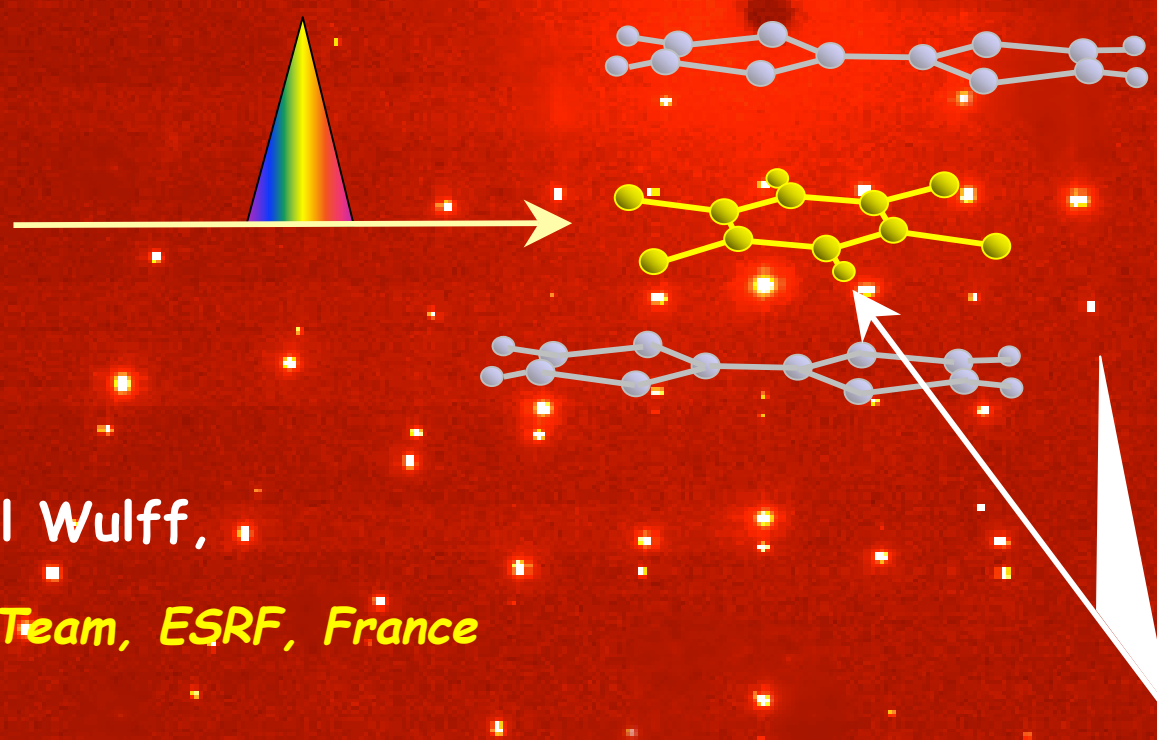
Probing Photo-induced solid-solid phase transitions by fast and ultra-fast time-resolved x-ray diffracti

E. Collet, L. Guérin, M. Buron, M.H. Lemée-Cailleau, H. Cailleau

Groupe Matière Condensée et Matériaux, University of Rennes 1, France

Shin-Ya Koshihara,

ERATO JST, KAST+TITech, Tokyo, Japan



Michael Wulff,

ID09B Team, ESRF, France

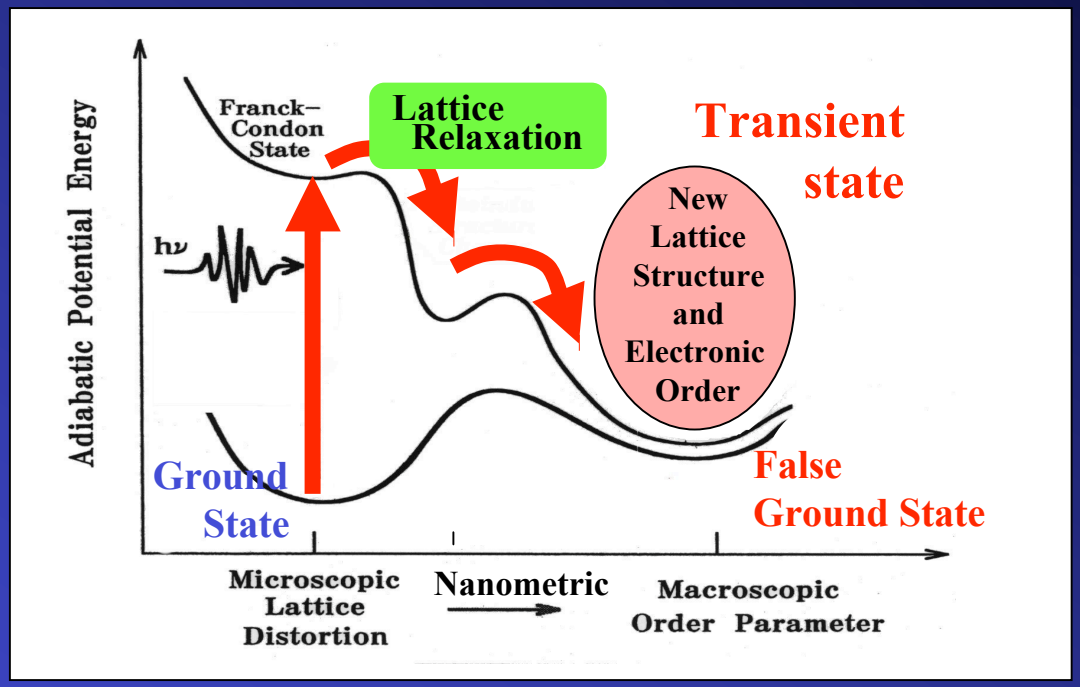
Photoinduced solid state phase transitio

Out of equilibrium and multi-scale process in solids

Self-amplification of excited state

K. Nasu (2001)

J. Phys.: Condens. Matter.

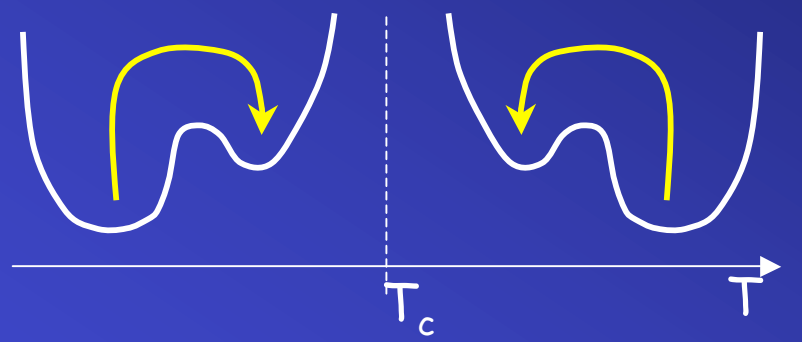


High density electronic excitation triggering structural instability :

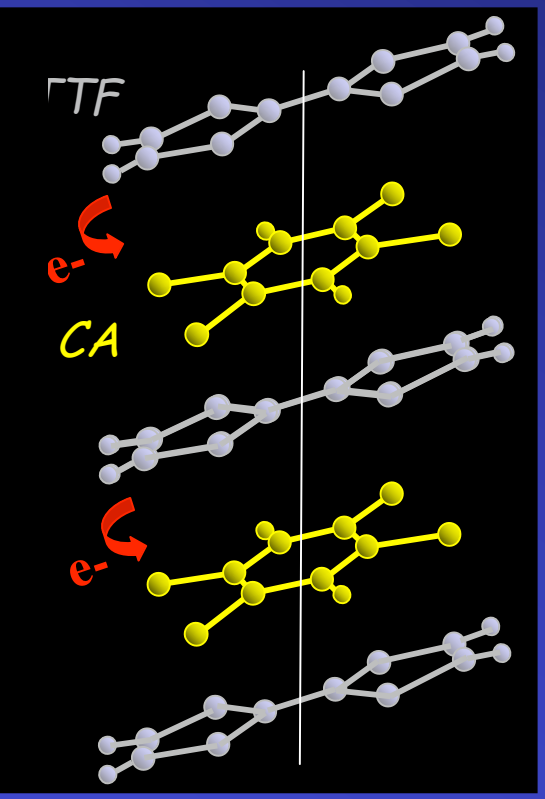
insulating ⟶ metal

insulating ⇄ insulating

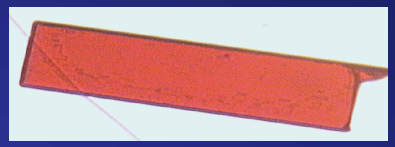
Solid state molecular switching



PHOTOINDUCED PHASE TRANSITION IN CT MOLECULAR SYST

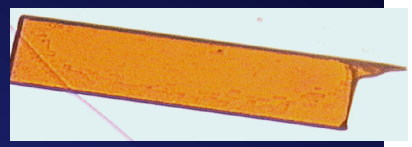


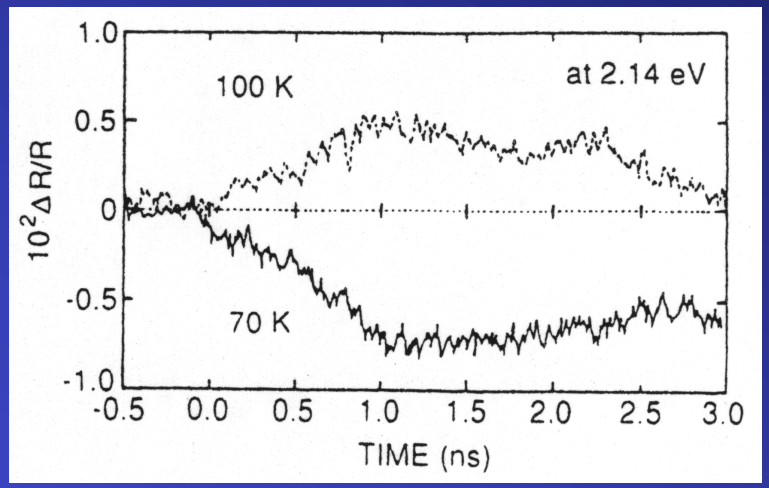
IONIC low T phase

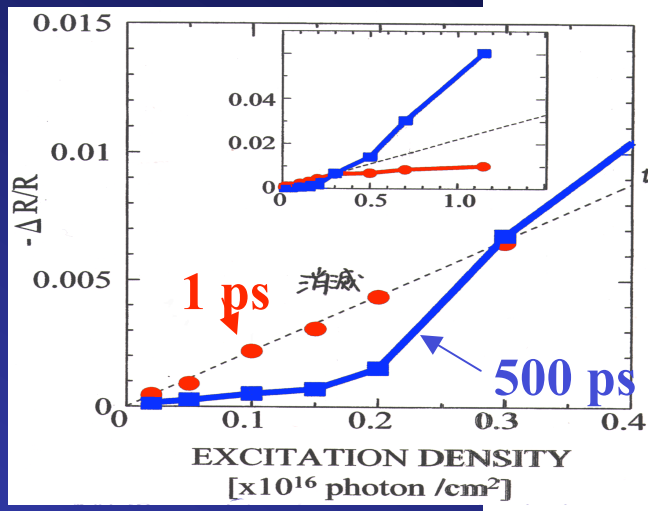


81 K

NEUTRAL high T phase







*S. Koshihara et al, J. Phys. Chem. B**103**, 2592 (1999)*

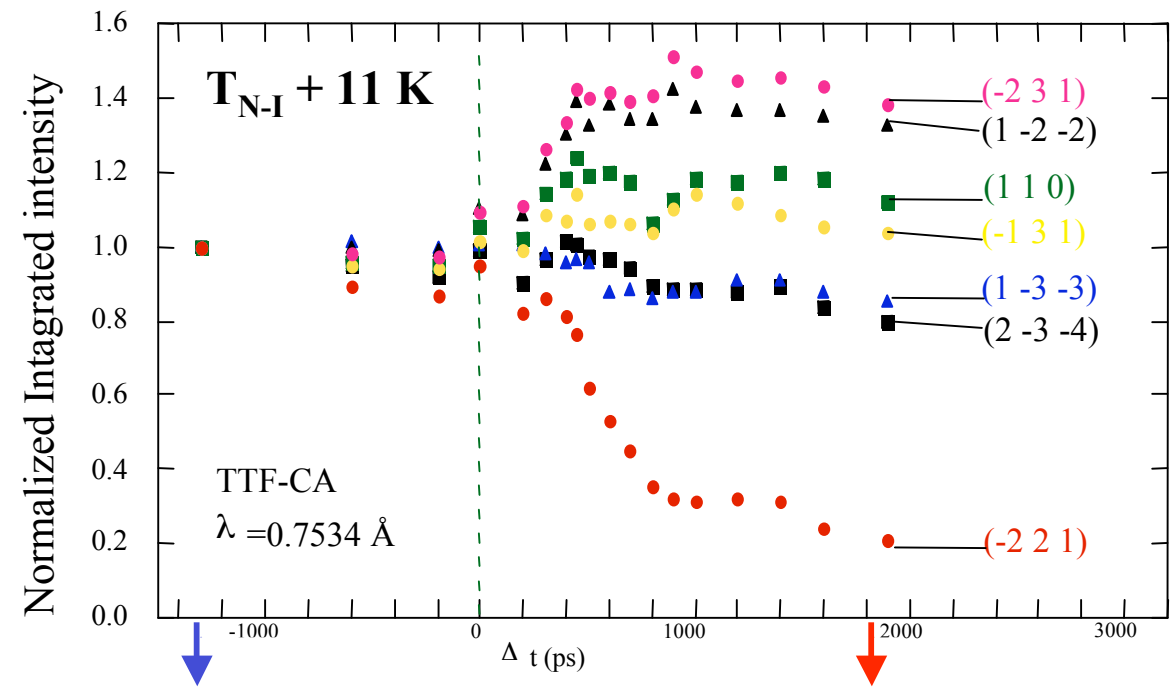
Okamoto et al,PRL(20

- ▷ **Highly cooperative : few 100 molecules / photon**
- ▷ **very fast : few 100 ps**
- ▷ **Highly non-linear : threshold behavior and $h\nu_{pump}$ dependence**

STRUCTURAL STUDY OF THE PHOTO-INDUCED N-I TRANSITION: TTF-CA

pump -Xray probe experiment ID09 ESRF

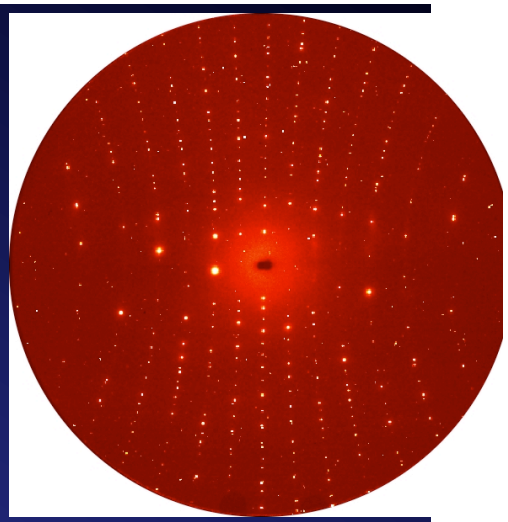
1st monochromatic experiment



Neutral state (high temperature)

Pulse laser 300 fs λ=800 nm

Ionic state (photo-induced)



X-ray Pulses 100 ps

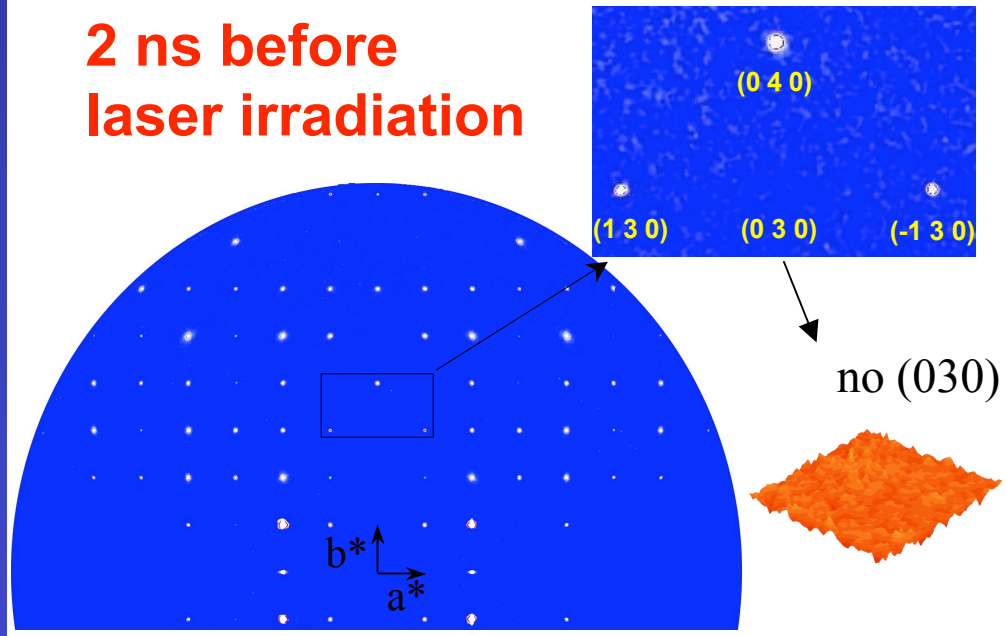
Structural reorganization :
3D domains
Large part transform

E. Collet et al, Science 300 61

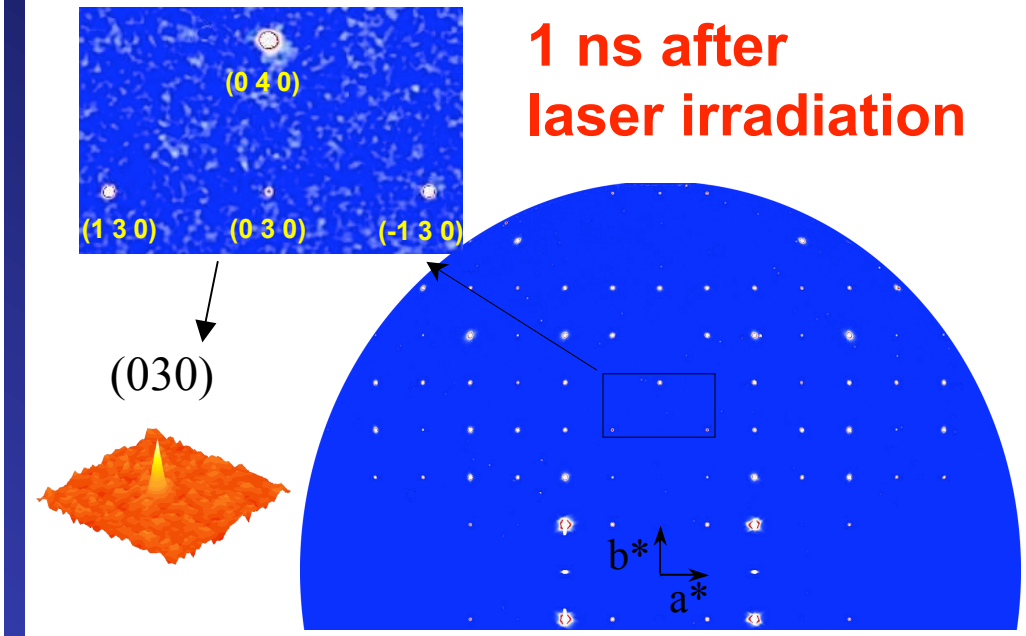
PHOTO-INDUCED STRUCTURAL ORDER

Complete data collection : scattered intensity in the reciprocal space.

2 ns before laser irradiation



1 ns after laser irradiation



Neutral phase

Space group **$P2_1/n$**

(0 k 0) : k = 2n+1 **absent**

(h 0 l) : h+l = 2n+1 **absent**

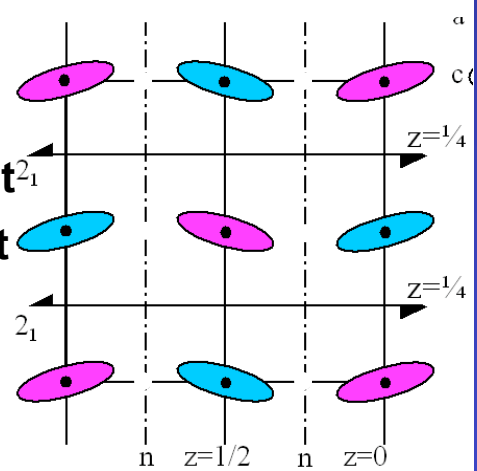
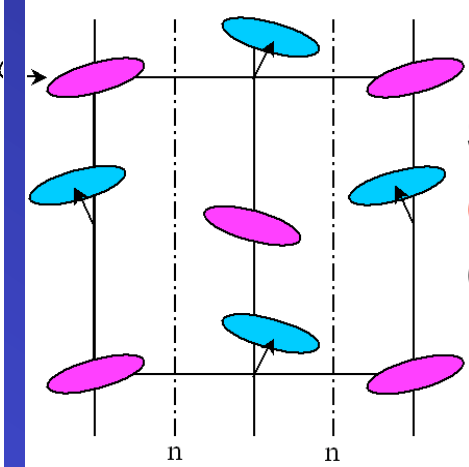


Photo-induced ferroelectric order



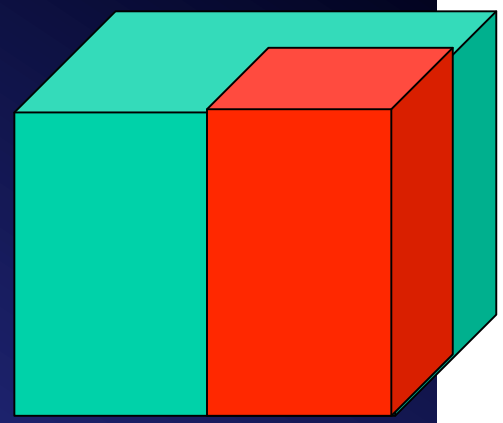
Space group **Pn**

(0 k 0) : k = 2n+1 **present**

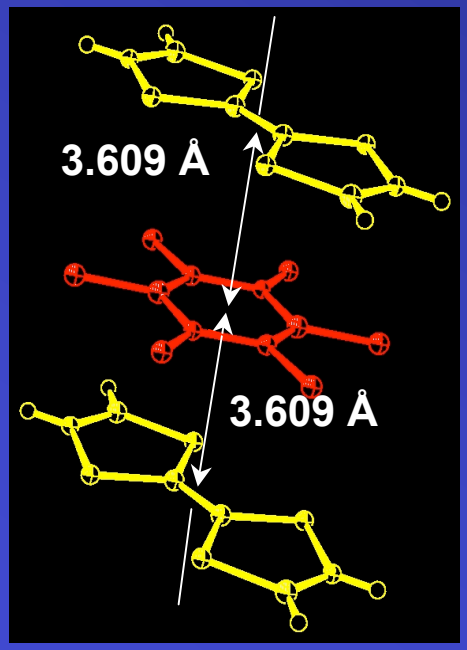
(h 0 l) : h+l = 2n+1 **absent**

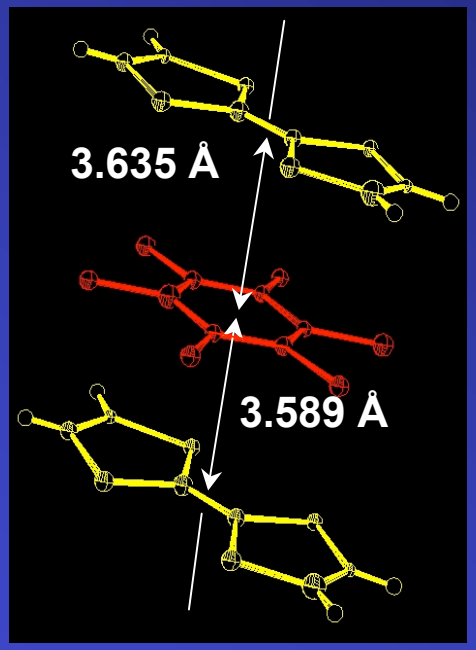
E. Collet et al, Science 300 612 (2003)

Crystal structure with 100 ps time resolution: refinement of homogeneous state



Δt= -2 ns **Δt= +1 ns**

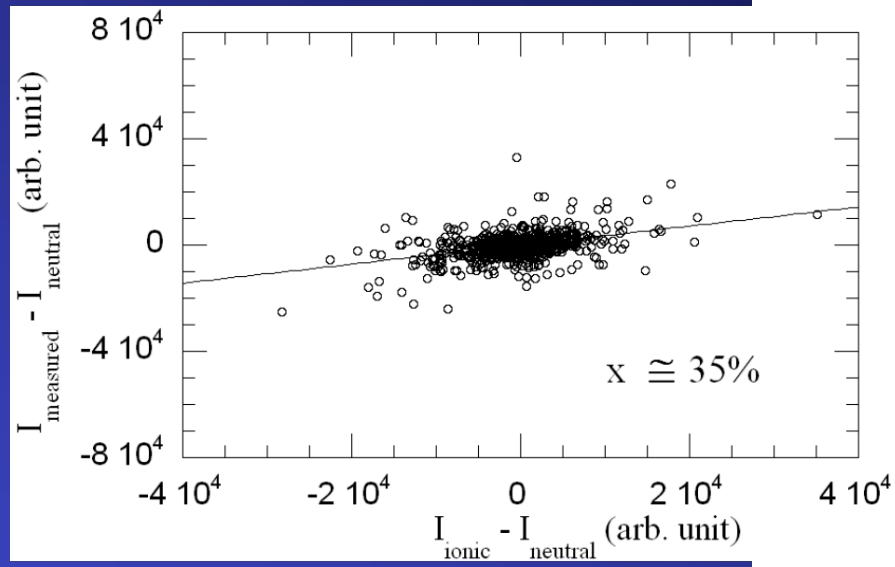




N phase ***I photo-induced ferroelectric state***

coexistence of N_{para} and I_{ferro} p

$I(hkl) = X\, I_{Iferro}(hkl) + (1-X)\, I_N(hkl)$



X = 35 %

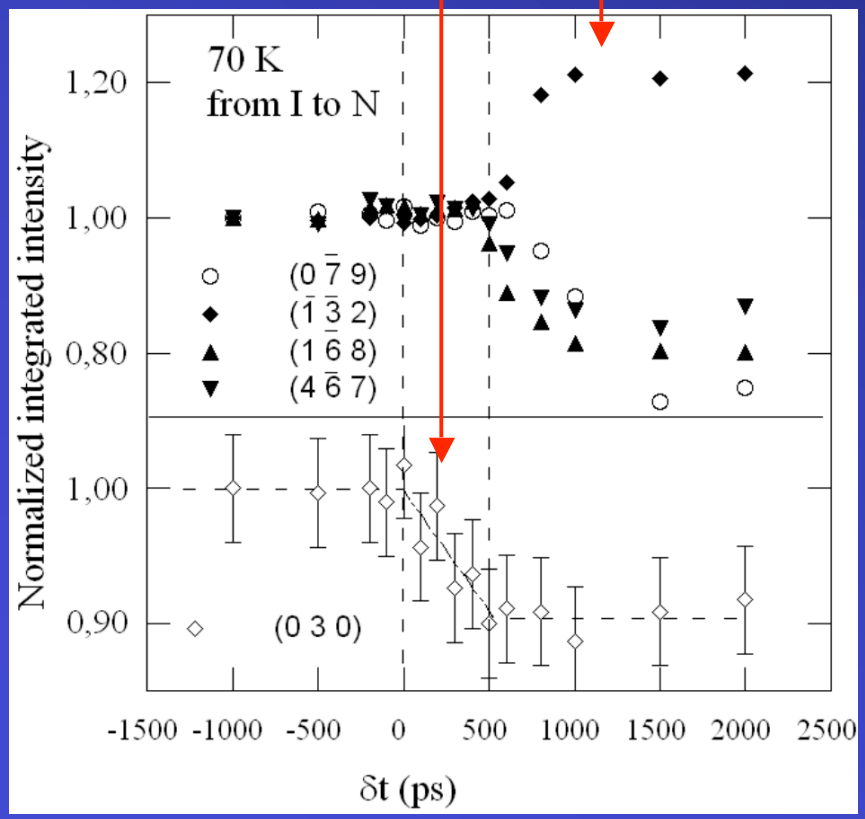
Lost of inversion center due to dimerization process

L. Guerin et al, Chem Phys (2004)

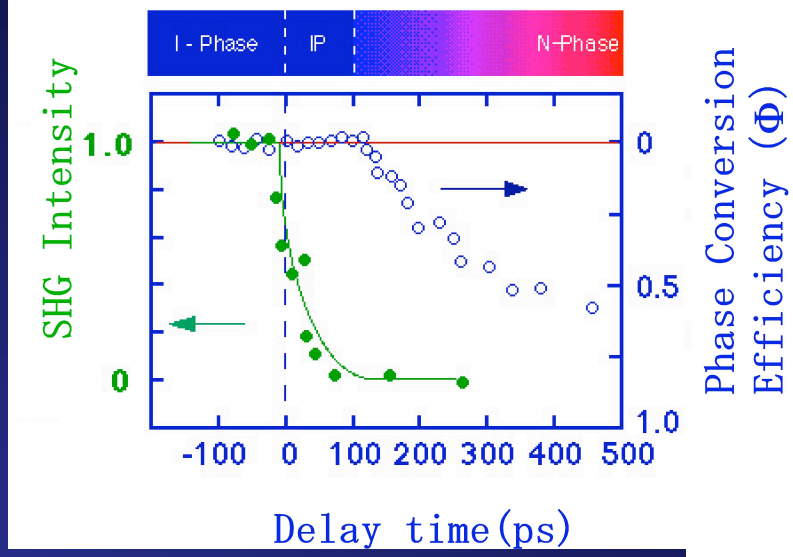
Opposite I-to-N photo-induced transformation : TTF-CA 70 K

- intermediate disordered state ?

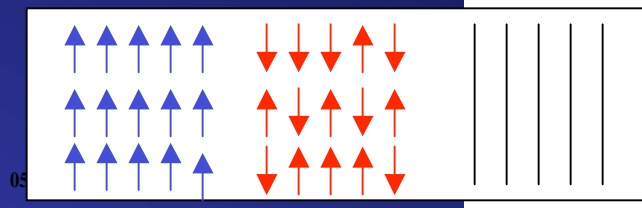
Change of symmetry + Change of state



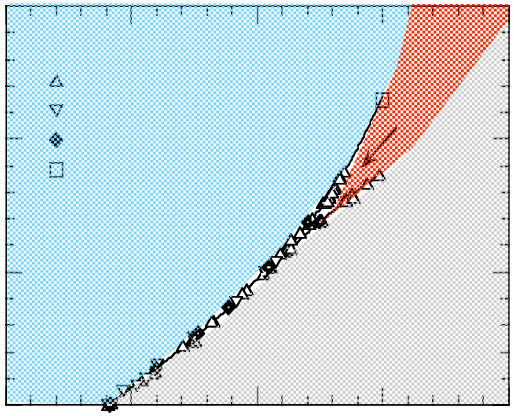
L. Guérin, E. Collet et al, Chem Phys. Special issue (2004)



T. Luty et al, Europhysics Lett., 59

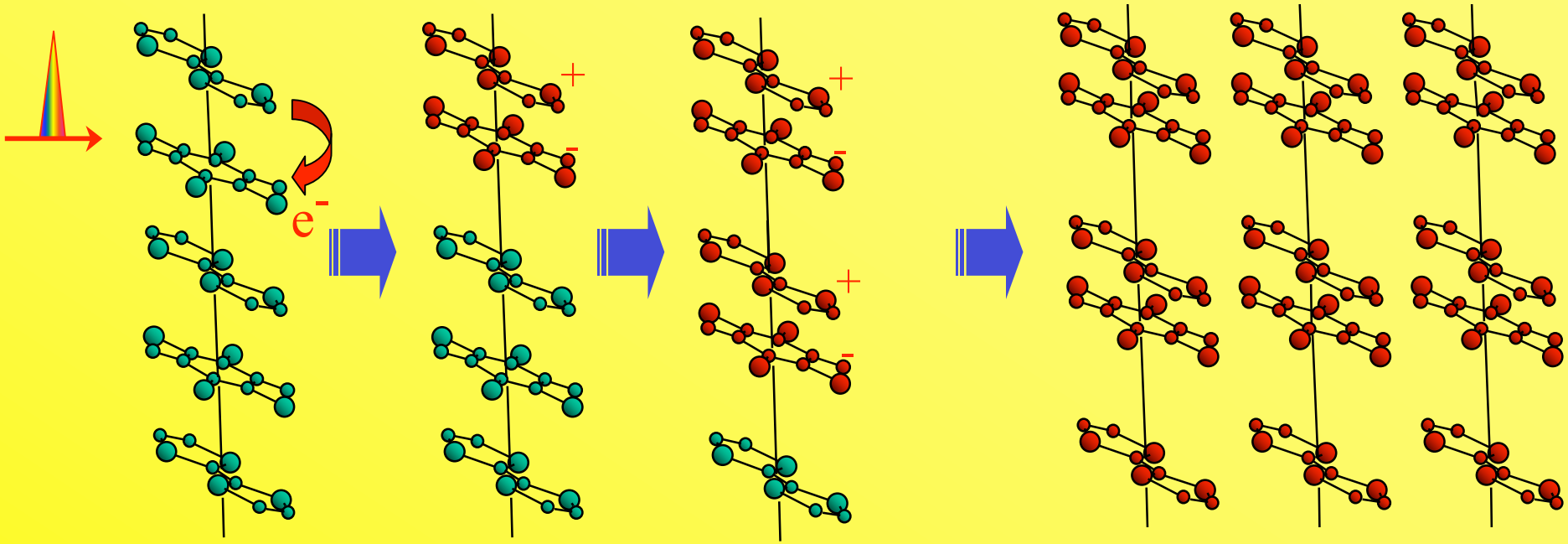


Phase diagram at thermal equilibrium



M.H. Lemée-Cailleau et al, PRL 79 16

What is the mechanism???



100 fs-1 ps

100 ps

photoinduced cooperative molecular switching along the chain : 1D process

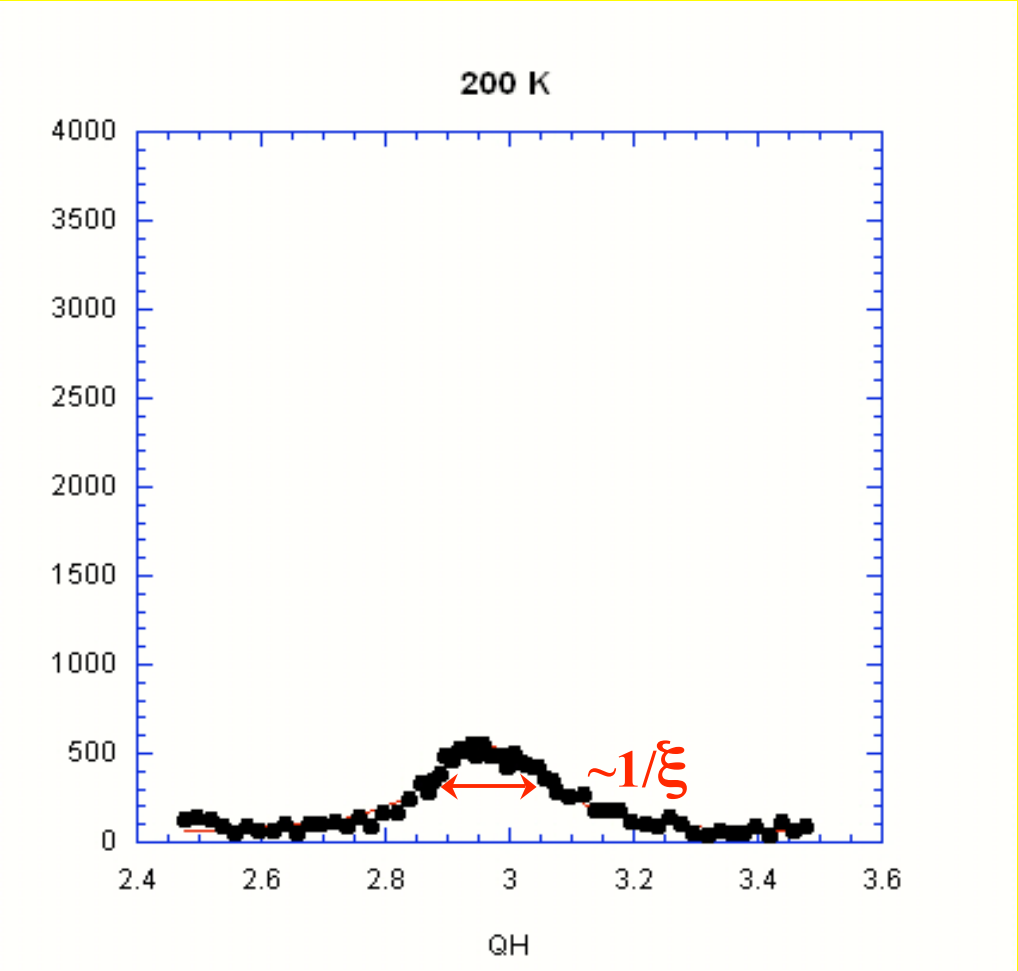
3D ordering of ionic dimers

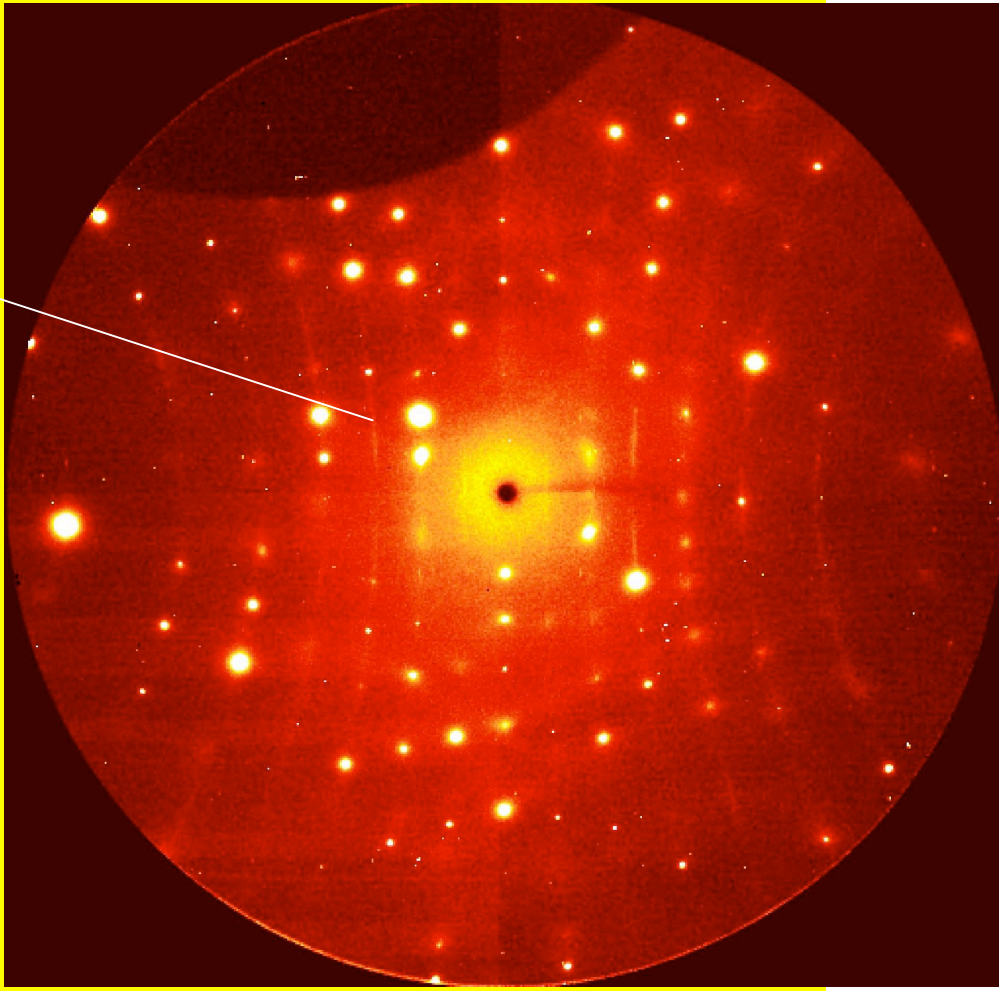
1D local order exist at the <u>very first step</u> : correlation/diffuse scattering???

C. Siders and A. Cavalleri, Science 300 (2003)

Importance of the time resolution

Ex : signal dependence
with the size of the excitations





ξ

… D° A° $(D^+A^-)(D^+A^-)(D^+A^-)(D^+A^-)(D^+A^-)$…

E. Collet et al, *Europhys. Lett.* 57 (2002)

DEVELOPMENT OF PICOSECONDE DIFFRACTION MEASUREMENTS:

KEK Photon Factory Advanced Ring : S. Koshihara and S. Adachi

SOLEIL Cristal Beamline (50 ps) : S. Ravy, E. Collet, H. Cailleau
in collaboration with M. Wulff

CONCLUSIONS AND PERSPECTIVES

- **X-ray diffraction :**

  photo-induced structural change: intra and inter-molecular reorganization

- **Materials :**

  physical properties driven by light

- **X-ray source :**

  development of new sources and beamlines

DREAMS

- **Beyond the average structure**

  diffuse scattering associated with the local Excitons (1st step) : *flux*

- **Beyond atomic resolution**

  towards electronic resolution : *stability*

- **Towards the early events**

  coherent domino effect : *time resolution*

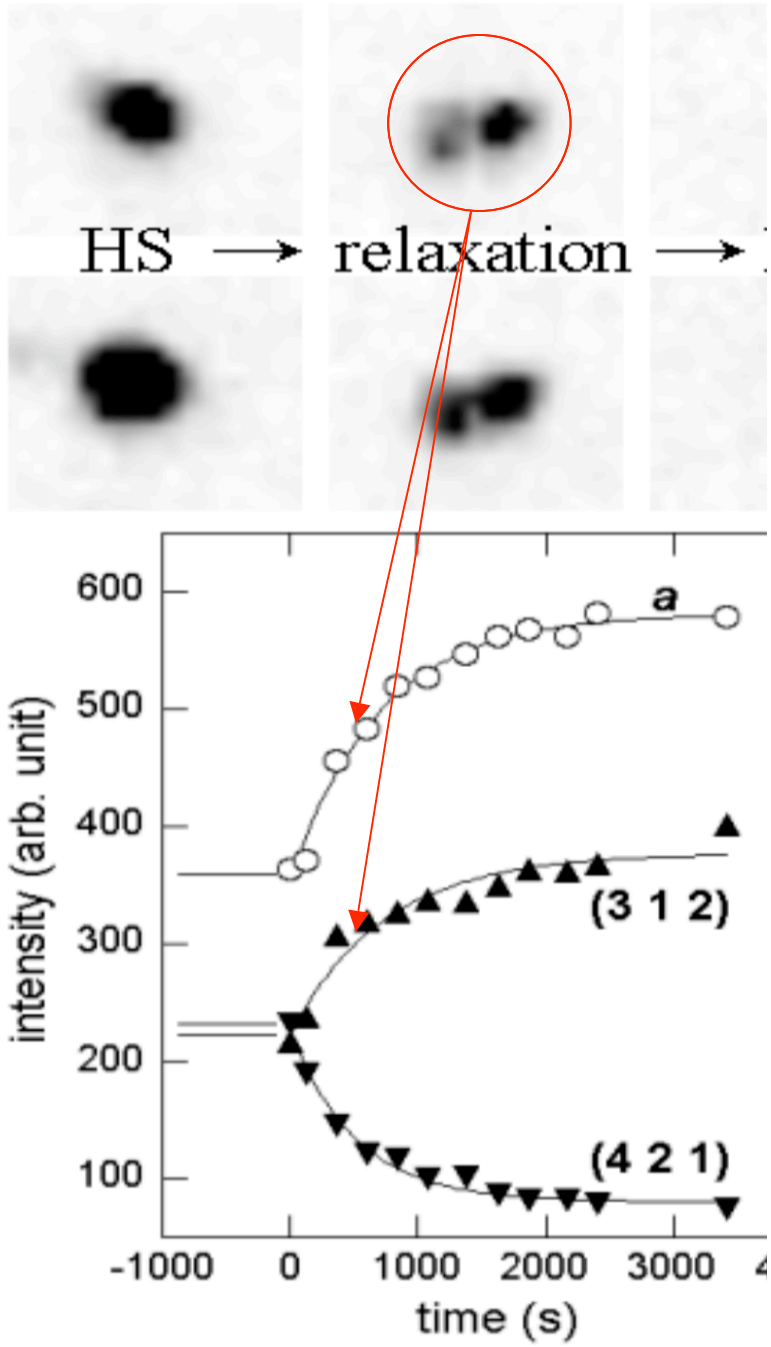
Example : photoinduced spin transition

Nucleation of domains mechanism

Evolution of the lattice parameters
in the photoinduced state

Changes of the 'average' position of the peaks

Changes of the intensities :
the structural reorganization
modify the structure factor
Contribution of HS and LS domains



N. Huby, L. Guerin, E. Collet et al, in Phys. Rev. B 69 020101(R) (2004)