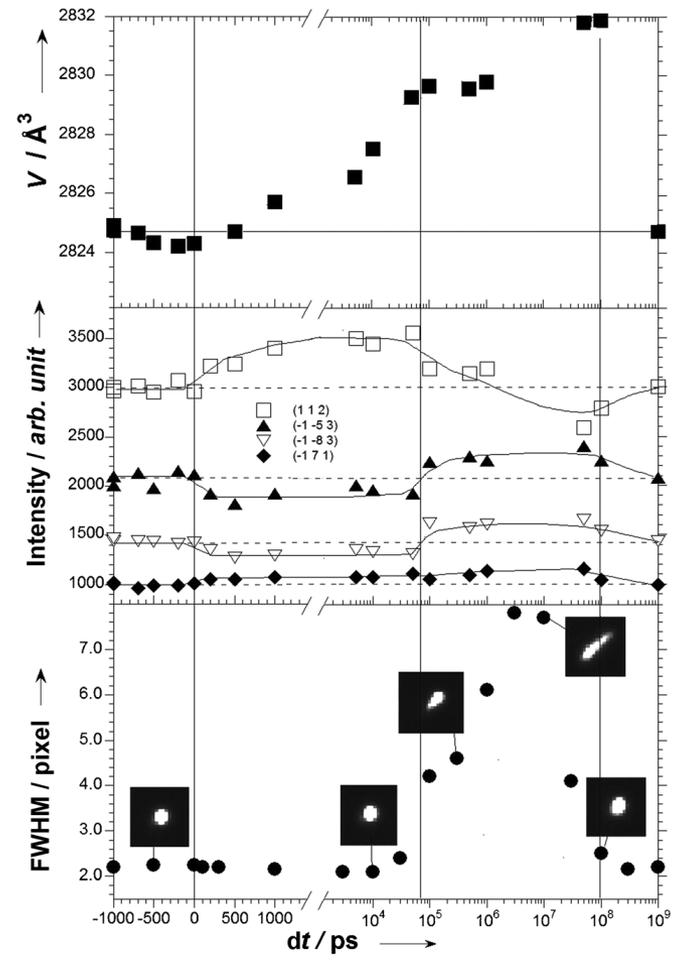


Bertoni *et al.*, Nature Mat. **15** (2016)

Enachescu *et al.*, PRB **95**, 224107 (2017)

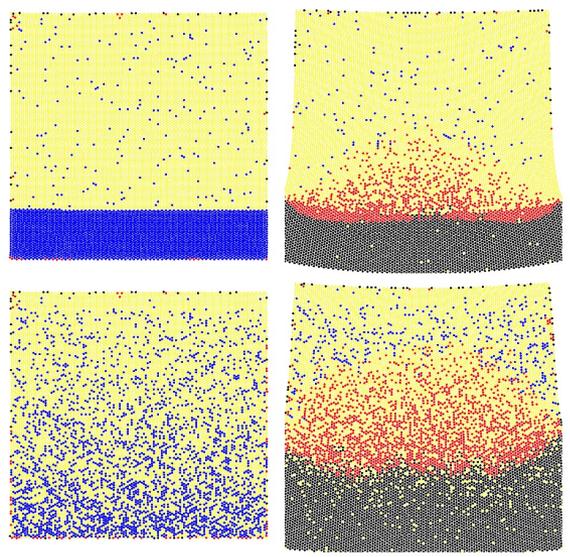


$$\langle F_{hkl} \rangle(dt) = X_{HS}(dt) F_{hkl}^{HS}(dt) + [1 - X_{HS}(dt)] F_{hkl}^{LS}(dt)$$

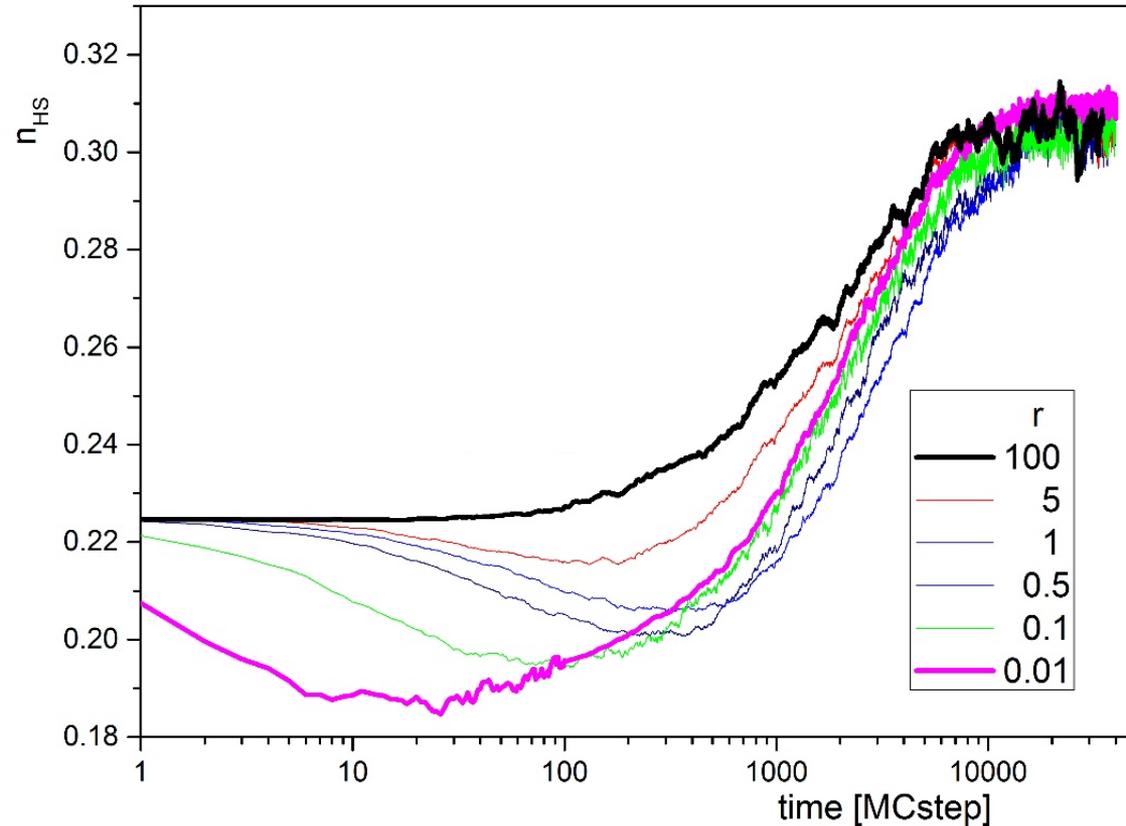


Collet *et al.*, Chem. Eur. J. **18** (2012)

- Excitation with gradient, case of single-crystal
- Stressed molecules unstable between LS/HS, must be of interest



Enachescu *et al.*, PRB **95**, 224107 (2017)



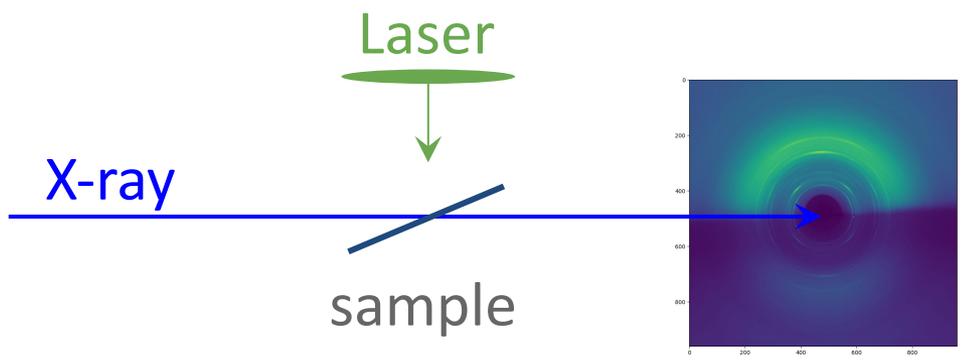
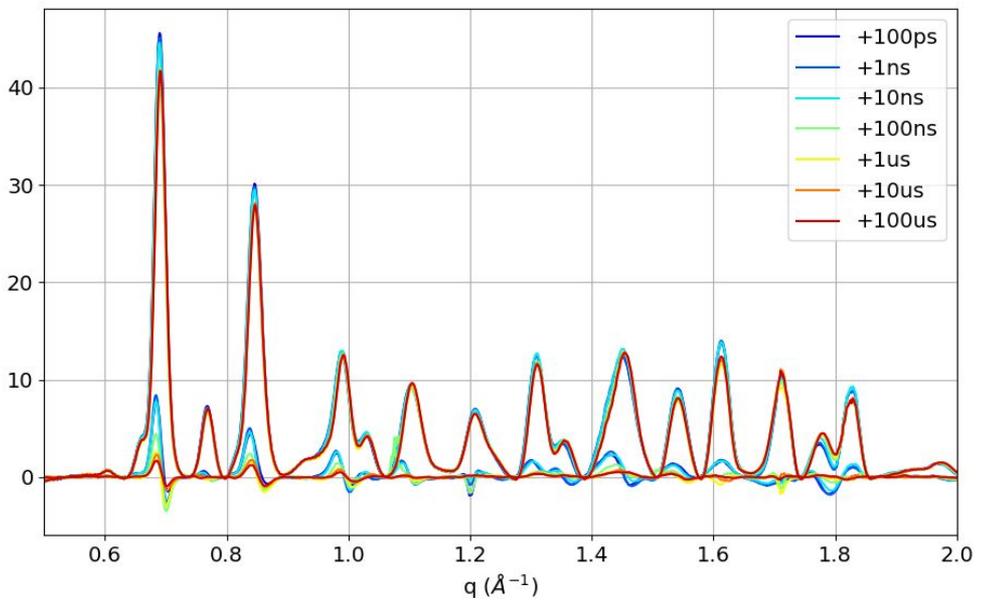
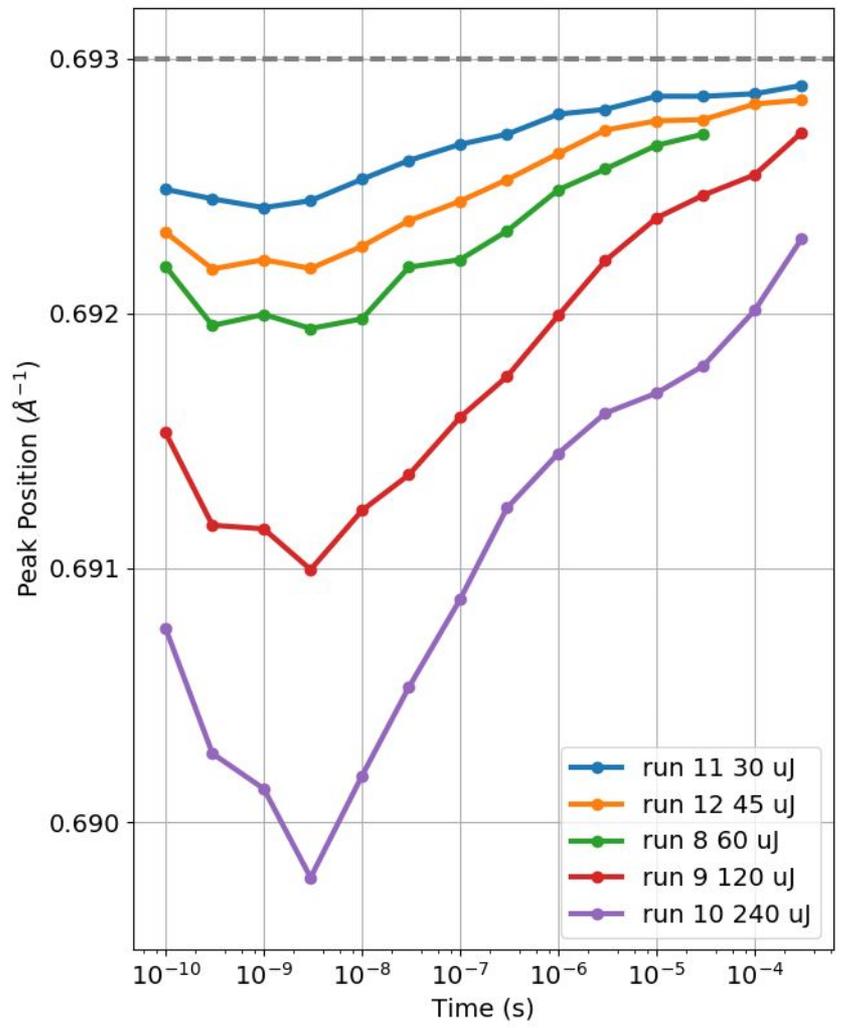
$$r = \frac{\text{steps\_solving\_lattice}}{\text{steps\_Monte\_Carlo}}$$

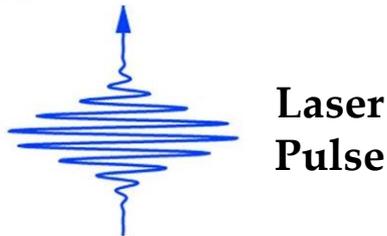
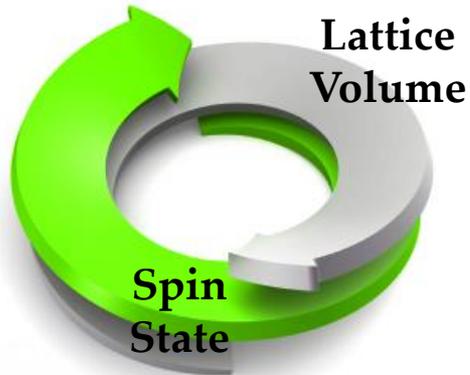
$r < 1$  slow lattice, fast molecular switch

$r > 1$  lattice and molecules equilibrated

Enachescu *et al.*, Phys. Rev. B (accepted)

# Time resolved powder XRD





- Triggering feedback mechanism between volume-molecular bond (spin state)
- Isostructural transition with laser fluence threshold
- Prolongation of induced state
- Cooperative effect leading to higher yield

## Outlook

- Latency time for coupling volume and spin state
- From ball-spring to phenomenological model
- Trying other class of volume changing materials



- ❖ **IPR, Rennes (FR)** : Celine Mariette, Roman Bertoni, Marco Cammarata, Eric Collet, Herve Cailleau, Marina Servol, Laurent Guerin, Marylise Buron, Xu Dong, Alix Volte
- ❖ **ICMMO, Orsay (FR)** : Marie-Laure Boillot
- ❖ **ICMCB, Pessac (FR)** : Jean-Francois Letard, Guillaume Chastanet
- ❖ **ESRF, Grenoble (FR)** : Michael Wulff, ID09 team
- ❖ **UAM, Poznan (PL)** : Jacek Kubicki
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- ❖ **UTokyo, Tokyo (JP)** : Seiji Miyashita

