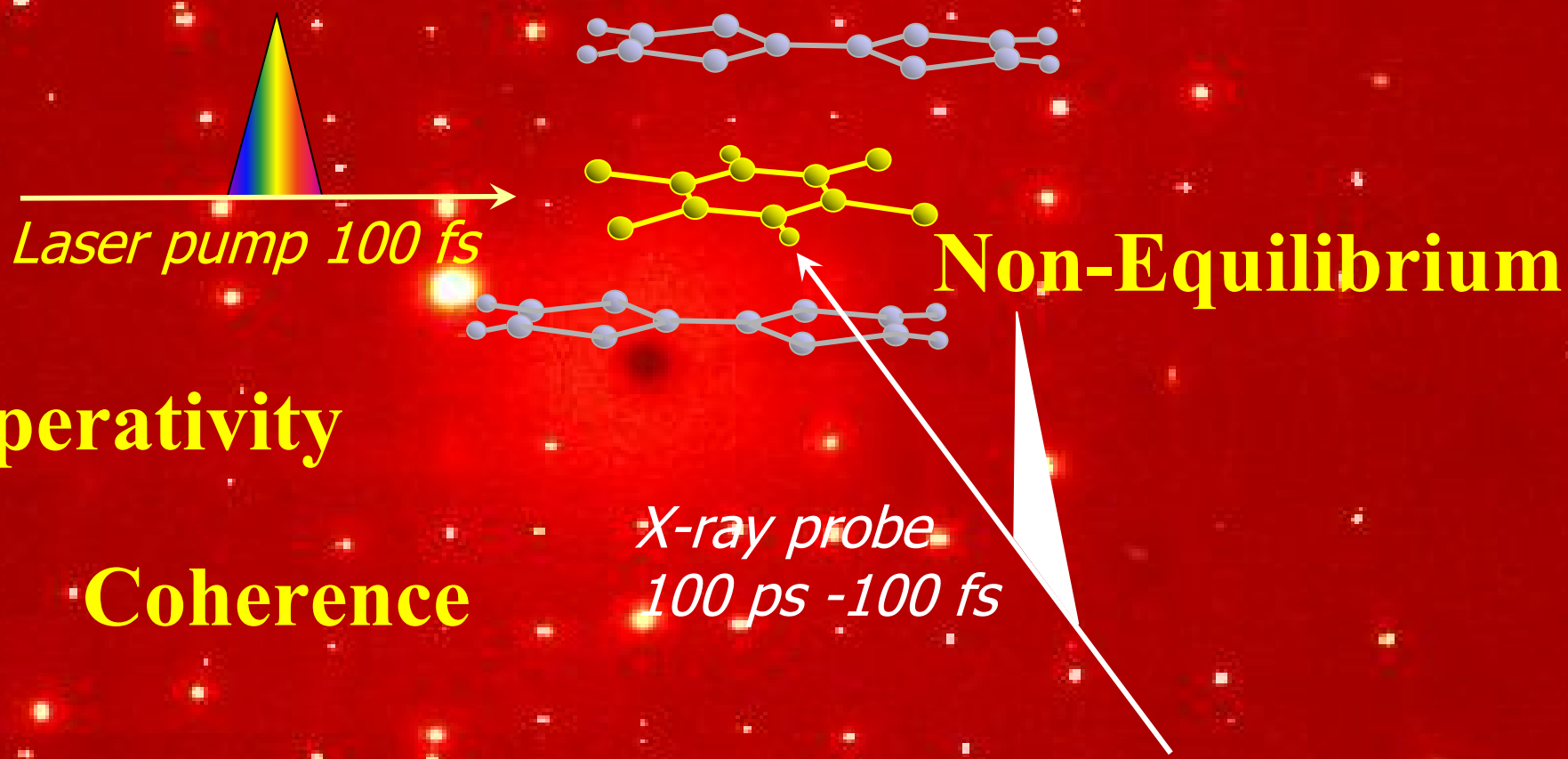
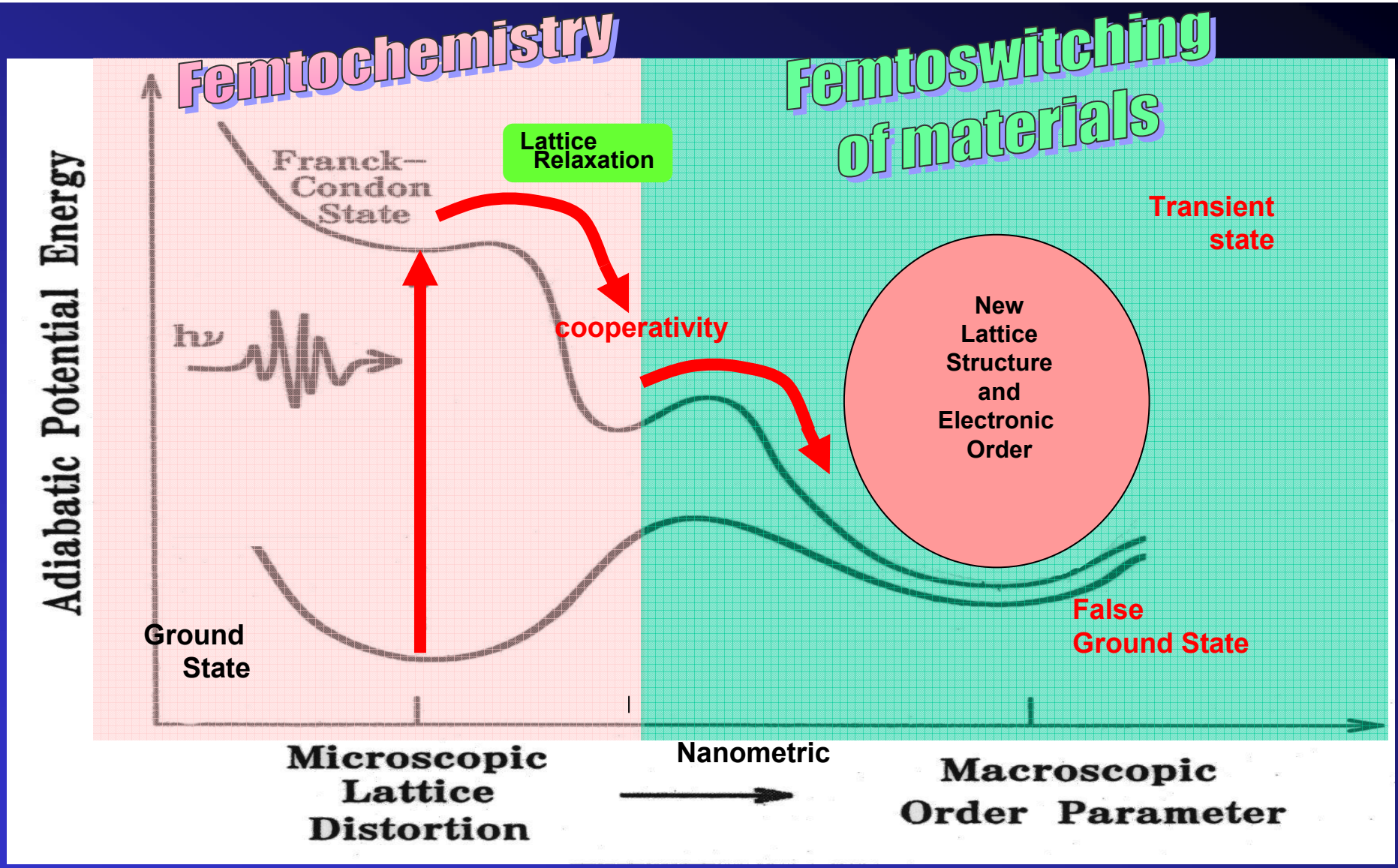
EVOLUTION AND CONTROL OF PHOTOINDUCED TRANFORMATIONS IN MOLECULAR MATERIALS :

Experiments for Tracking and Understanding their Non-Equilibrium Cooperative and Coherent Dynamics

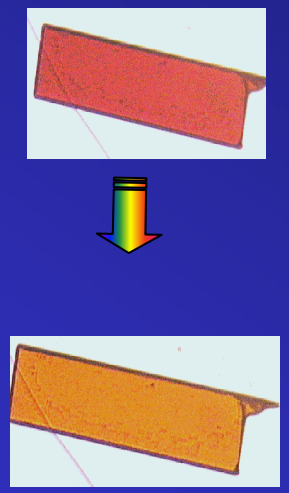




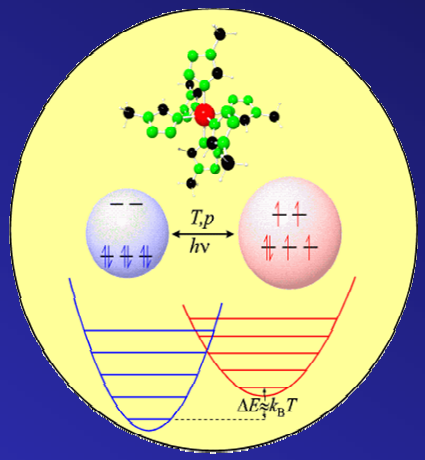
from K. Nasu

Taking advantage of cooperative interactions in the solid state (active medium) to trigger with a light pulse the switching of the macroscopic state of a material, and then of its physical properties (magnetic, optical, conduction,…)

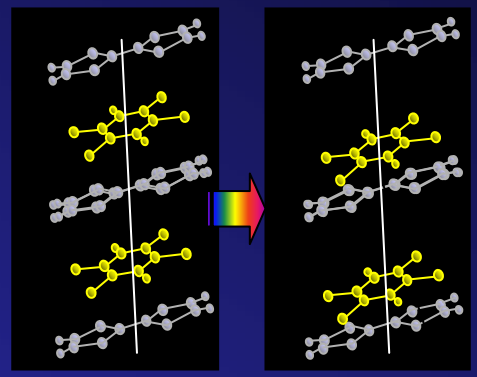
Chromism



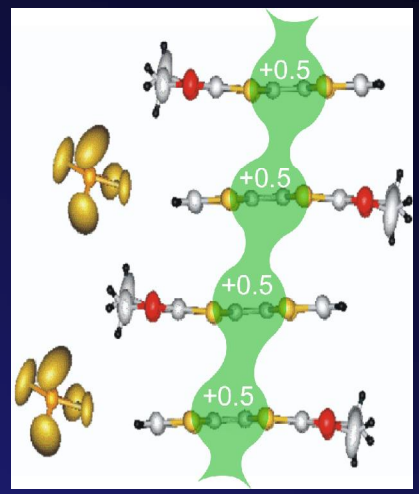
Magnetism



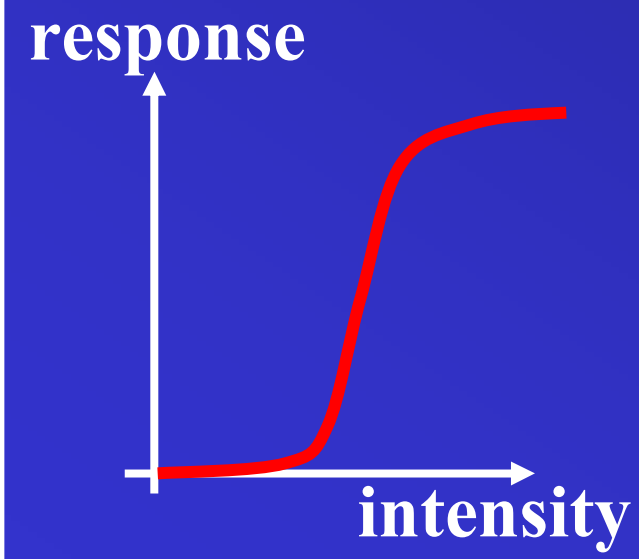
Ferroelectricity



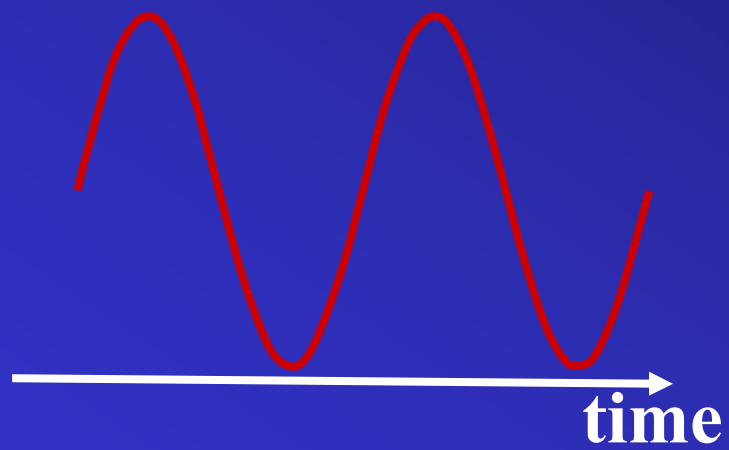
Conductivity



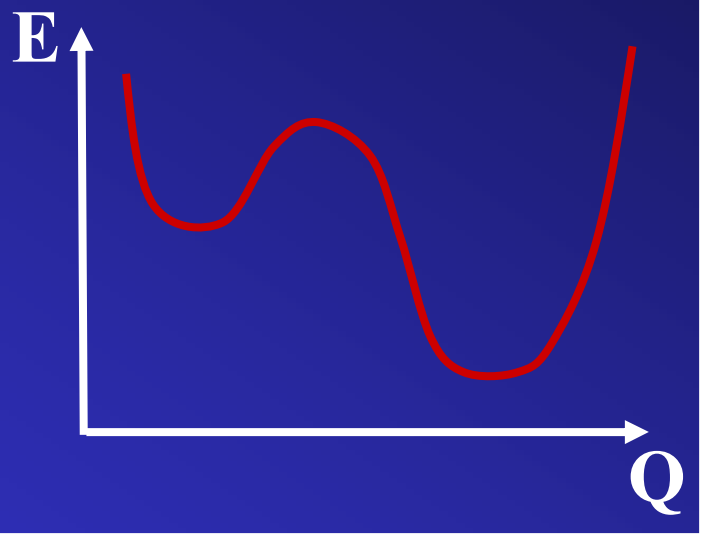
Cooperativity



Coherence



Non-Equilibrium



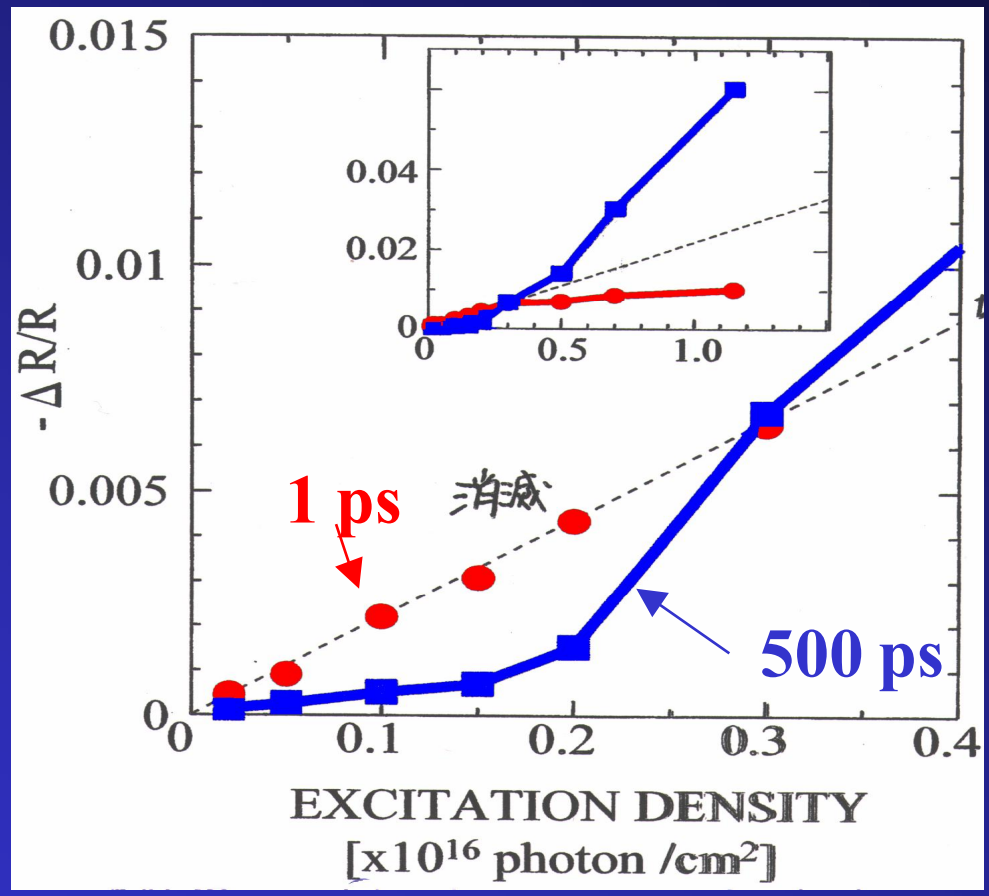
Cooperativity
« More is different » (PW Anderson)

- cooperative interactions drive the emergence of remarkable features such as phase transitions or non-linear dynamical instabilities, as well as ultra-fast photo-induced phase transitions beyond the femtochemistry of independent molecules
- namely, the medium is no more passive but active throught positive feedback, inducing an effective field at the origin of strong responsiveness

Non-linear response to excitation density

Self-amplification and threshold

The simultaneous absorption of a huge number of photons yields more than the sum over individual events

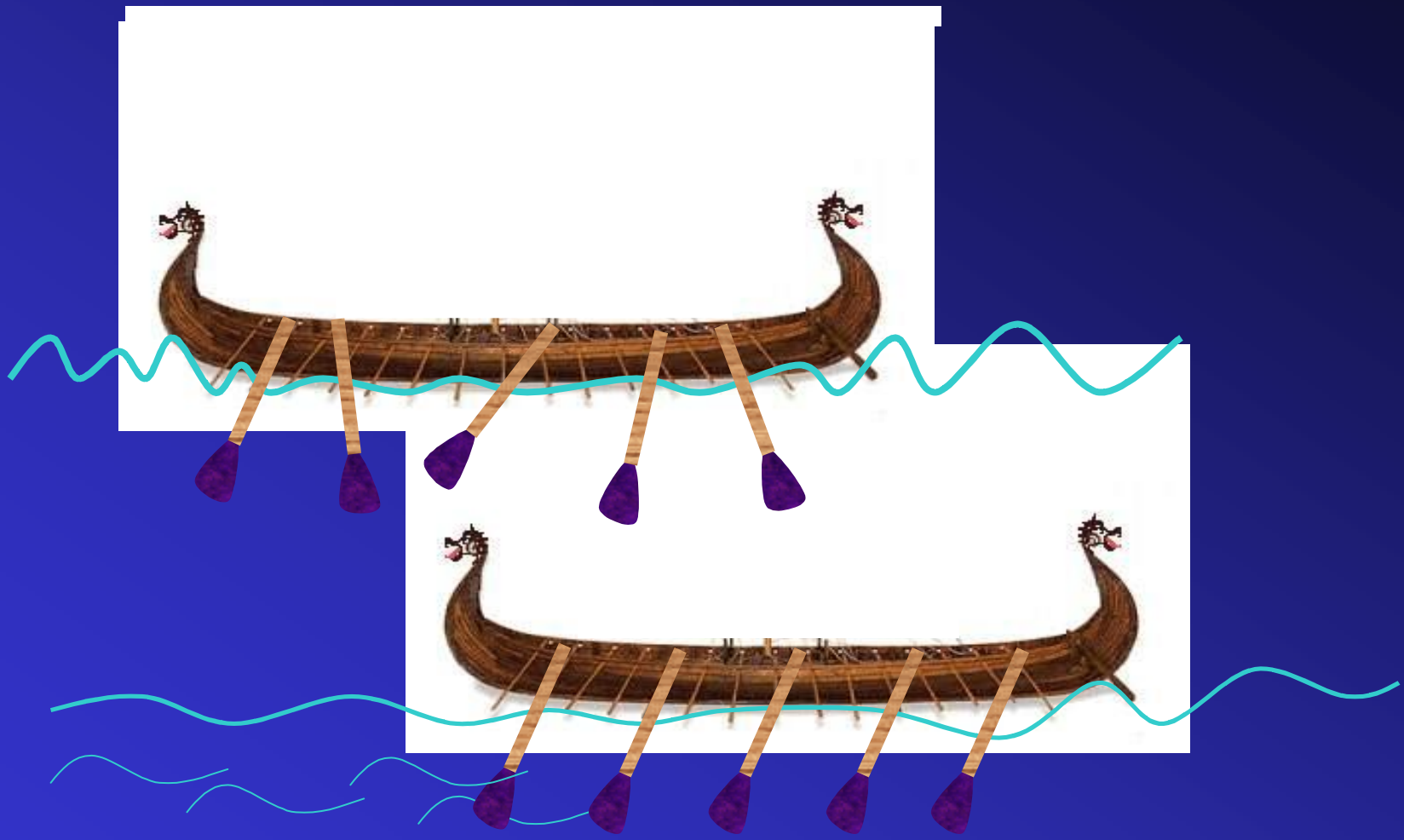


H. Okamoto et al, Univ. Tokyo
Phys. Rev. Lett. (2002)

Coherence (non-thermal)

- physics of coherent processes triggered by ultra-short laser pulse is different
- the different dynamics are no more stochastic as at thermal equilibrium but instead become deterministic
- manipulating coherence is a big challenge since laser is not a mere heat source, instead it may coherently direct the system along the desired pathways on the potential energy surface

Coherent vs Incoherent Motions



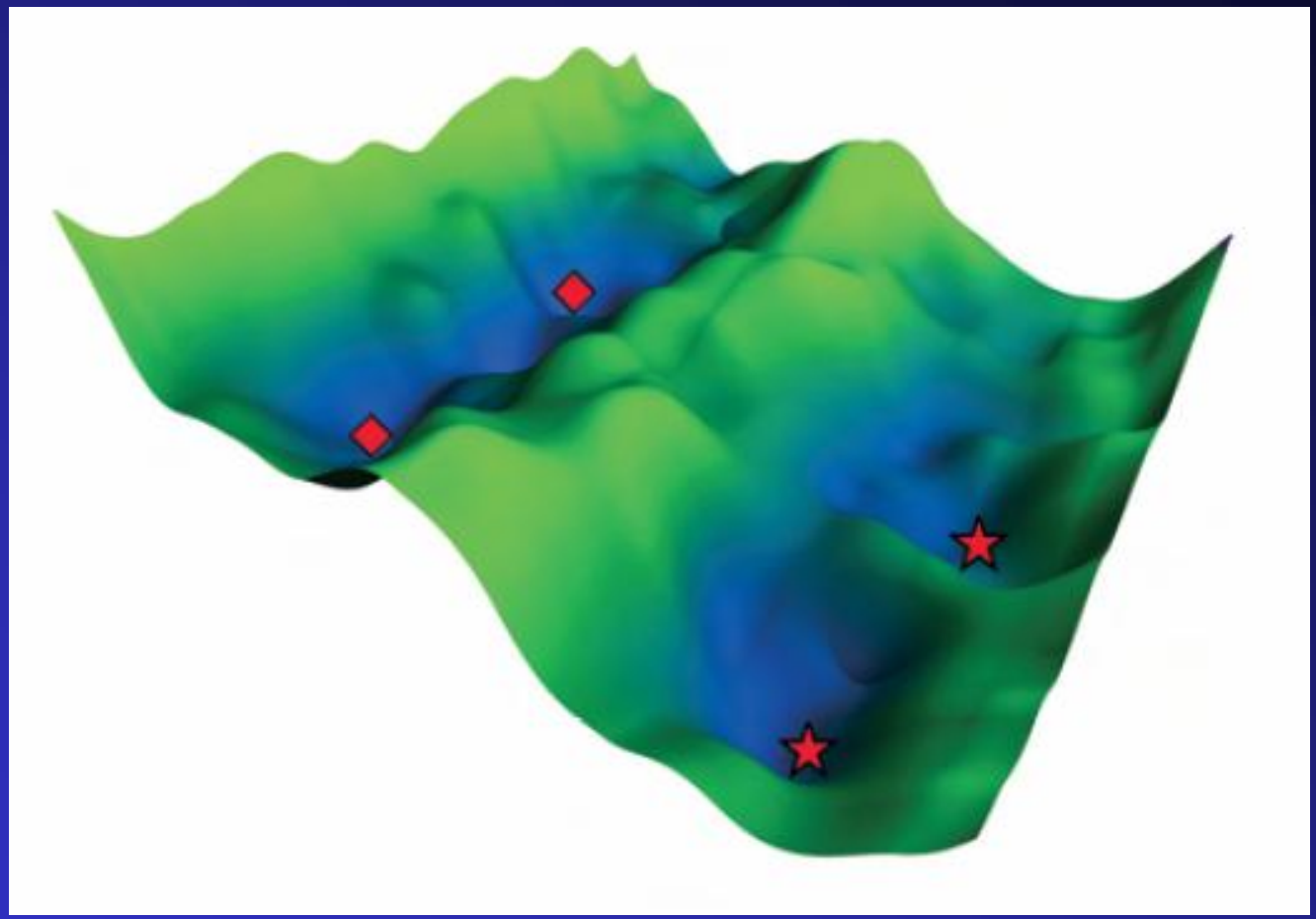
The physical effect is very different

Far away from equilibrium

- the aim of photo-induced collective and/or cooperative phenomena in materials is to force the system towards a new macroscopic state far away from thermal equilibrium
- beyond our current understanding of matter based on thermal equilibrium properties
- actually different subsystems of different nature, such as electrons, spins, phonons, molecular configurations, cell deformation,…play their part but on different time scales

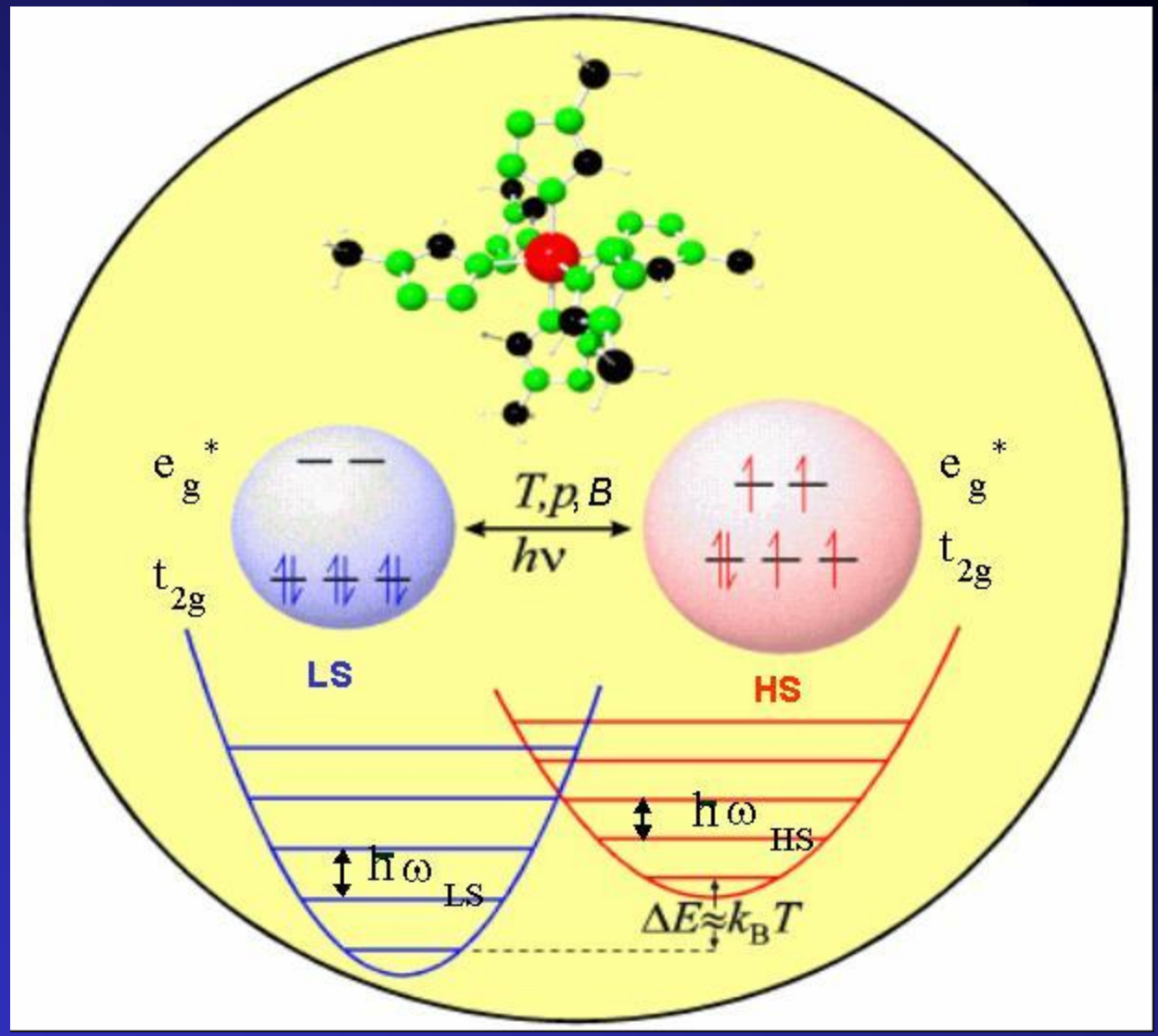
POTENTIAL-ENERGY LANDSCAPE

What kind
of
potential-energy?

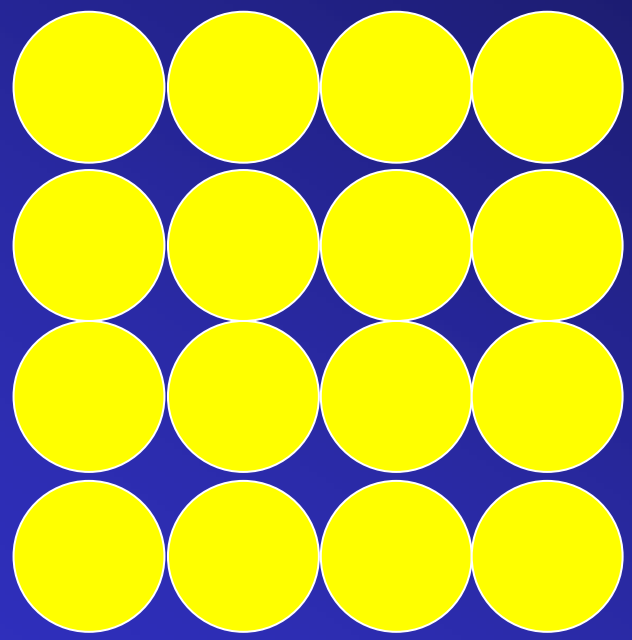


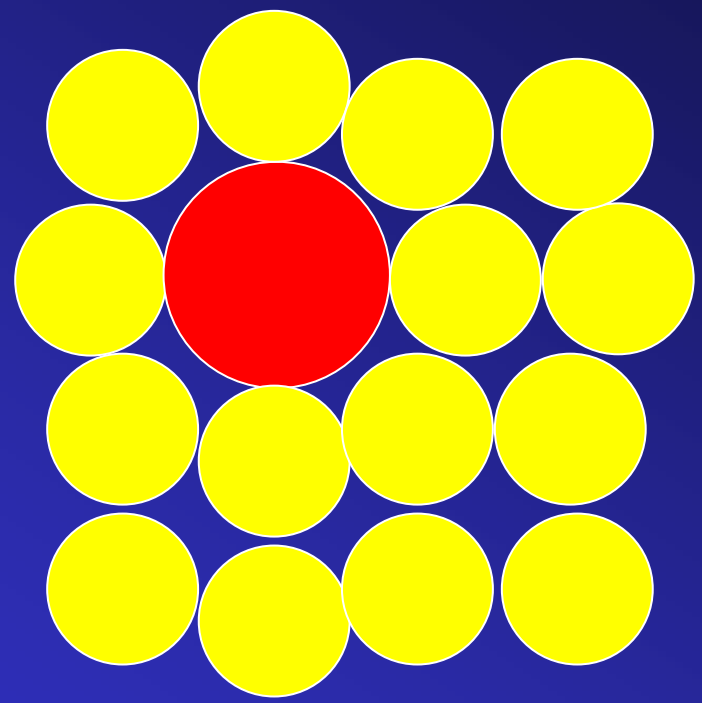
What are the relevant physical parameters which govern the out of equilibrium dynamics? What are the consecutive steps which take place? On which lenght and time scales? When thermalization occurs? And for which kind of subsystem?

The prototype of molecular bistability in the solid state : spin crossover crystals



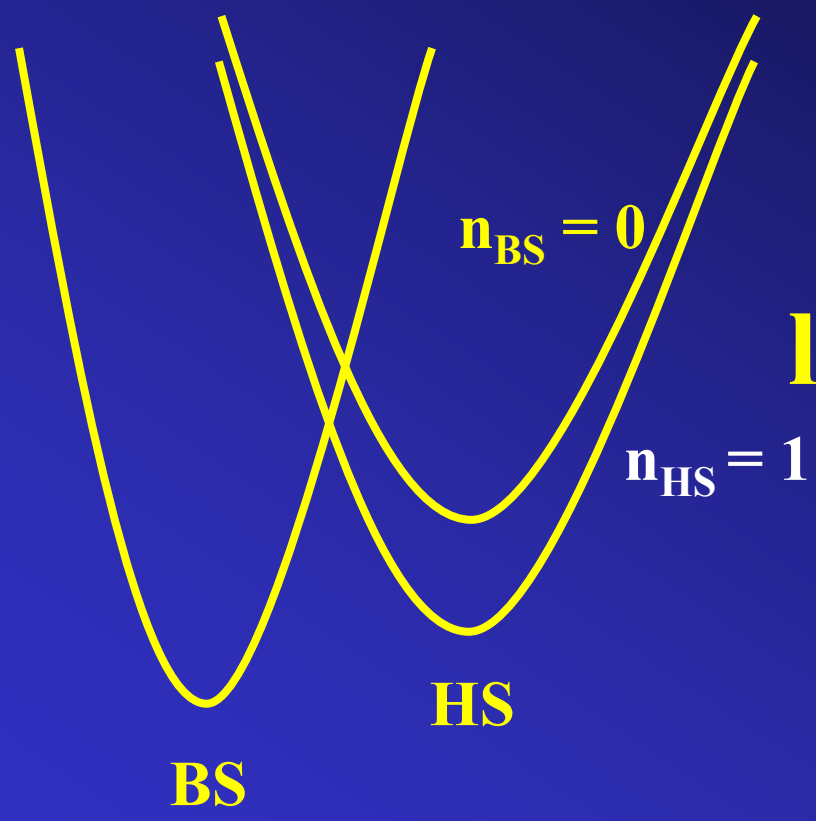
Co-operativity in spin crossover crystals: long-range elastic interactions





Active medium

Positive feedback



increasing n_{HS} lowers E_{HS} (equilibrium) and increases $\Delta E_{HS\text{-}BS}$ (kinetics)

Simple illustration of feedback effect

PHOTO-STATIONARY STATES

No more thermodynamic potential but dynamic potential (from the kinetic equation)

$dx/dt = f(x) = - dV(x)/dx$

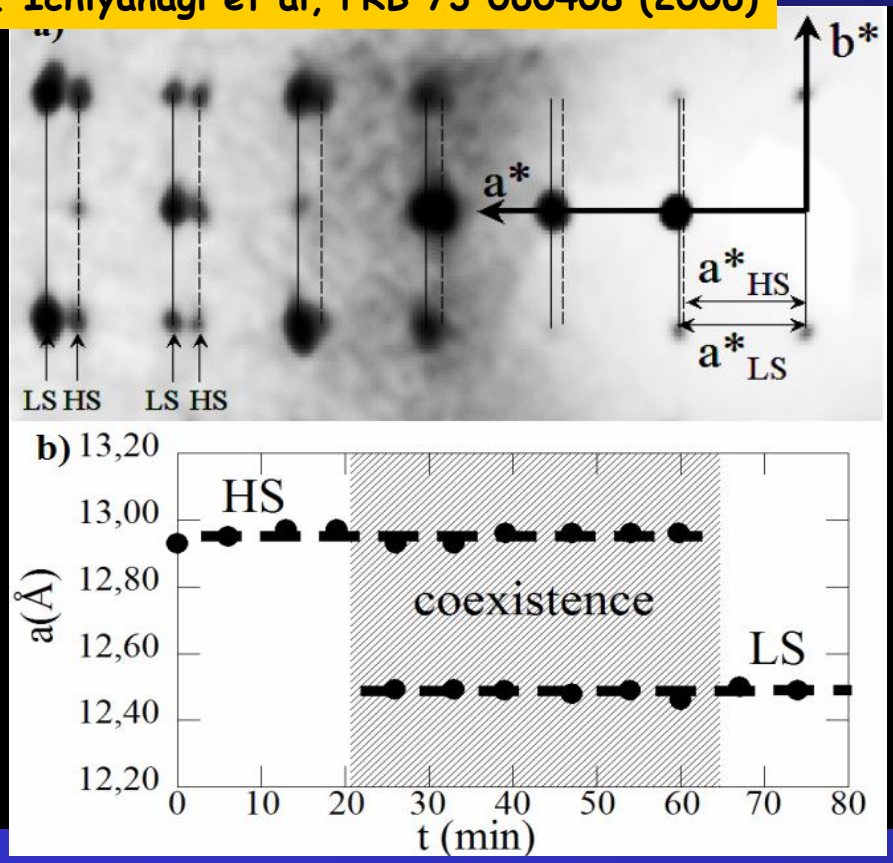
Light-driven bistabily can occur in case of non-linear kinetic law

The control parameters are photon flux and temperature

Mechanism driving the photoinduced macroscopic switching and relaxation in $[Fe(PM\text{-}BiA)_2(NCS)_2]$ compounds

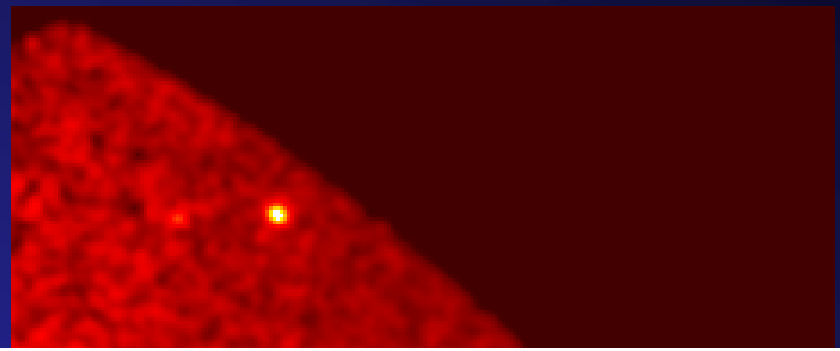
Orthorhombic form :

K. Ichiyanagi et al, PRB 73 060408 (2006)



domain nucleation process associated with the coexistence HS and LS phases around the thermal and photoinduced transition

Monoclinic form :



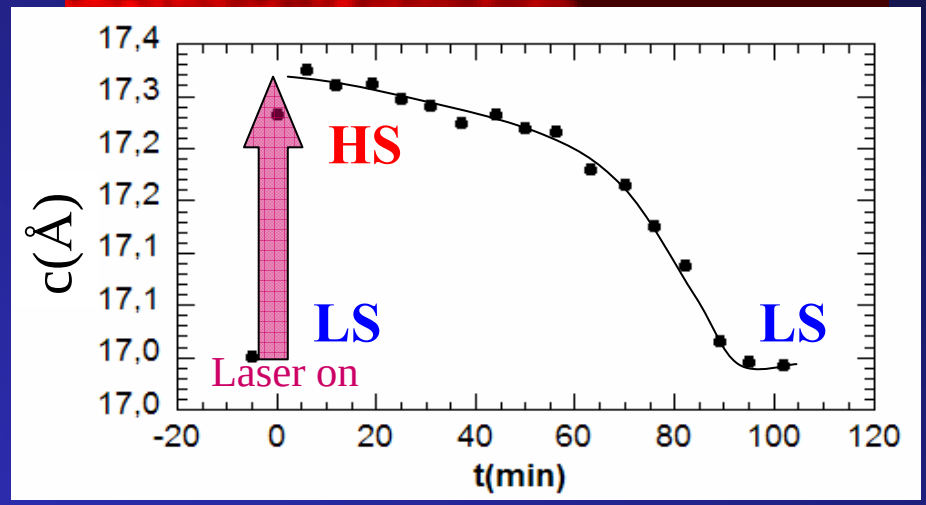


Photo-injection process where the concentration of HS molecules is gradually changed around the thermal and photoinduced transition

The domain nucleation process requires coperativity

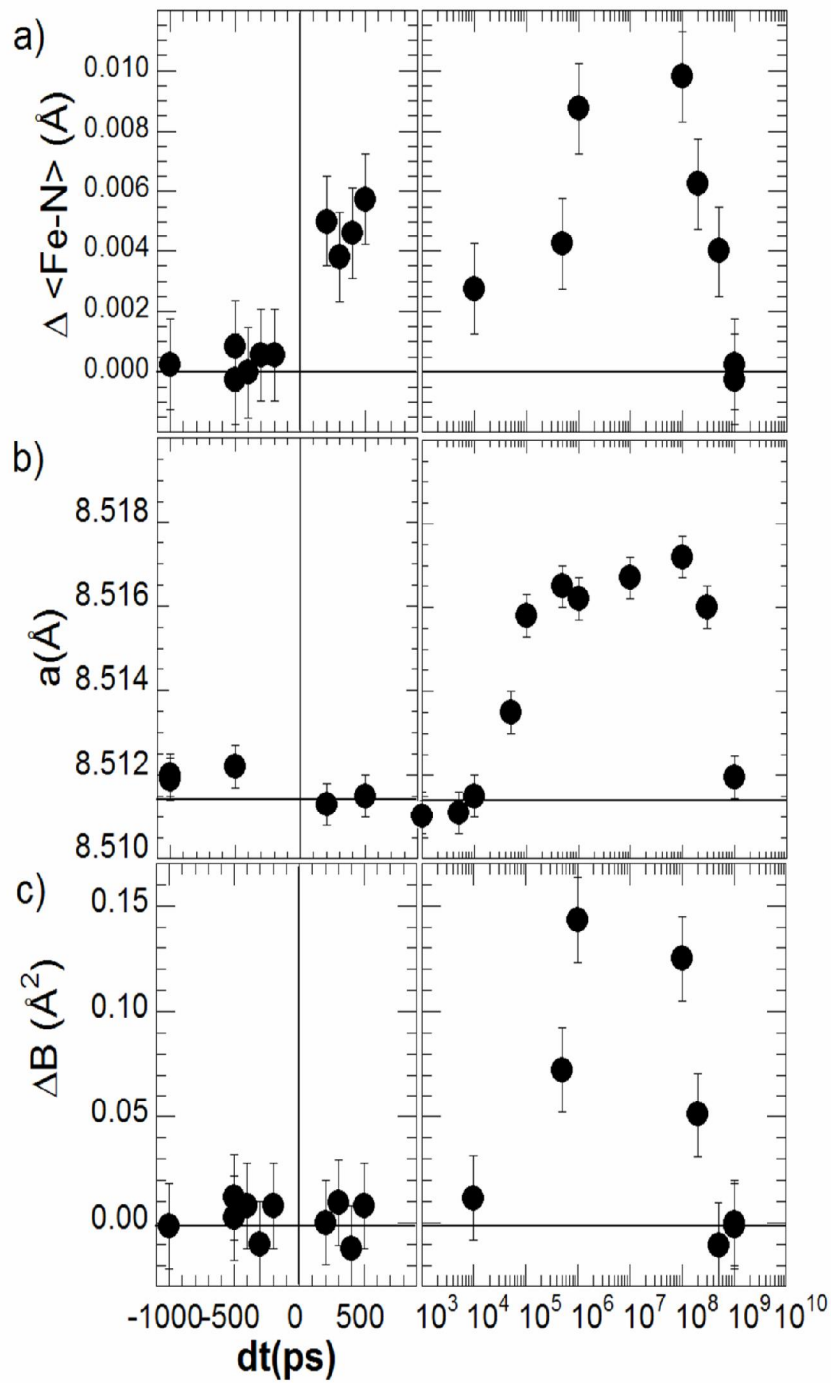
3 main steps :

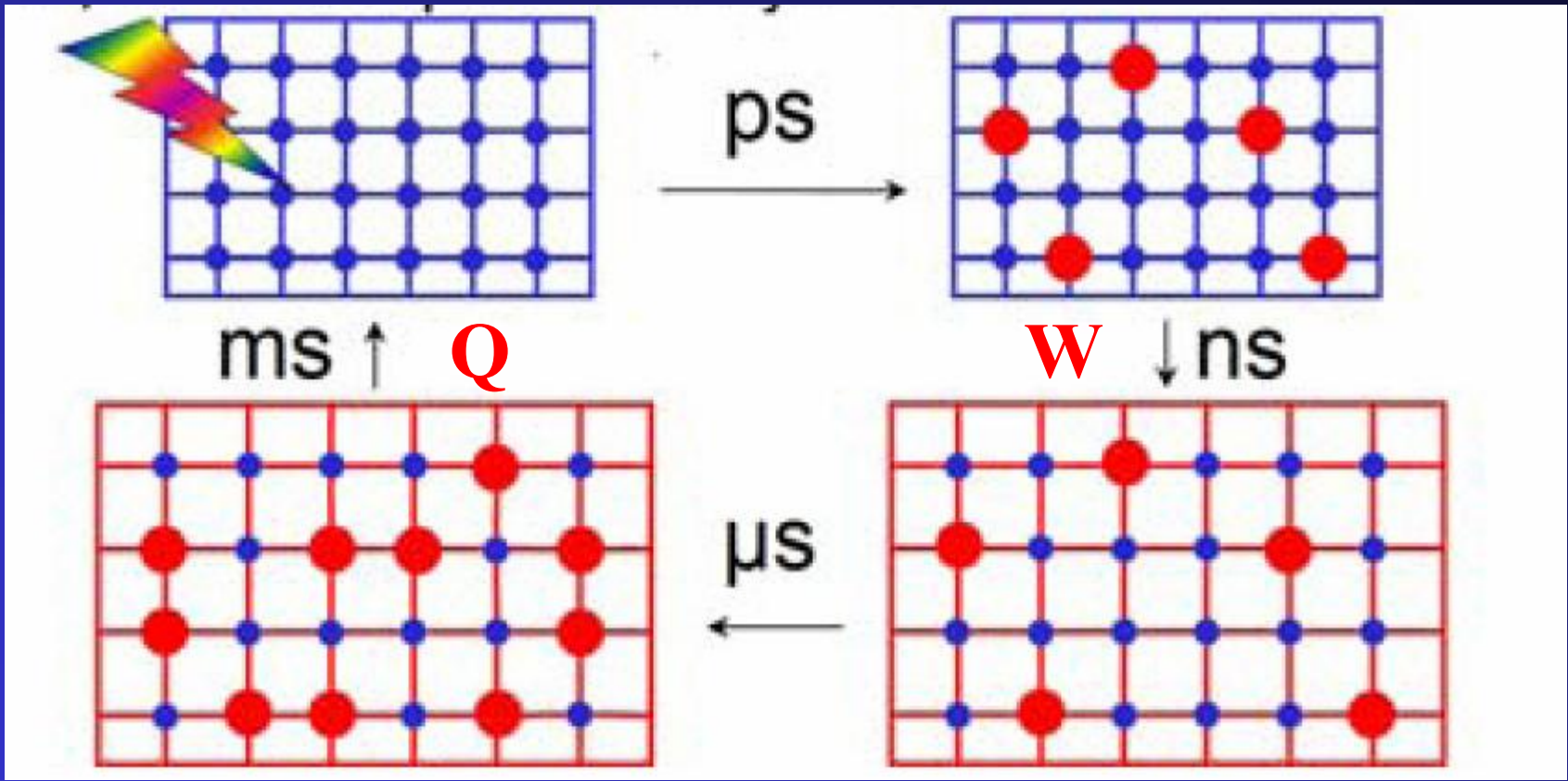
i) sub-ps molecular switching

ii) unit cell volume expansion on 10 ns time scale

iii) significant thermal effect on µs time scale

Phys. Rev. Letters 103, 028301 (2009)
Acta Crys. A 66, 189 (2010)





Out of equilibrium (thermo)dynamics

Consecutive different dynamicprocesses at different time-scales

Ultra-fast

Fast

Slow dynamics

10^{-15} s — Electronic motions

10^{-12} s — atomic motions, optical phonons

10^{-9} s — acoustic phonons, domain wall motions

10^{-6} s

10^{-3} s

1 s

Days

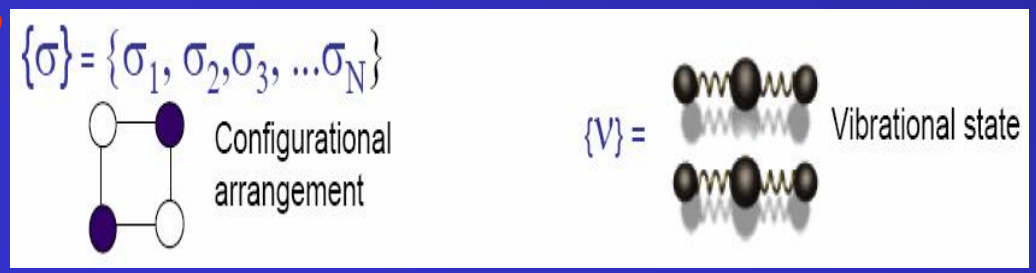
ultra-fast molecular switching (local)

thermalization of lattice at constant volume (isolated)

volume relaxation (adiabatic $\tau \approx l/v_s$)

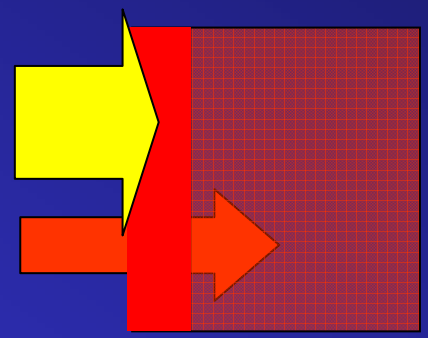
thermal molecular switching and heat diffusion

recovery of thermal equilibrium ($\tau \approx C/K$)



Light

X-ray



COMPLEX PATHWAY

The laser pulse prepares the material in a new electronic physical state. This determines the initial conditions for the evolution of the system. It follows a complex pathway from molecular to material scale through a sequence of dynamical processes. Not only is the pathway indirect, the potential energy landscape depends on time-scale: what degrees of freedom are involved in the subsequent dynamics or kinetics and which other are frozen, or quantum or statistical averaged? It spans from mechanical potential directing a deterministic dynamics to thermodynamic potential for kinetics towards equilibrium

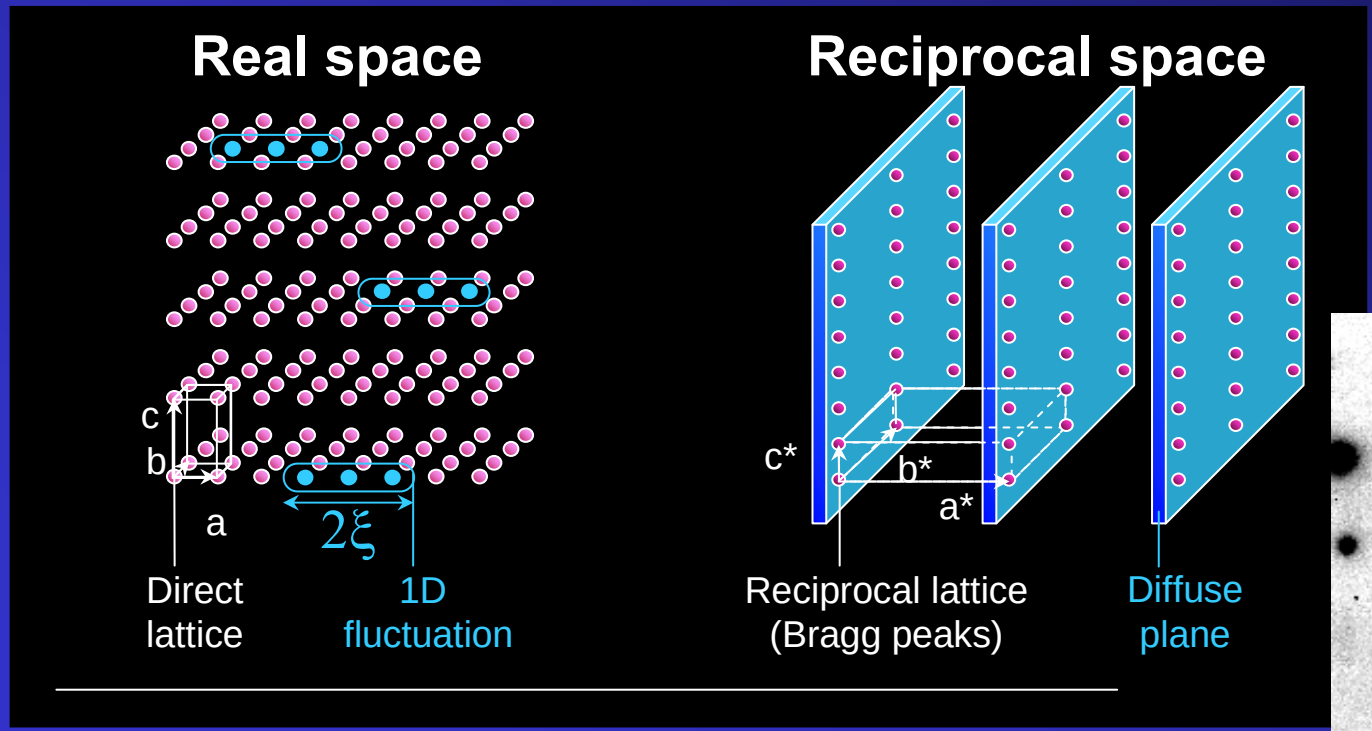
NEW CHALLENGE

The control of macroscopic photo-switching in materials requires the direct observation of ultrafast precursor phenomena which precede photoinduced phase transformation

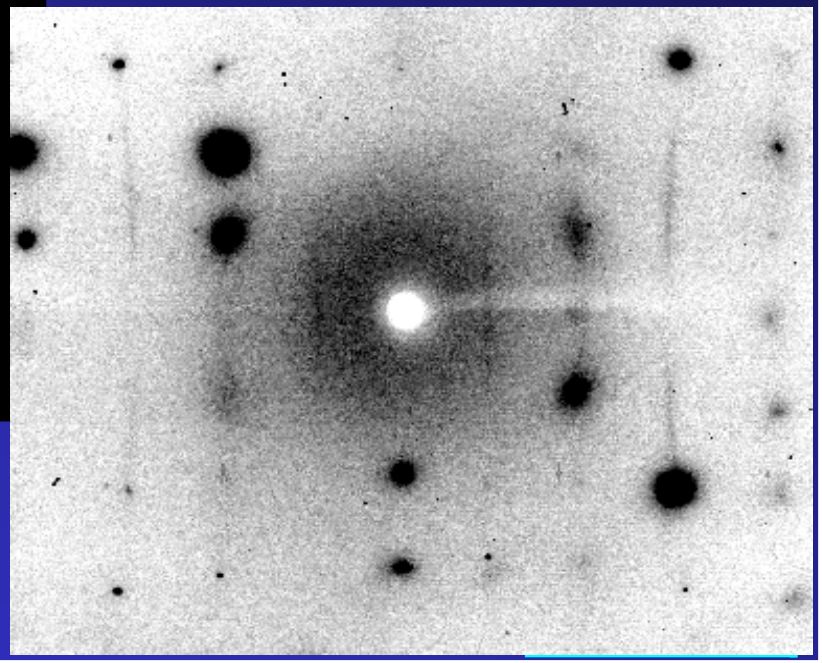
Mechanism of photoinduced phase transformations

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

1D object gives rise to diffuse planes

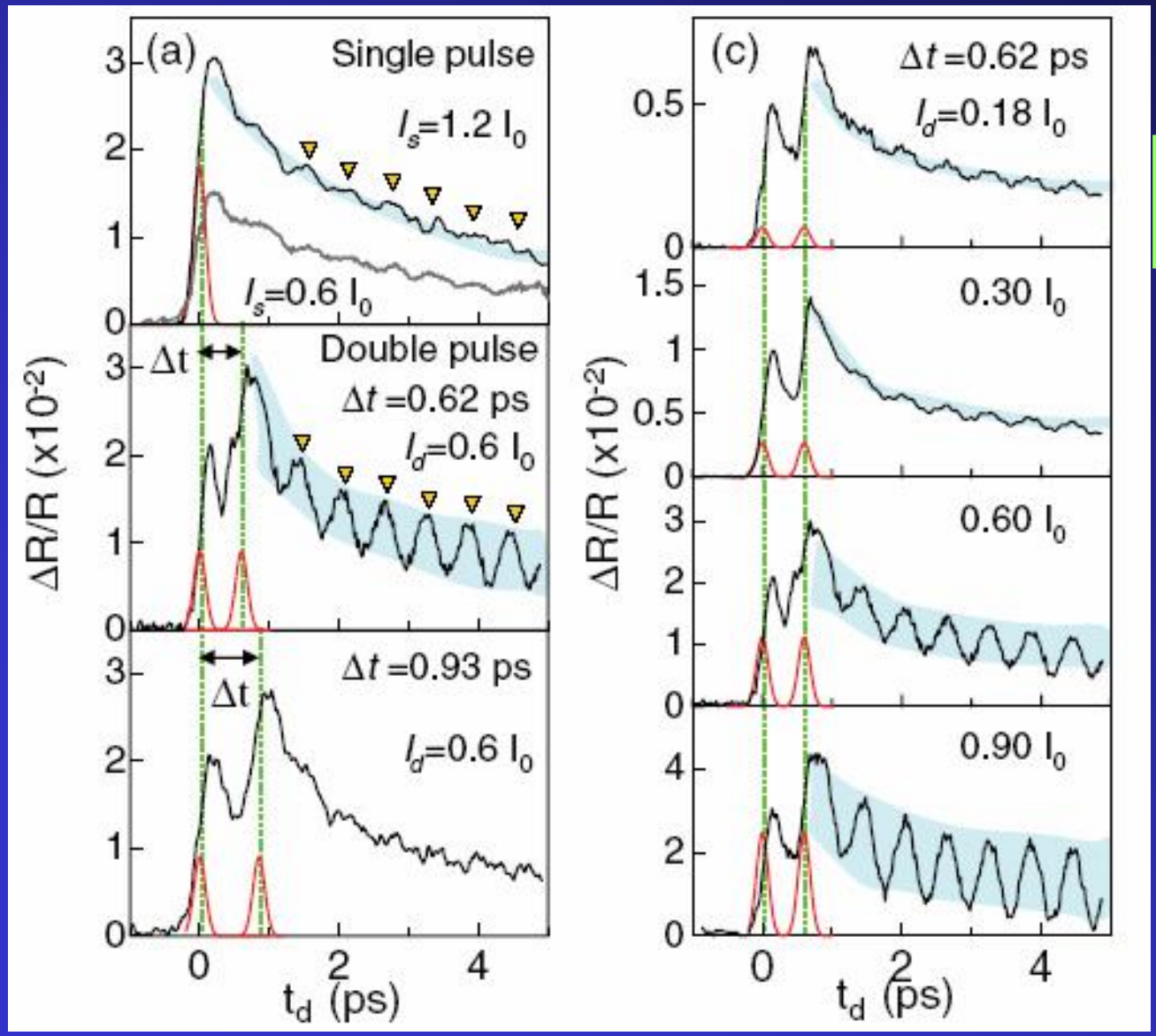


Watching precursor phenomena



Phys. Rev. Lett. 96, 205503 (2006)

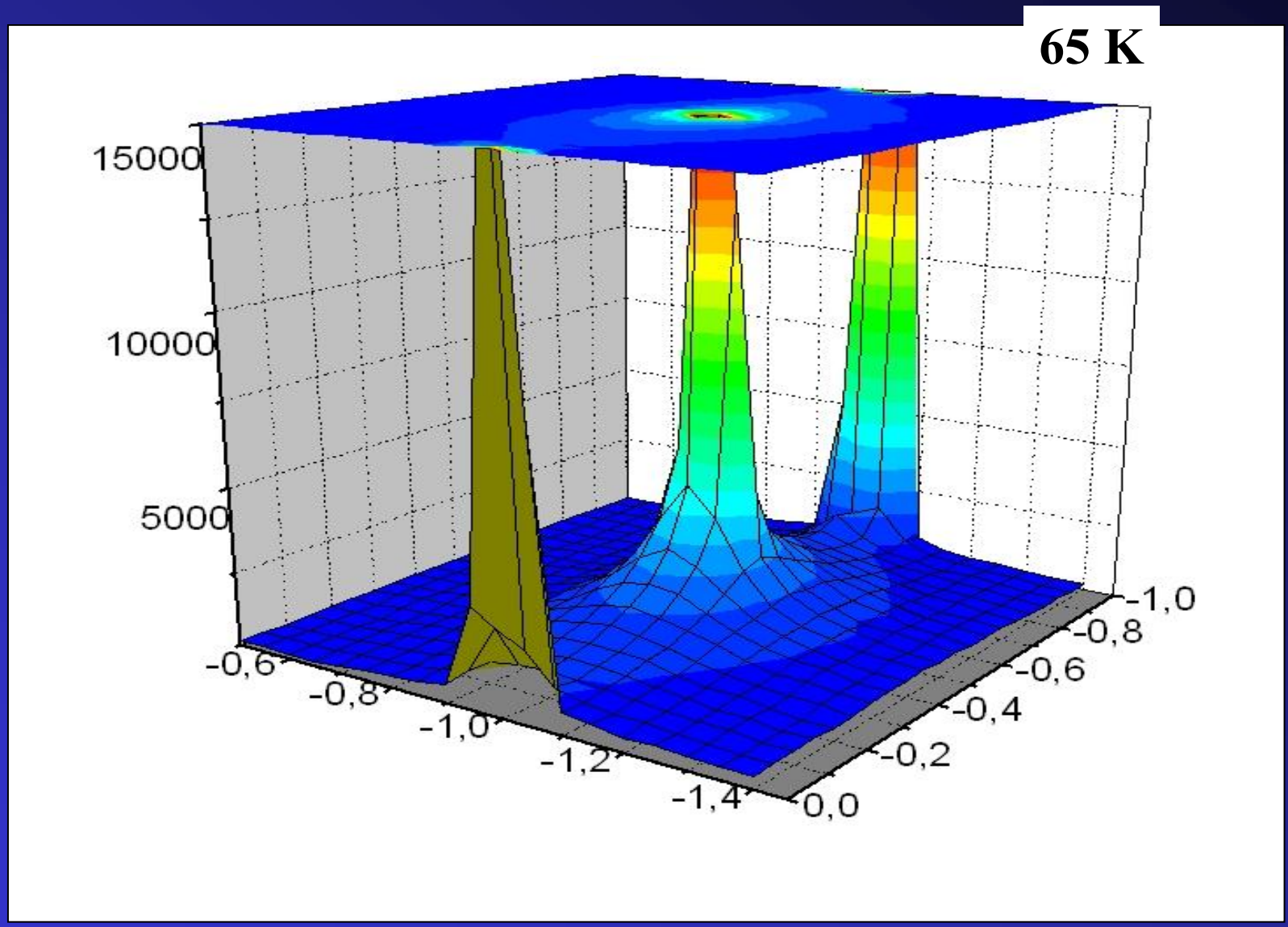
Going down to 100 fs time resolution to watch coherent dynamics



Iwai et al, PRL 96, 057403 (2006).

Two pulses excitation : non-linear increase of the oscillation amplitude

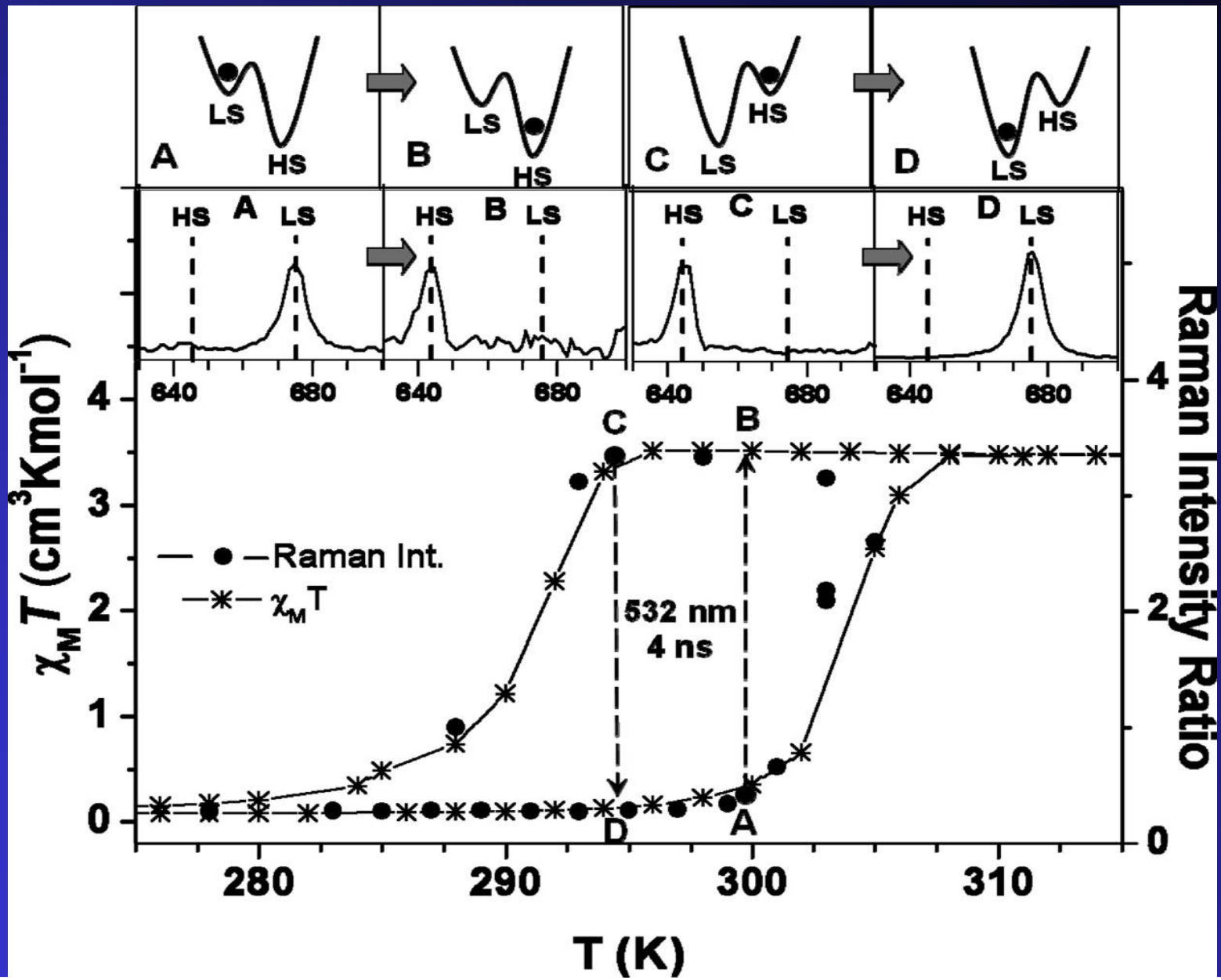
1D - 3D CROSSOVER (DMTTF-CA)



Another challenge : single shot experiment

Photoinduced switching inside thermal hysteresis

JACS 130, 9021 (2008)



Spin crossover nanoparticles

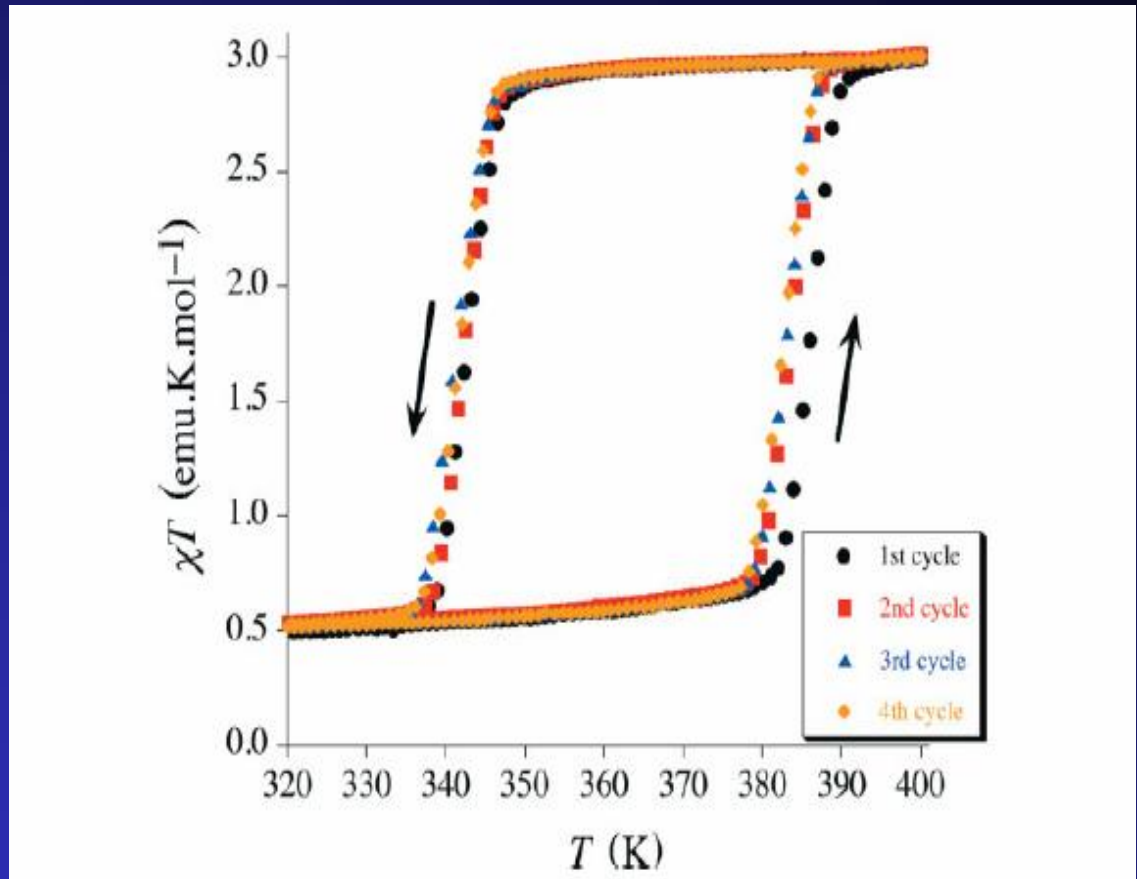


Figure 3. Magnetic thermal hysteresis for as-prepared $[Fe(Htrz)_2(trz)](BF_4)$ nanoparticles (magnetic moment represented per mole of Fe).

Hysteresis down to a few nm ($n_S \sim n_B$)

here size ~ 10 nm

E. Coronado et al Adv. Mater. 19, 1359 (2007)

Team and collaborations

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