Ultra-fast photoinduced gigantic metallization in quarter filled organic $\text{A}_2\text{B}$ salts: $(\text{EDO-TTF})_2\text{PF}_6$

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Photoinduced Phase Transition
Out of equilibrium processes at different scales

- Ground state
- Nanometric lattice relaxation
- New lattice structure and electronic order

Metal – insulator transition in \((\text{EDOTTF})_2\text{PF}_6\)

\((\text{EDOTTF})_2\text{PF}_6\)

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

A novel M-I transition

Multi-instability:

- Peierls transition
- Charge ordering
- Anion ordering

At 260K
Molecular deformation

\[ [0, +1, +1, 0] \text{ (BFFB) type Charge Ordering} \]

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 3 ps

Fast time dependance in reflectivity change

Phase conversion process completed in 1.5 ps

Highly efficient conversion:
- 50% change
- 1 photon/500 molecules
- Strong cooperativity

6. $10^{18}$ photons.cm$^{-3}$

1.72 eV

1.38 eV
Excitation intensity dependence

Nonlinear response is observed

Threshold like behavior: 1 photon/1500 molecules

Internal cooperative interactions

1.38 eV
3 ps

Life time depends on photoexcitation energy

Cooperative interactions occur 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

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

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-TTF)$_2$PF$_6$ crystal shows highly sensitive (50% efficiency for weaker excitation intensity than 1 photon/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 $\frac{1}{4}$ 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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Funds: Collège Doctoral Franco-Japonais
1: Quite similar to thermally induced I-to-M transition

2: Highly efficient and fast conversion with 800nm excitation

\[(\text{EDO-TTF})_2\text{PF}_6\]
\[T_{MI} = 280 \text{ K}\]
Pump: 1.55 eV, $E//b$

\[6.4 \times 10^{14}\]
Photons/cm$^2$

Probe: $E//b$

$T = 180 \text{ K}$
Cycle between I state and M photoinduced state

1. Bent molecules
   - Excitation by 1.56eV
   - Induced instability
   - Free charge trapping
   - Lattice relaxation
   - Vibration

2. Flat molecules
   - 0.56eV
   - 1.36eV