

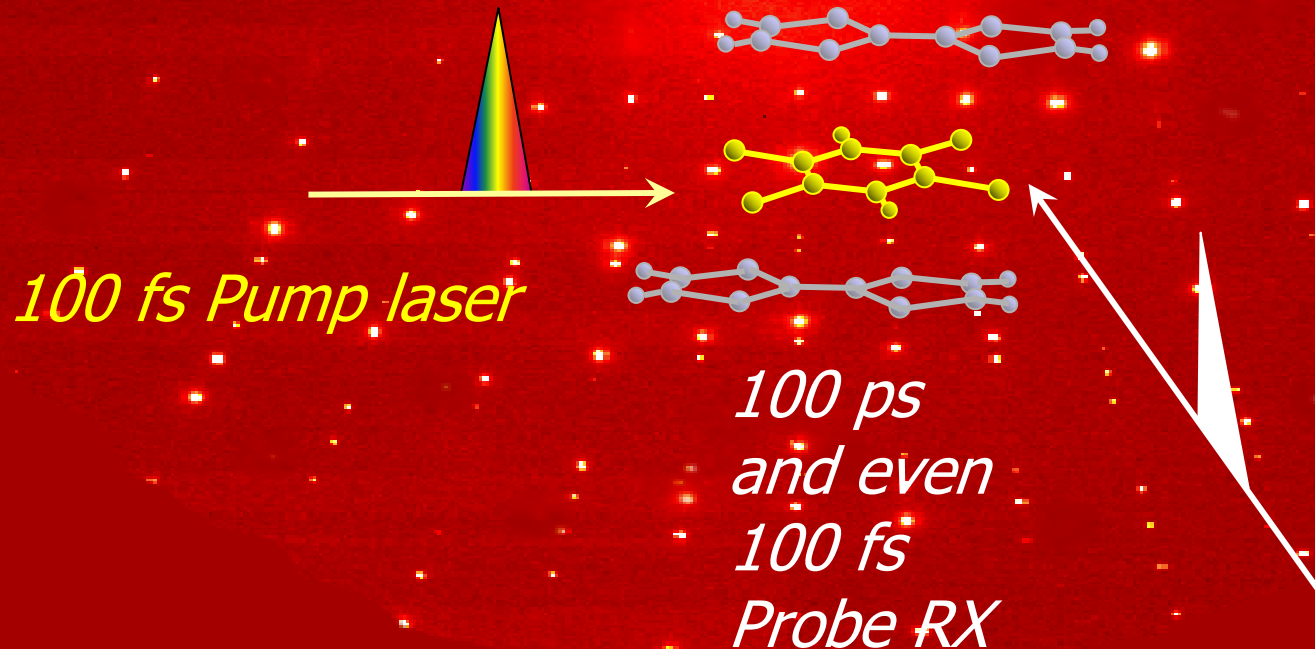
Probing photo-induced solid-solid phase transition by fast x-ray diffraction

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GMCM CNRS, University Rennes I France*

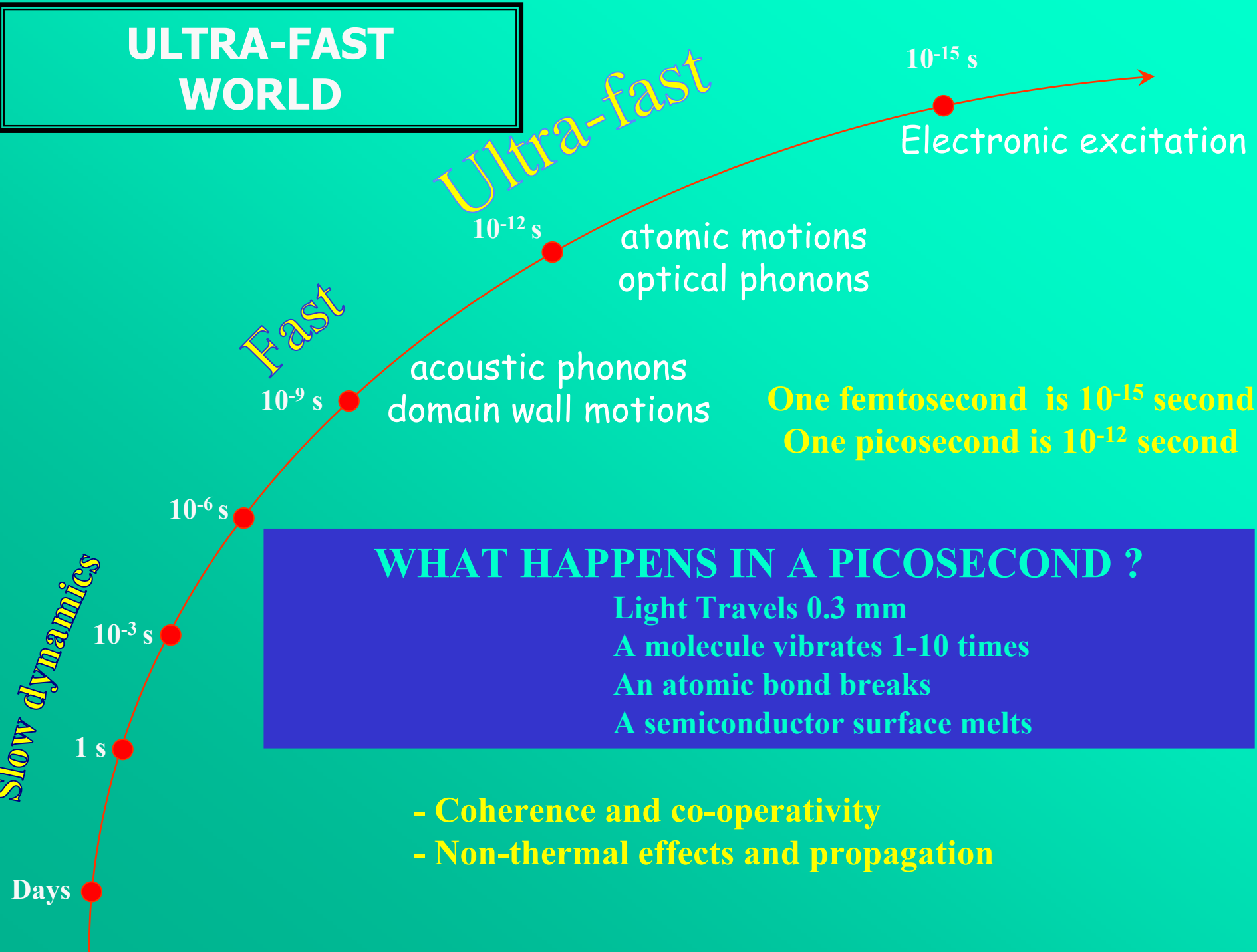
Michael WULFF, ID09B, ESRF Grenoble

Shin-Ya KOSHIHARA, KAST+TIT, Tokyo, Japan

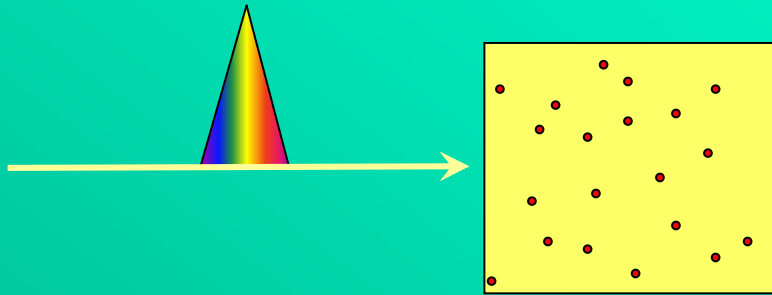
S. ADACHI, R. TAZAKI, J. TAKAHASI, KEK, Tsukuba, Japan



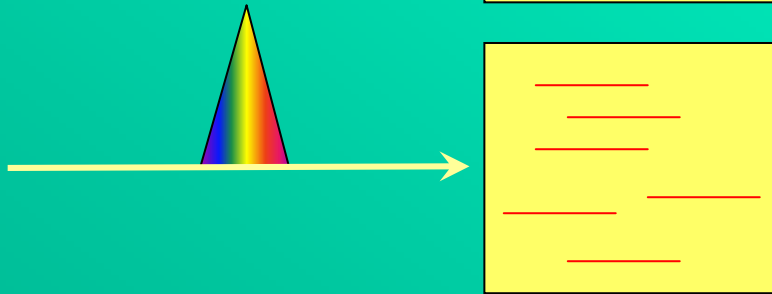
ULTRA-FAST WORLD



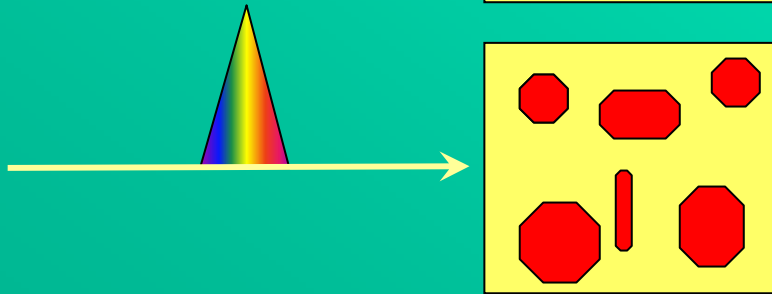
Different kinds of photo-induced processes : what happens when the sample is irradiated?



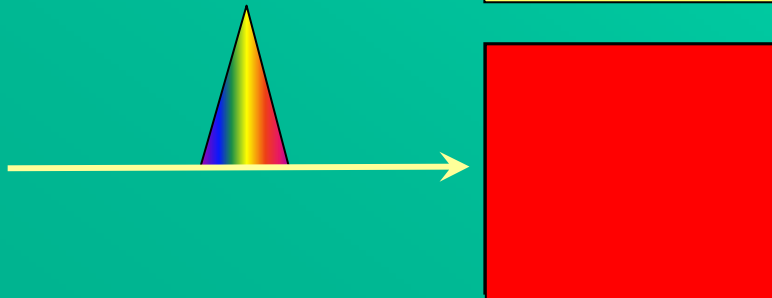
local transformations involving independent molecules (%)



Short range photo-induced order extending over few unit cells associated with cooperative phenomena



Coexistence of photo-induced and stable macroscopic domains (long range order)



Complete transformation of the material

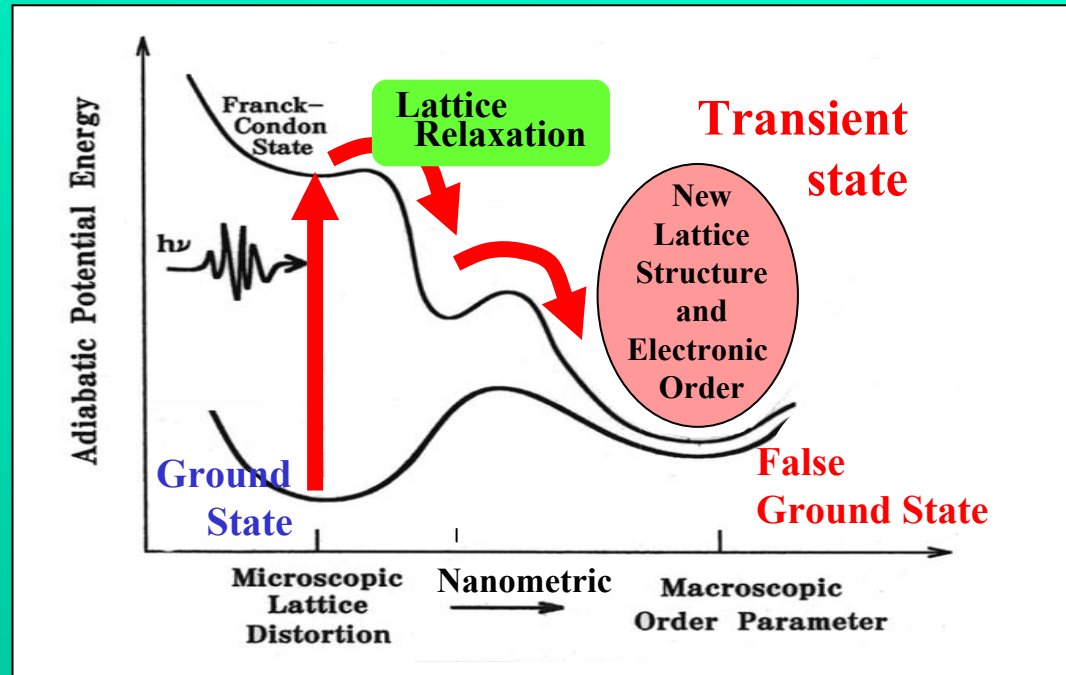
Photoinduced solid state phase transition

Out of equilibrium and multi-scale process in solids

Self-amplification
of excited state

K. Nasu (2001)

J. Phys.: Condens. Matter.

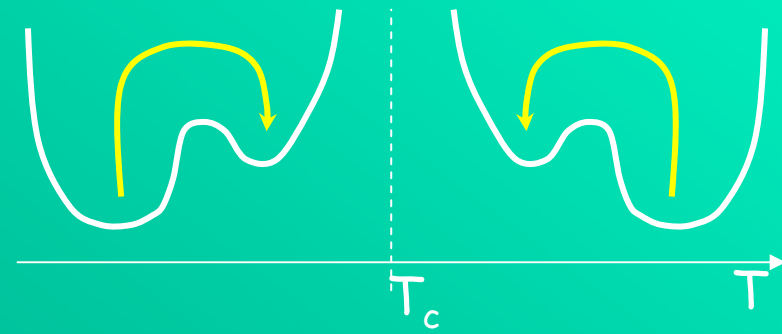


High density electronic excitation
triggering structural instability :

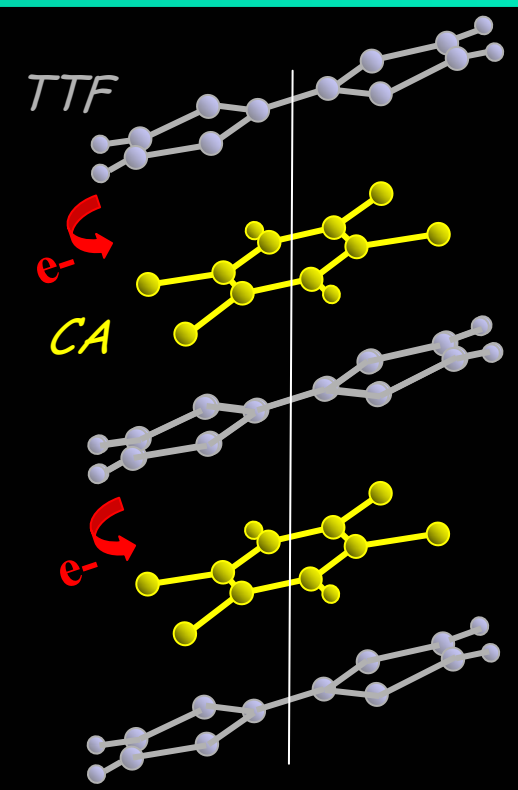
insulating \longrightarrow metal

insulating \longleftarrow insulating

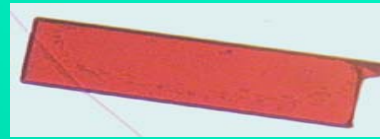
Solid state molecular switching



PHOTOINDUCED PHASE TRANSITION IN TTF-CA

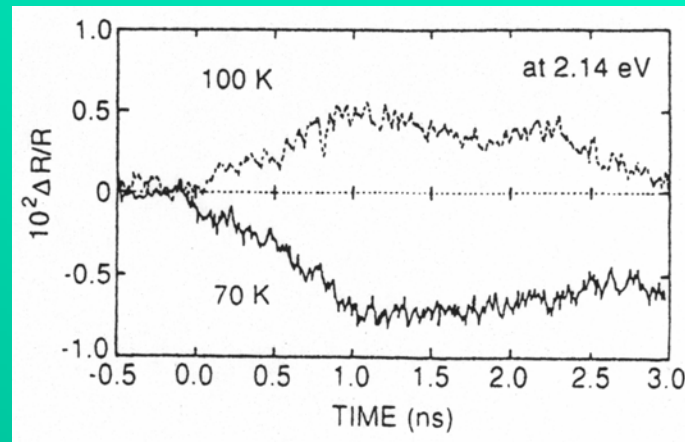


IONIC low T phase

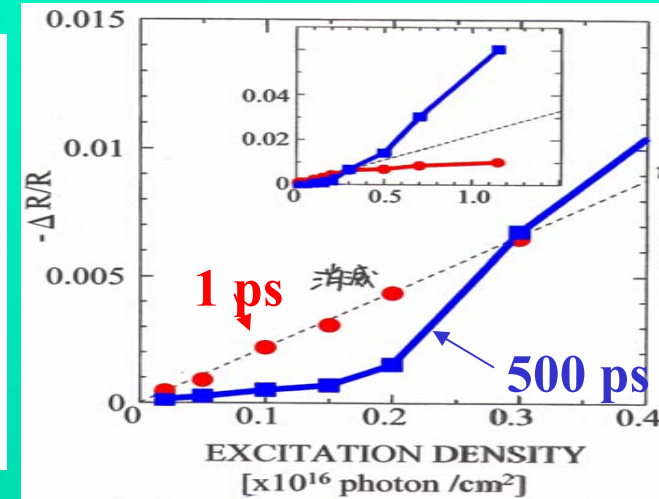


81 K

NEUTRAL high T phase



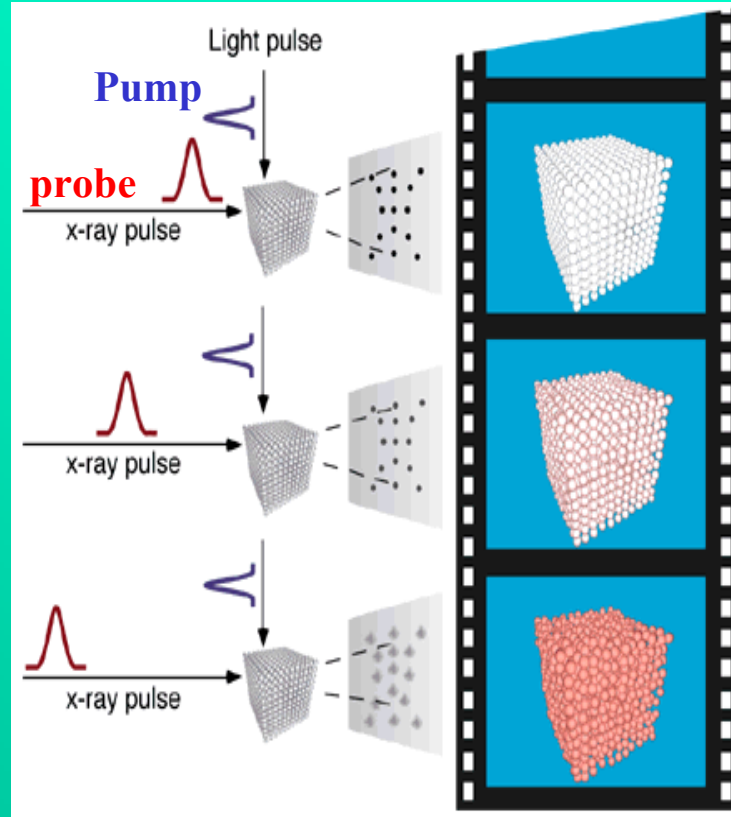
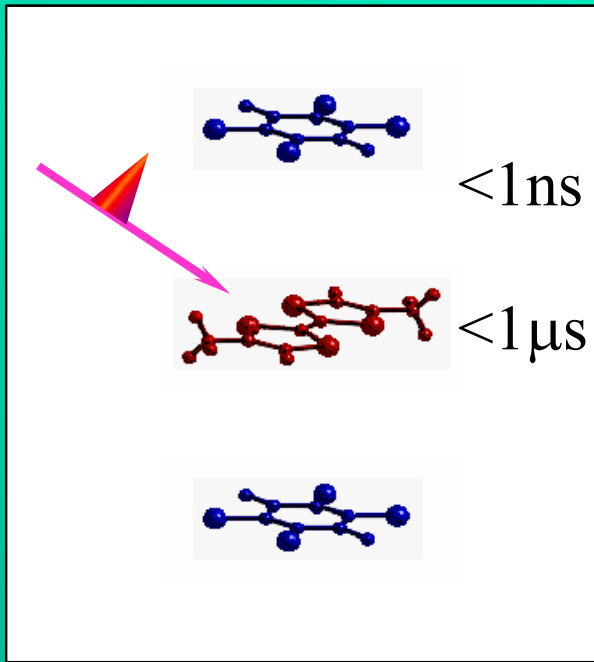
*S. Koshihara et al,
J. Phys. Chem. B103, 2592 (1999)*



*Iwai et al, PRL 88 057402
(2002)*

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

TIME-RESOLVED CRYSTALLOGRAPHY



X-ray sources :

- **synchrotron**

-> 50-150 ps

-> 100 fs

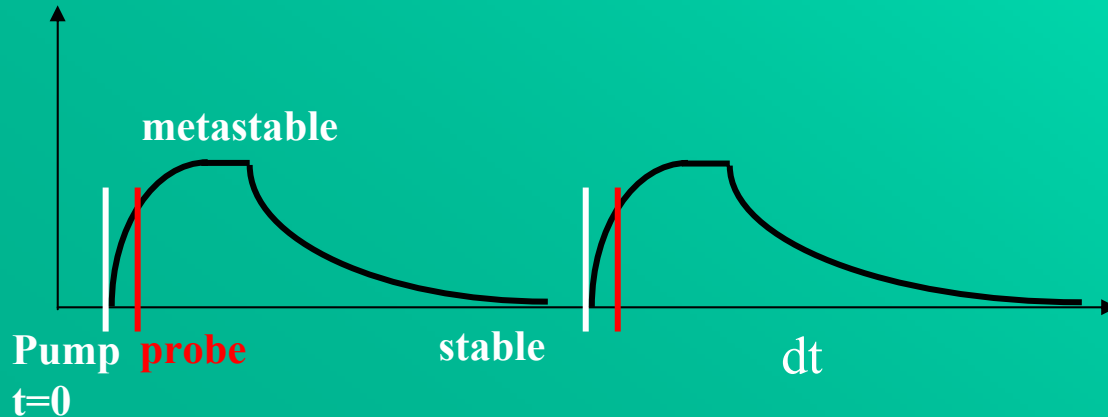
- **Laser systems**

-> 100 fs

- **Future sources**

-> 100 fs

Transformation coordinate

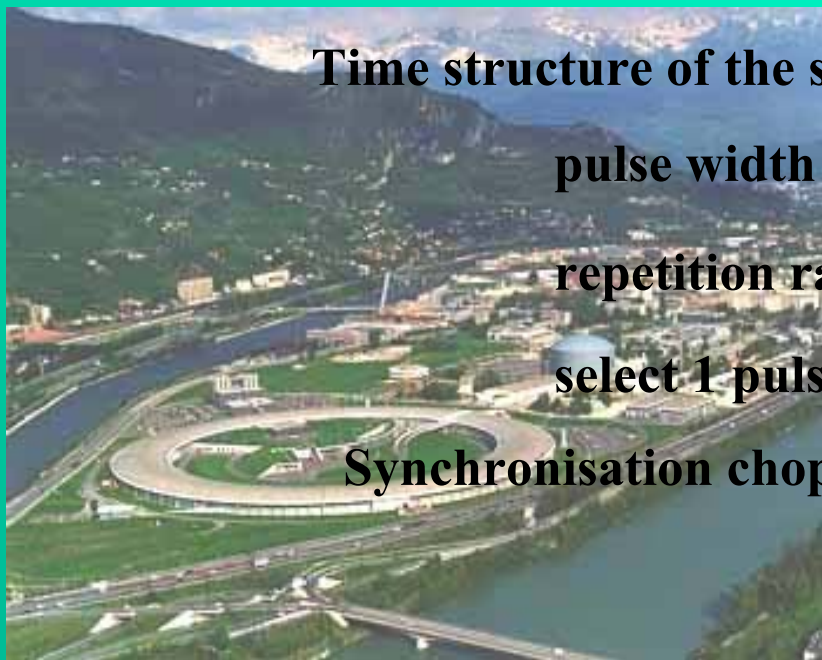


stroboscopic techniques

'Watching matter rearrange'
K. Nelson Science (1999)

Molecular movies

PICOSECOND CRYSTALLOGRAPHIC MEASUREMENTS ID09B ESRF



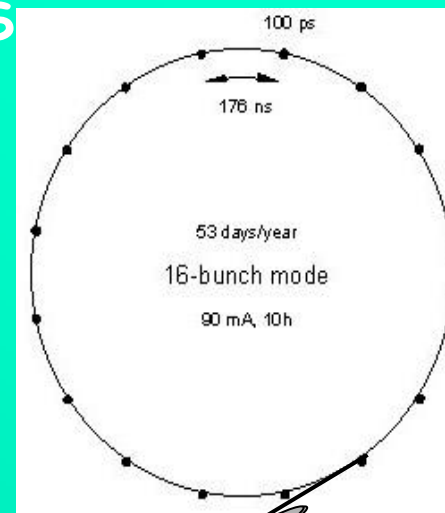
Time structure of the synchrotron radiation :

pulse width : 100 ps

repetition rate : 1kHz (896.6 Hz)

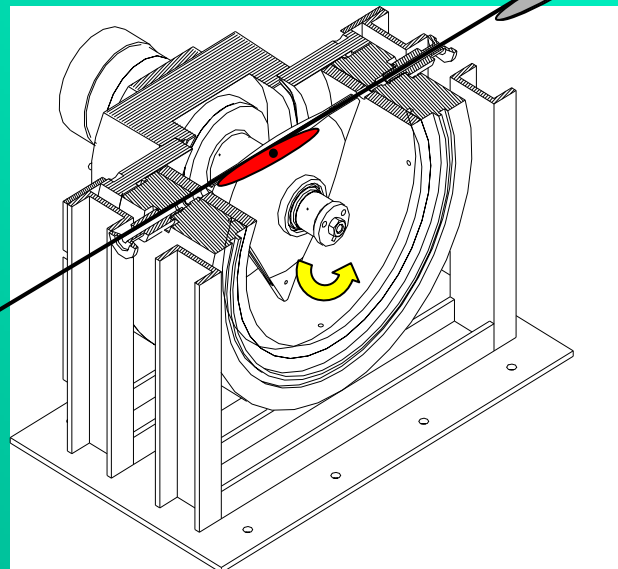
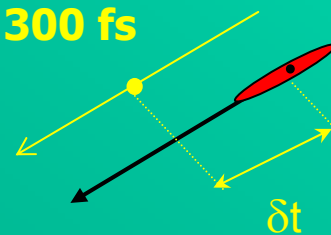
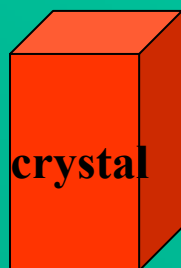
select 1 pulse over 6400 !

Synchronisation chopper/Laser

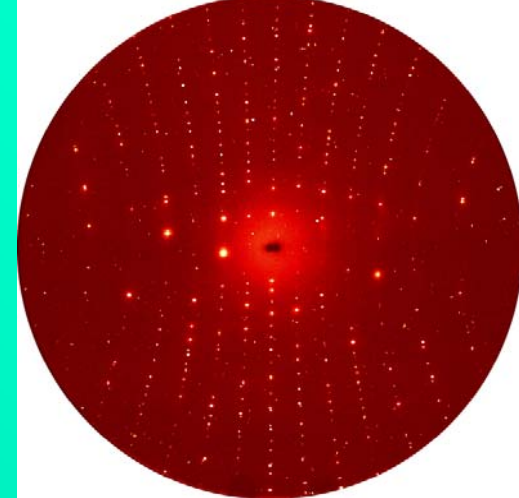


**X-ray Pulse
100 ps**

**Laser
pump
300 fs**



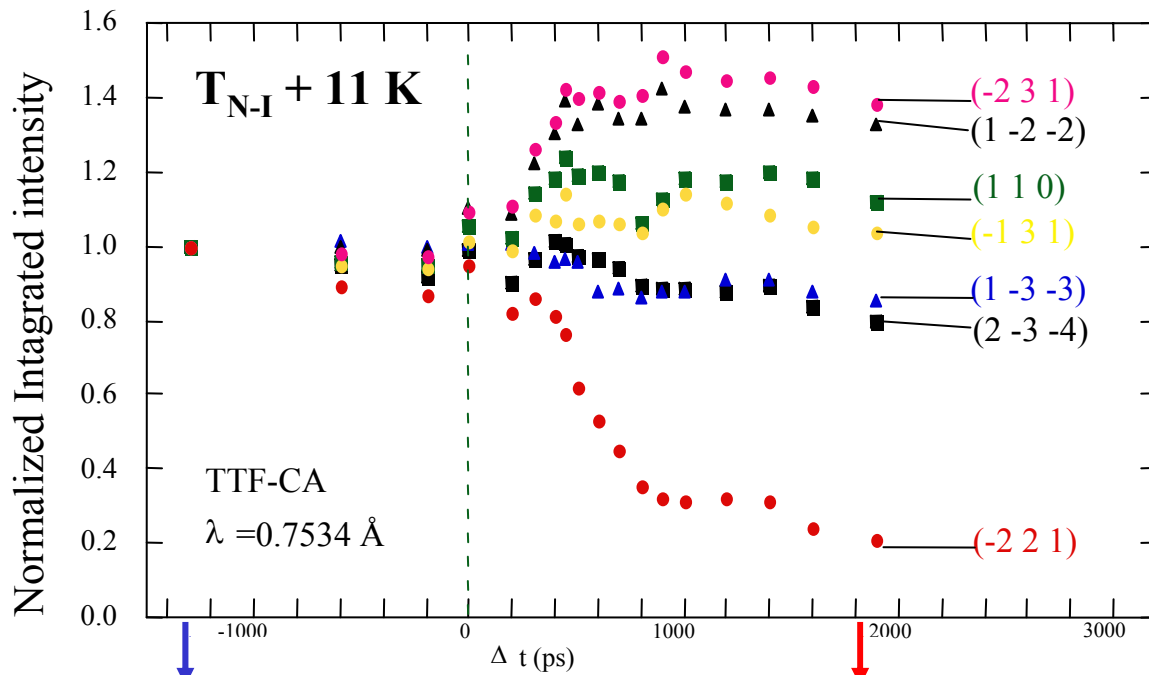
STRUCTURAL STUDY OF THE PHOTO-INDUCED N-I TRANSITION: TTF-CA



X-ray Pulses 100 ps

1st monochromatic experiment

ID9 ESRF



Neutral state

(high temperature)

Pulse laser 300 fs
 $\lambda = 800 \text{ nm}$

Ionic state

(photo-induced)

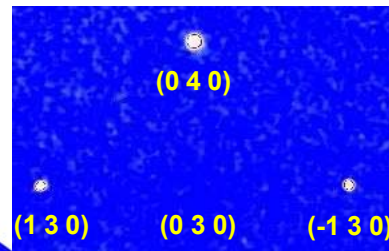
Structural reorganization :
3D domains

Large part transformed

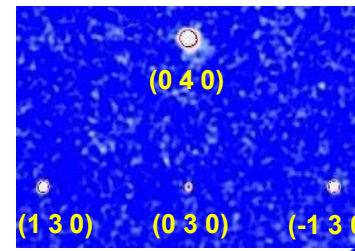
PHOTO-INDUCED STRUCTURAL ORDER !

Complete data collection : scattered intensity in the reciprocal space.

**2 ns before
laser irradiation**



**1 ns after
laser irradiation**



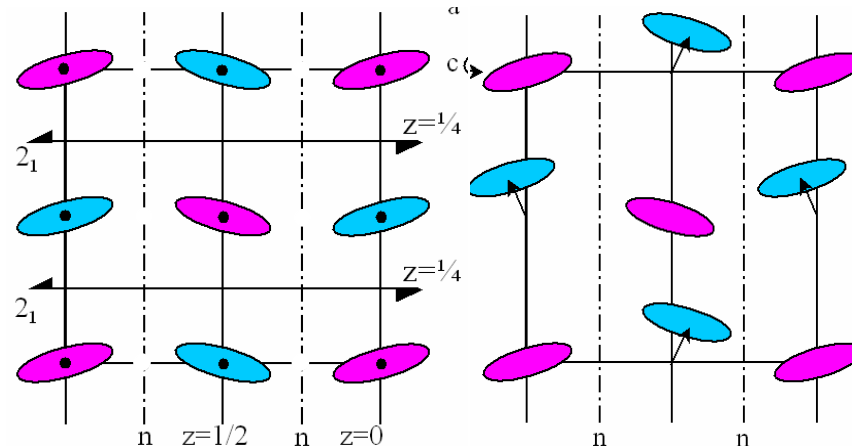
no (030)

(030)



Neutral phase

Space group $P2_1/n$
 $(0\ k\ 0) : k = 2n+1$ absent
 $(h\ 0\ l) : h+l = 2n+1$ absent

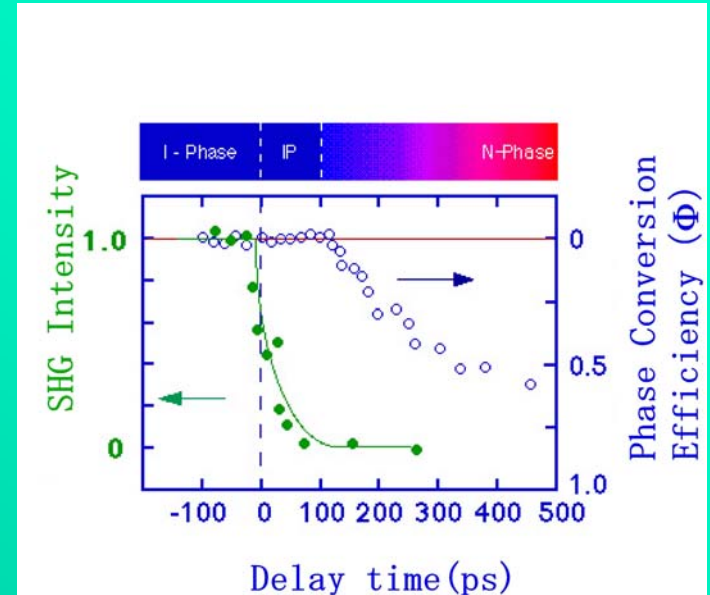
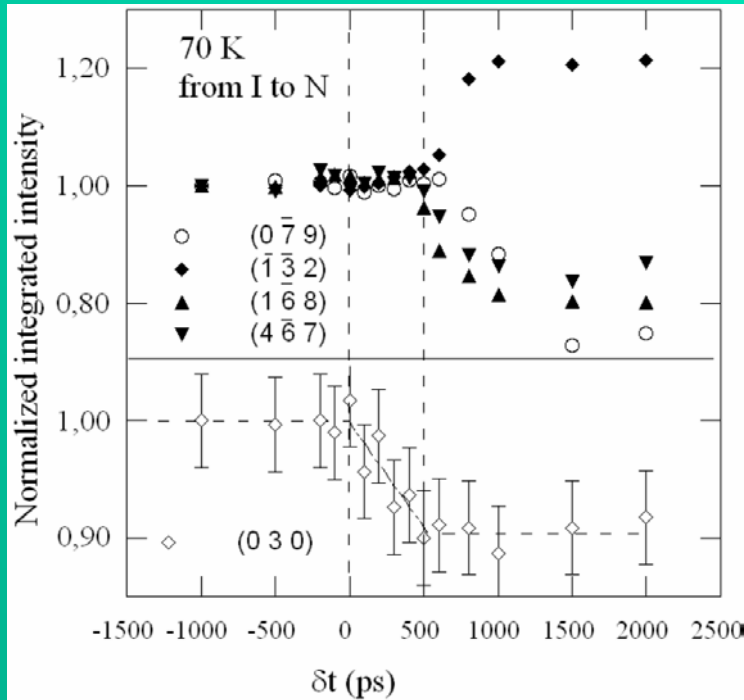


Space group Pn
 $(0\ k\ 0) : k = 2n+1$ **present**
 $(h\ 0\ l) : h+l = 2n+1$ absent

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

- *intermediate disordered state ?*

Change of symmetry + Change of state



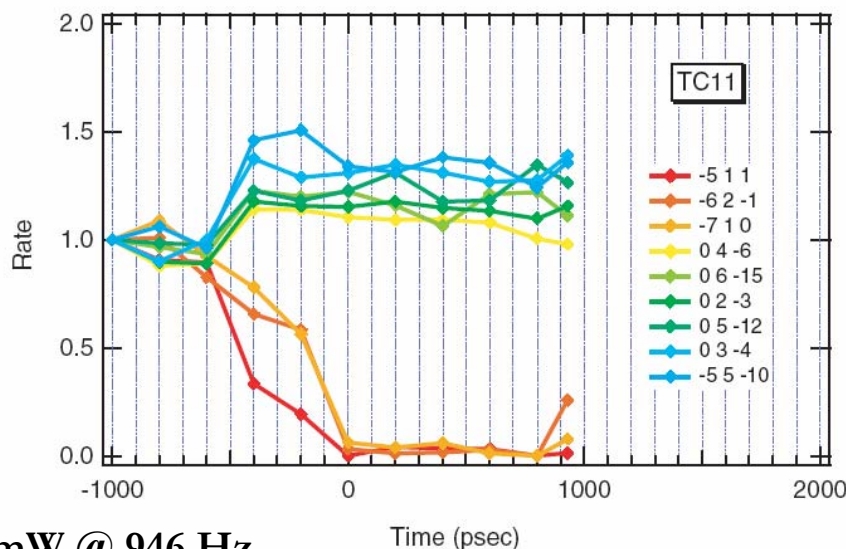
T. Luty et al, Europhysics Lett., 59 (2002)

L. Guérin et al, Chem Phys. 299 163 (2004)

Results obtained on TTF-CA
have been reproduced in KEK
Tsukuba (Japan)

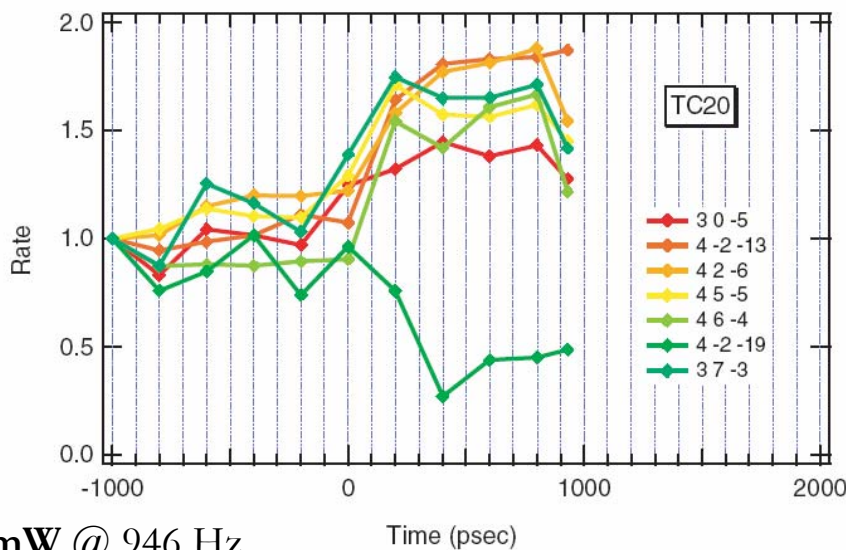
Today, only 1 beam line at KEK
for time-resolved XAFS
and time-resolved diffraction

In a near future, two beam lines
200 days/year for time resolved
measurements



225mW @ 946 Hz

In 1mm ϕ



175mW @ 946 Hz

In 1mm ϕ

TO CONCLUDE :

A new exciting tool exists for probing structural changes at the atomic level as they take place in condensed matter.

Fast and ultra-fast diffraction techniques, combined with time resolved optical measurements, are the key for elucidating the light pulse control of phase transitions, i.e. for controlling ultra-fast macroscopic switching of materials

Challenge for the future :

In addition to 100 ps synchrotrons (ESRF, KEK (Japan)), 30 ps synchrotron (Soleil), combining the high quality of synchrotron beam (flux, divergence,..) and the time scale reached by 100 fs sources

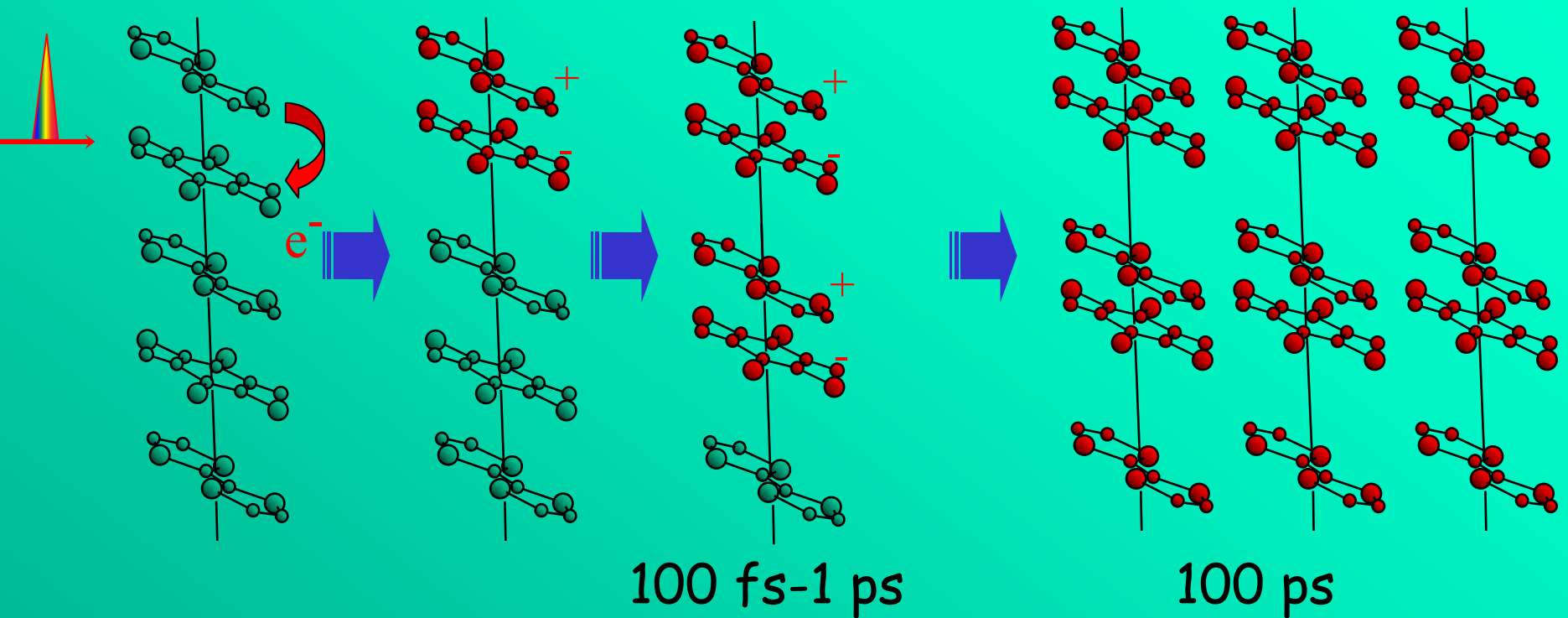
SPPS in Standford

slicing (Soleil, Berkeley)

Development of 100 fs laser-produced plasma sources (LOA, ...)

Large scale projects : FREE ELECTRON LASER (X-FEL)

What is the mechanism???



photoinduced cooperative molecular
switching along the chain :
1D process

3D ordering
of ionic dimers

1D local order exist at the very first step : diffuse scattering???