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

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100 fs Pump laser

100 ps and even 100 fs Probe RX
ULTRA-FAST WORLD

- Coherence and co-operativity
- Non-thermal effects and propagation

WHAT HAPPENS IN A PICOSECOND?

- Light Travels 0.3 mm
- A molecule vibrates 1-10 times
- An atomic bond breaks
- A semiconductor surface melts
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)

High density electronic excitation triggering structural instability:

- insulating $\rightarrow$ metal
- insulating $\leftrightarrow$ insulating

Solid state molecular switching
PHOTOINDUCED PHASE TRANSITION IN TTF-CA

IONIC low T phase

NEUTRAL high T phase

81 K

1 ps

500 ps


Iwai et al, PRL 88 057402 (2002)

Highly cooperative: few 100 molecules / photon

very fast: few 100 ps

Highly non-linear: threshold behavior and $h\nu_{pump}$ dependence
TIME-RESOLVED CRYSTALLOGRAPHY

X-ray sources:
- synchrotron
  -> 50-150 ps
- Laser systems
  -> 100 fs
- Future sources
  -> 100 fs

Transformation coordinate

Pump probe metastable
→ 0 s → 1 ns → 1 µs

stroboscopic techniques
‘Watching matter rearrange’
Molecular movies
Time structure of the synchrotron radiation:

- pulse width: 100 ps
- repetition rate: 1 kHz (896.6 Hz)
- select 1 pulse over 6400!

Synchronisation chopper/Laser

- Laser pump: 300 fs
- Crystal
- δt
- X-ray Pulse 100 ps

PICOSECOND CRYSTALLOGRAPHIC MEASUREMENTS
ID09B ESRF

53 days/Year
16-bunch mode
90 mA 10 h
STRUCTURAL STUDY OF THE PHOTO-INDUCED N-I TRANSITION: TTF-CA

1st monochromatic experiment

1st monochromatic experiment

ID9 ESRF

X-ray Pulses 100 ps

Structural reorganization: 3D domains

Neutral state (high temperature)  Ionic state (photo-induced)

TTF-CA

\( \lambda = 0.7534 \text{ Å} \)

Normalized Integrated intensity

Neutral ionic

\( 0.0 \quad 0.2 \quad 0.4 \quad 0.6 \quad 0.8 \quad 1.0 \quad 1.2 \quad 1.4 \quad 1.6 \)

\( -1000 \quad 0 \quad 1000 \quad 2000 \quad 3000 \)

\( t \) (ps)

\((-2 \ 3 \ 1)\)

\((1 \ -2 \ -2)\)

\((1 \ 1 \ 0)\)

\((-1 \ 3 \ 1)\)

\((1 \ -3 \ -3)\)

\((-2 \ -3 \ -4)\)

\(-2 \ 2 \ 1)\)

T\(_{N-I} + 11 K\)

Pulse laser 300 fs

\( \lambda = 800 \text{ nm} \)

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

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


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 1mmϕ

175mW @ 946 Hz In 1mmϕ
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 Stanford
  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

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

3D ordering of ionic dimers

100 fs - 1 ps

100 ps