Ultra-fast photoinduced gigantic metallization in quarter filled organic A_2B salts: $(EDO\text{-}TTF)_2PF_6$

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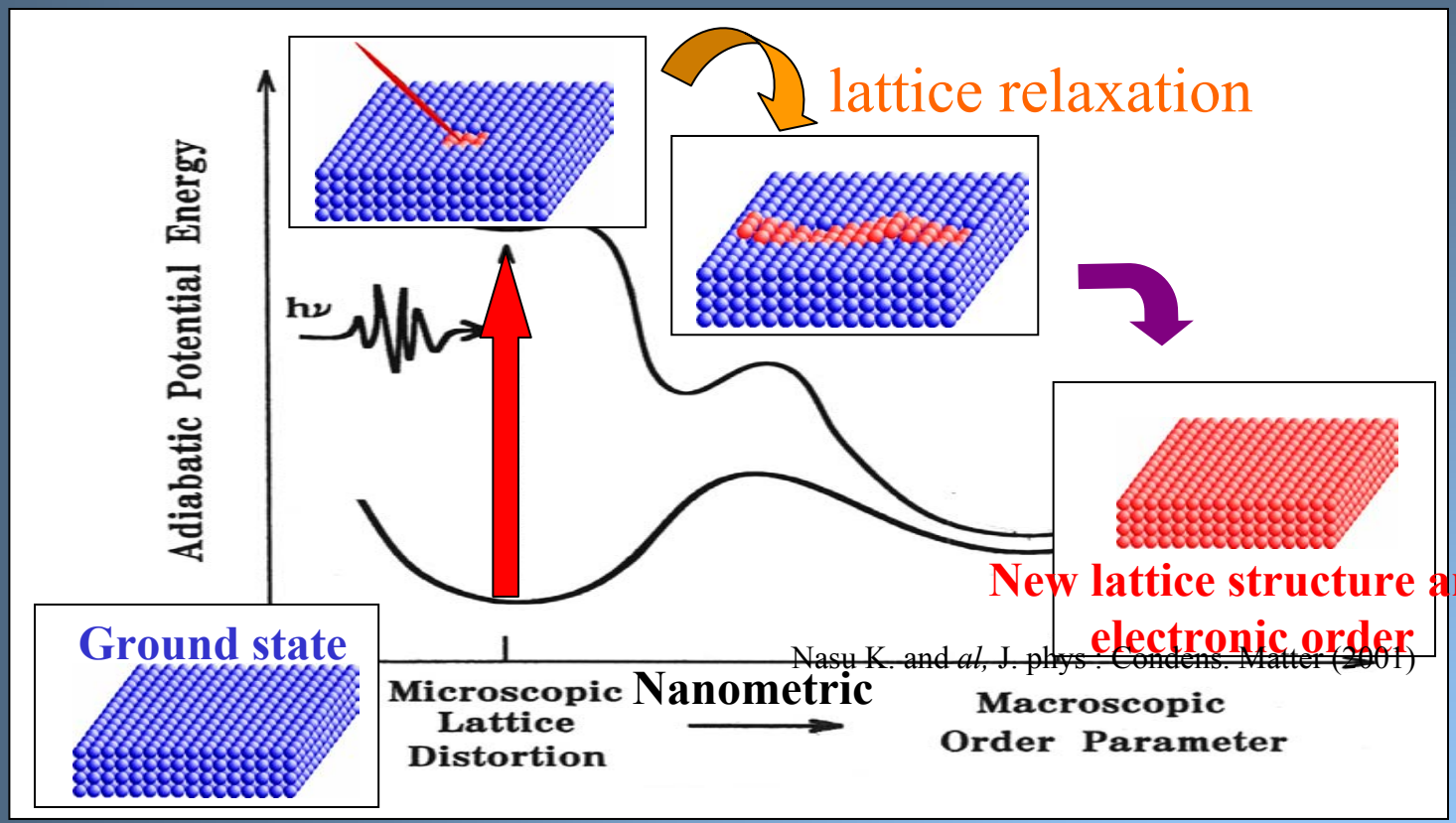
Photoinduced Phase Transition

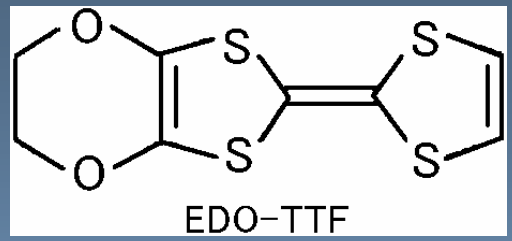
Out of equilibrium processes at different scales

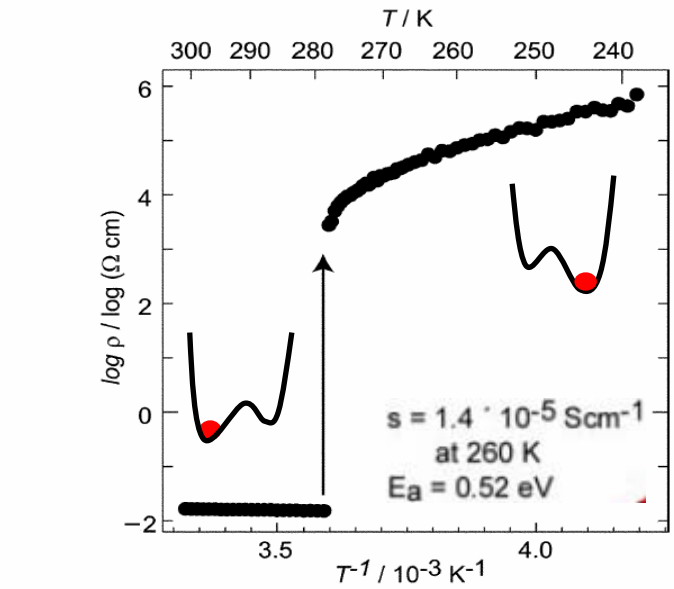


Nasu K. and *al*, J. phys : Condens. Matter (2001)

Metal – insulator transition in $(EDOTTF)_2PF_6$

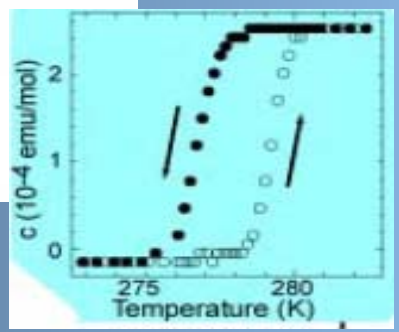
$(EDOTTF)_2PF_6$



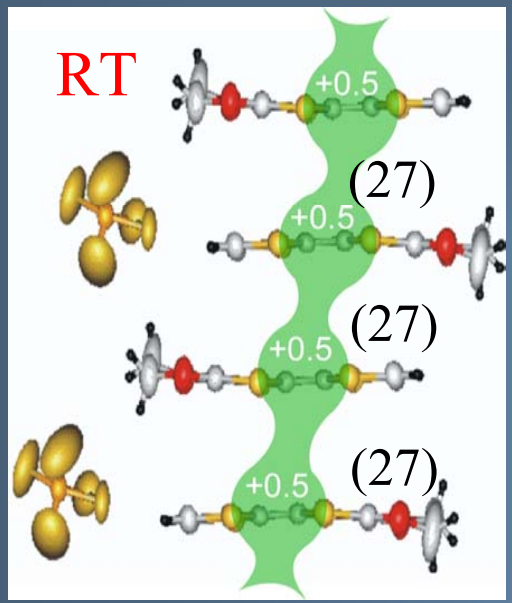


A. Ota, J. Mater. Chem. **12** (2002)

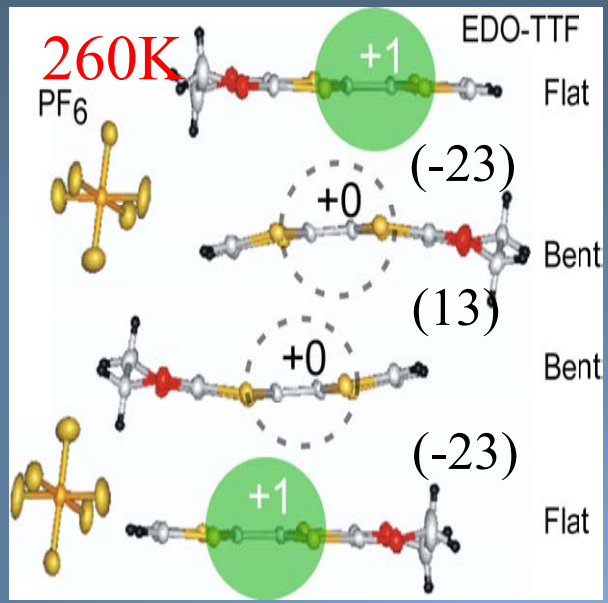
A noble Metal – Insulator Transition accompanied with multi-instability at 280K



A novel M-I transition



Metal



Insulator

Multi-instability:

Peierls transition
Charge ordering
Anion ordering

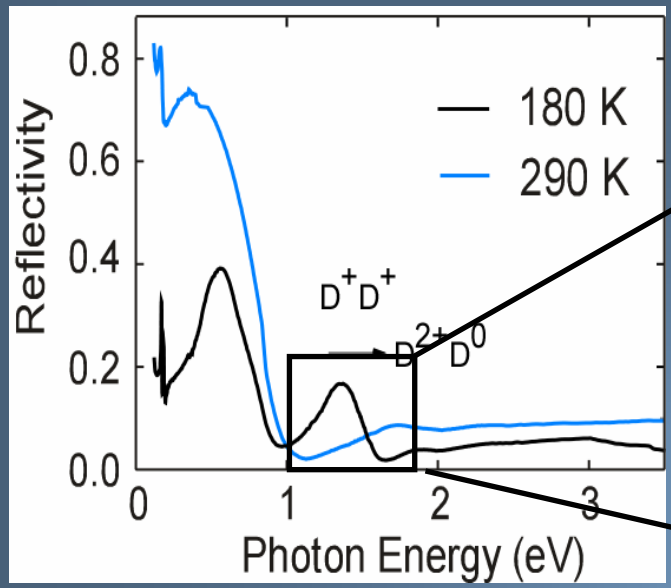
At 260K Molecular deformation

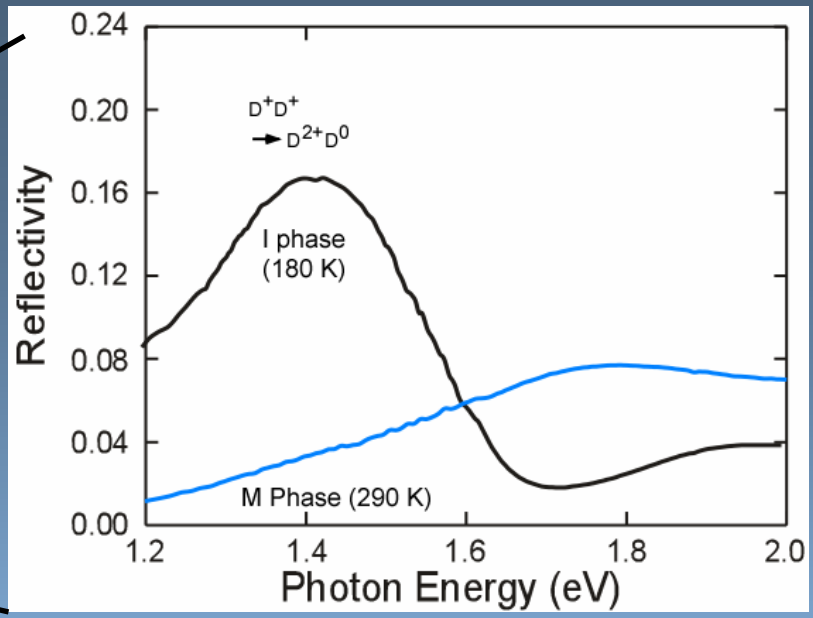
-F-F-B)-(B-F-F-B)-(B-

[0,+1,+1,0] (BFFB) type Charge Ordering

J. Mater. Chem., (2002) 12, 2600

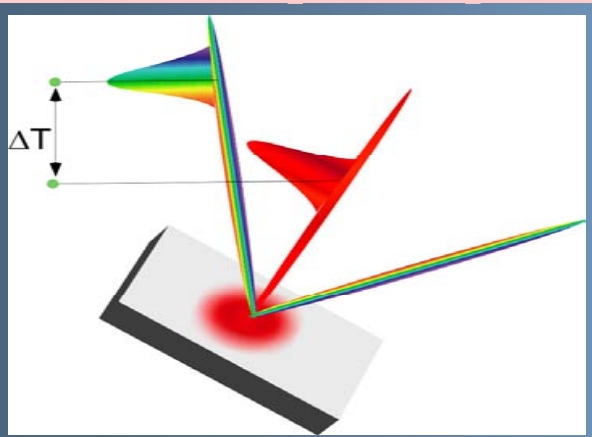
How can the transition be probed?



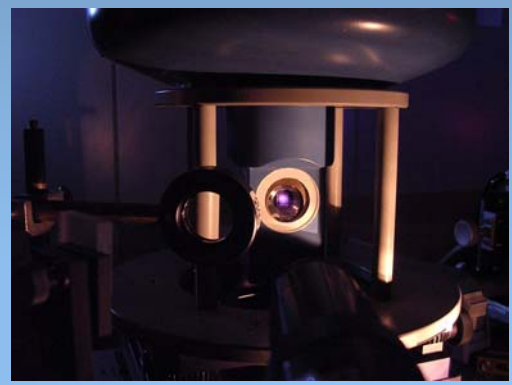


Large change in the 0.8 – 1.8 ev region (important for application)

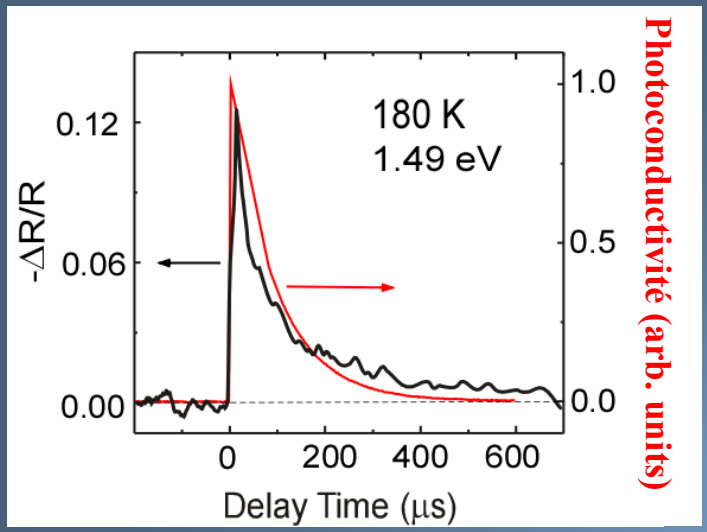
Time-resolved optical spectroscopy



Femtosecond laser 70 fs
- pump : 800 nm
- probe : continuum

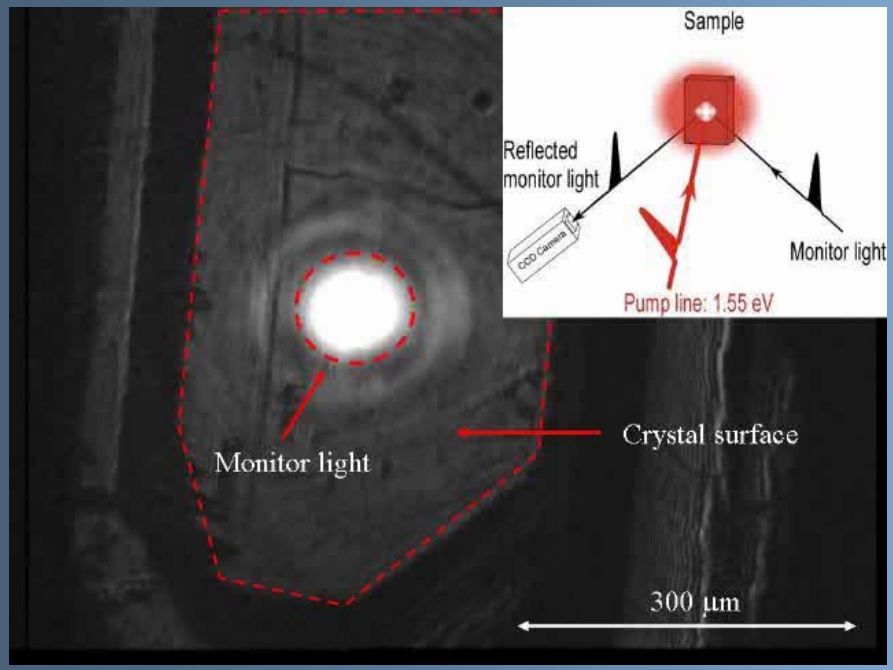


Access to different times of the transition with 100 fs resolution



Jump of the photoconductivity

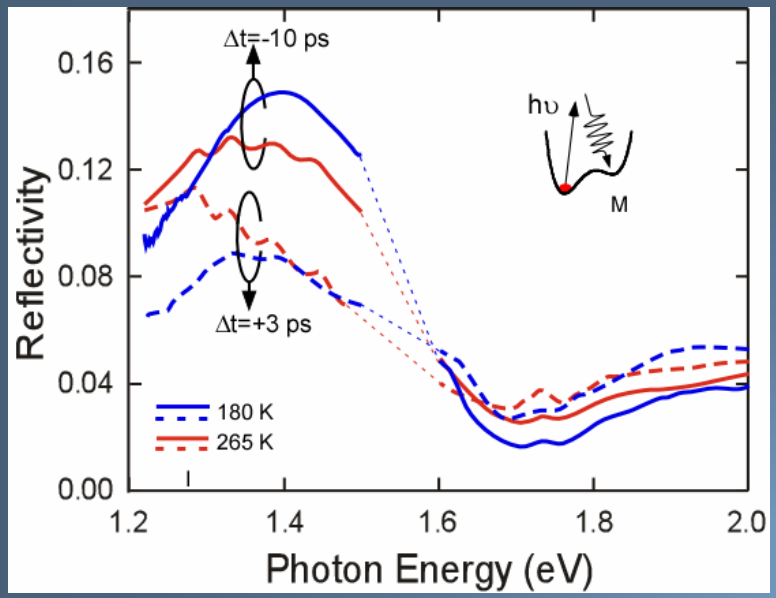
Insulator to metal transition associated with change of the reflectivity



Large change of the reflectivity easily probed using CCD camera

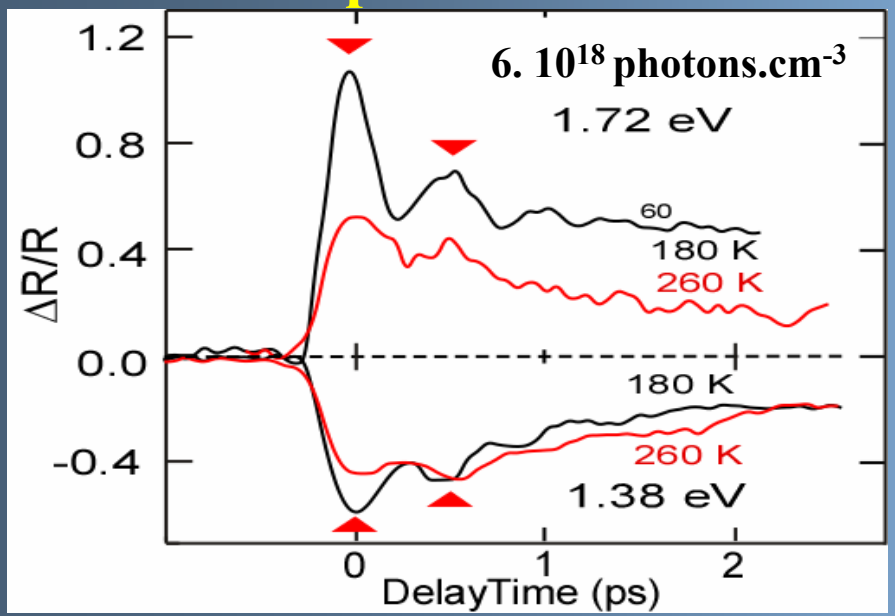
Chollet et al. Science **307**, 84 (2005)

Spectral changes



CO melting accompanied by I-M phase conversion occurs within 3ps

Fast time dependance in reflectivity change



Phase conversion process completed in 1.5 ps

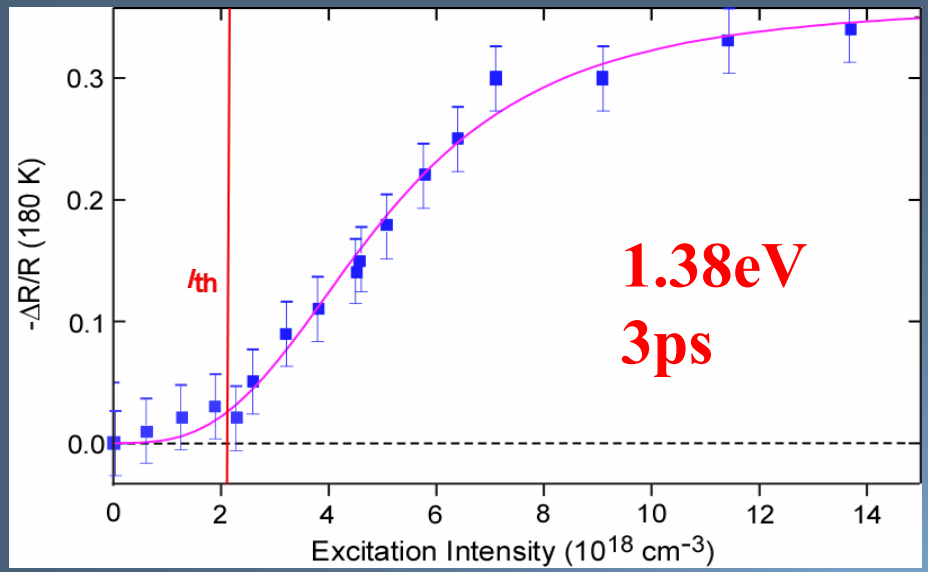
Highly efficient conversion :

50% change

1 photon/500molecules

Strong cooperativity

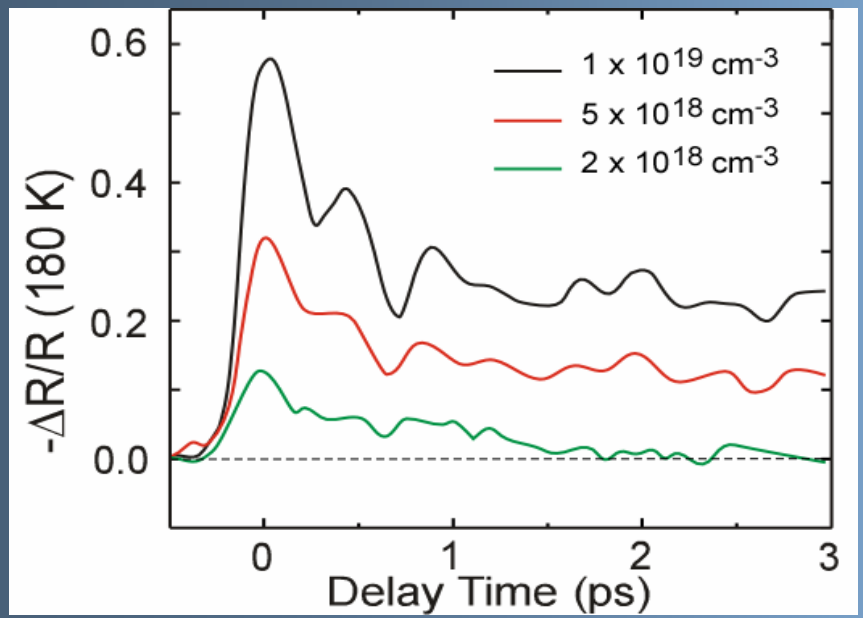
Excitation intensity dependance



Nonlinear response is observed

Threshold like behavior :
1photon/ 1500 molecules

Internal cooperative interactions

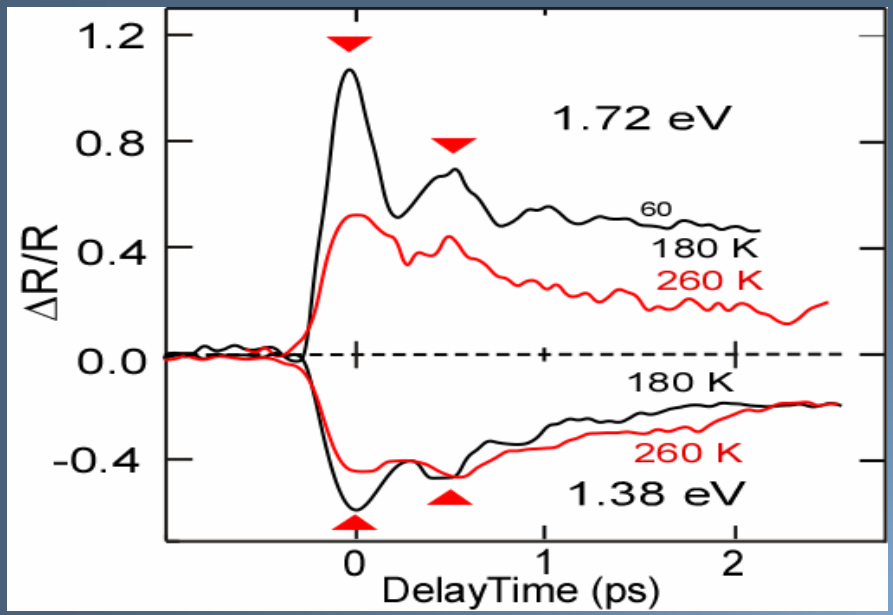


Life time depends on photoexcitation energy

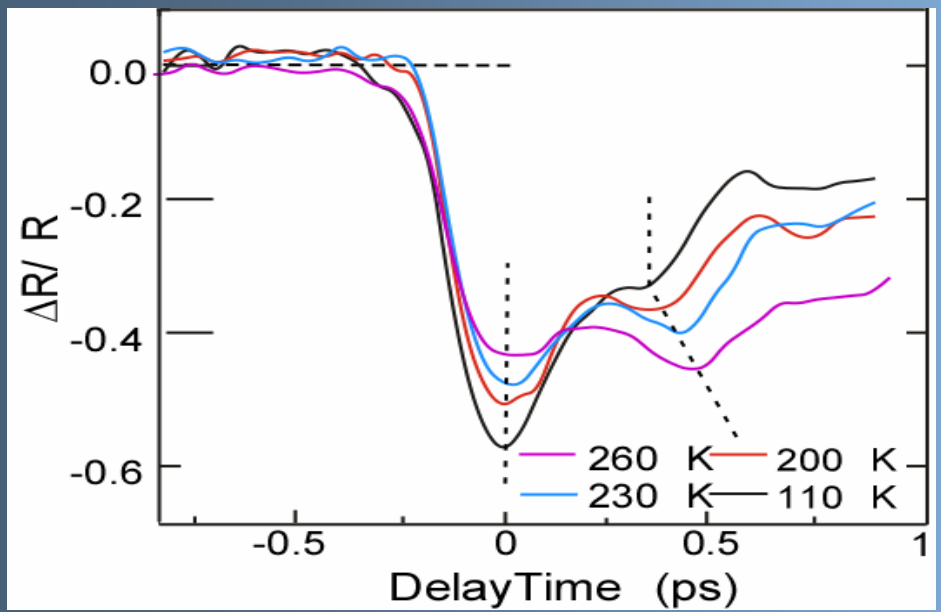
Cooperative interactions occurs in the relaxation process

Quick recovery time for application in phase- switching devices

Vibrational structure of the photo-induced I-M transition



Period of vibration :
independant of probe photon energy

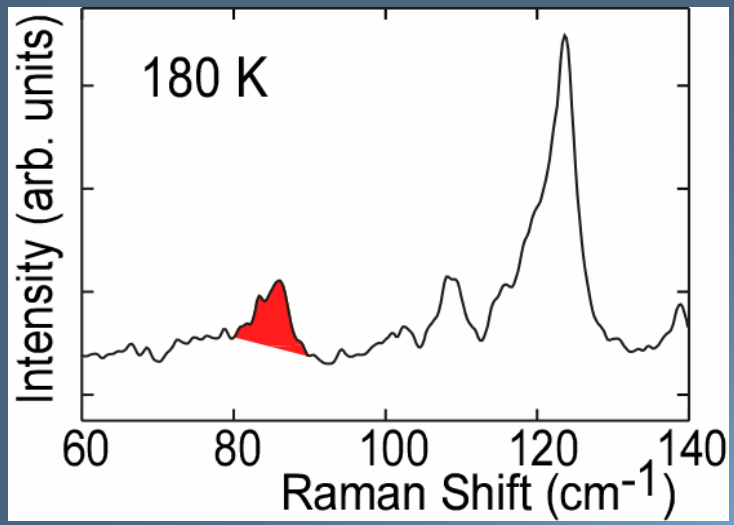


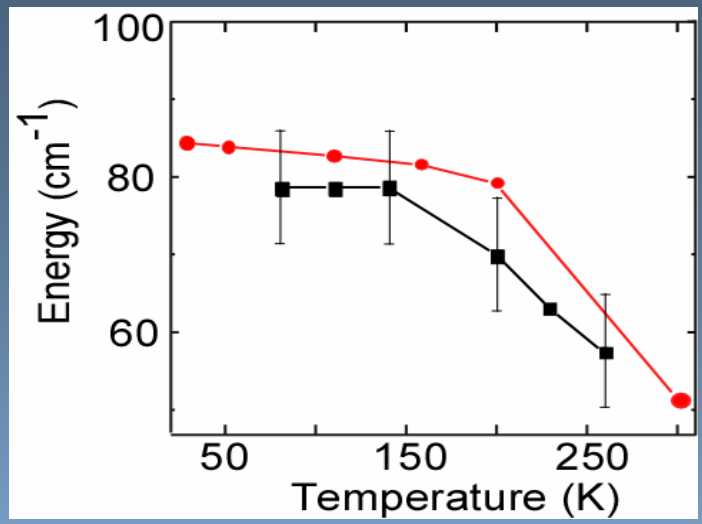
Temperature dependant

Softening of the phonon mode while Increasing temperature

Chollet et al. Science **307**, 84 (2005)

Mechanism of the photo-induced transition





Hasegawa, thesis (2004)

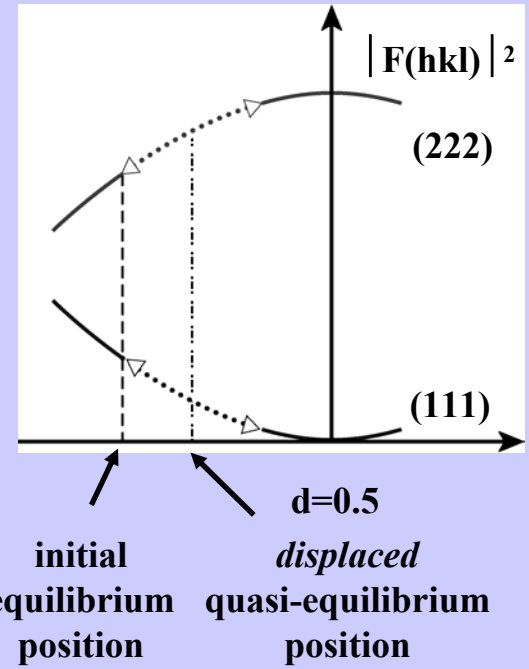
The optical phonon mode corresponds to the bending mode of EDOTTF molecules
Strong coupling between CO and molecular deformation

Incoherent vs coherent phonon process :

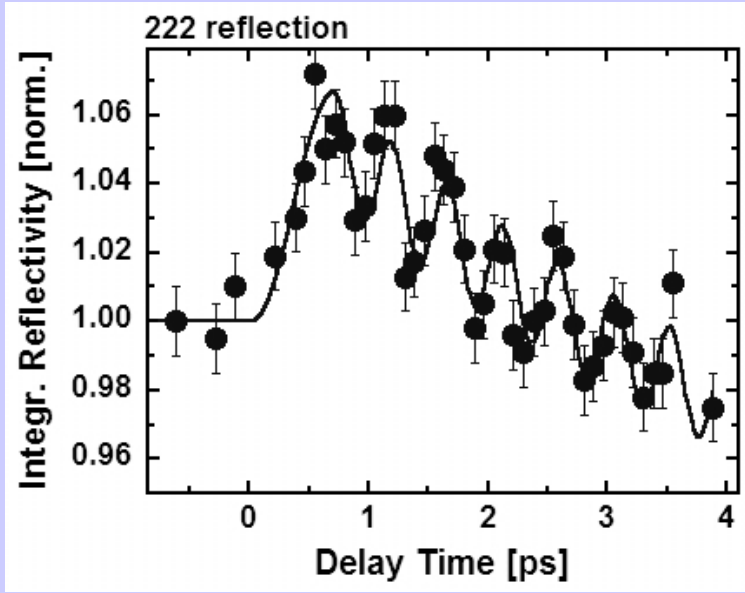
- Speed of domain growth limited by incoherent process
- Meso-size domain mediated by coherent phonon induced just after photo-excitation

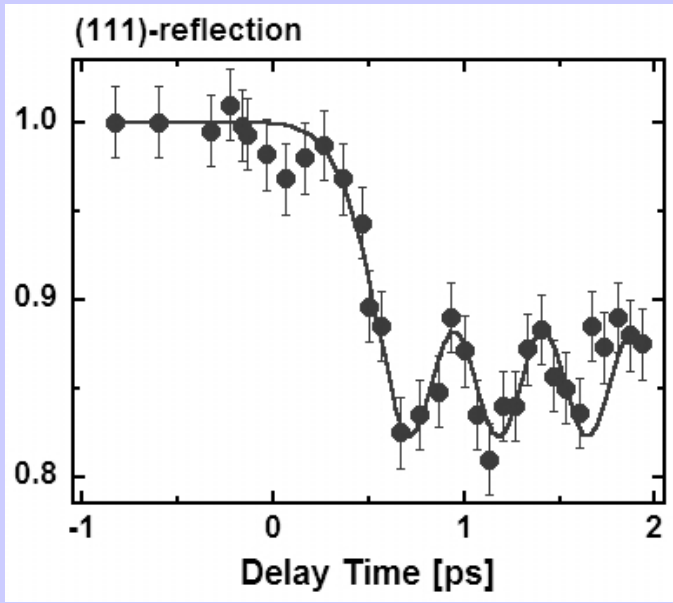
Coherent optical phonons observed in Bismuth

K. Sokolowski-Tinten et al., Nature **422**, 287 (2003)



d, distance between atoms 1 and 2





Weak rhombohedral distortion of the CFC unit-cell
Atom 1 at (0,0,0), atom 2 close to (0.5,0.5,0.5)

Summary

$(EDO\text{-}TTF)_2PF_6$ crystal shows highly sensitive (50% efficiency for weaker excitation intensity than 1photon/500 molecules) I (CO)-to-M like PIPT within 1 ps

Such highly sensitive and ultra-fast response may be characteristics of "molecular deformation (lattice) – charge – spin" coupling in ¼ filled system.

Nonlinear response to excitation intensity has been observed (importance of co-operativity)

E-L interaction via an optical coherent phonon mode plays an important role in the Photoinduced transition.

Femto-sec. X-ray crystallography is a key for solving mechanism.

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Ryoko Tazaki

MI transition probe by photo-excitation

1:Quite similar to thermally induced I-to-M transition

2:Highly efficient and fast conversion with 800nm excitation

$(EDO\text{-}TTF)_2PF_6$

(T_{MI} = 280 K)

Pump:1.55 eV, $E//b$

6.4×10^{14} Photons/cm^2

Probe:$E//b$

T = 180 K

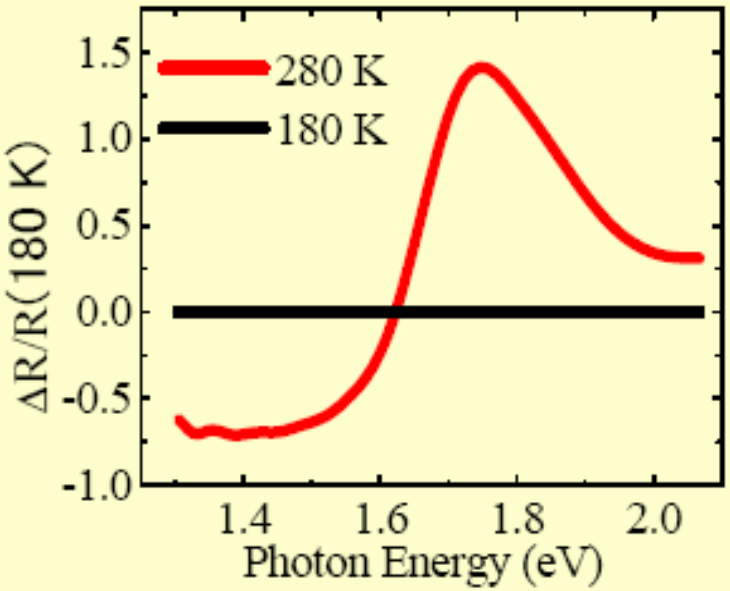
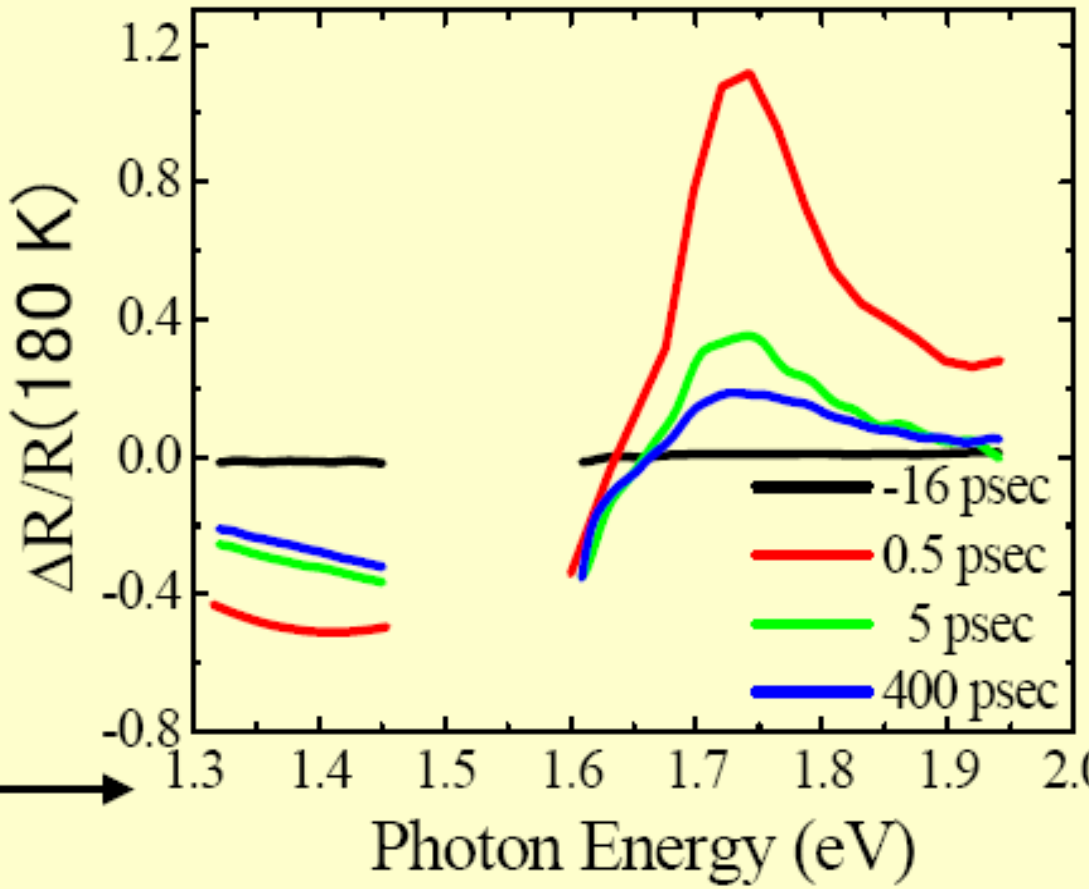
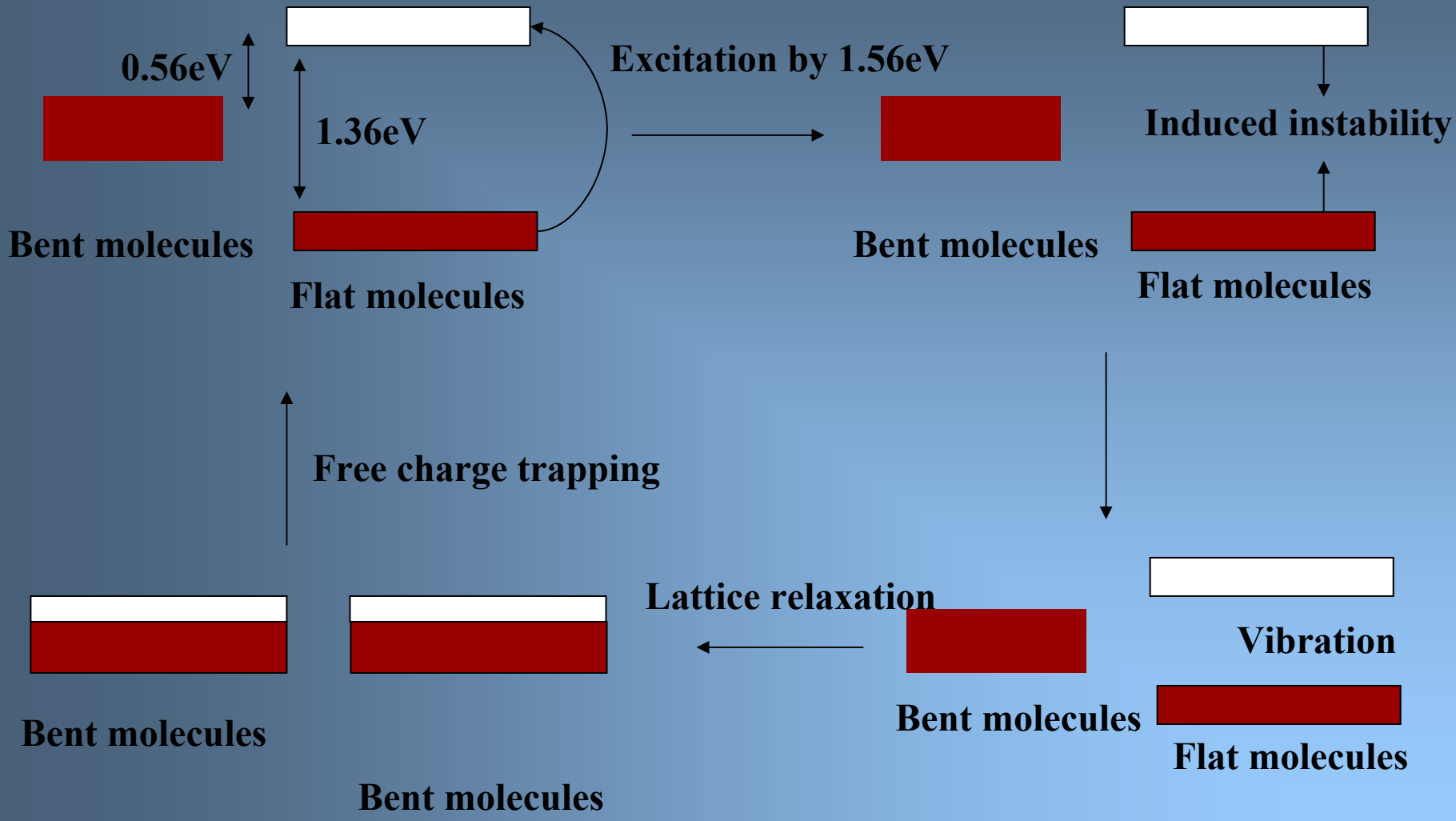


Photo-induced spectral change →



Cycle between I state and M photoinduced state



Hasegawa, thesis (2004)