The Role of the Time-Resolved Crystallography Based on SOR-Laser Combined Technology in Nano-Scale Materials Science

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&

ERATO, JST

Contents

1: Characteristics of Photo-Induced Phase Transition

Cooperative interaction between ‘materials’ and ‘light’

2: Examples

2-1:Photo-induced Ferro-electricity in Neutral-Ionic Transition System

2-2:Ultra-fast (THz), highly sensitive and non-equilibrium melting of Charge Order in Organic Super Conductor Candidate (EDO) (Metal-Insulator Transition)

3：Summary

Importance of X-ray for materials research from view point of new axis ‘Cooperative Light Excitation’.

Collaborators

Dr. Eric Collet, Dr. Marie-Hélène Lemée-Cailleau, Dr. Marylise Buron-Le Cointe, Professor Hervé Cailleau, Profrssor Simone Techert, Dr. Michael Wulff, Professor Tadeusz Luty

Professor G.Saito, Professor H.Yamochi, Mr.A.Ota (Kyoto Univ.) and Dr. G.Shao

Mr.T.Hasegawa (Tokyo Inst. Tech.)

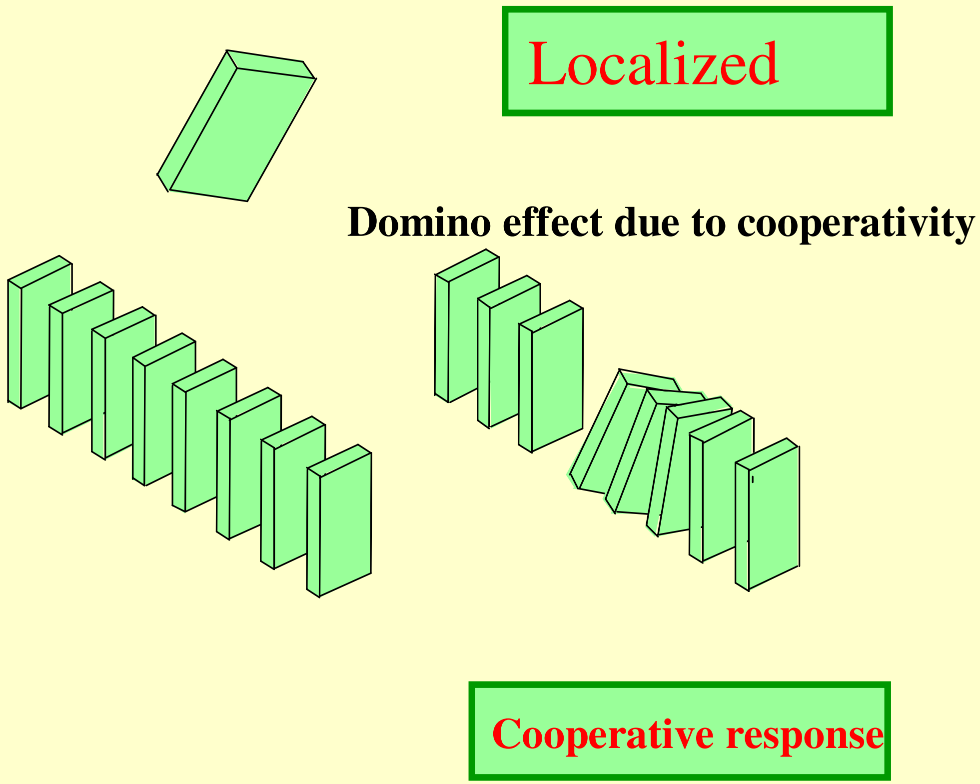
Professor S.Adachi, Professor H.Sawa, Miss R.Tazaki, Dr. J.Takahashi, Dr. S.Nozawa and Dr. M.Daimon (KEK & ERATO)

My group

Dr. T.Ishikawa, Mr.M.Kurita, Mr.N.Uchida, Mr. S.Fukaya, Mr. H.Shimoda, Mr. Y.Sakano, Mr. M.Chollet and Mr.L.Guerin

What is photo-domino ?

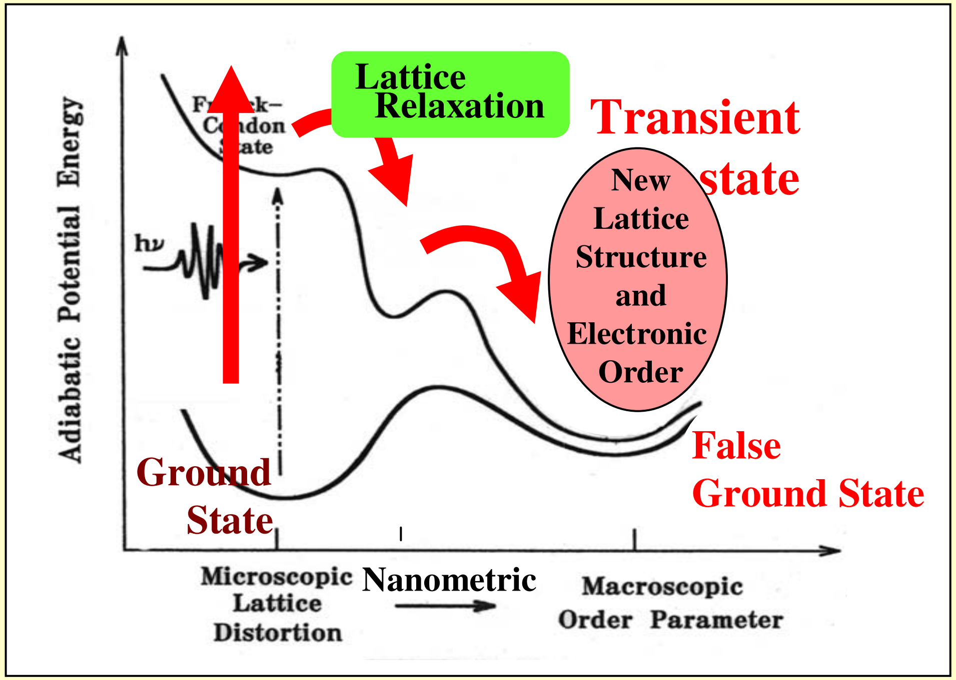
- **Cooperative response due to cooperative interaction**
- **Control of electron-lattice-spin (multi-)coupling by internal correlation effect**
- **Pulse width of 1ps corresponds to the energy of 33 cm^{-1} for elementary excitations**
- **Various Application**



Photoinduced solid state phase transition

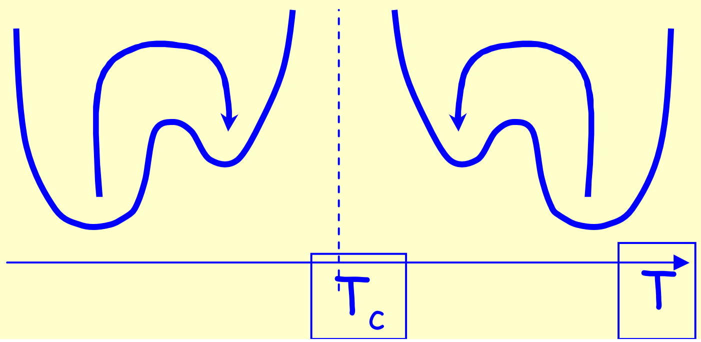
Out of equilibrium and multi-scale process in solids :

Nonequilibrium behavior in relaxation process of photo-excited species ; Energy relaxation via specialized mode and its selection (coherent relaxation)



Relation even with Coherence

Solid state molecular switching

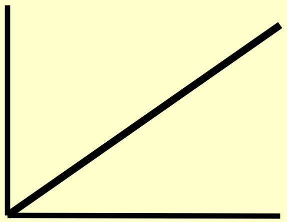


Characteristics of Photo-Domino

(1) Threshold

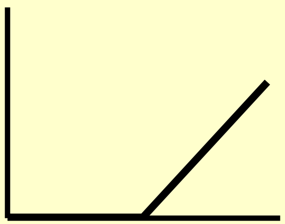
Ordinary Photo-induced

Effect



Excitation Intensity

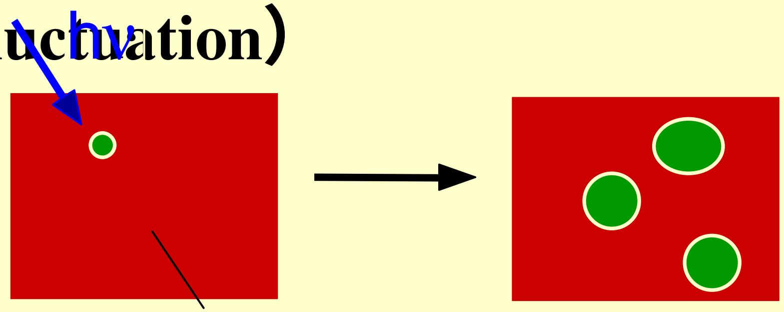
Photo-induced Phase Transition (PIPT)



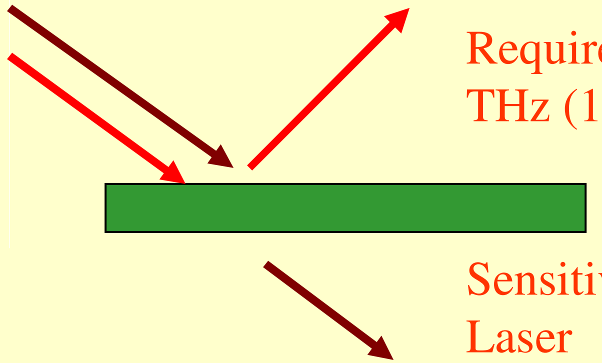
Excitation Intensity

(2) Dynamical phase separation, Phase switching dynamics

(Relation with internal fluctuation)



(3) Photonic Switching Effect



Required Switching Speed : THz (10^{-12}sec.)

Sensitive response for diode Laser

2:Examples of Materials Design for Strongly Electron-Lattice Coupled System

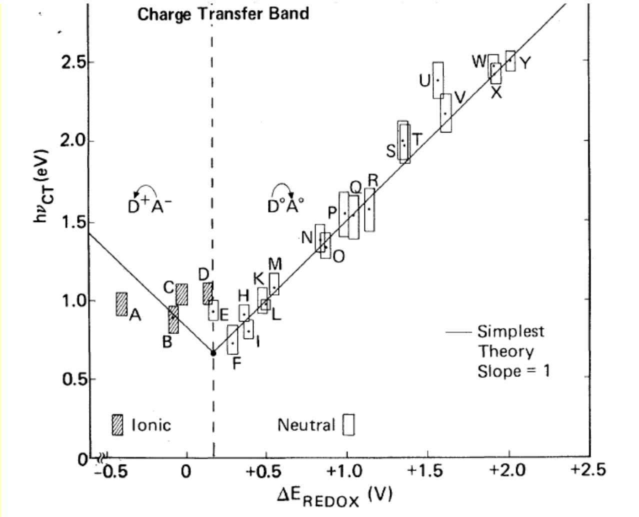
"Why molecules make solid ? "

Three Classifications 1: Molecular Solid 2:Covalent Bond 3:Ionic

"To be or not to be, that is the question for molecules"

Discovery of a Neutral-to-Ionic Phase Transition in Organic Materials

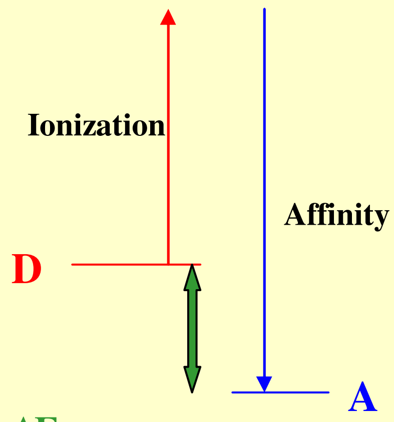
J. B. Torrance,[a] J. E. Vazquez, J. J. Mayerle, and V. Y. Lee
IBM Research Laboratory, San Jose, California 95193
(Received 25 August 1980)



Symbol	Compound	*N/I*
A	TMPD-tetrafluoroTCNQ	*I*
B	dimethylphenazine-TCNQ	*I*
C	TMPD-TCNQ	*I*
D	TMPD-chloranil	*I*
E	TMDAP-TCNQ	*N*
F	TTF-chloranil	*N*
G	TTF-fluoranil	*N*
H	DibenzeneTTF-TCNQ	*N*
I	DEDMTSeF-diethylTCNQ	*N*
J	TMDAP-fluoranil	*N*
K	TTF-dichlorobenzoquinone	*N*
L	perylene-tetrafluoroTCNQ	*N*
M	perylene-DDQ	*N*
N	perylene-TCNE	*N*
O	perylene-TCNQ	*N*
P	TTF-dinitrobenzene	*N*
Q	perylene-chloranil	*N*
R	pyrene-TCNE	*N*
S	pyrene-chloranil	*N*
T	anthracene-chloranil	*N*
U	hexamethylbenezene-chloranil	*N*
V	naphthalene-TCNE	*N*
X	anthracene-PMDA	*N*
Y	anthracene-tetracyanobenzene	*N*
Z	phenanthrene-PMDA	*N*

PRL 46 (1981) 253

Phase transition between 1 and 3



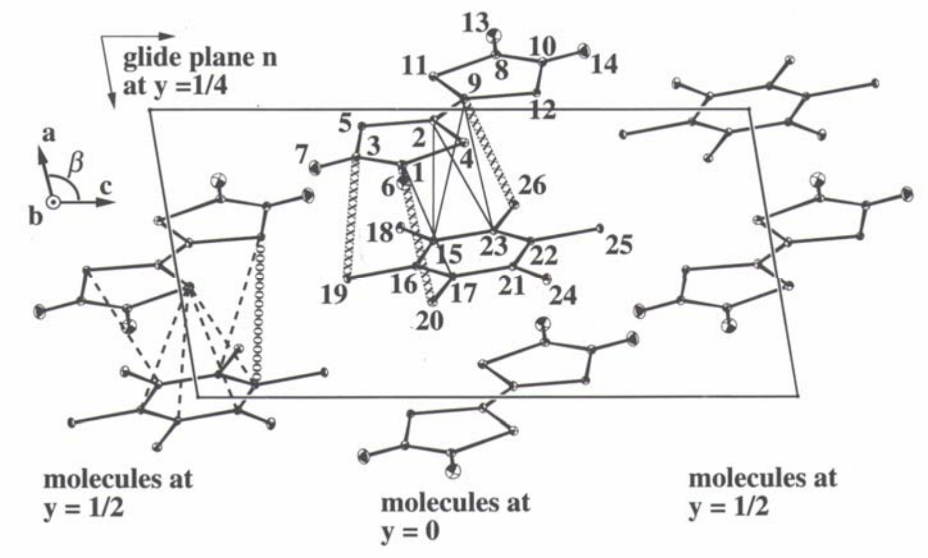
ΔE_{redox}

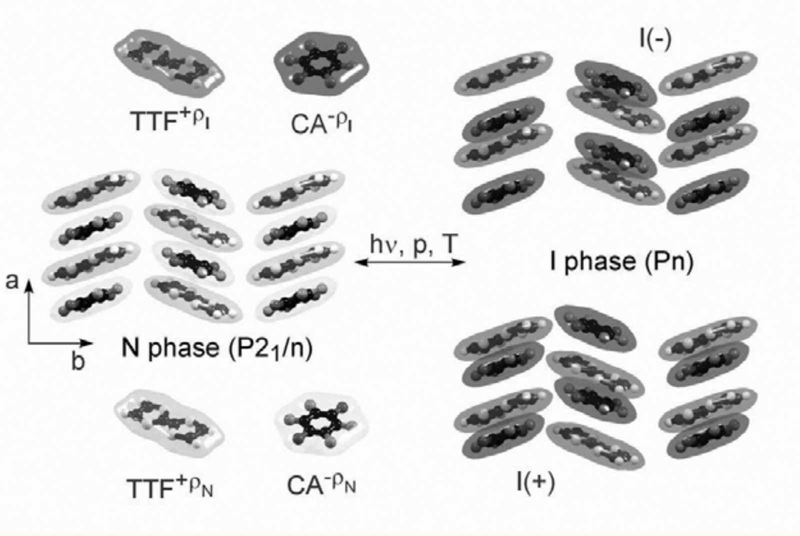
and Balance due to cooperative interaction

N-I Transition in TTF-CA(Photo-ferroelectricity)

- Mixed stack of Donor (TTF) and Acceptor (CA)
- At high temperature (>82K) Neutral

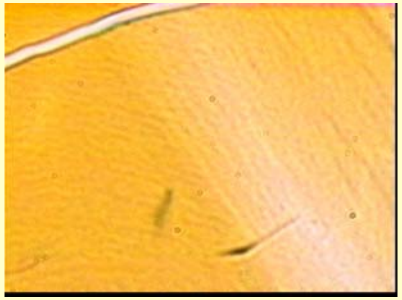
At low temperature Ionic

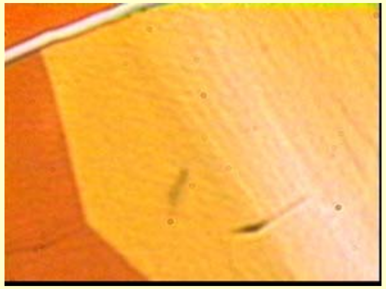




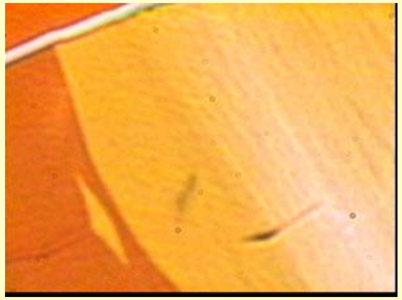
… D° A° D° A° (D⁺A⁻) (D⁺A⁻) (D⁺A⁻) D° A° D° A° …

Movie of cooperative CT





Photonic switching between N and I phase is possible ?



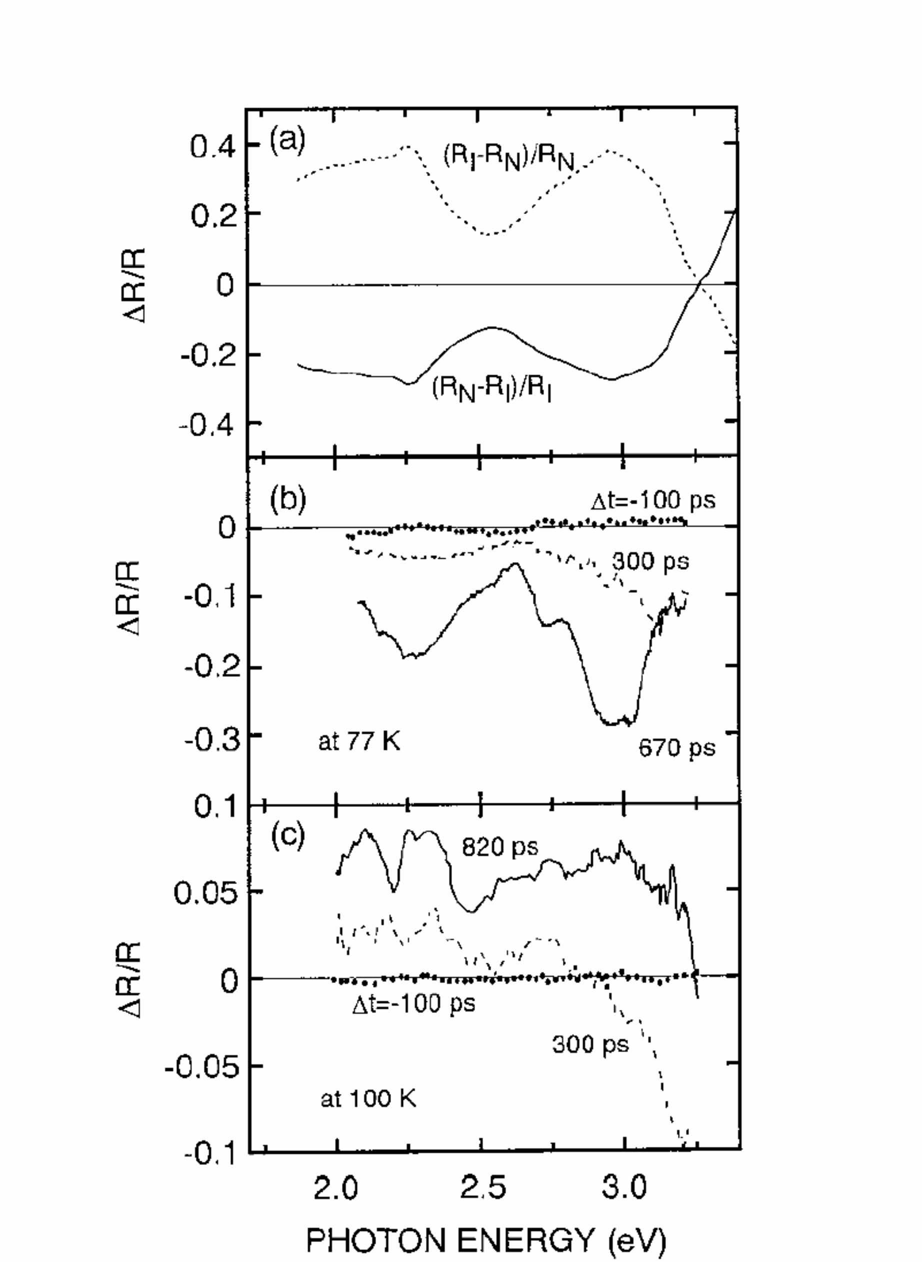
$D^0A^0D^0A^0D^0A^0D^0$

$D^0A^0D^0A^0D^0A^0D^0$

$D^+A^-D^+A^-D^+A^-D^+$

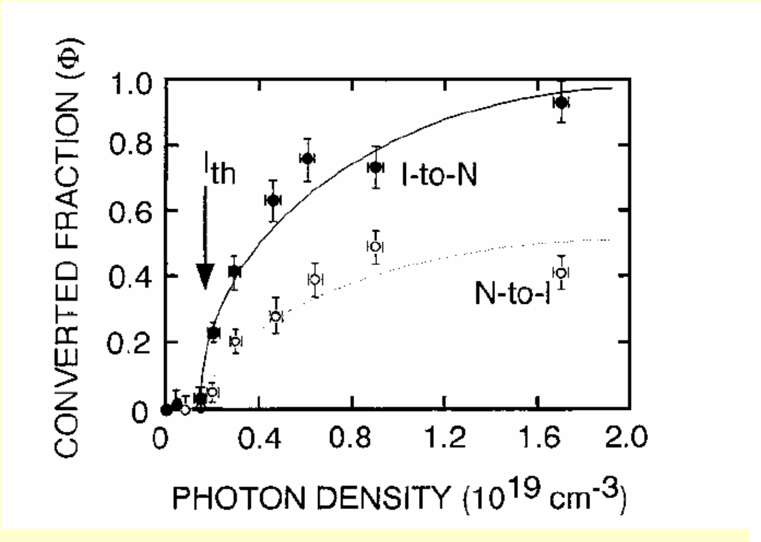
$D^+A^-D^+A^-D^+A^-D^+$

YES!



Cooperative CT induced by fs laser pulse

Nonlinear response
(Threshold)



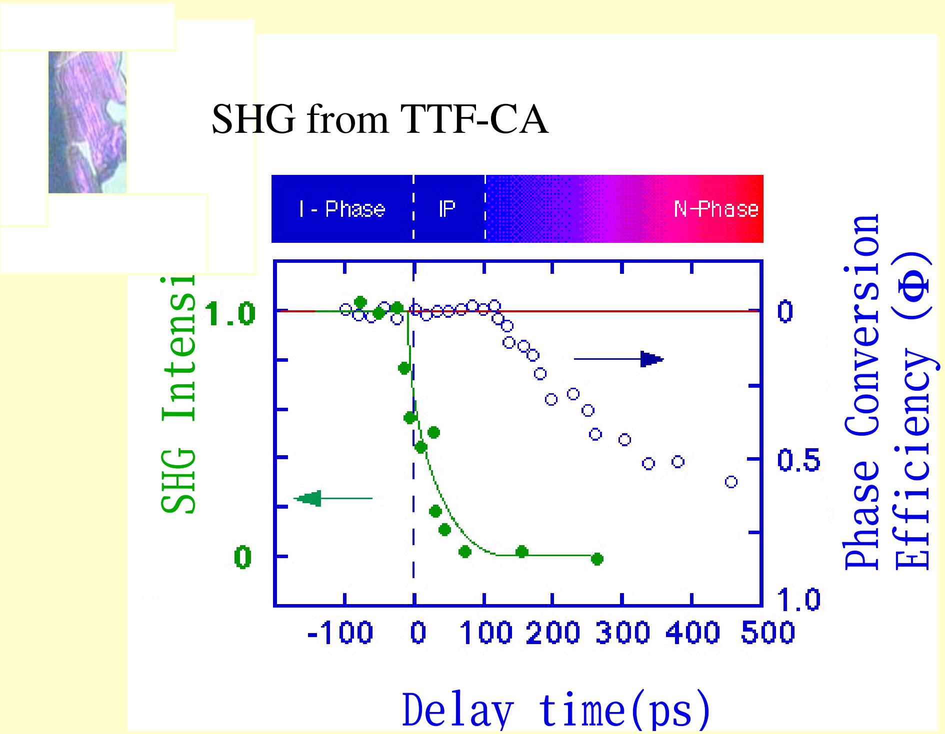
Structure has changed ?

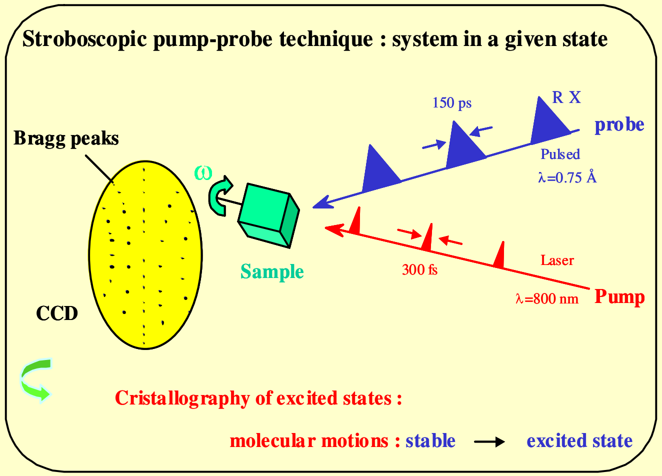
（key factor for nonlinear optics）

J.Phys.Chem. FEATURE ARTICLE 103,(1999) 2592

Key Technology is Molecular Movie

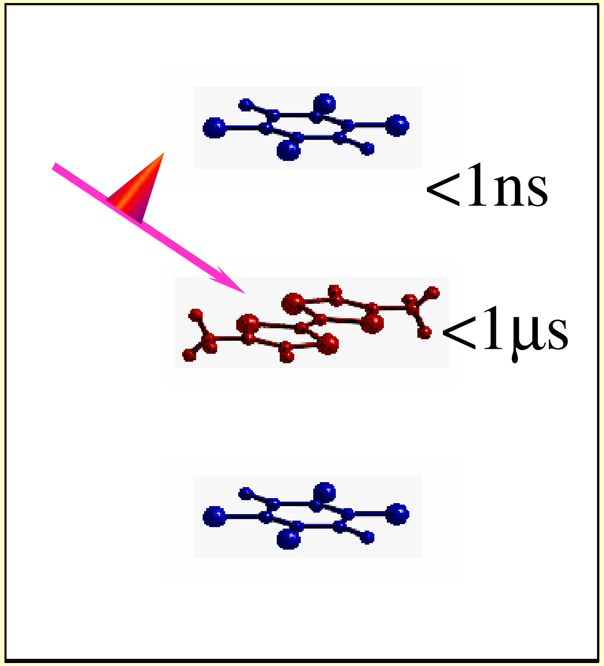
- **Structural cange occurs accompanied with CT ?**
- **Long range order may be generated under non-equilibrium condition ?**
- **Optical control of nonlinear optical property (SHG) is possible ?**

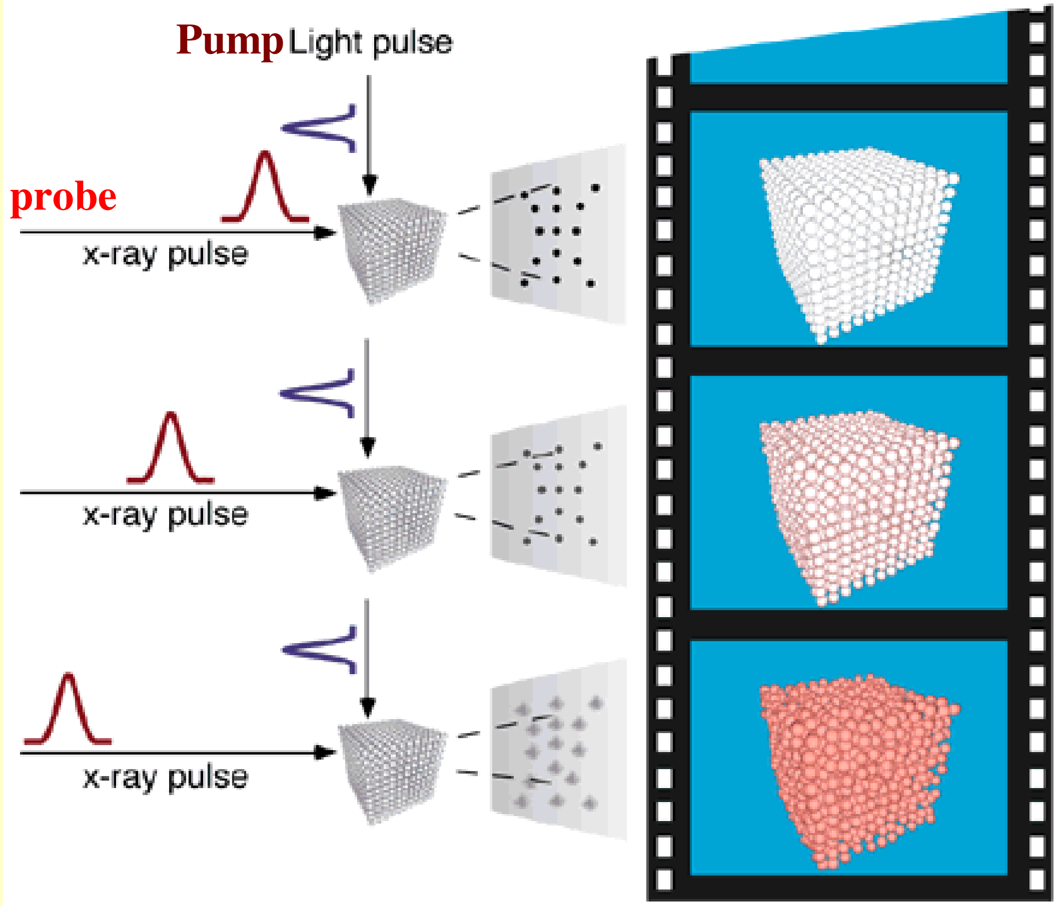




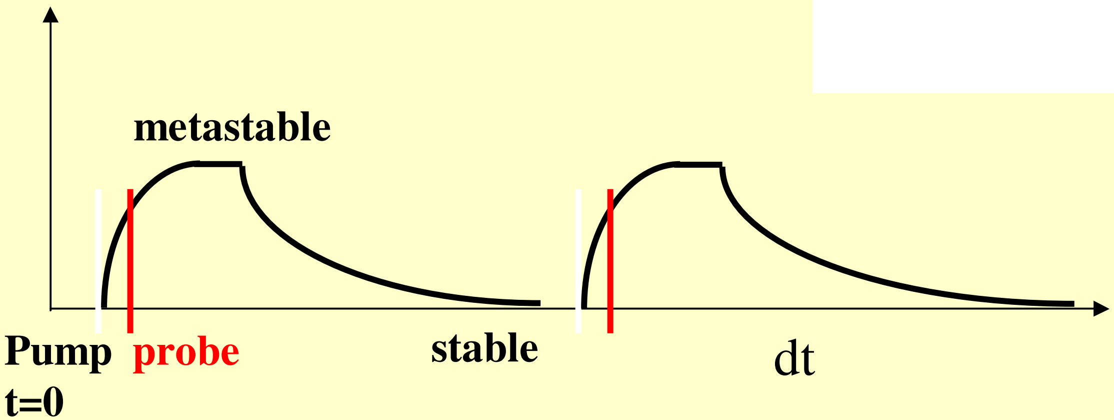
—Cartoon from *Life*, February, 1896. The New Roentgen Photography.
"Look Pleasant, Please."

TIME-RESOLVED CRYSTALLOGRAPHY





Transformation coordinate



stroboscopic techniques

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

Molecular movies

Delay-time modulation spectroscopy using a cw mode-locked Nd:YAG laser synchronized with the synchrotron radiation pulses (invited)

Tadaoki Mitani, Hiroshi Okamoto, Yoshihiro Takagi, Makoto Watanabe, and Kazutoshi Fukui

Institute for Molecular Science, Okazaki 444, Japan

Shinya Koshihara

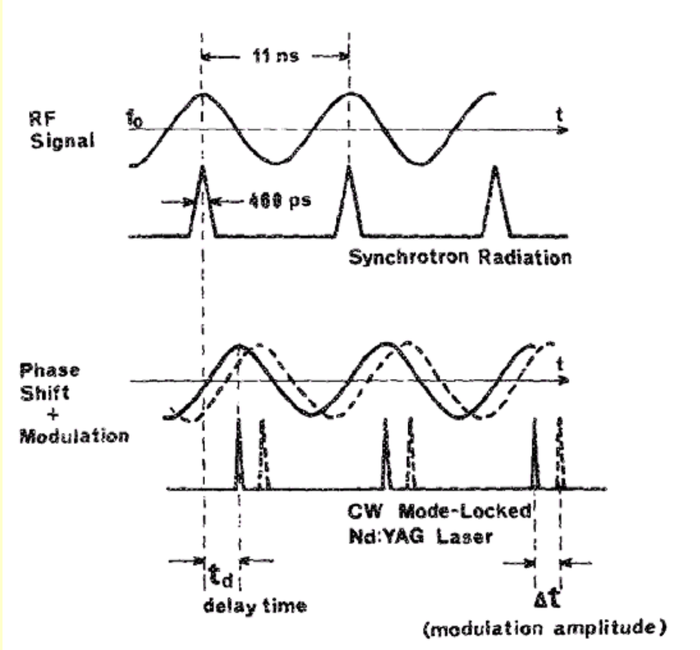
Faculty of Science, University of Tokyo, Tokyo 113, Japan

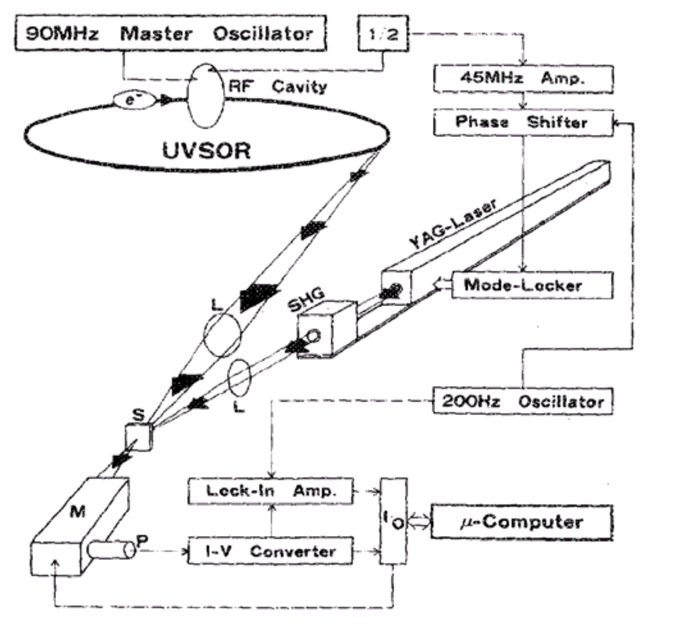
Chihiro Ito

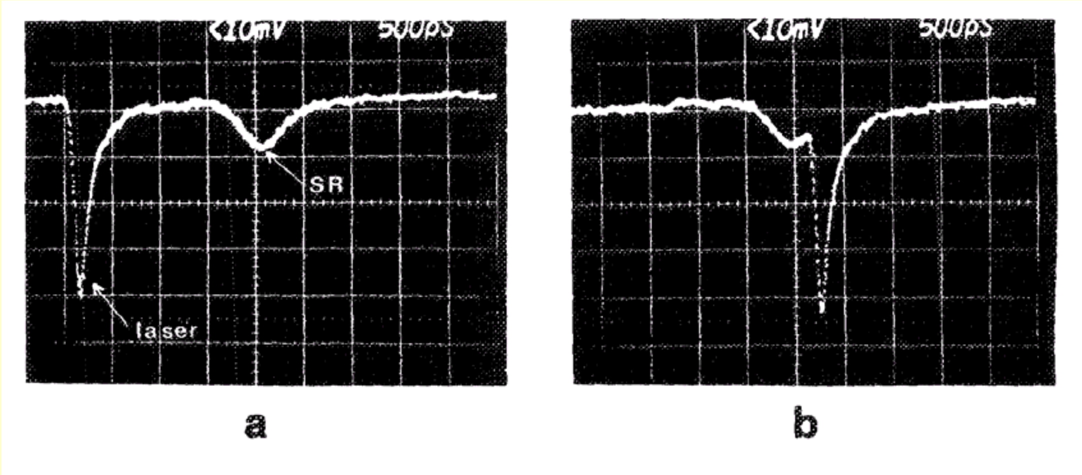
Faculty of Science, Nagoya University, Nagoya 464, Japan

(Presented on 1 September 1988)

Rev. Sci. Instrum., Vol. 60, No. 7, July 1989

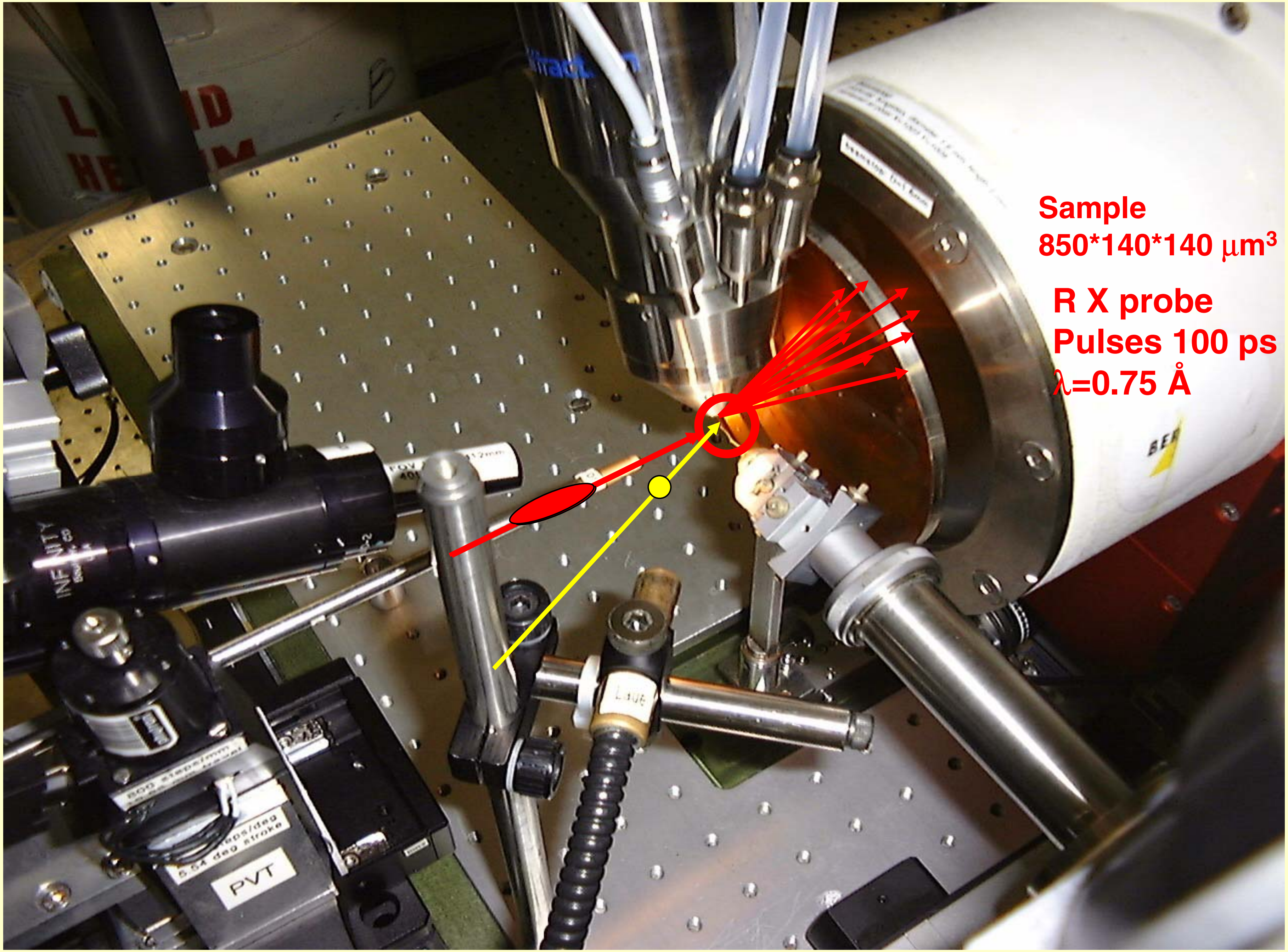




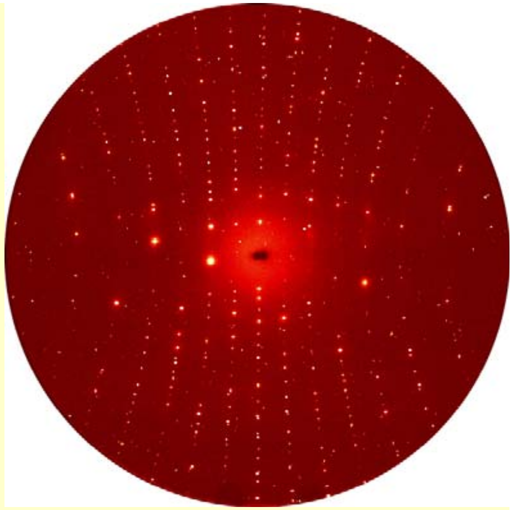


Technique for synchronization between SOR and mode-locked laser in 'IMS' has been established in 1987.

Experimental set-up : ID09B beamline at the ESRF



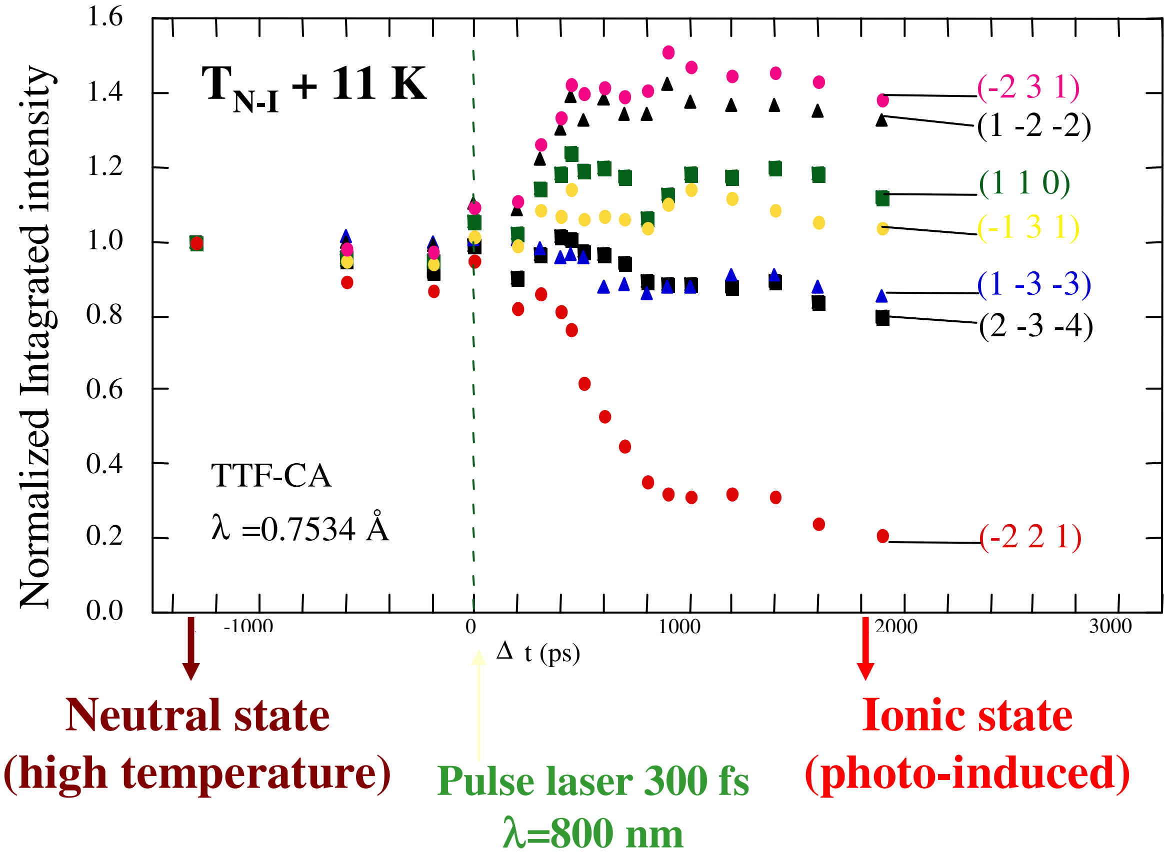
STRUCTURAL STUDY OF THE PHOTO-INDUCED N-I TRANSITION: TTF-CA



X-ray Pulses 100 ps

Monochromatic experiment

ID9 ESRF

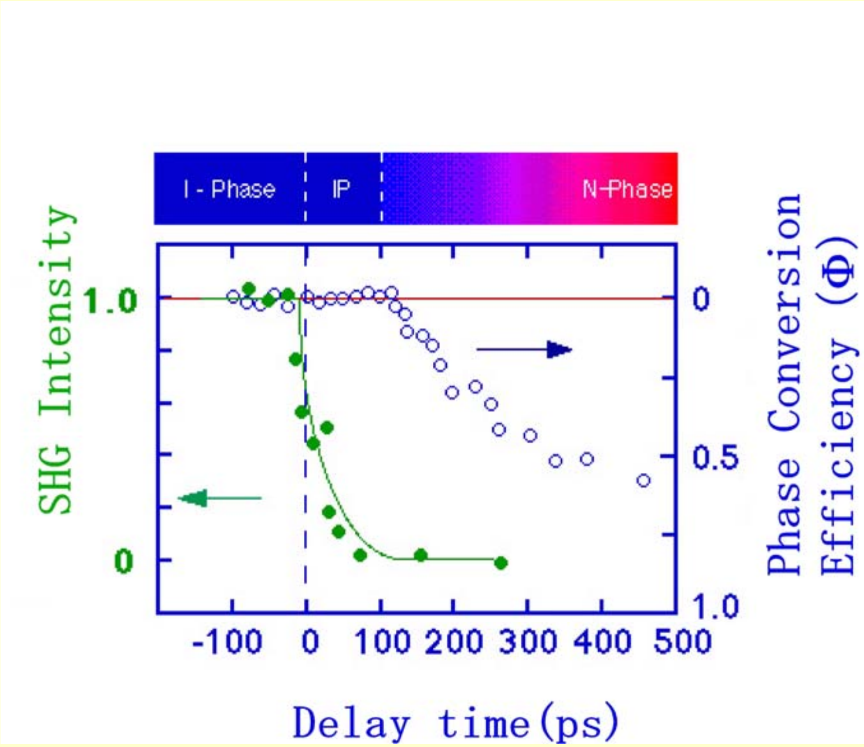


Structural reorganization
3D domains

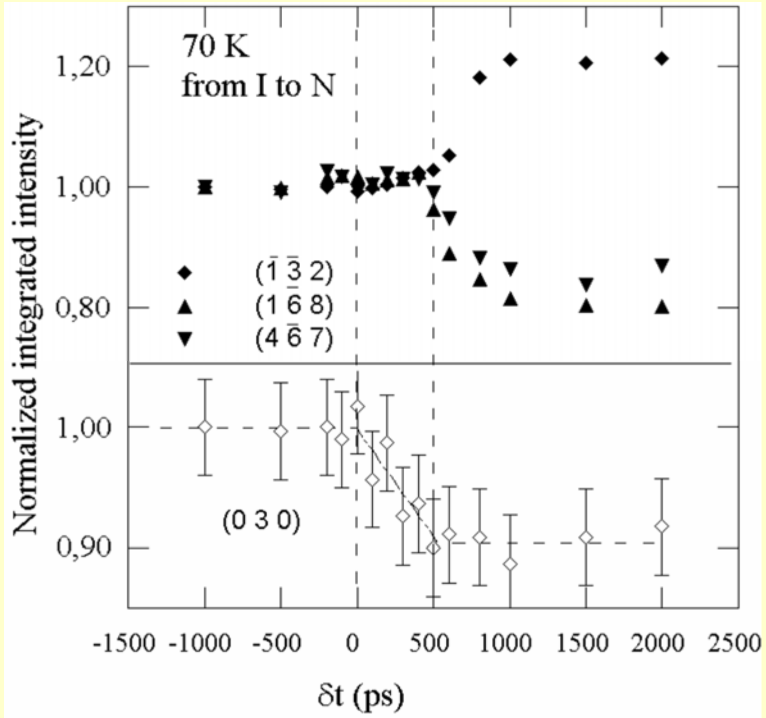
Large part transformed

time-scale similar to previous reesults

Transition in I to N direction



Europhysics Lett., 59 (2002) 619.

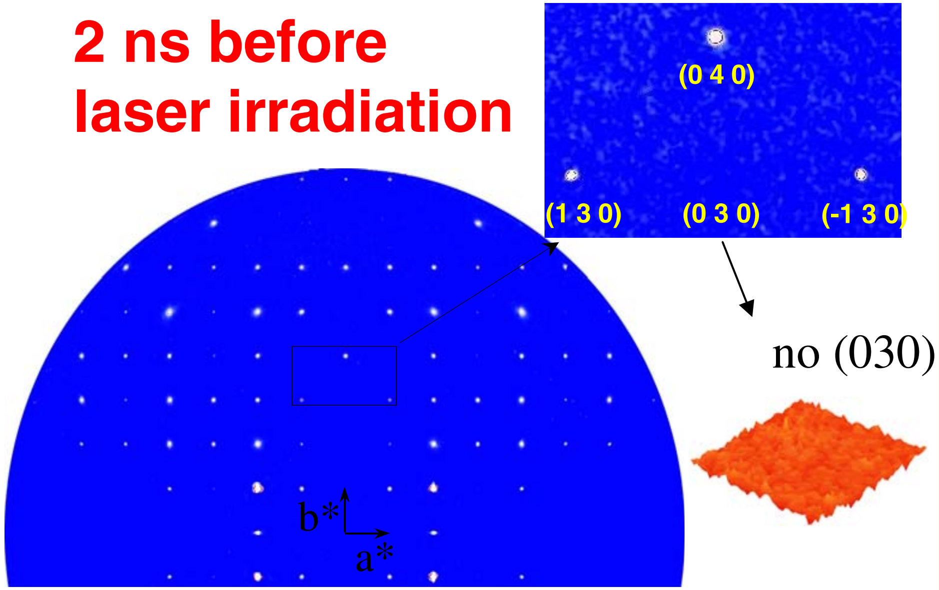


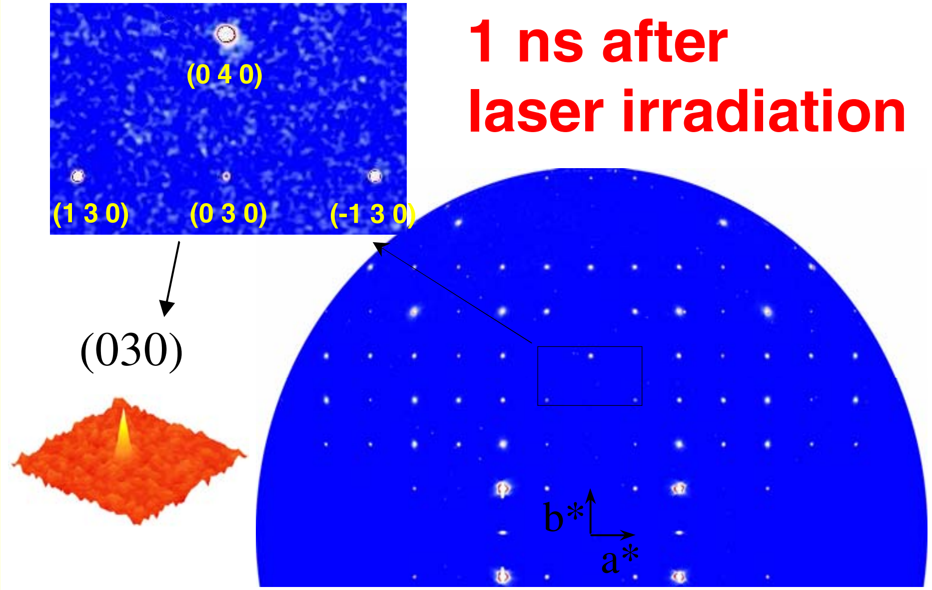
L.Guerin et.al. Chem. Phys. In press

Already published in Web form

PHOTO-INDUCED STRUCTURAL ORDER OBSERVED AT ID-09 IN ESRF

Complete data collection : scattered intensity in the reciprocal space.





Neutral phase

Space group P2$_1$/n

(0 k 0) : k = 2n+1 absent

(h 0 l) : h+l = 2n+1 absent

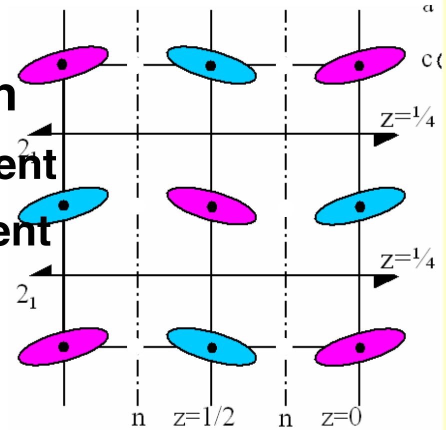
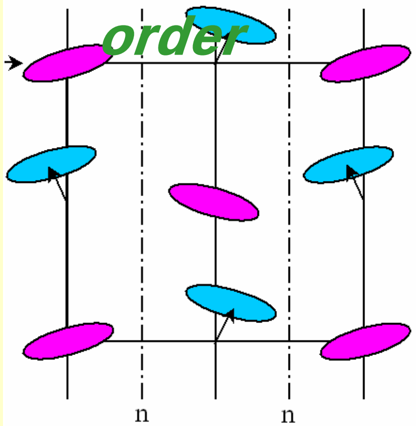


Photo-induced ferroelectric order

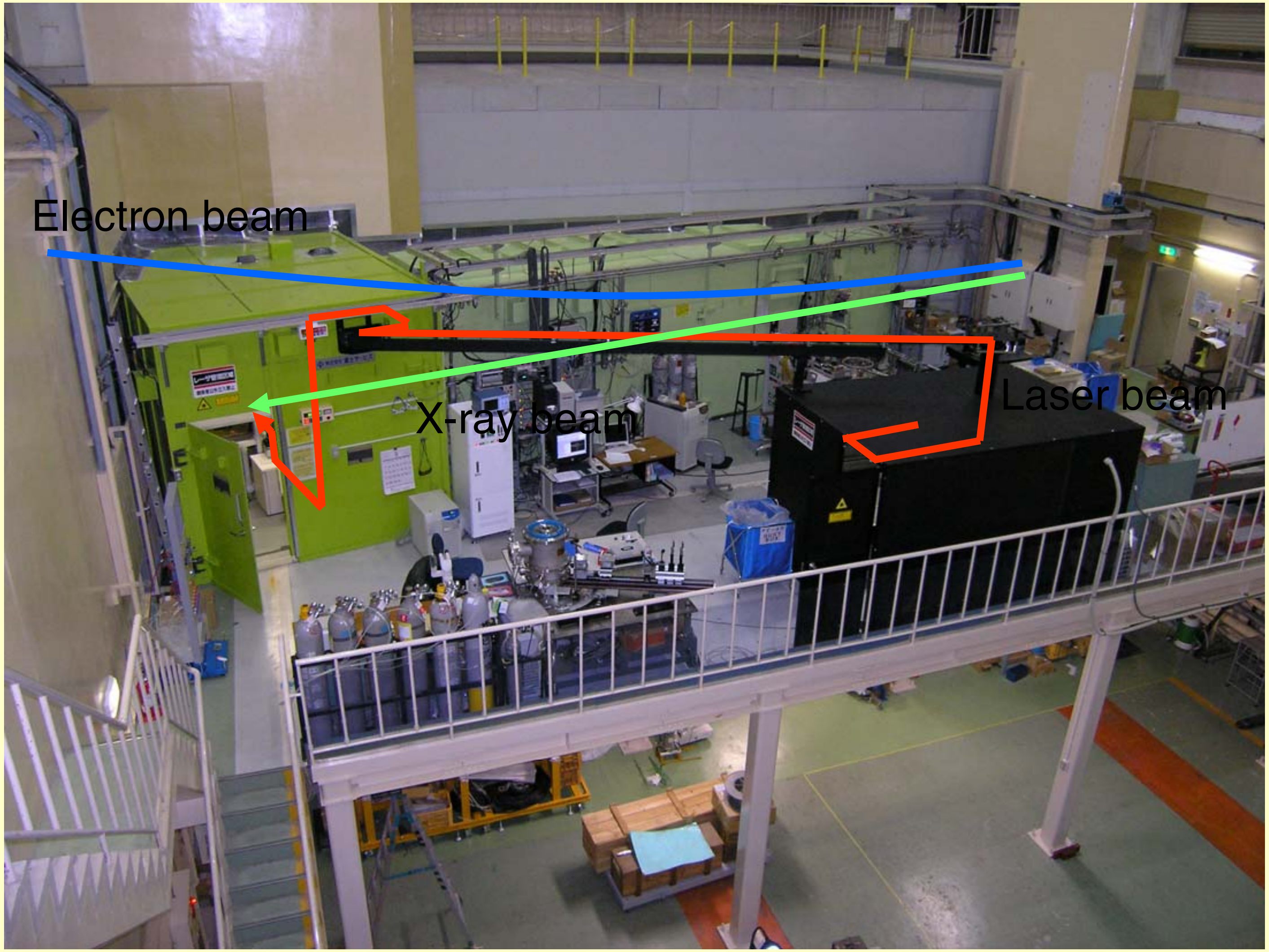


Space group Pn

(0 k 0) : k = 2n+1 present

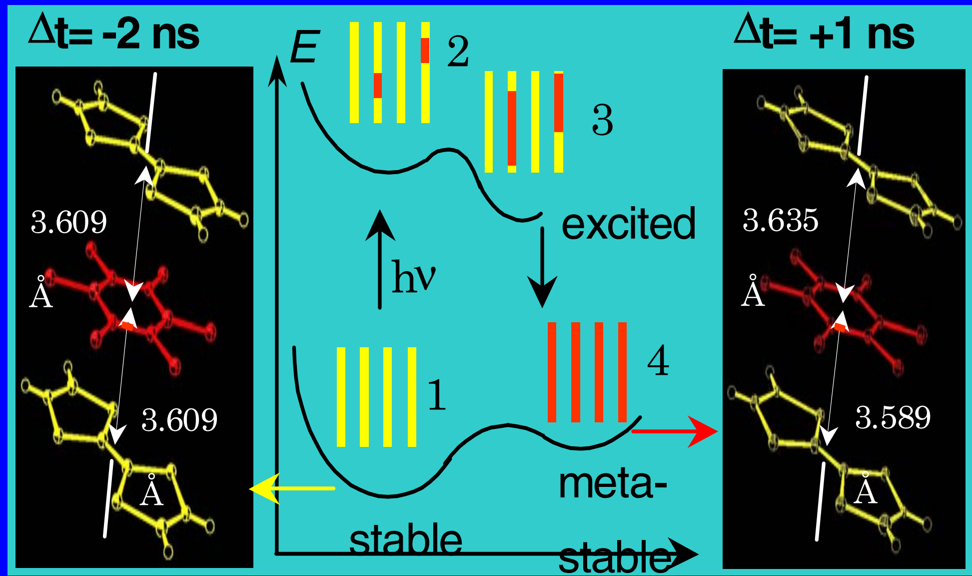
(h 0 l) : h+l = 2n+1 absent

Molecular Movie Apparatus Everyday Working in KEK-AR



Summary for TTF-CA

- Photo-induced ferroelectric order has been confirmed
- Total volume change induced by photo-excitation seem to be very small
- Gigantic changes in various property as a results of cooperative CT, structural and Spin (dimerization) interactions.



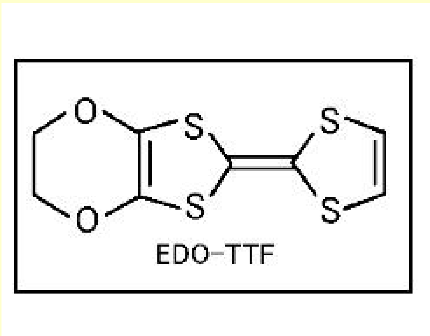
J.Phys.Chem. FEATURE ARTICLE 103,(1999) 2592

Europhysics Lett., 59 (2002) 619.

Science, 300(2003)612.

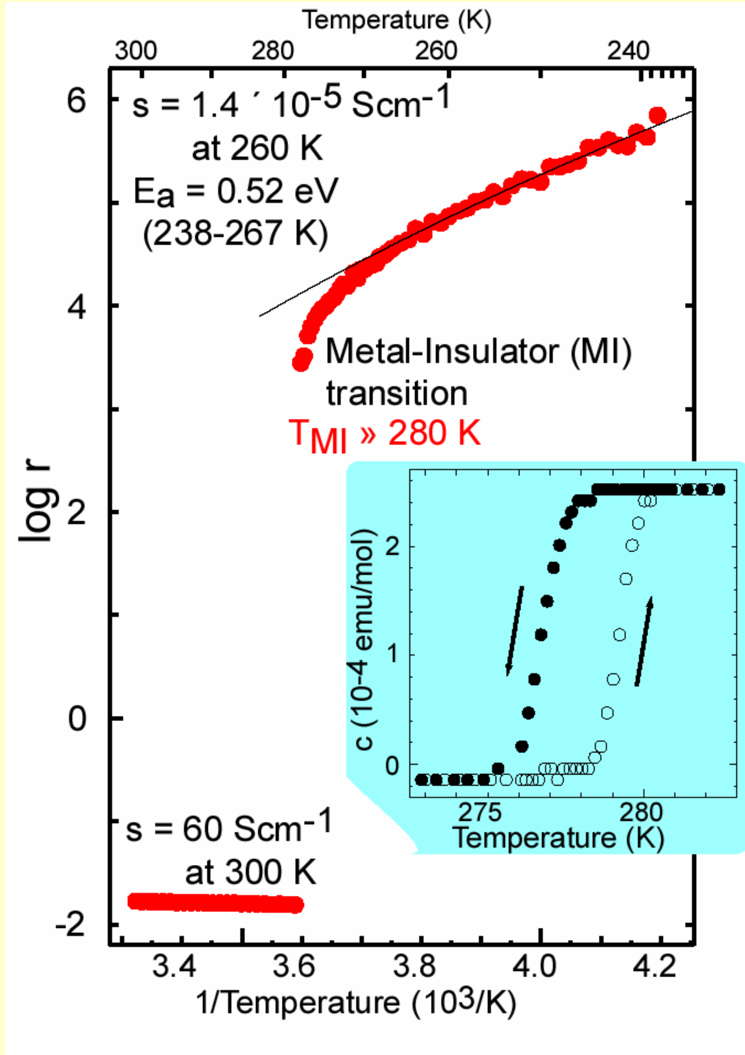
Why $(EDO)_2PF_6$ is important for the study of Photo-Domino effect?

A noble metal (M) insulator (I) transition (Charge Order:CO) accompanied with multi-instability at 280K



What occurs in a system with multi-cooperativity by photo-excitation ?

Non-equilibrium Melting of CO !

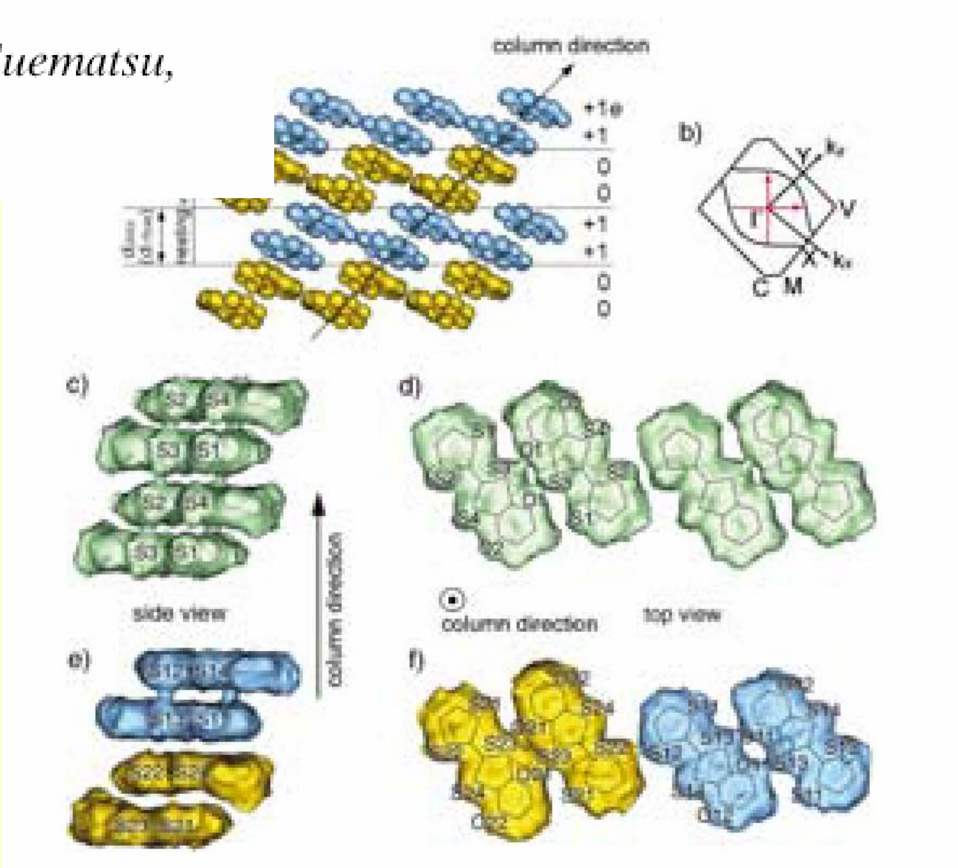


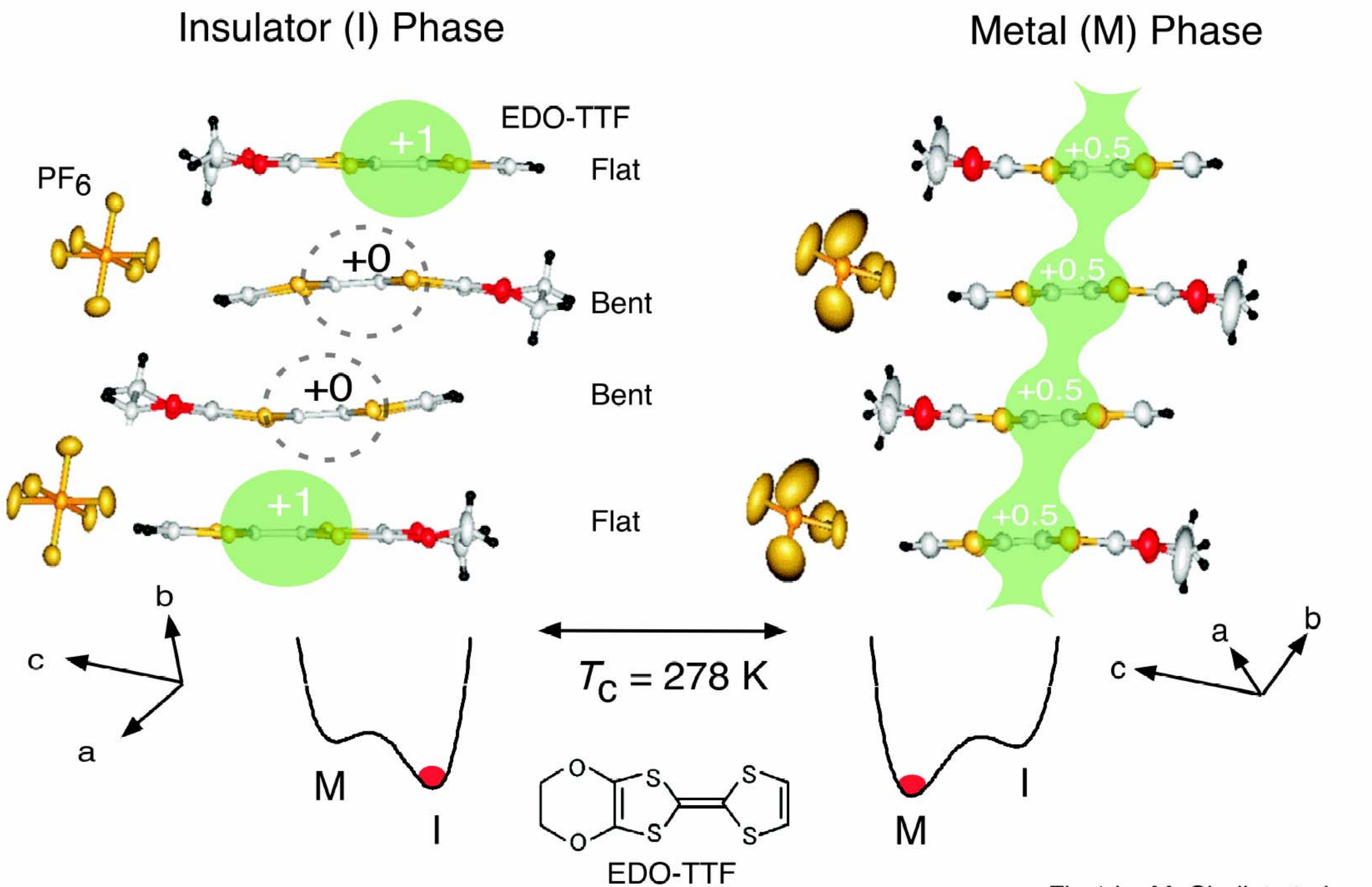
Powder MEM based electron density

Direct Observation of Bonding and Charge Ordering in $(EDO\text{-}TTF)_2PF_6$

*Shinobu Aoyagi, Kenichi Kato, Akira Ota, Hideki Yamochi, Gunzi Saito, Hiroyoshi Suematsu, Makoto Sakata, and Masaki Takata**

Angew. Chem. Int. Ed.
2004, 43, 3670 – 3673

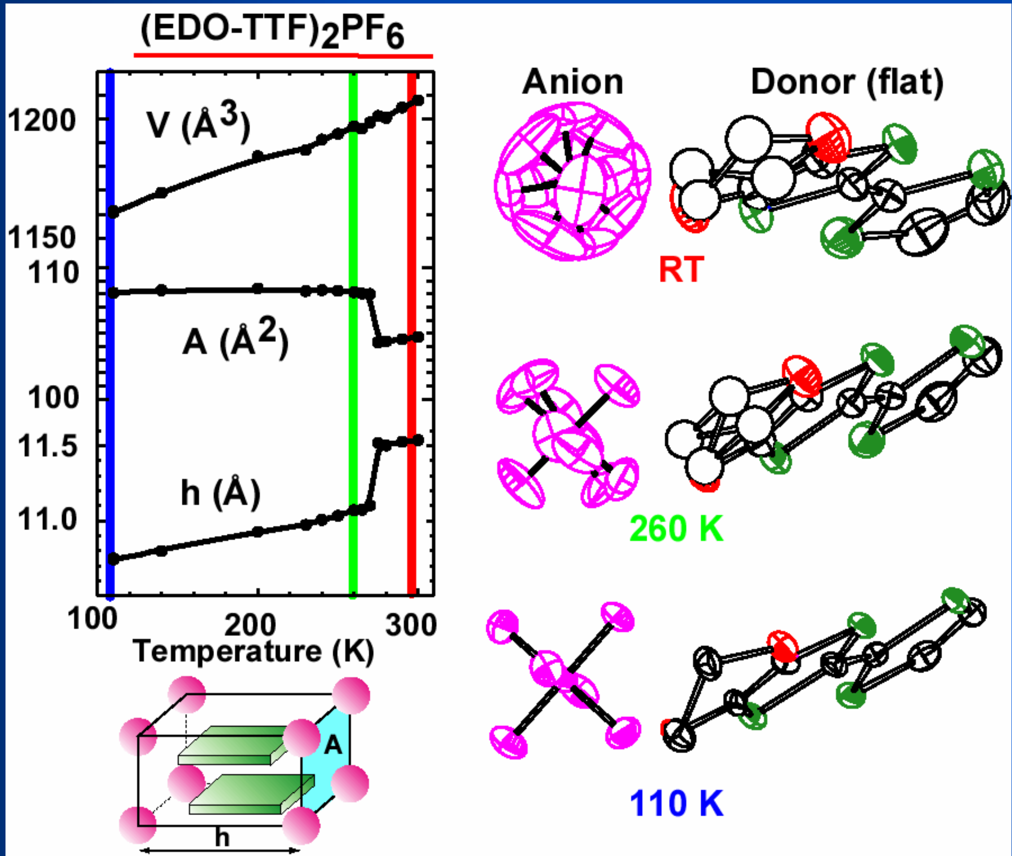




Science 307 (2005) 86.

Link service by AAAS: http://www.coechem6.titech.ac.jp/kenkyu1.htm

Temperature dependence of the crystal structure



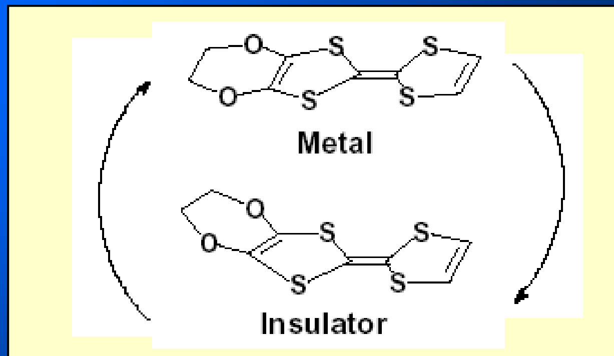
A novel MI transition

Cooperative nature with the molecular deformation

Peierls transition

Charge Ordering

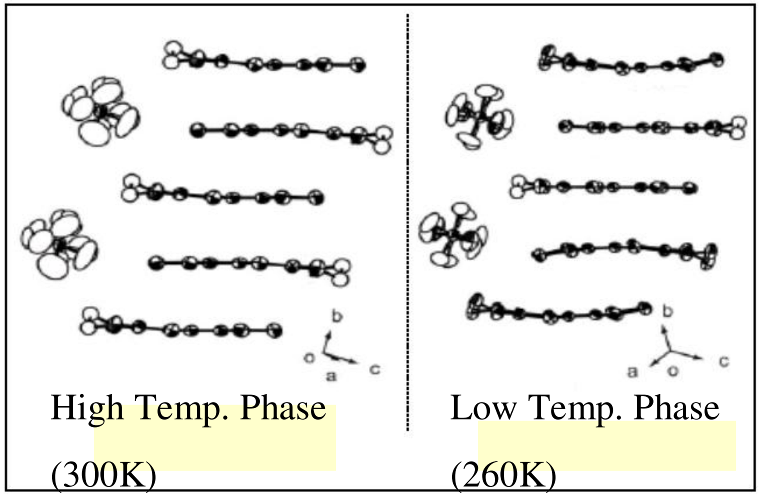
Anion Ordering



○The same type of MI transition was observed at 268K in EDO_2AsF_6 .

○At RT, the salt of ClO_4 was isostructural to that of the insulating phase of the salt of PF_6 and AsF_6 .

Crystal structures of $(EDO\text{-}TTF)_2PF_6$ at RT and at 260K



A. Ota, H. Yamochi, and G. Saito, J. Mater. Chem. **12** 2600 (2002).

Multi-instability:

Charge ordering, Anion ordering,

Changes in the magnetic character,

Molecular conformation

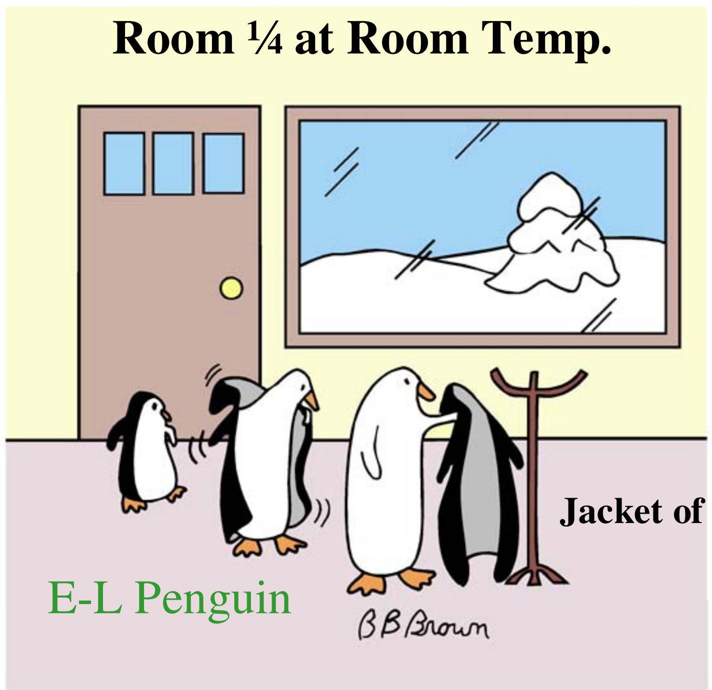
At 260K

Molecular deformation

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

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

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



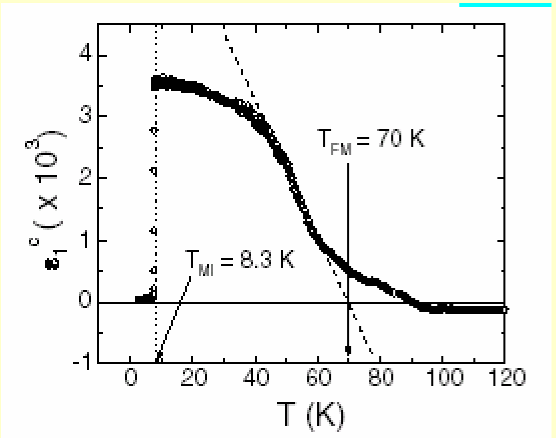
Anomalous response in ¼ systems

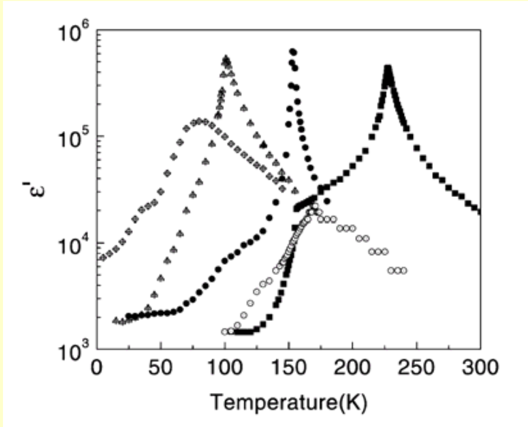
It is necessary to focus on “Mott-CO-Metal” critical point

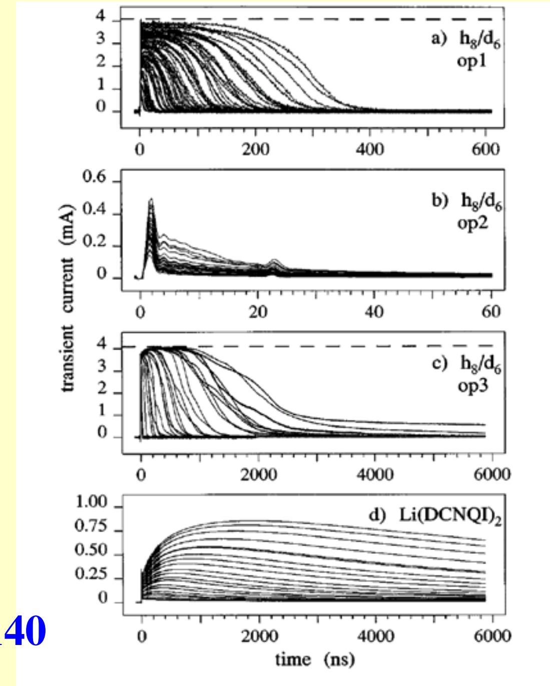
The ferroelectric Mott-Hubbard phase in organic conductors.

S. Brazovskii [a] P. Monceau [b] F. Nad [c]

Syn.Met. 137 (2003) 1331







Anomalous Dielectric Response in the d Correlated Metallic State of -(BEDT-TSF)$_2$FeCl$_4$

Hiroshi MATSUI et.al. JPSJ 70 (2001) 2501

PRL 81（1998）140

Optically Reversed Peierls Transition in Crystals of Cu(dicyanoquinonediimine)2

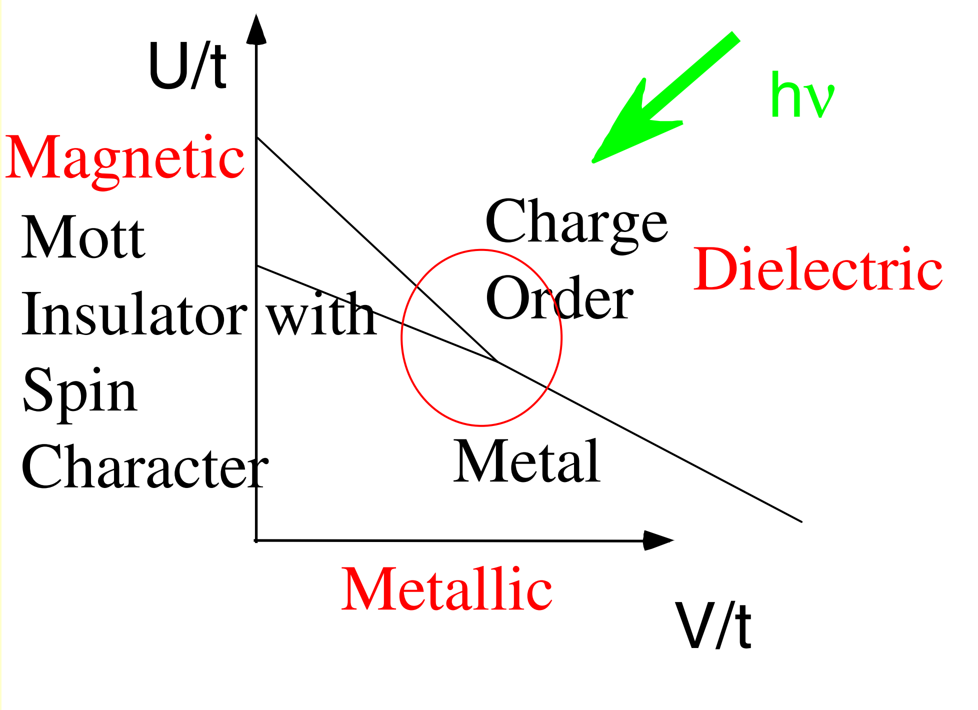
F. O. Karutz, J. U. von Schütz, H.Wachtel, and H. C. Wolf

Target point based on 6th sensitivity of experimentalist:

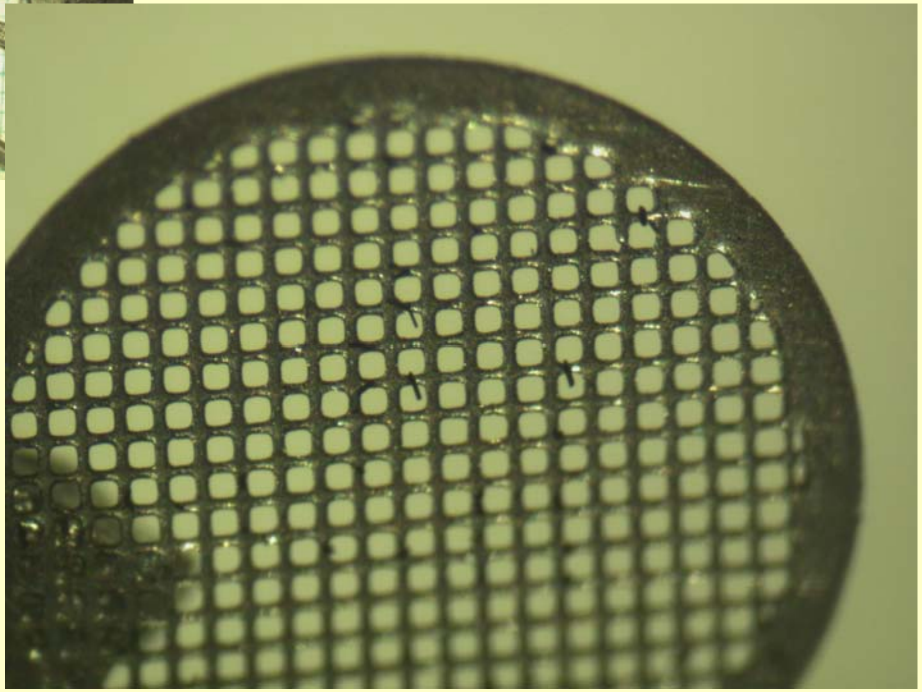
Multi-instability of Charge, Spin and Lattice

in Photo-excited state

第 5 図
ギリシャ神話の三身神ヘカテ。
励起子研究でのワニヤ励起子(正面)，フレンケル励起子(側面)，電荷移動型励起子(背面)にたとえられる。



To eat, or not to eat, that is question.



M-I transition probe by photo-excitation

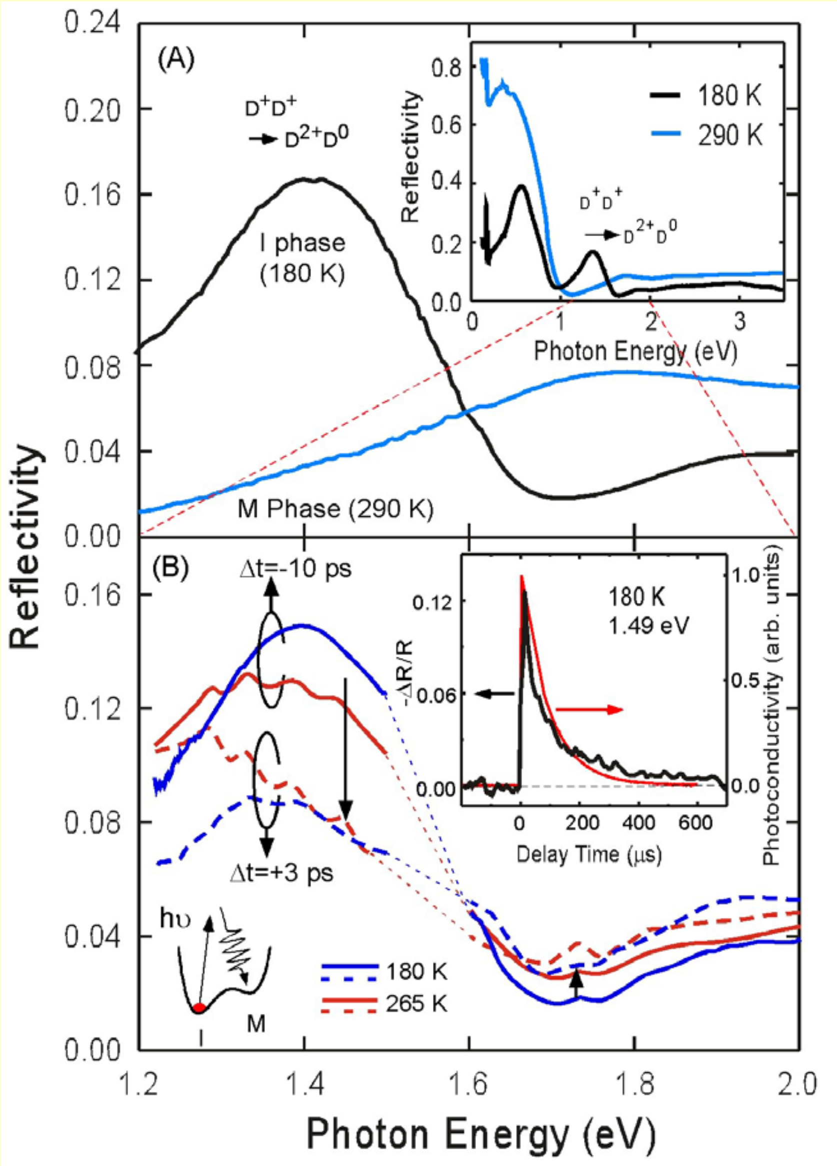


Fig.2 by M. Chollet et.al.

$(EDO-TTF)_2PF_6$

(T_{MI} = 280 K)

Pump:1.55 eV, *E*//*b*

6.4×10^{14} Photons/cm^2

Probe:*E*//*b*

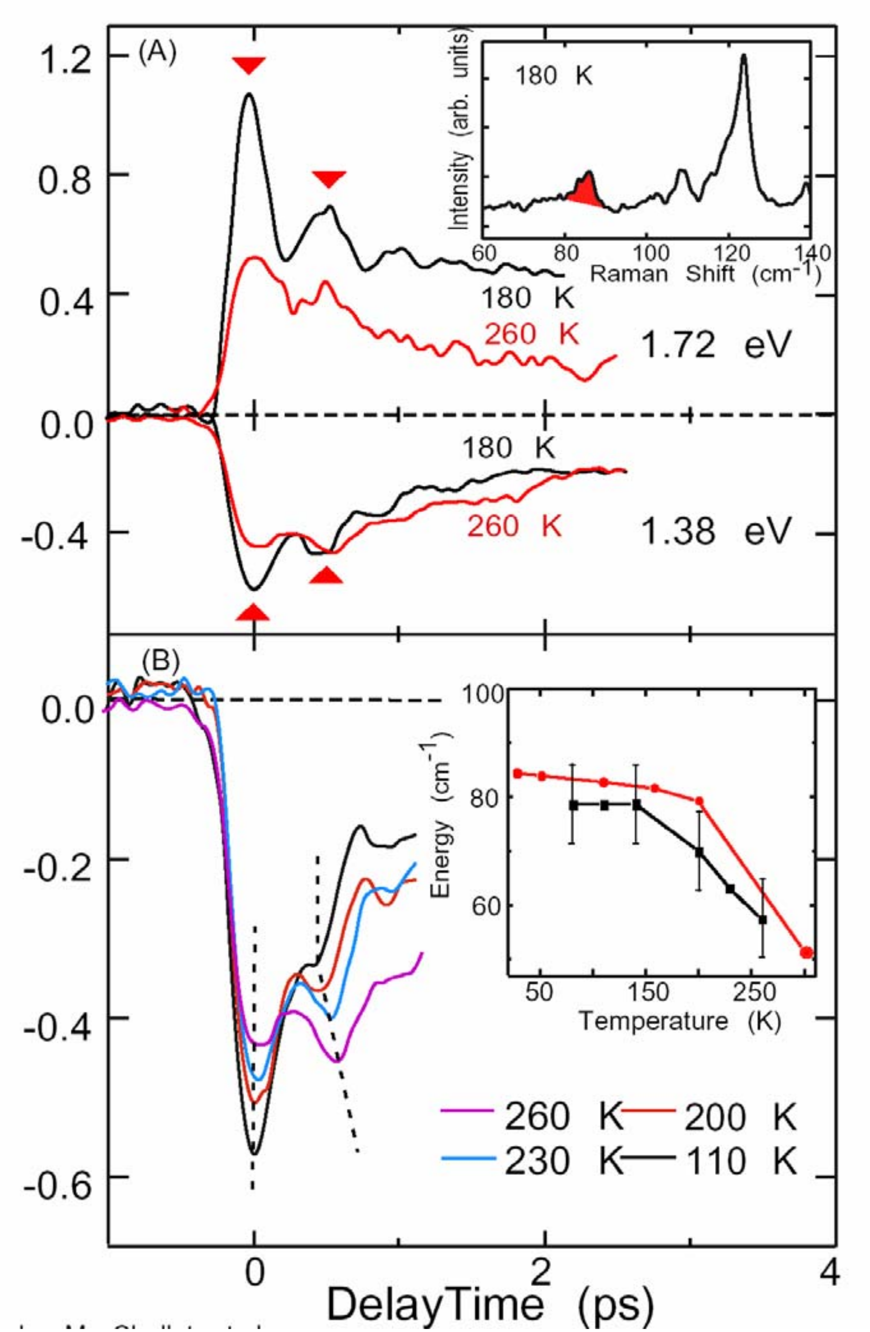
T = 180 K

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

2:Highly efficient and fast conversion with 800nm excitation

(a few ten μJ/cm^2 pulse:1 photon for every few hundreds molecules)

Fast Time-dependence in reflectivity change



Pump:1.55 eV, *E//b*

6.4×10^{14} Photons/cm^2

Probe:*E//b*

T = 180 K

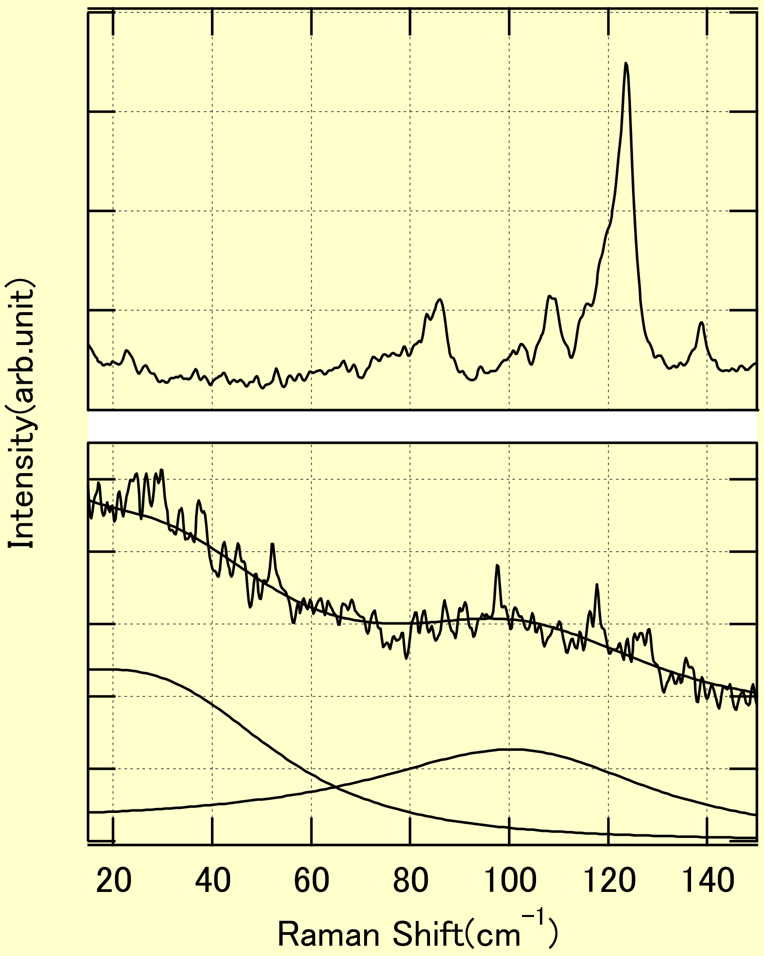
Vibration structure scarcely depends on probe wavelength

Some vibration in electronic structure

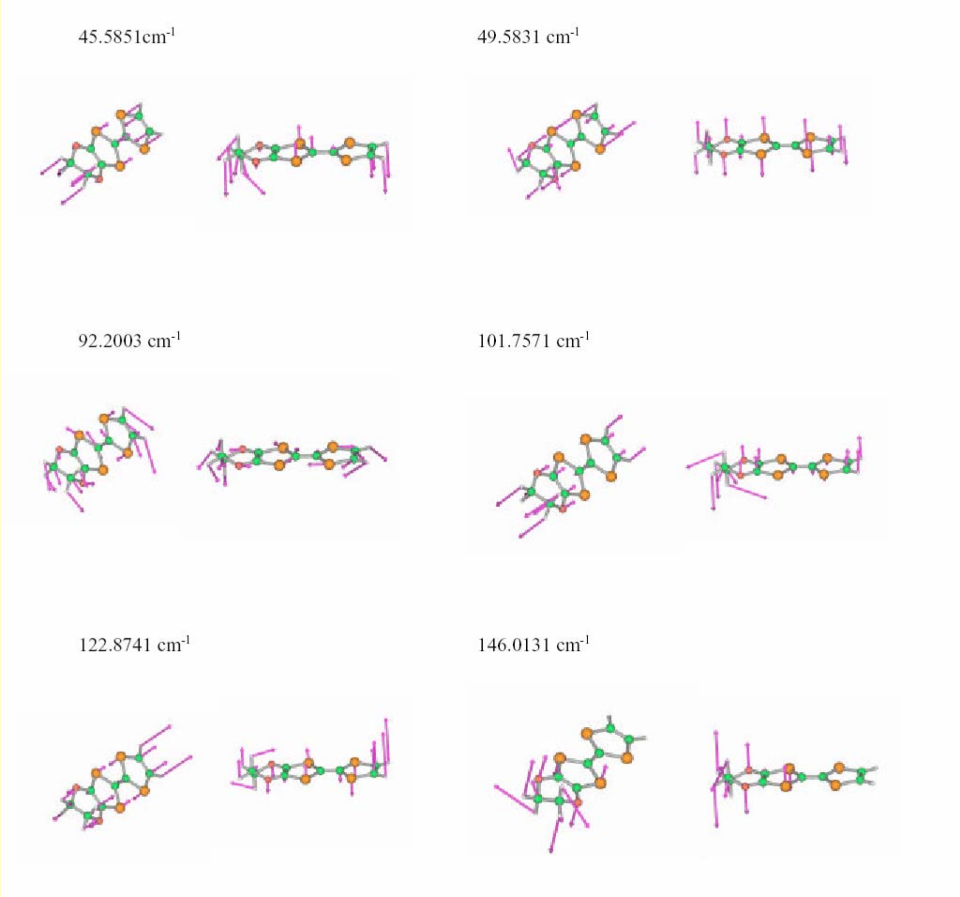
A few Raman lines in LT−phase was confirmed in 35−140 cm^{-1} region:

Important role of Coherent phonon for ultra fast phase conversion !

Raman Spectra in Low Frequency Region Observed by Low Temperature Micro-Raman System

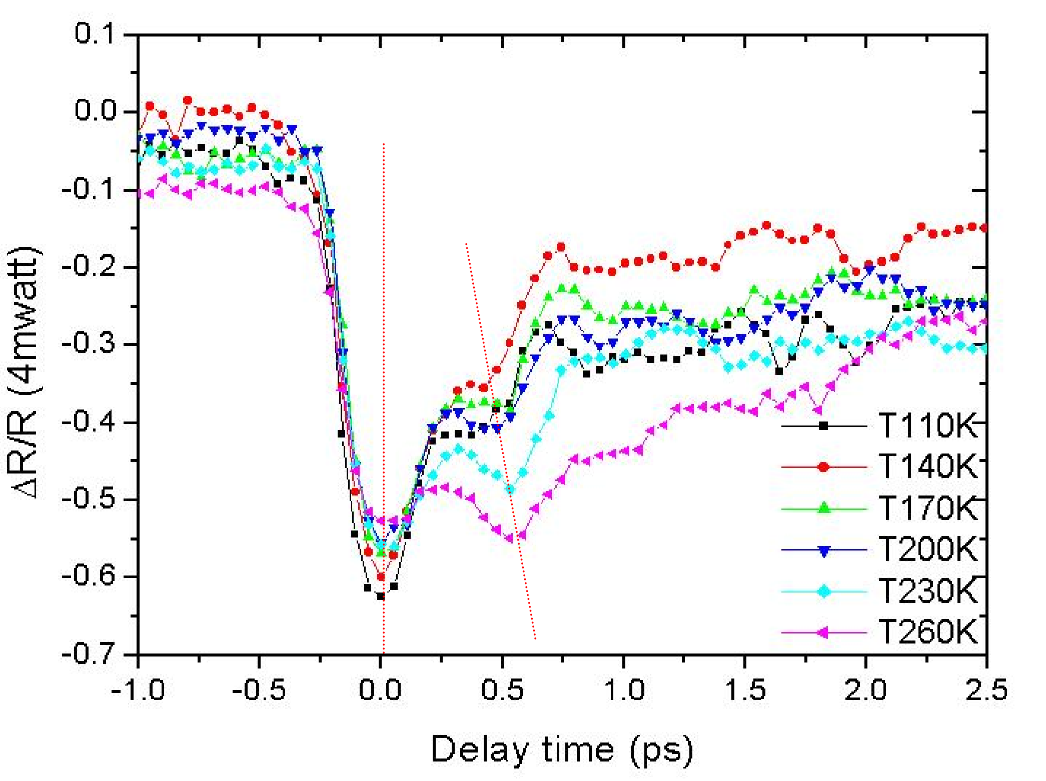


By Mr. T.Hasegawa in Iio Lab. , T.I.Tech.

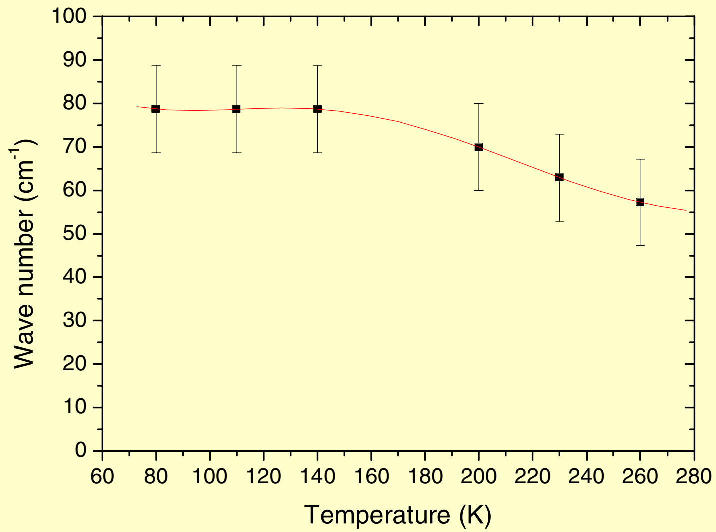


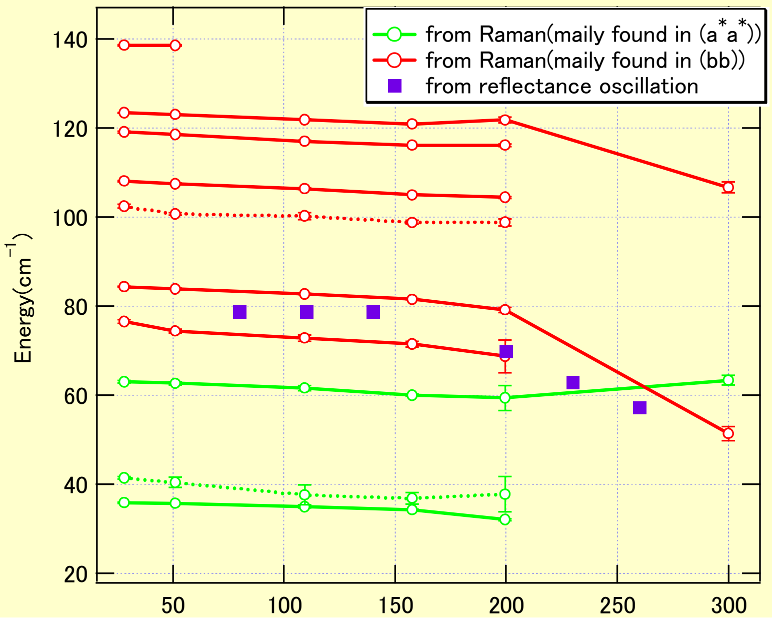
Molecular vibrational mode of EDO-TTF cation (with a help of Dr.Kawai, T.I.Tech. for the use of WS)

Temperature dependence



The period of the first vibration seems to depend on the temperature

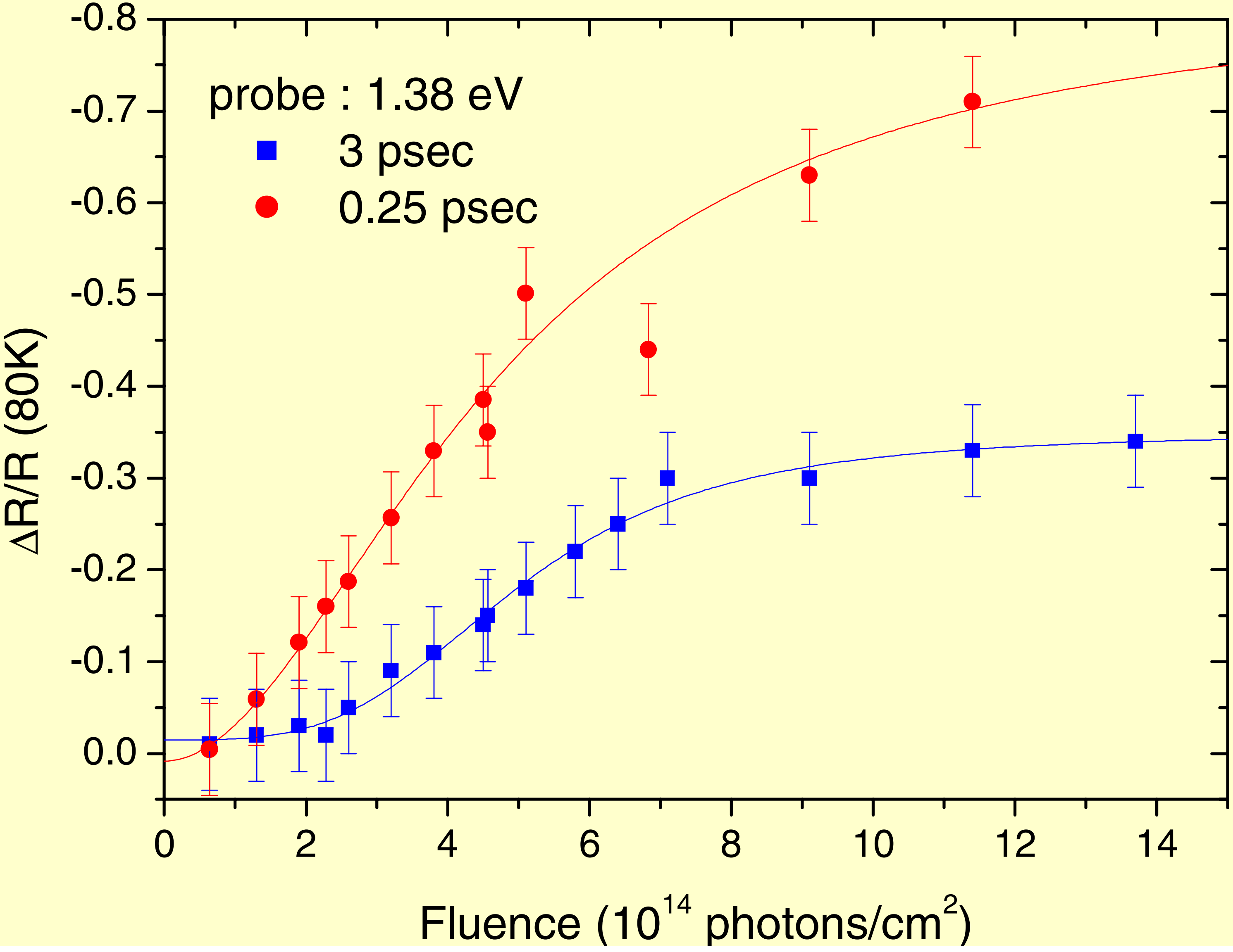




Softening of the phonon mode was clearly observed as the temperature increases.

Excitation Intensity Dependence

Nonlinear response was clearly observed at rather large Δt.



Both phase conversion and relaxation process strongly depend on the excitation intensity

(and electric field, bias current etc.)

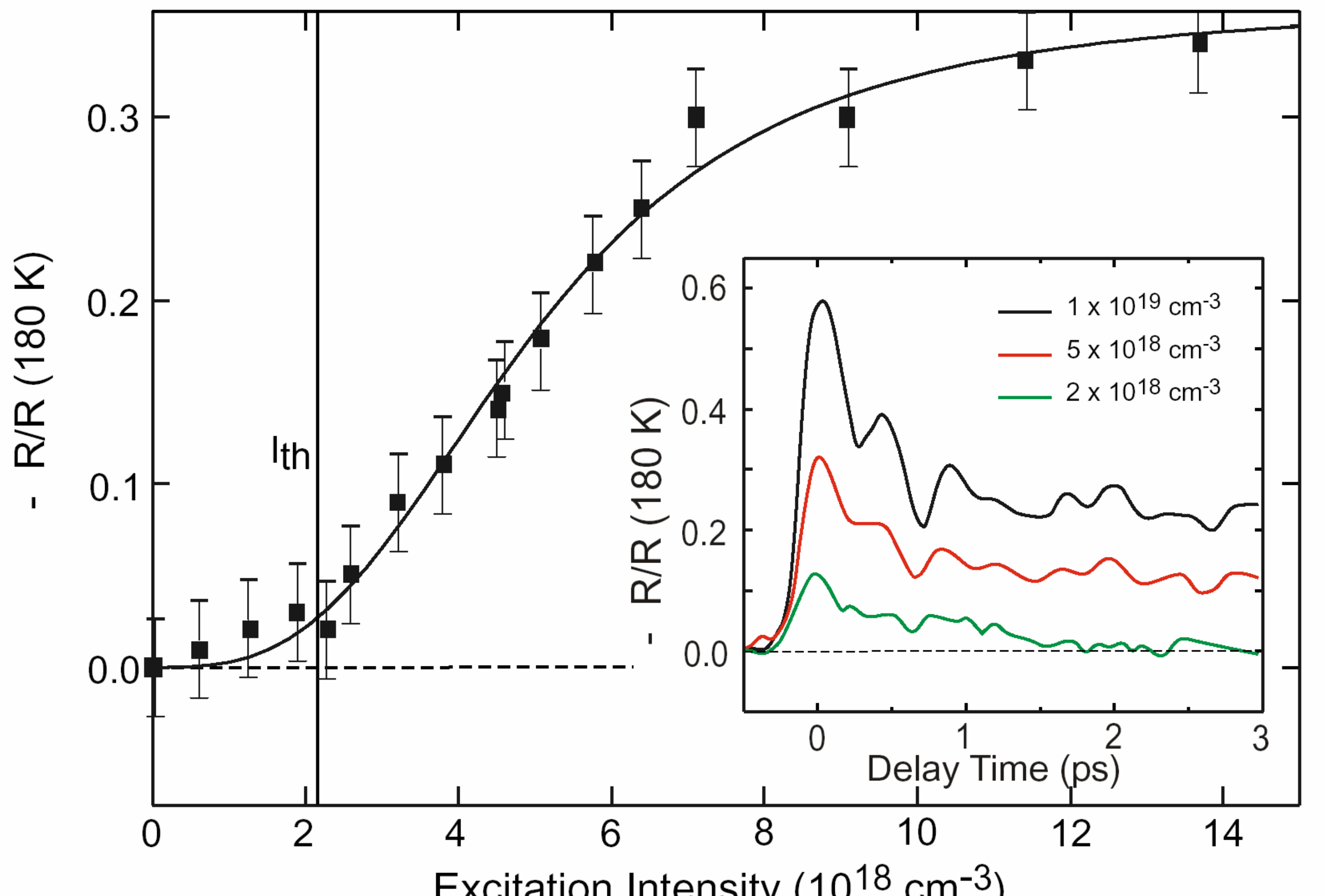


Fig 4 by M. Chollet et al.

Time dependence

Pump:1.55 eV, *E*//*b*

6.4×10^{14} Photons/cm^2

Probe:*E*//*b*

T = 180 K

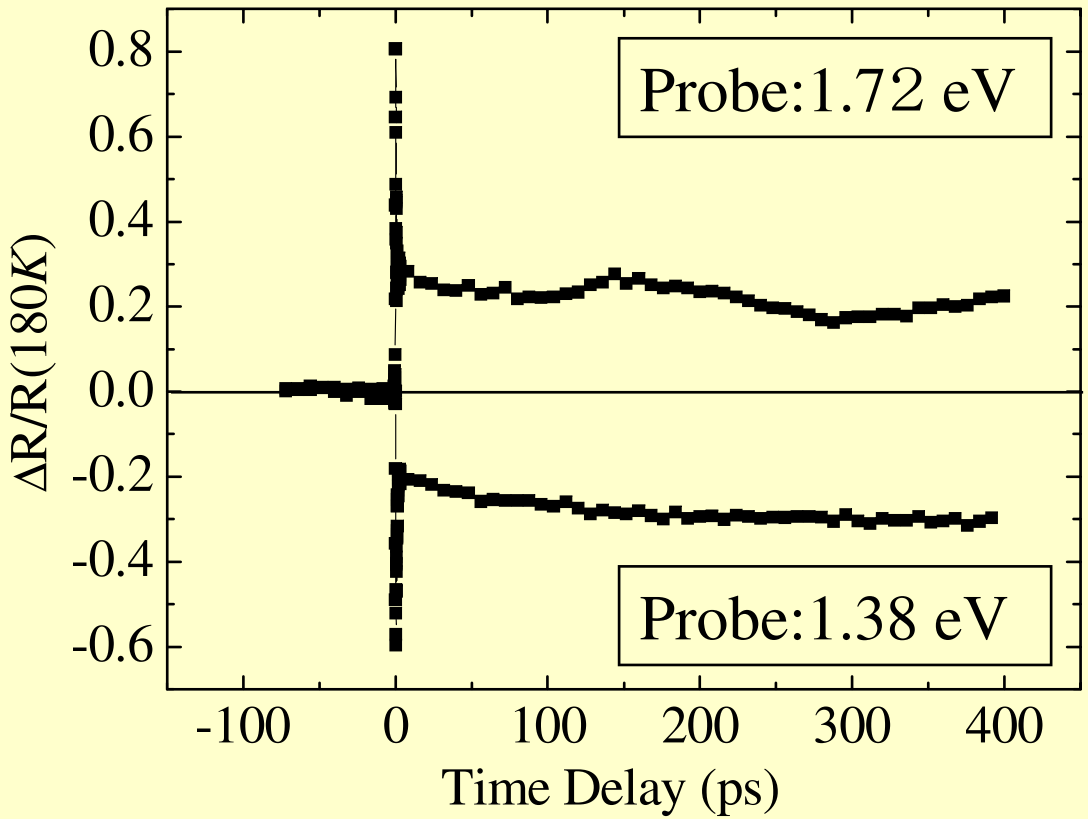
200ps vibration at 1.72 eV

But not at 1.38 eV

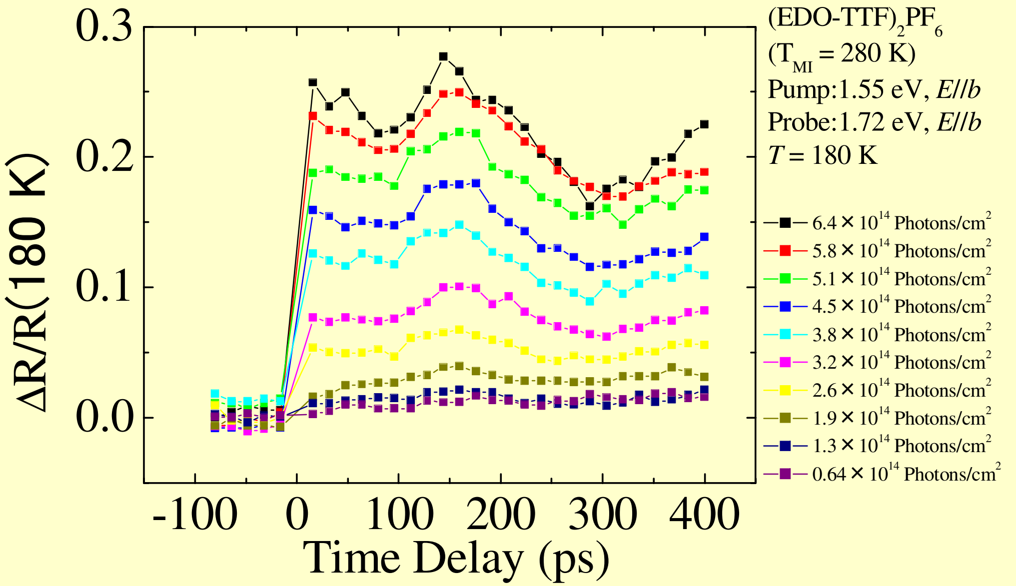
↓

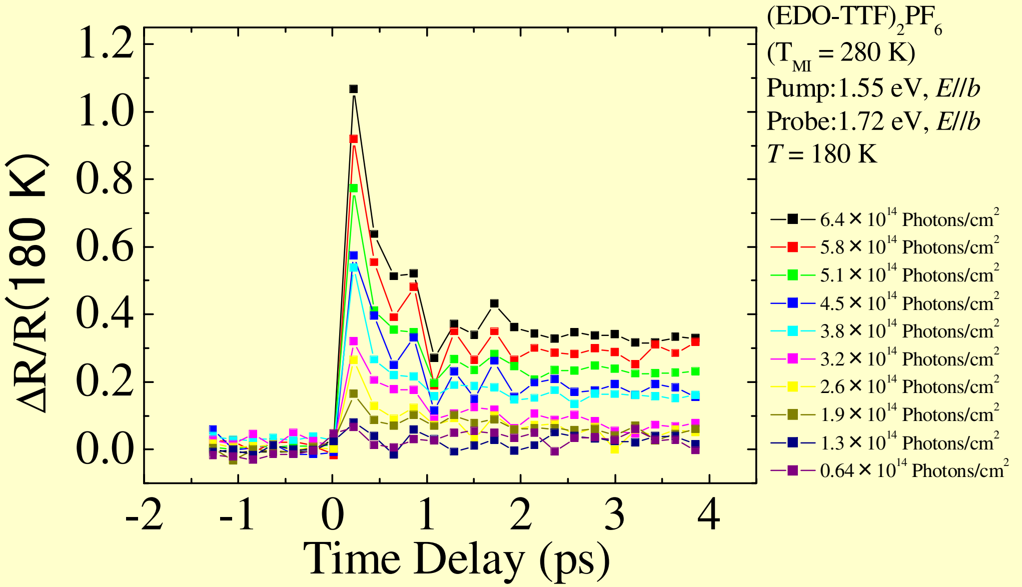
Accoustic wave?

Interference at domain wall ?



Excitation Intensity Dependence (at 1.72 eV)

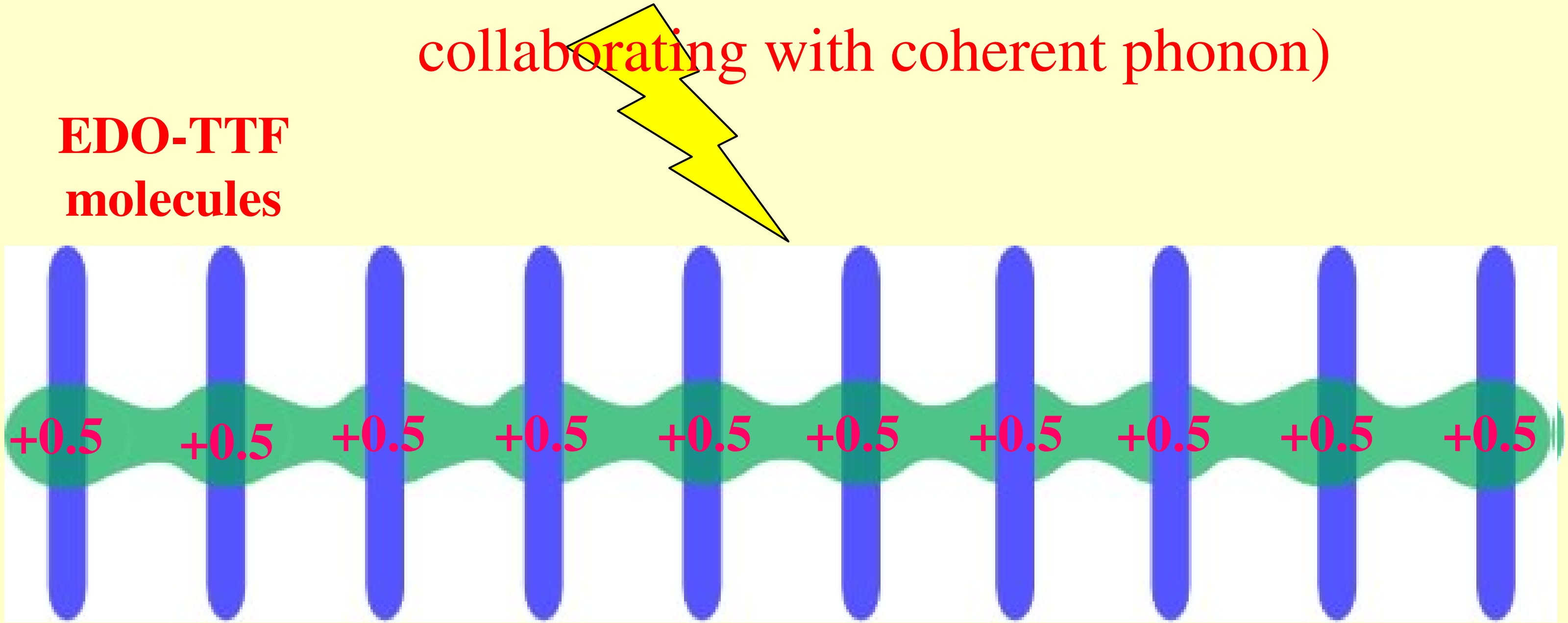




Schematics for photo-domino (Photo-Induced I-M transition)

(Cooperative melting of Charge Order

collaborating with coherent phonon)



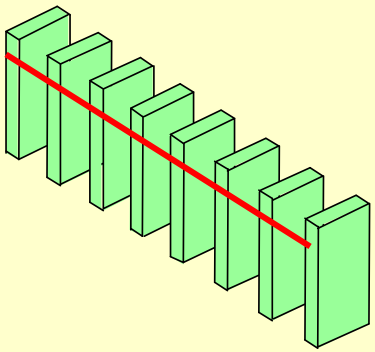
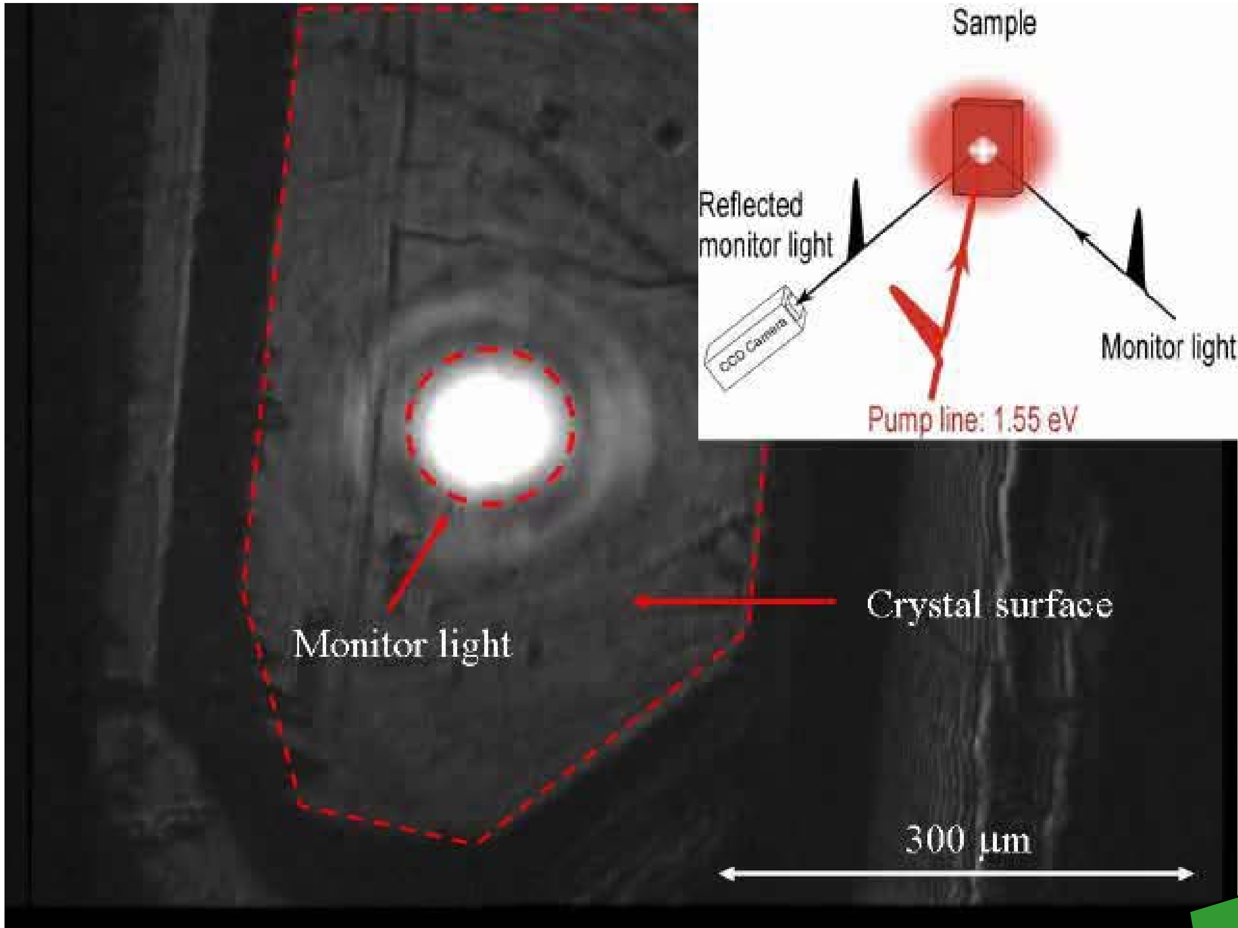
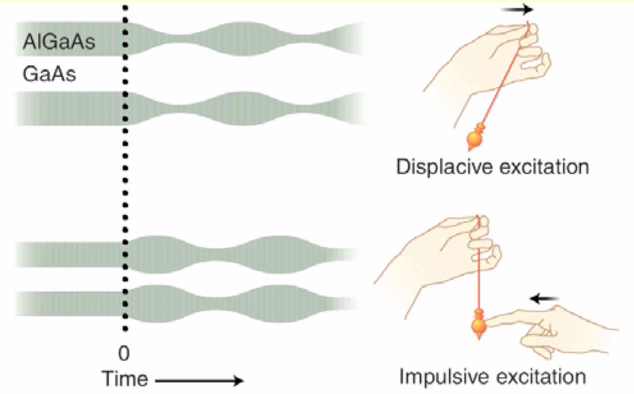


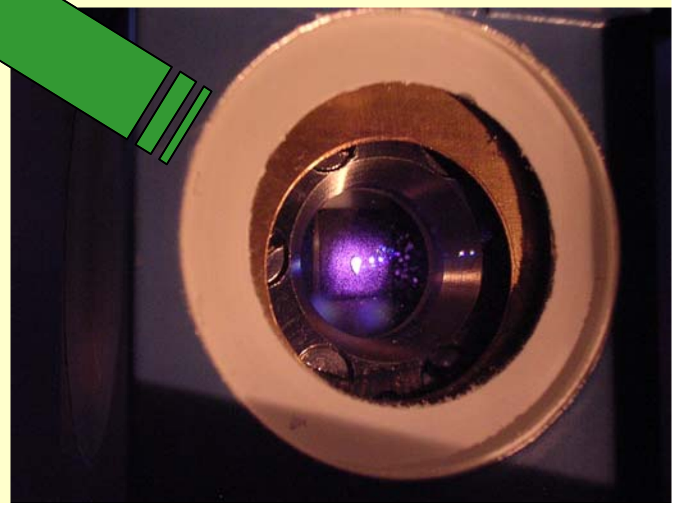
Photo-domino on phonon coherence (POPC) mediated by k=0 phonon mode via E-L collaboration ?





How crystals oscillate. (Left) Displacive and impulsive excitations can be distinguished by the phase of the oscillations. The distortions are greatly exaggerated in these drawings to show that displacive excitations oscillate as cos(ωt), whereas impulsive excitations oscillate as sin(ωt). **(Right)** A pendulum can be used to demonstrate the two excitation mechanisms.

Science 306 (2004) 1691



Molecular and lattice structure are really vibrating as an origin of the stability of PIPT process ?

Electronic distribution is really correlated with lattice ?

Summary

$(EDO\text{-}TTF)_2PF_6$ crystal shows highly sensitive (50% efficiency for 1photon/1000 molecules) I (CO)-to-M like PIPT within 1 ps combined with coherent phonon propagation (POPC Mechanism)

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

（Mode selection for energy relaxation combined with sub-nano scale materials design）

Femto-sec. X-ray crystallography will be a key for solving mechanism. (Science 307 (2005) 86.)

Link service: http://www.coechem6.titech.ac.jp/kenkyu1.htm

How the same class of materials can generate what a different impression !?

Monet

Renoir

¼ system can become the bridge among scientific fields just like the famous one located near Paris ?

Importance of Non-equilibrium and Ultrafast Dynamics

(Application in Fine Machining)

Top of the match stick



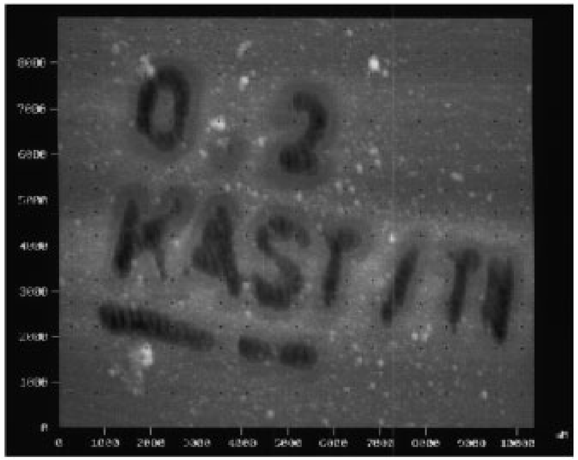
Excited by 100fs light pulse of 800nm (1mW, 1kHz)


Fired

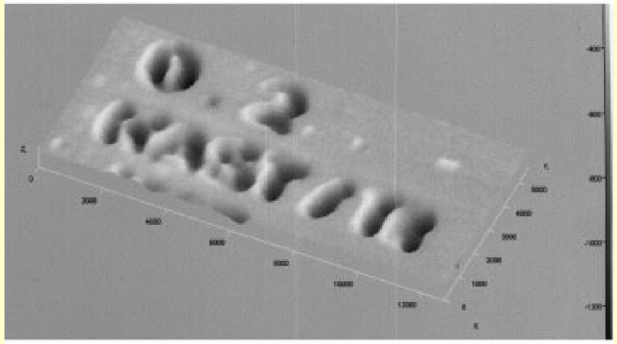
Excited by CW light of 800nm

with the same intensity (1mW)

a)



b)



(a) **Nano-machining of diamond-single crystal by fs-pulse with 800nm, 100fs and 0.05mW**

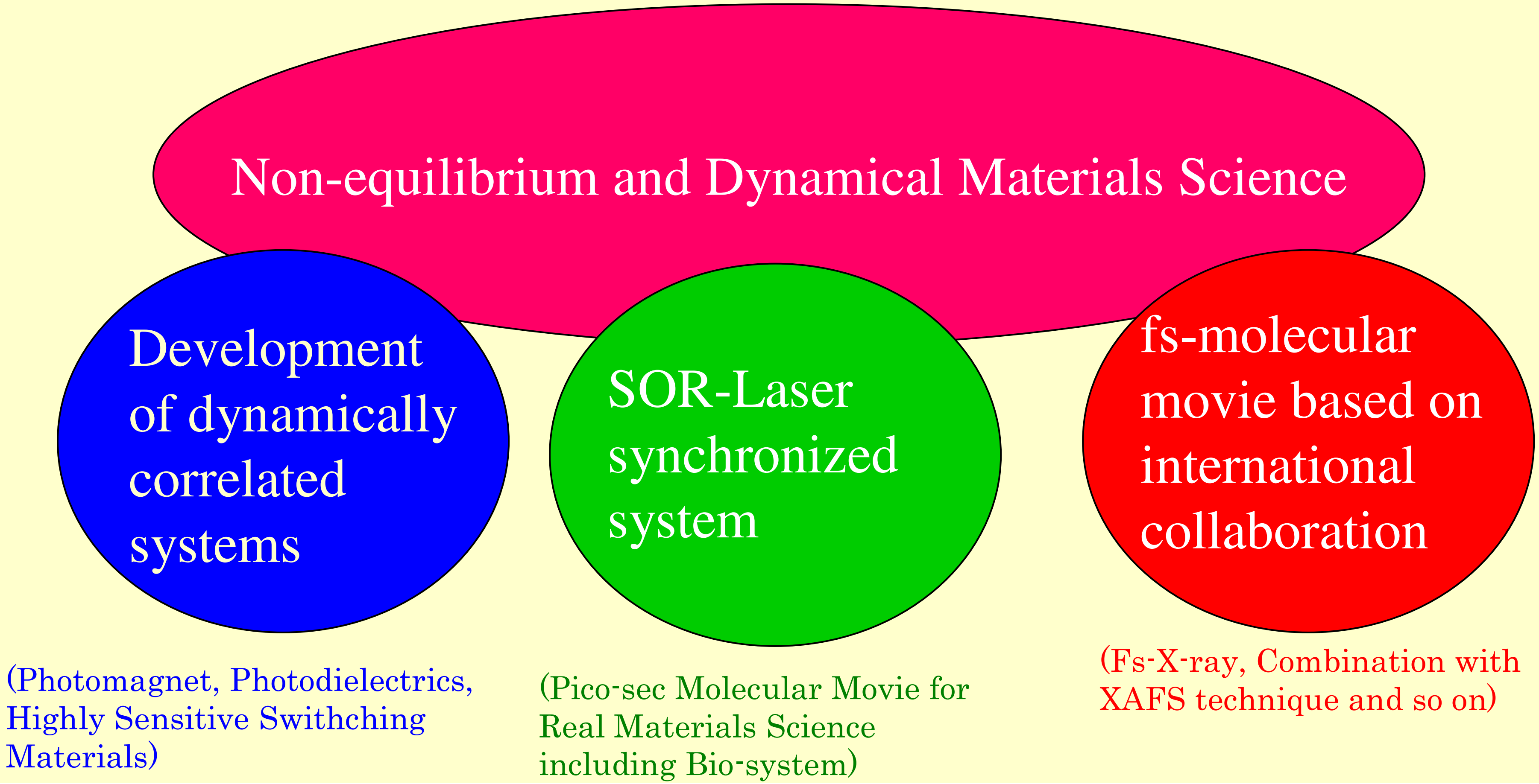
(b) **Observation by confocul microscope**

M.Takesada and S.Koshihara *Look Japan* April 2001 http://www.lookjapan.com/LBst/01AprNT.htm

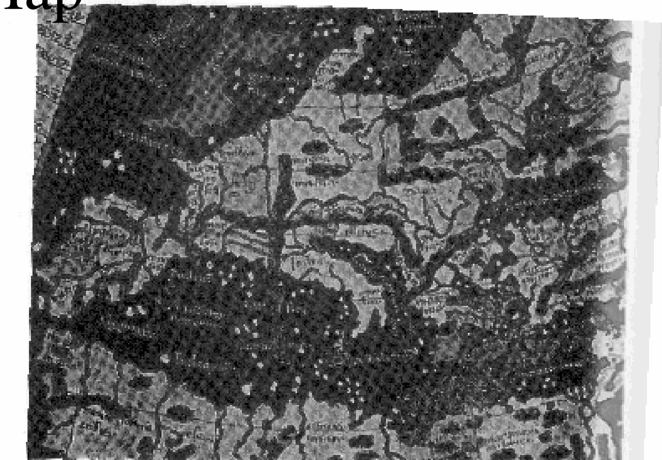
M.Takesada et.al.,

***Jpn.J.Appl.Phys.* 42** (2003) 4613

New Collaboration with Materials science (Small Science) and Accelerator Science (Big Science)



Map


プトレマイオス地図の一例(ヨーロッパとその周辺)

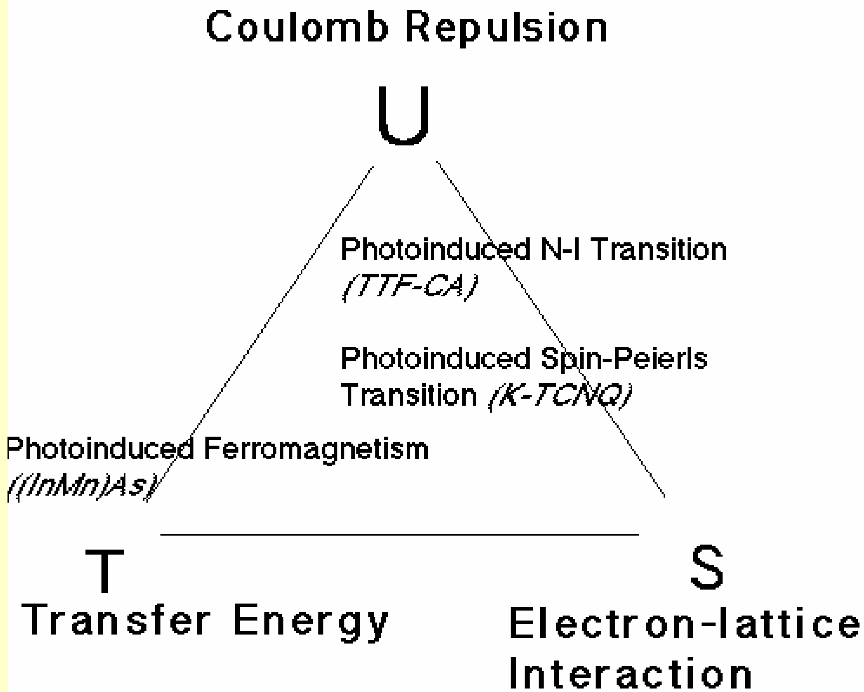

「ここはアレクサンドロスが、アレクサンドロスよどこまで行くのか、という神託を聴いた

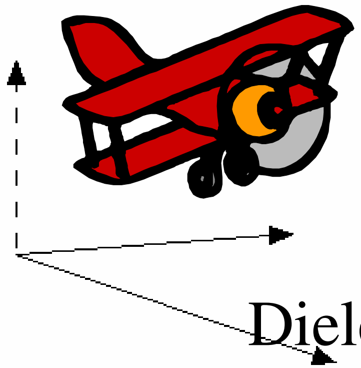
Appearance of Airplane

‘ローマ人の物語X’

by Shiono

物質の地図





Light can become a new axis ?

Dielectric system originated from correlation effect

The End

Thank you for your attention