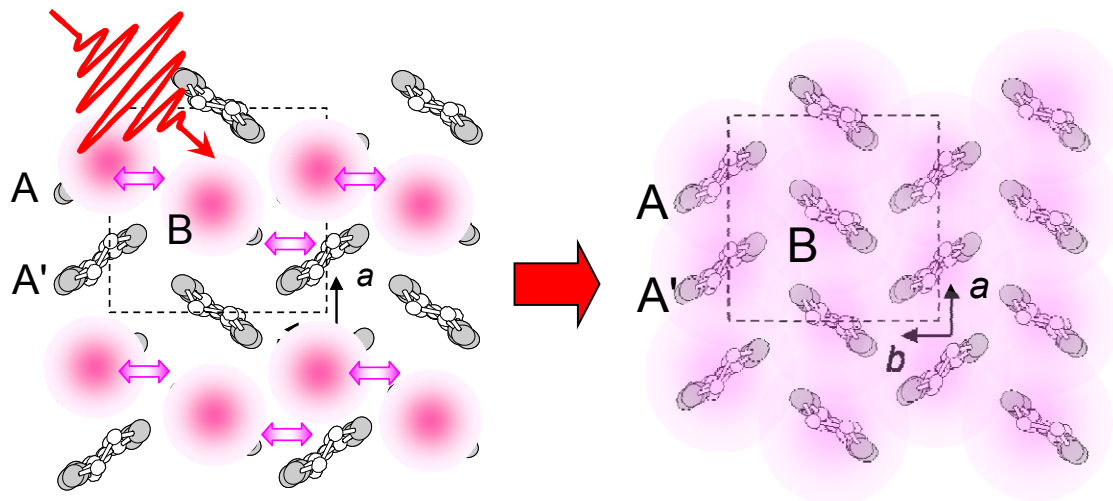
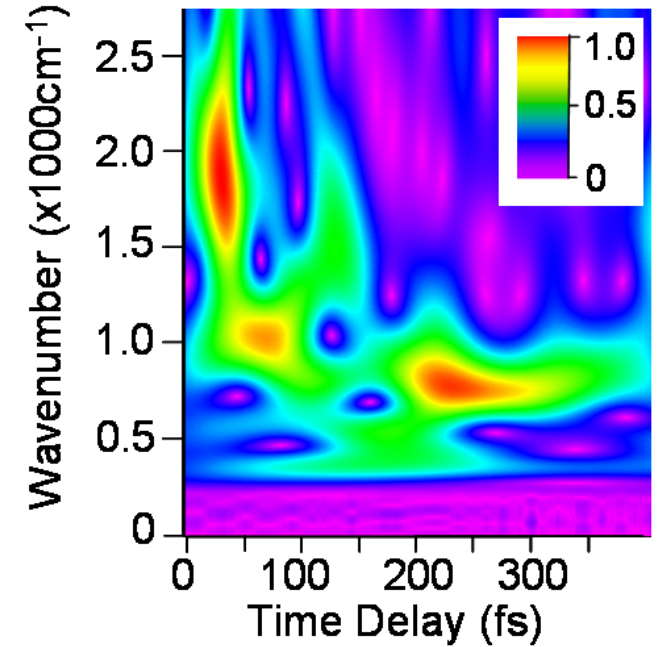
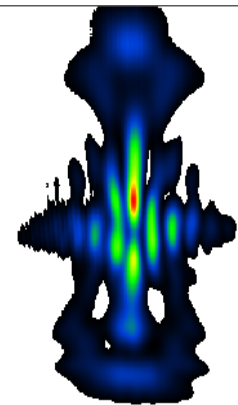
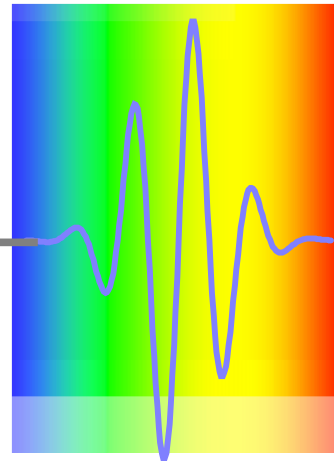
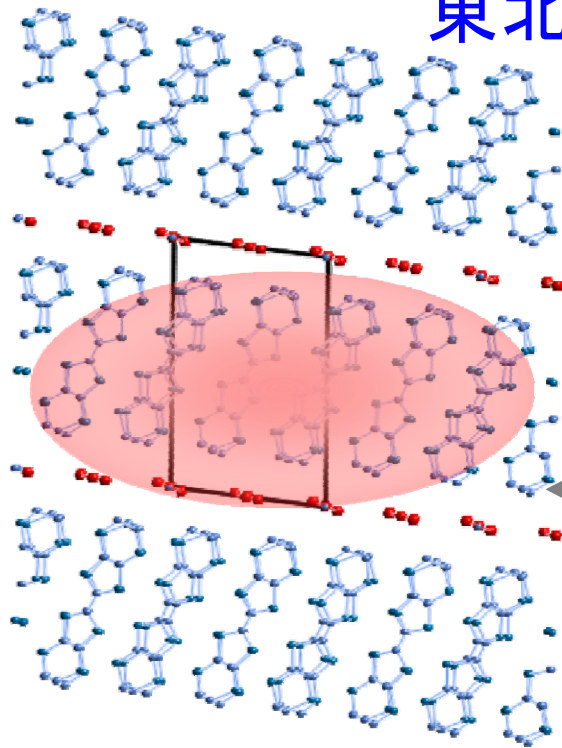


極超短パルス光で見る、操る強相関電子系の光誘起相転移

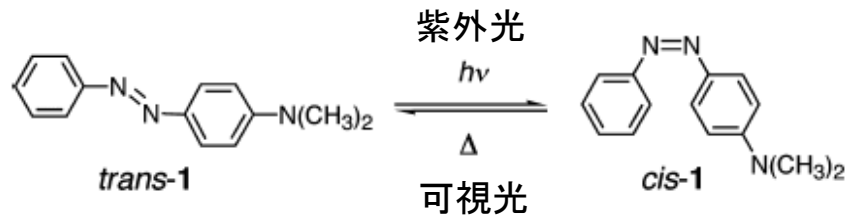
東北大理、CREST 岩井伸一郎



- i) はじめに; 強相関電子系の光誘起相転移
- ii) 光誘起相転移のはじまりを捉える
- iii) 光励起で秩序をつくる?
- iv) まとめ

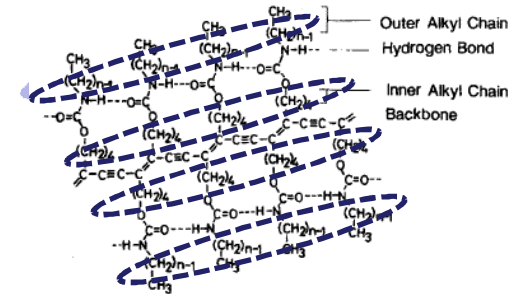
光による物質の変化

アゾベンゼン(シストランス異性化)



G.S. Hartley J. Chem. Soc. 633 (1938).

ポリジアセチレン(側鎖構造の変化)



Koshihara et al., PRL68, 1148 (1990),
J. Chem. Phys. 92, 7581 (1990).

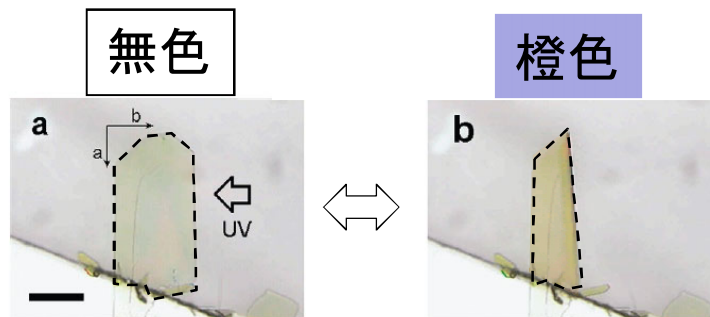


写真: H. Koshima et al., JACS 131, 6890 (2009).

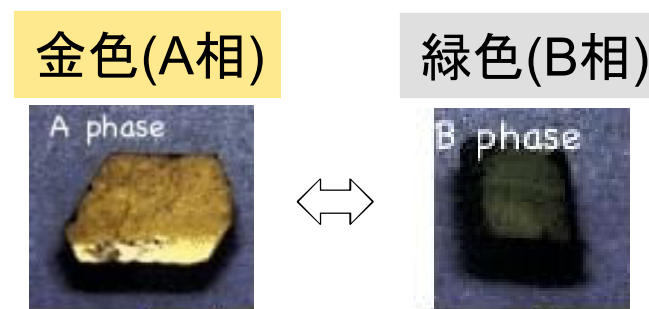


写真: 和歌山大 伊東研 HP

強相関電子系物質の光誘起相転移(遷移金属化合物)

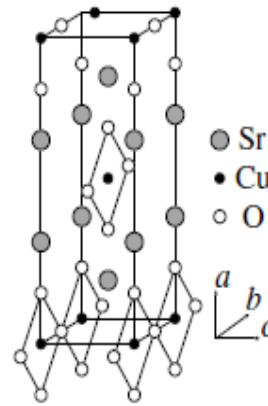
・銅酸化物 : 高温超伝導

光ドーピングによる金属化

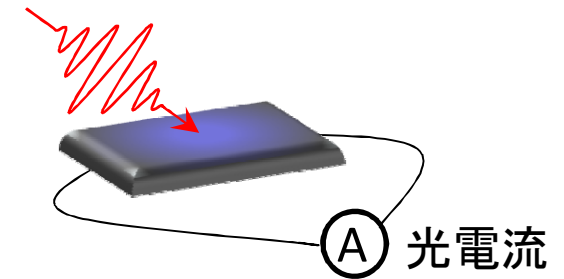
Yu et al., PRL **67**, 2581 (1991).

Matsuda et al., PRB **50**, 4097 (1994).

Ogasawara et al., PRL **85**, 2204 (2000).



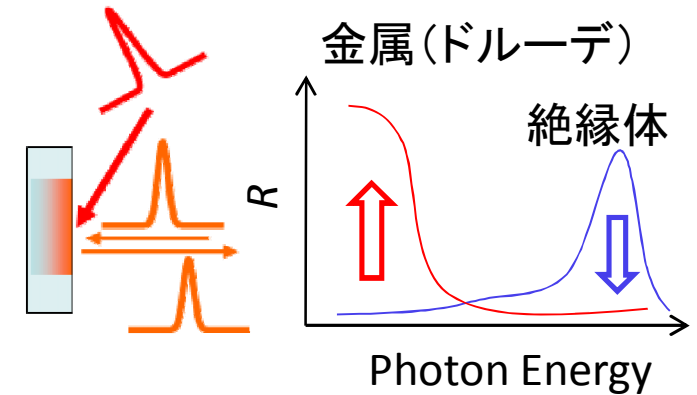
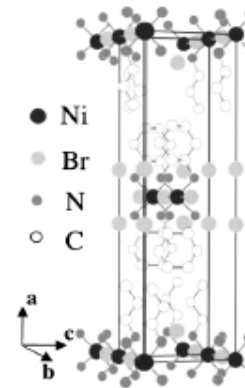
光-伝導



・ニッケル錯体

ドルーデ的金属の超高速スイッチング

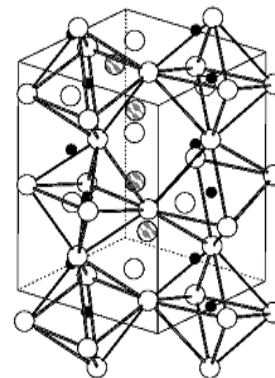
Iwai et al., PRL **91**, 057401 (2003).



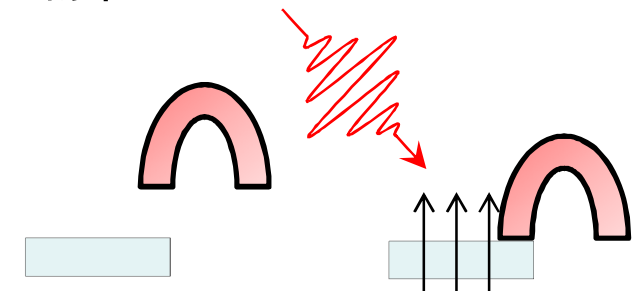
・マンガン酸化物 : 超巨大磁気抵抗

強磁性金属への転移

Fiebig et al., Science **280**, 1925 (1998).

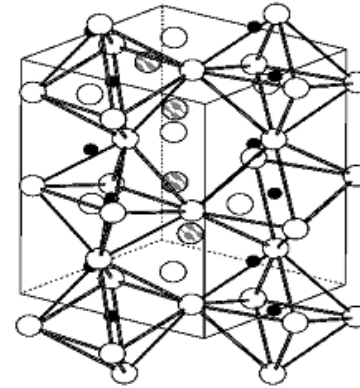
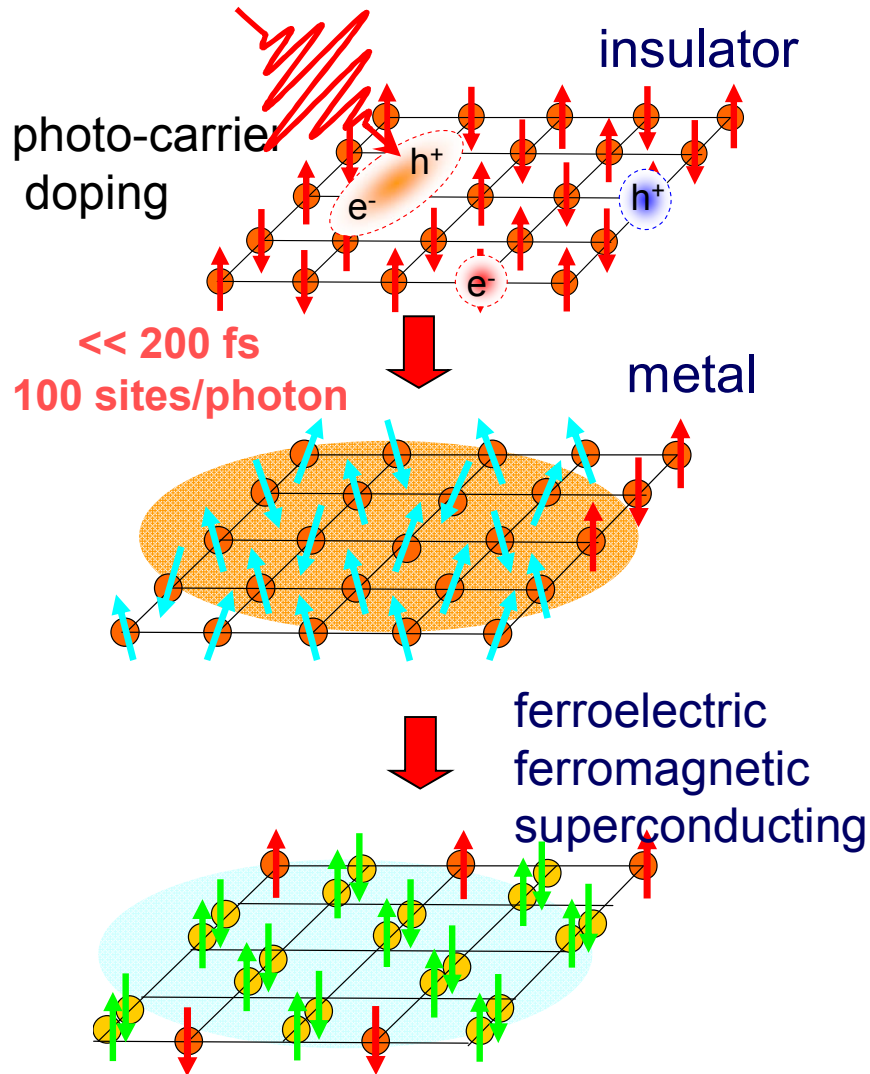


光-磁性

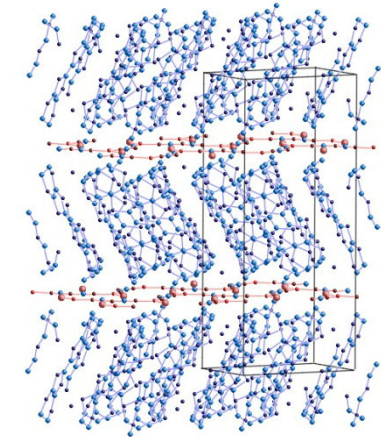


Photoinduced insulator-to-metal transition (PIMT)

Melting & Reconstruction



• Oxides



• Organic salts

Fiebig, APB(2000).
 Ogasawara, PRB(2001)
 Cavalleri, PRL(2001).
 Iwai, PRL(2003).
 Perfetti, PRL(2005).
 Polli, Nature at.(2007).
 Fausti *et al.*, Science (2011).
 etc.....

Chollet, Koshihara
 Science (2005).
 Tajima JPSJ(2005).
 Iwai, PRL(2007, 2009).
 Okamoto, PRL(2007).
 Onda, Koshihara (2008).

- Control of opto-/electric properties
- Discovery of new material phases

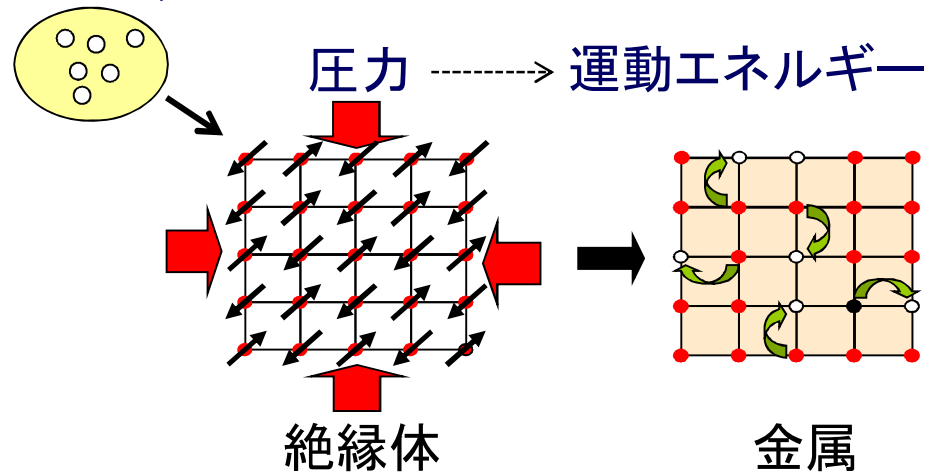
Theory:
 Ishihara, Takahashi, Yonemitsu, Iwano

強相関電子系物質の絶縁体-金属転移

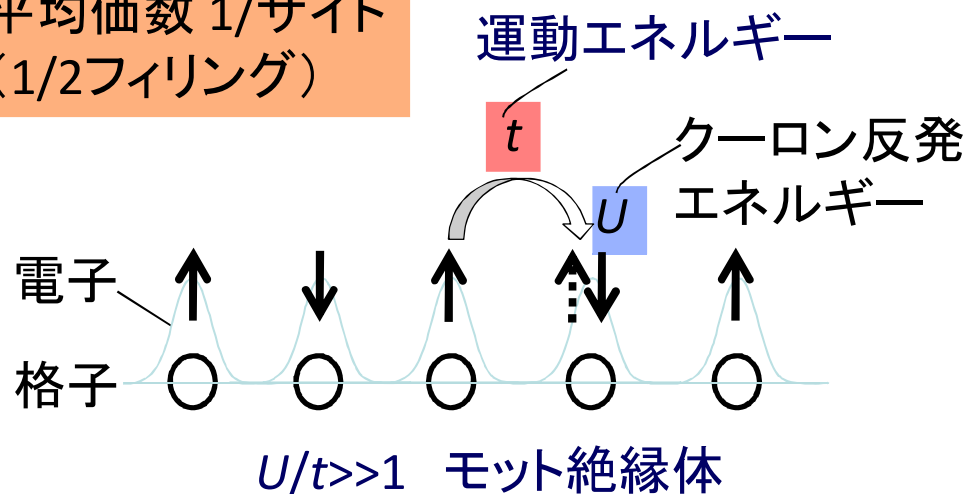
拡張ハバードモデル

$$H_{EH} = -\sum_{ij} t_{ij} (c_i^* c_j + c_j^* c_i) + \sum_i U_i n_{i\uparrow} n_{i\downarrow} + \sum_{ij} V_{ij} n_i n_j$$

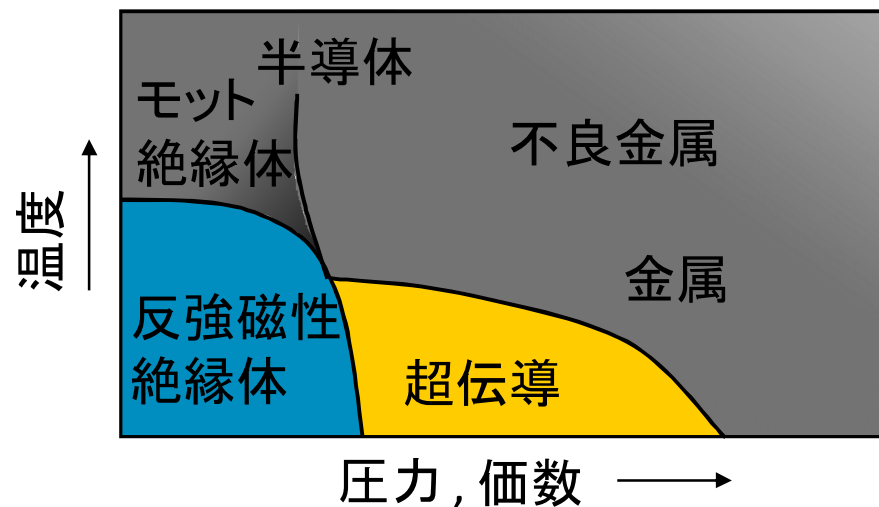
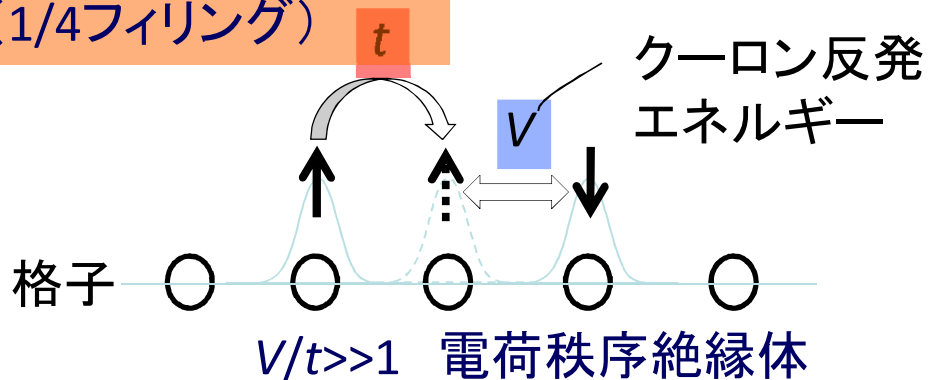
キャリアドーピング → 電子の占有数



平均価数 1/サイト
(1/2フィリング)

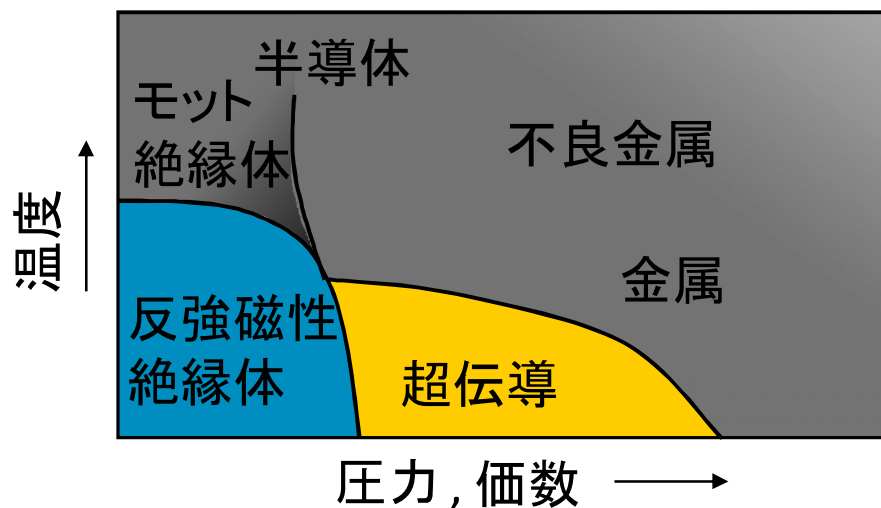
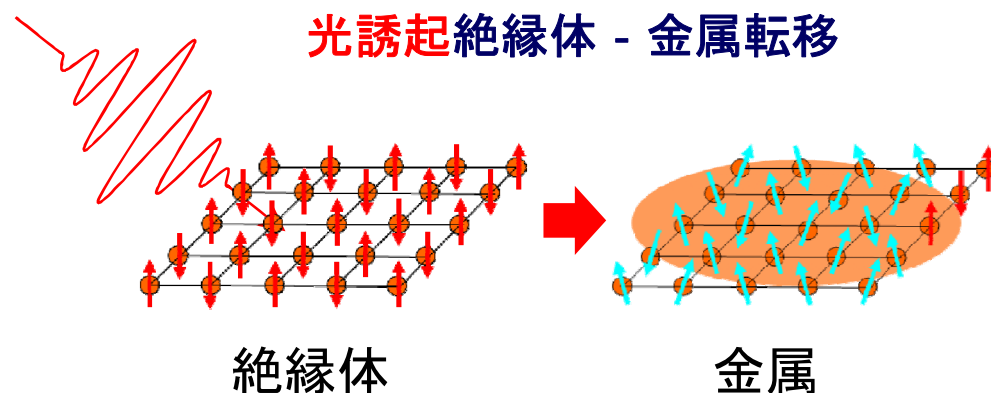
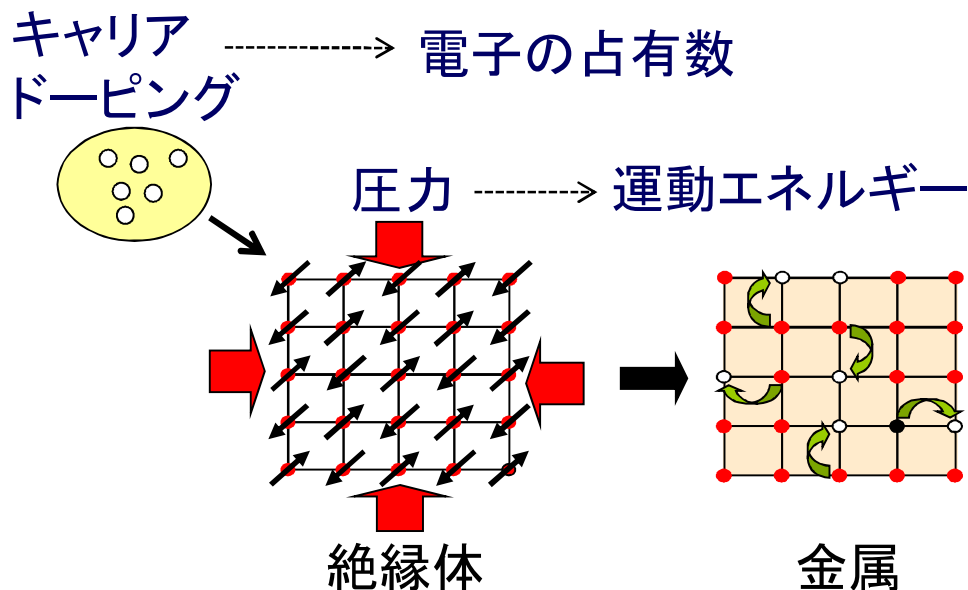


平均価数 0.5/サイト
(1/4フィリング)



絶縁体-金属転移: 強磁性、強誘電、超伝導

強相関電子系物質の絶縁体-金属転移



秩序の融解や再構築の機構？

- ・光ドーピング？
(バンドの占有が1/2や3/4からずれる)
- ・光バンド幅制御？
(構造変化によって t が変化)

絶縁体-金属転移: 強磁性、強誘電、超伝導

i) 光による秩序の融解はどのように始まるのか？

極超短パルス光(パルス幅~3光サイクル)によるスナップショット観測

- ・電荷秩序 α -(ET)₂I₃, θ -(ET)₂RbZn(SCN)₄
電子のコヒーレントダイナミクス
- ・ダイマーモット絶縁体 κ -(d-ET)₂Cu[N(CN)₂]Br)
電子-格子結合系の非線形ダイナミクス

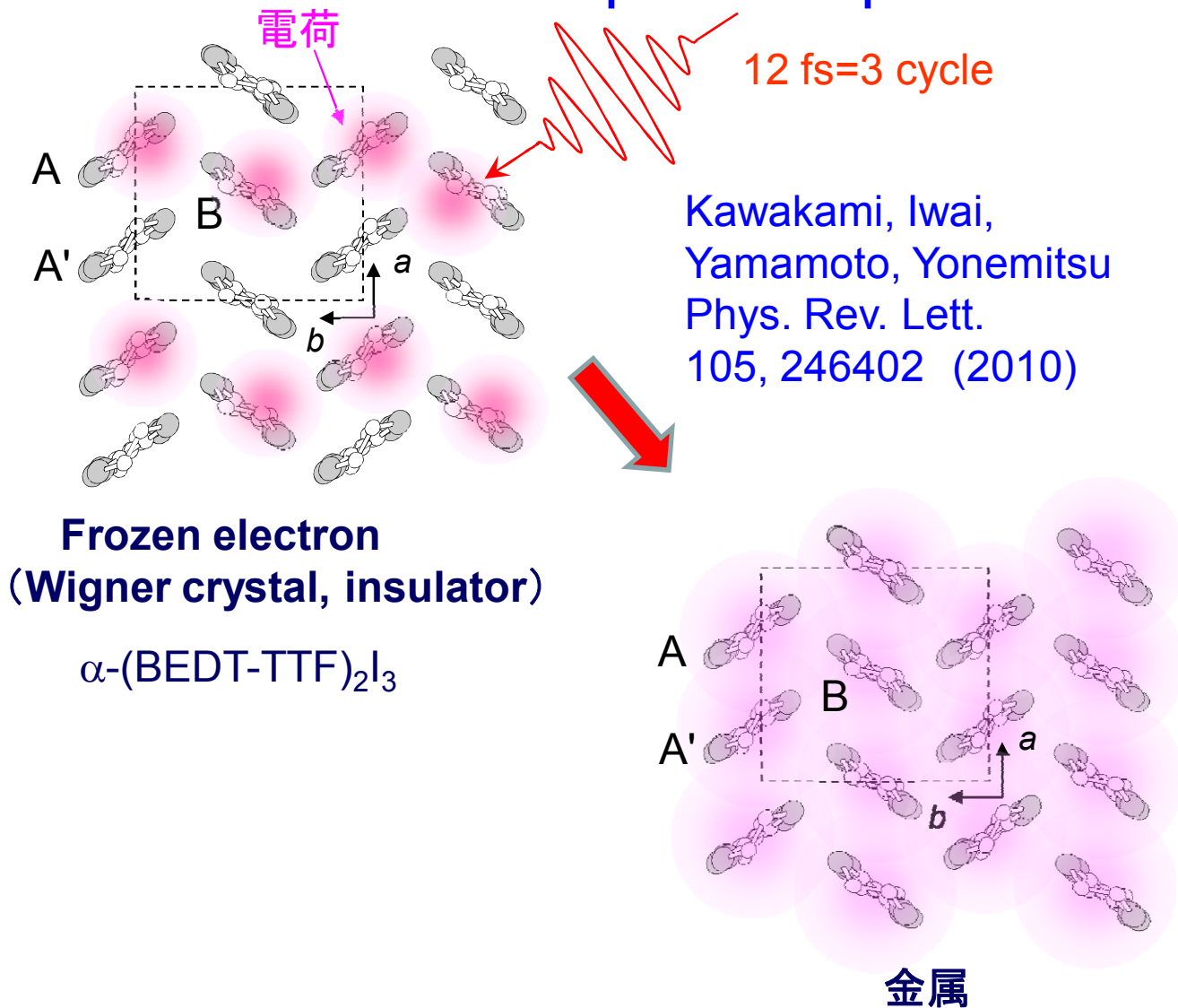
ii) 光による秩序(揺らぎ)の形成は可能か？

光励起-THzプローブ分光

- ・ダイマーモット絶縁体(電子誘電体) κ -(ET)₂Cu₂(CN)₃

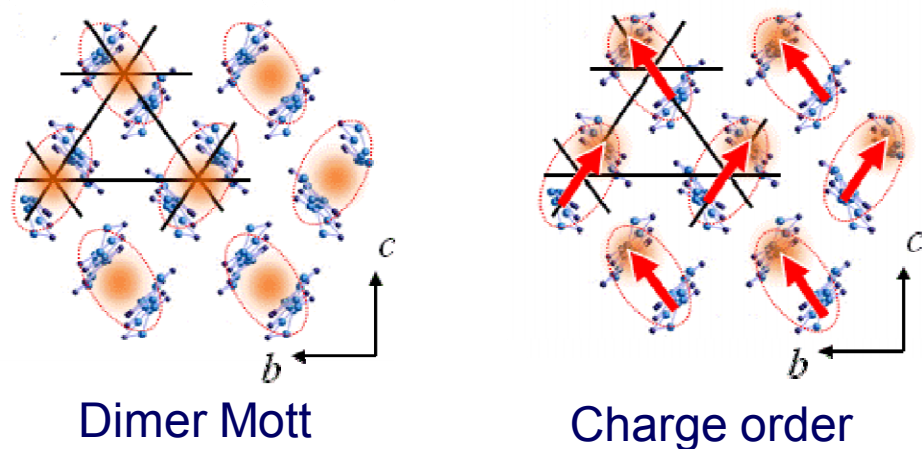
How is the order melted ?

Ultrafast snapshot of photoinduced phase transition



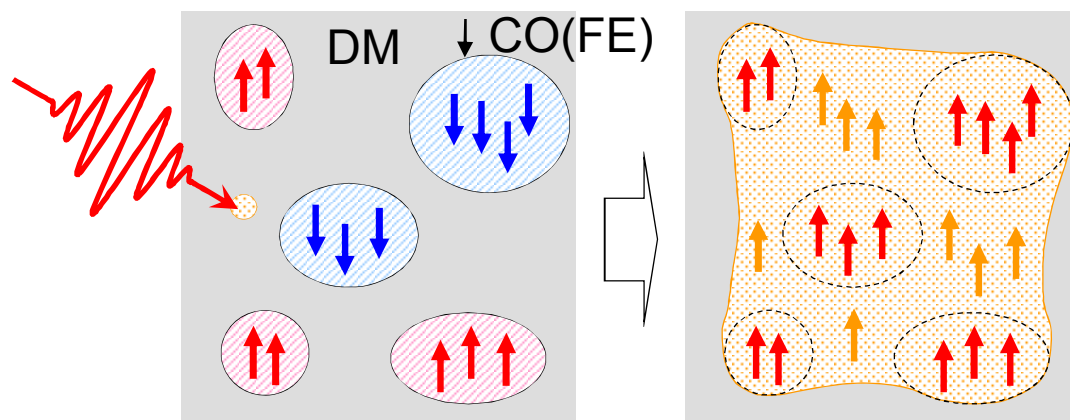
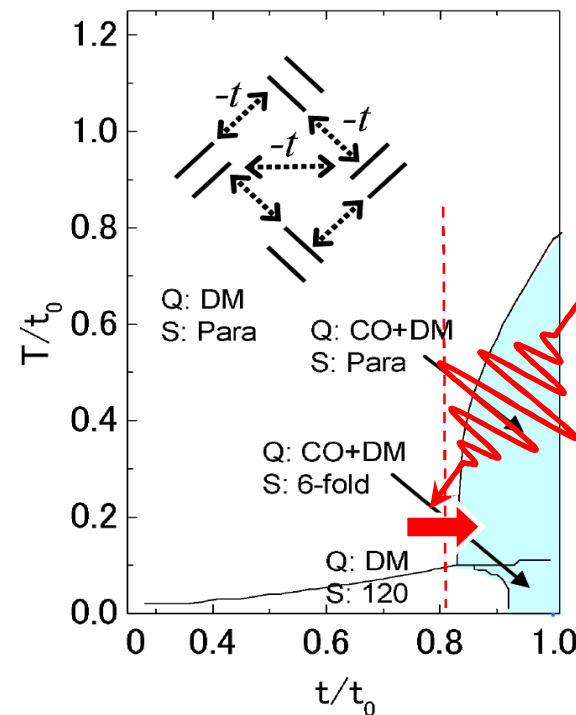
**Melting of frozen electron is
initiated by coherent oscillation of correlated electron !**

Photoinduced ordering is possible ?



Triangular Dimer Mott insulator
 (κ -(BEDT-TTF) $_2$ Cu $_2$ (CN) $_3$)

competition between 2 phases



Collapse of order DM \rightarrow Stabilization of order CO (FE)

Naka, Ishihara
 JPSJ **79**, 063707 (2010).

T. Sasaki (IMR),
 S. Ishihara (Tohoku U.)

Collaborators

Tohoku Univ. Y. Kwakami, T. Fukatsu, Y. Sakurai, H. Unno
H. Nakaya, K. Itoh, H. Itoh

S. Ishihara



Institute of Molecular Science (IMS)
K. Yamamoto, K. Yakushi

K. Yonemitsu



Institute for Material Research (IMR)

T. Sasaki, N. Yoneyama, N. Kobayashi

Thank to K. Iwano (KEK), Y. Shimoi (AIST)
A. Takahashi (Nara), H. Kishida (Nagoya), H. Seo (Riken)
T. Arima (Tokyo University), N. Ikeda (Okayama University)

i) 光による秩序の融解はどのように始まるのか？

極超短パルス光(パルス幅~3光サイクル)によるスナップショット観測

- ・電荷秩序 α -(ET)₂I₃, θ -(ET)₂RbZn(SCN)₄
電子のコヒーレントダイナミクス
- ・ダイマーモット絶縁体 κ -(d-ET)₂Cu[N(CN)₂]Br)
電子-格子結合系の非線形ダイナミクス

ii) 光による秩序(揺らぎ)の形成は可能か？

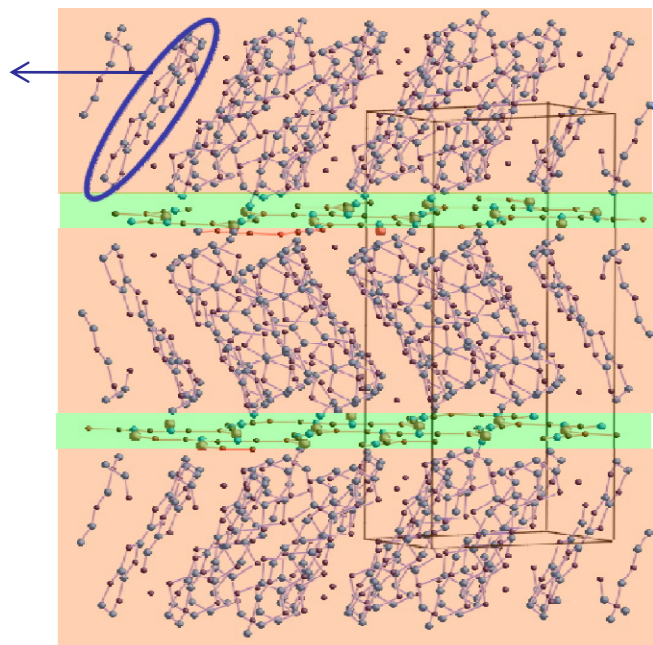
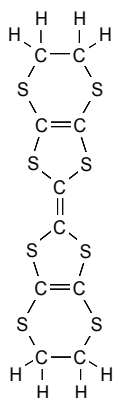
光励起-THzプローブ分光

- ・ダイマーモット絶縁体(電子誘電体) κ -(ET)₂Cu₂(CN)₃

Organic conductors (3/4 filling)

ET (: bisethylenedithio-tetrathiafulvalene)

ビス エチレンジシオ-テトラシアフルバレン

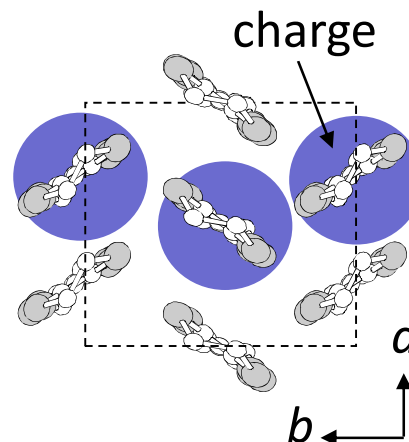


Donor

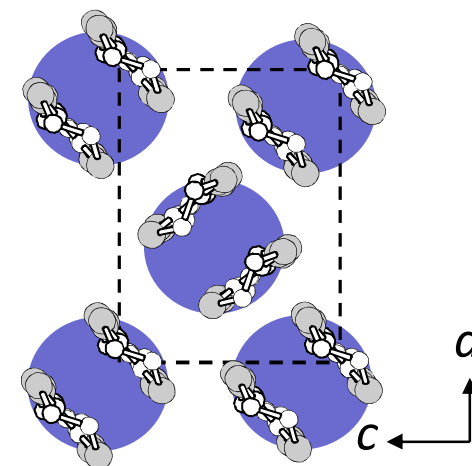
Acceptor

Molecular charge = 0.5

Charge order



Mott insulator



Fukuyama, Seo, Hotta.

D_2A : 3/4 filling

Various phases:

Metal, Charge order, Mott insulator
Ferroelectricity,
Superconductivity

Large responses to light and field

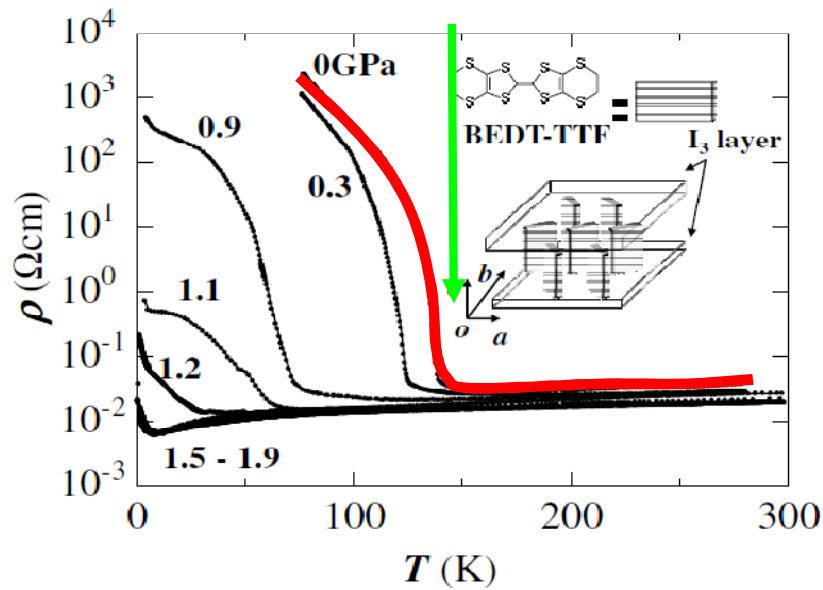
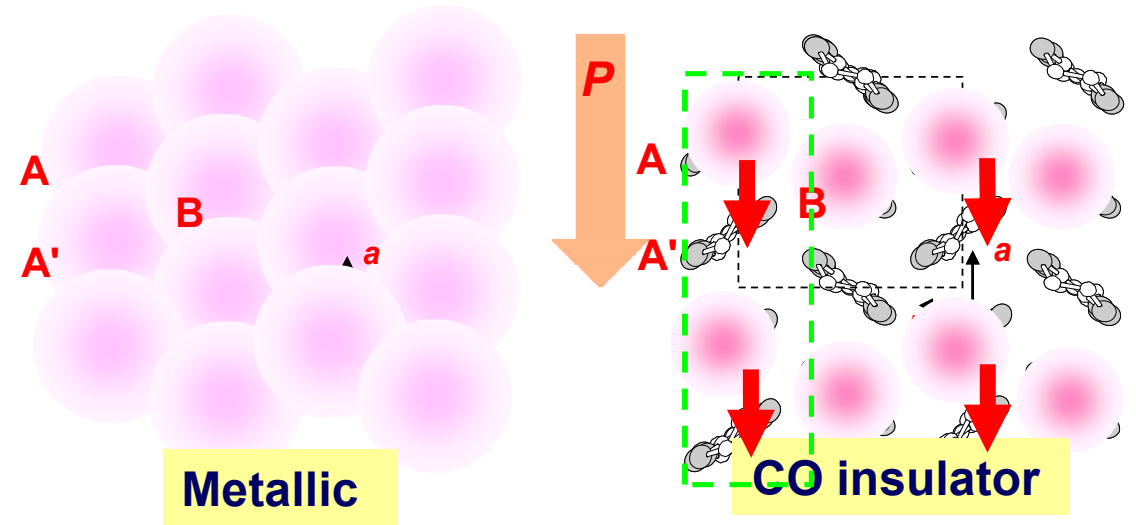
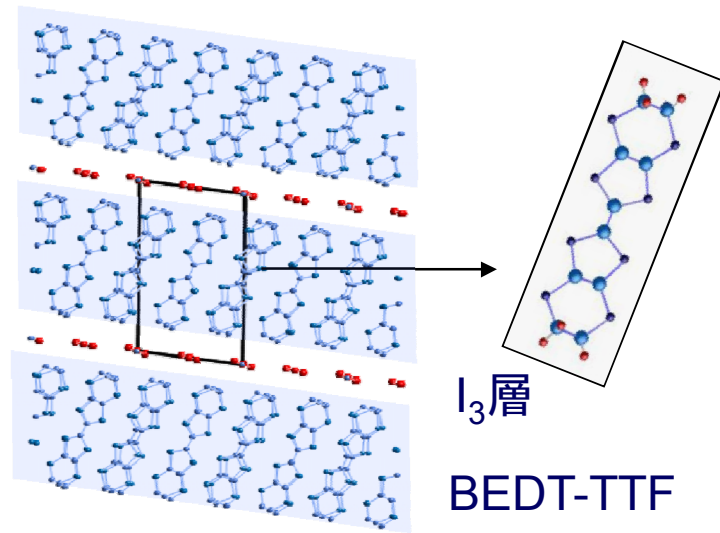
$(EDO-TTF)_2PF_6$ Photoinduced phase transition

Chollet et al., Science **307**, 86 (2005).

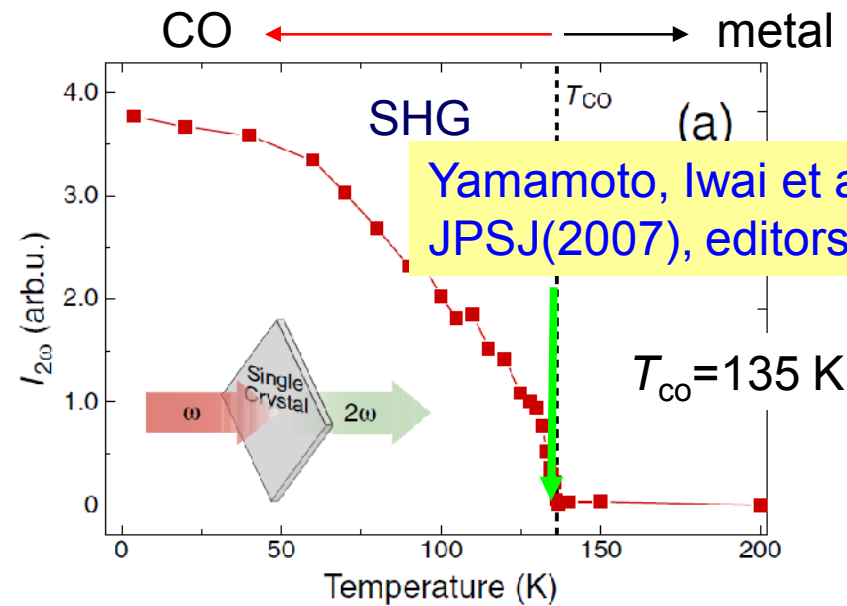
θ - $(ET)_2CsCo(SCN)_4$ Nonlinear conductivity

F. Sawano et al., Nature **437**, 522 (2005).

Ferroelectric charge order (CO-FE) in α -(BEDT-TTF)₂I₃



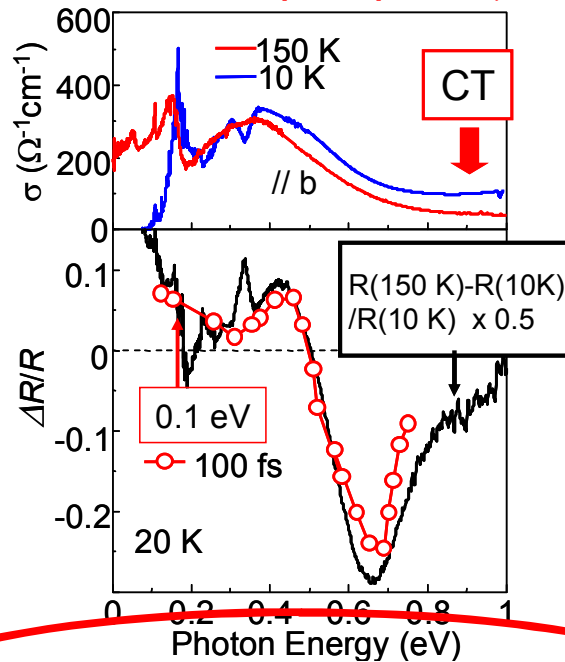
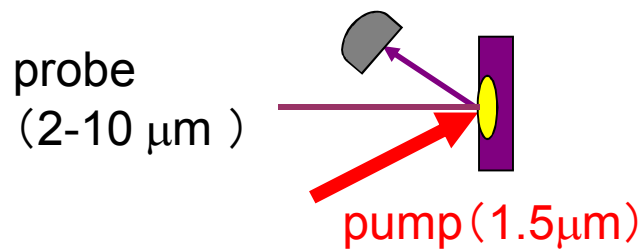
Tajima et al. EPL80,47002(2007)



Electron Ferroelectricity

c.f. (TMTTF)₂X (1-D system) Monceau et al. PRL(2001)

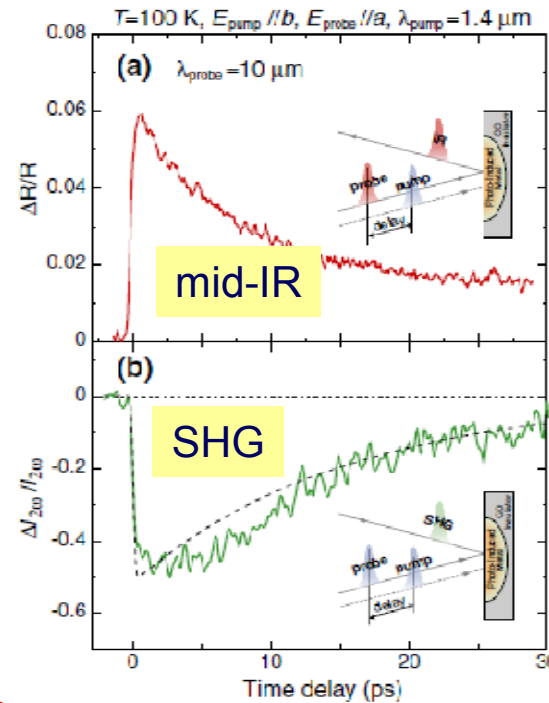
Melting of charge order(CO)—ferroelectricity (FE)



$\eta \sim 50\text{-}100$ molecule/photon

Mid-IR reflectivity

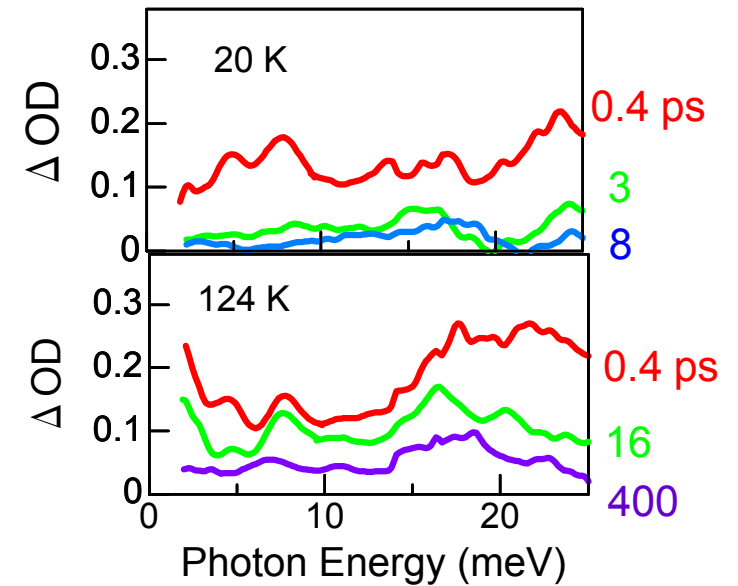
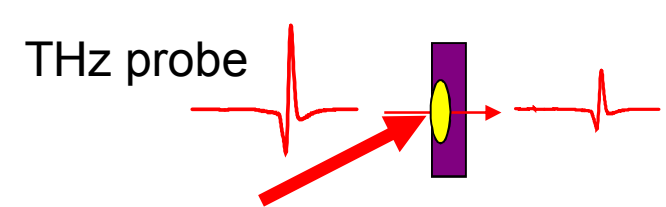
Iwai *et al.*, PRL **98**, 097402 (2007)
PRB **77**, 125131 (2008)



Collapse of FE

SHG probe

Yamamoto *et al.*
JPSJ **77**, 074709 (2008)



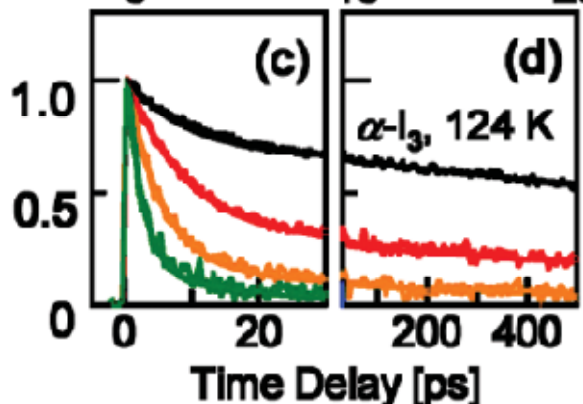
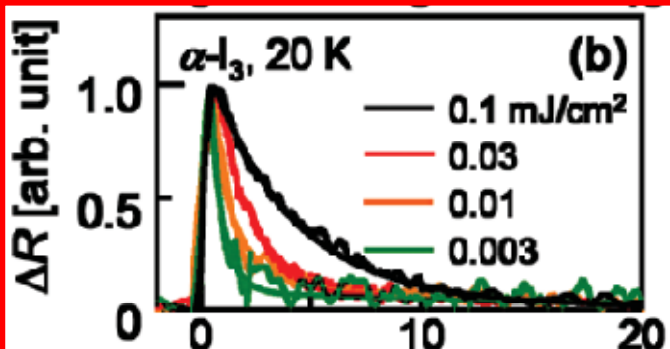
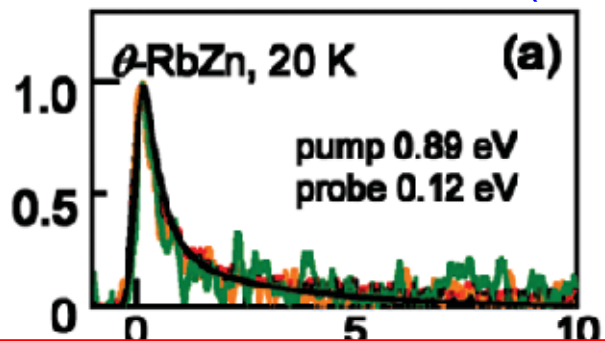
Metallization

THz probe

Nakaya *et al.*
PRB **81**, 155111 (2010)

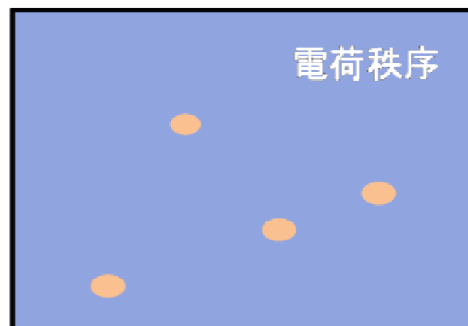
Cooperative and critical nature (α -(ET)₂I₃, θ -(ET)₂RbZn(SCN)₄)

Iwai et al. PRL98, 097402(2007)



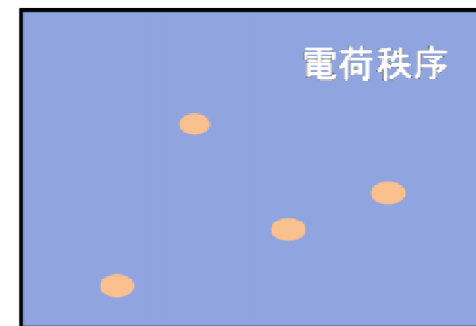
Weak exc. 1 photon/
(0.003 mJ/cm²) \sim 15000 molecule

α -(ET)₂I₃

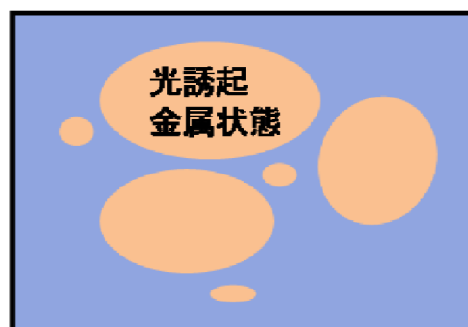


短寿命(\sim ps)

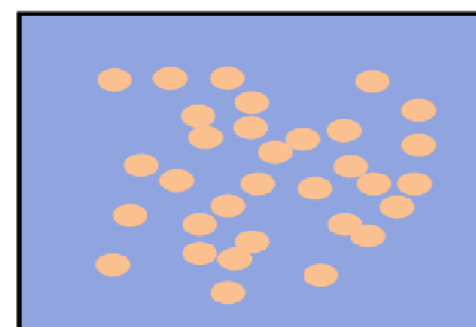
θ -(ET)₂RbZn(SCN)₄



短寿命(\sim ps)



長寿命(\sim ns)

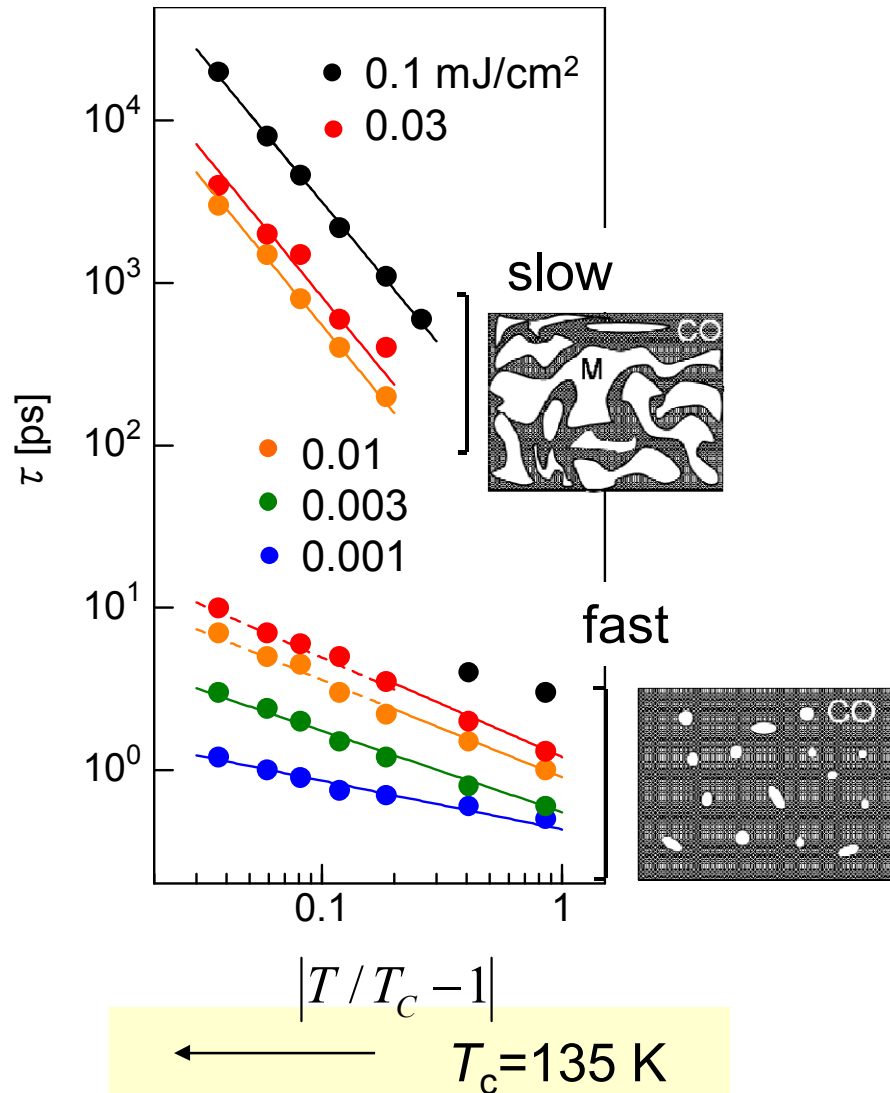


短寿命(\sim ps)

Strong exc. 1 photon/
(0.1 mJ/cm²) \sim 500molecule

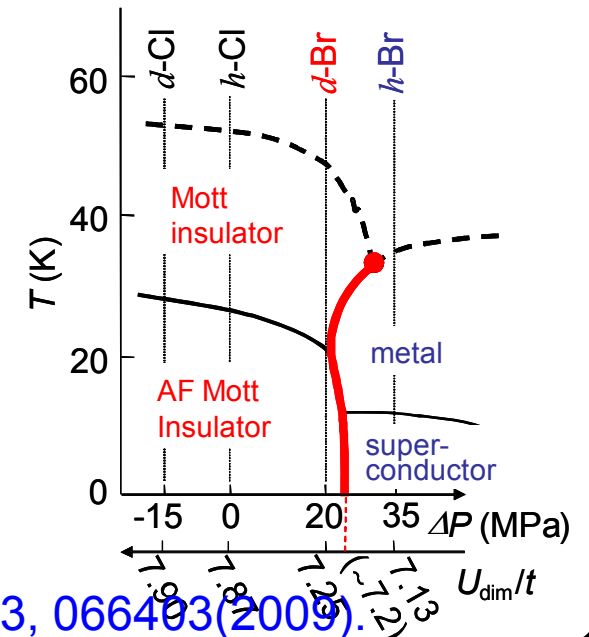
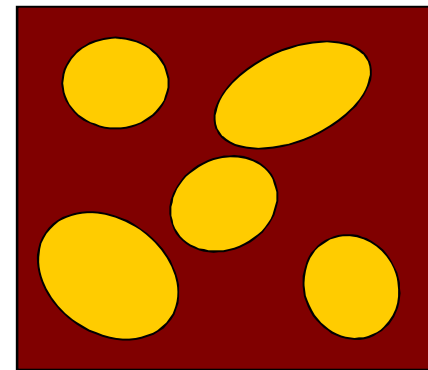
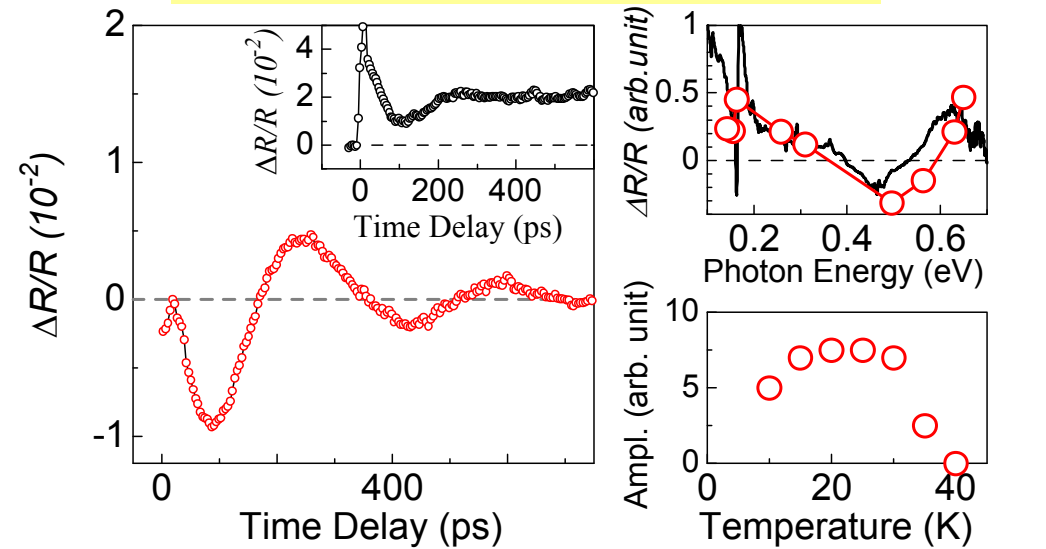
Slower dynamics of Photo-induced metallic state

α -I₃; Critical Slowing



Iwai et al. PRL98, 097402(2007)

κ -(d-Br): DW oscillation

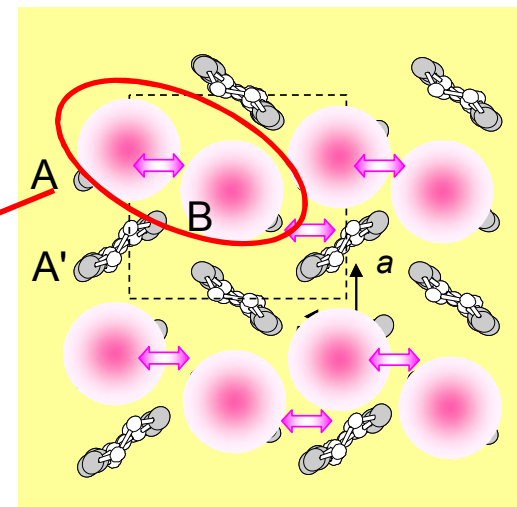
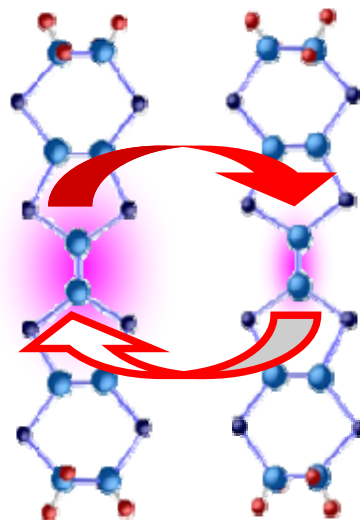


Kawakami et al. PRL103, 066403(2009).

Objective; Capture the primary dynamics of PIMT

i) Intermolecular electron motion

- Time scale \rightarrow 20~40 fs
(CO gap 0.1-0.2 eV)



II) Intramolecular vibration

- C=C stretching vibration ($1300-1500\text{ cm}^{-1}$) (ν_3)

Electron-Molecular Vibration (EMV) coupling

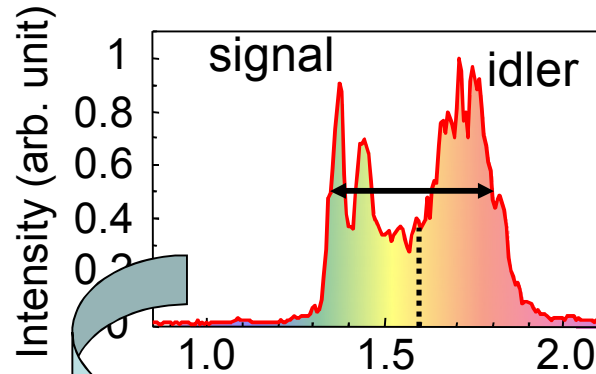
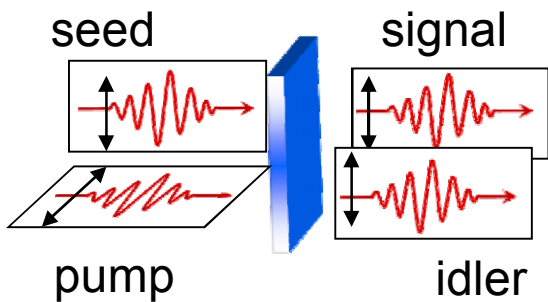
- period \sim 20 fs



10 fs pulse in IR region (few-optical-cycle)

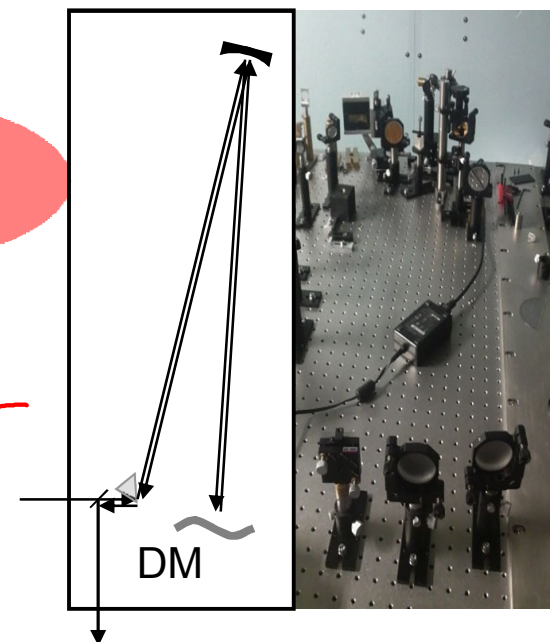
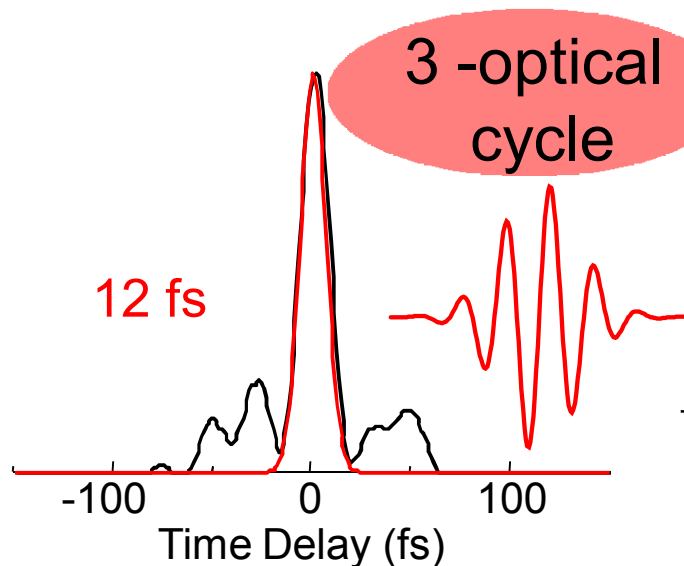
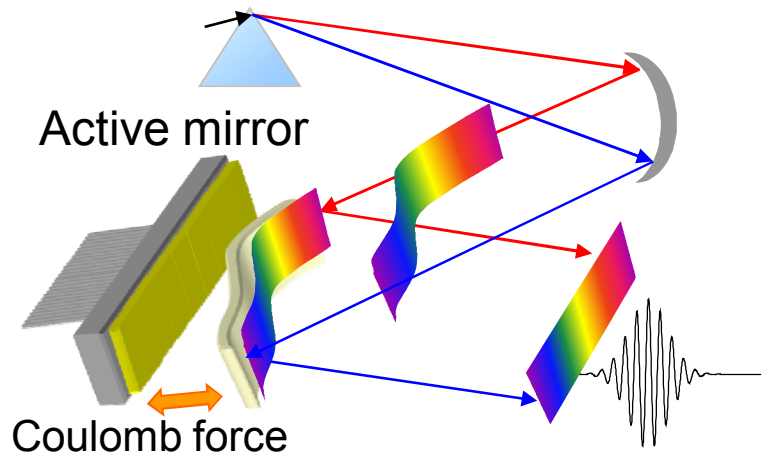
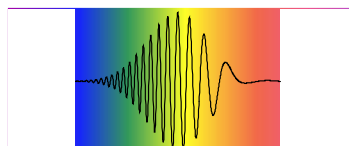
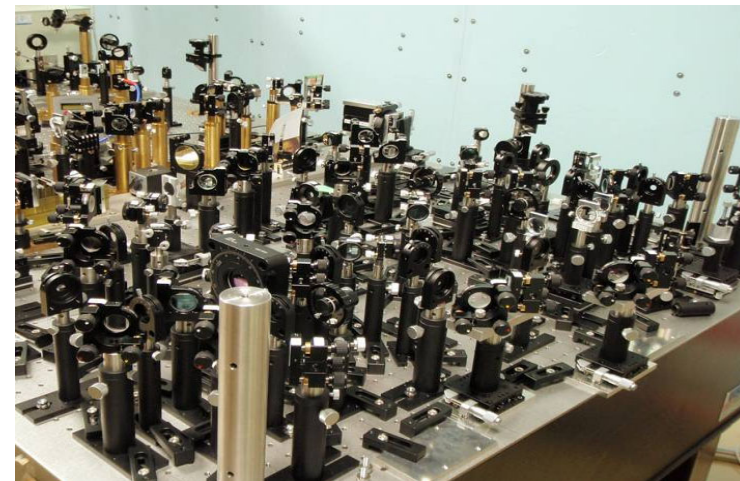
Technical issue; Super broadband (1~2 μm) OPA

Degenerate OPA (type1 BBO)

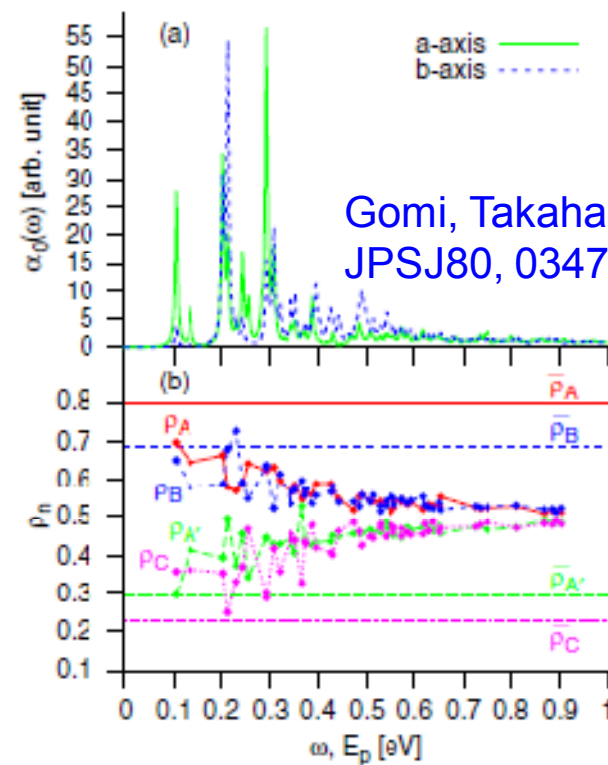
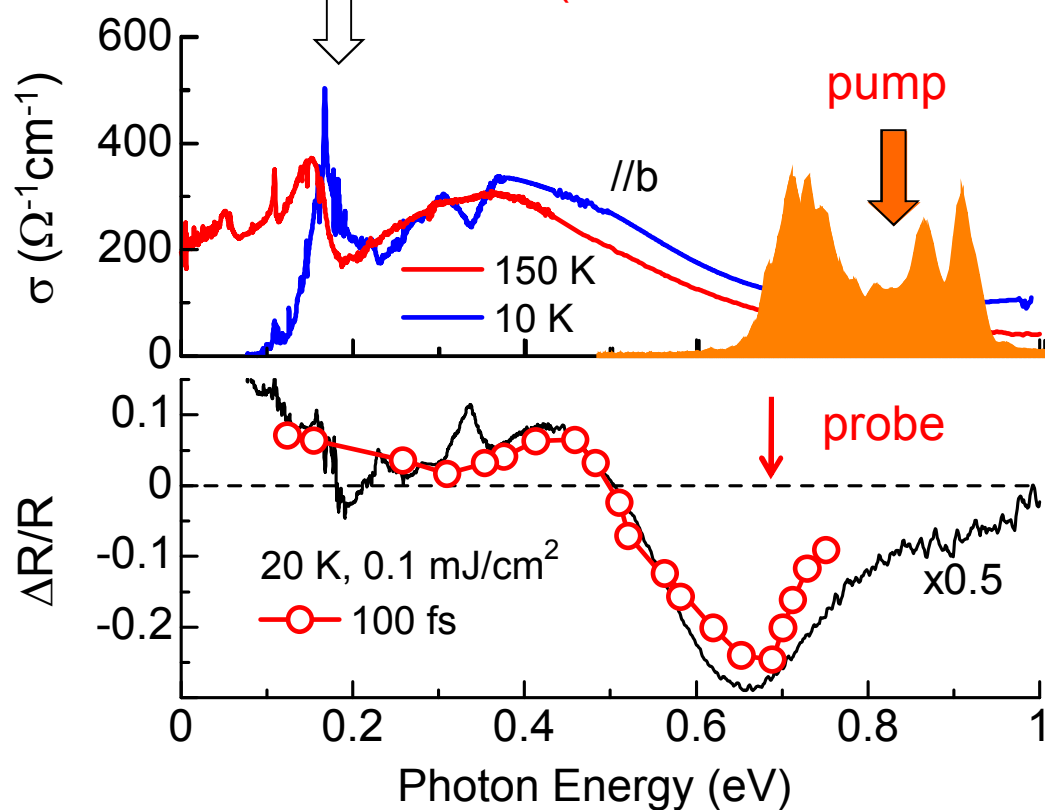
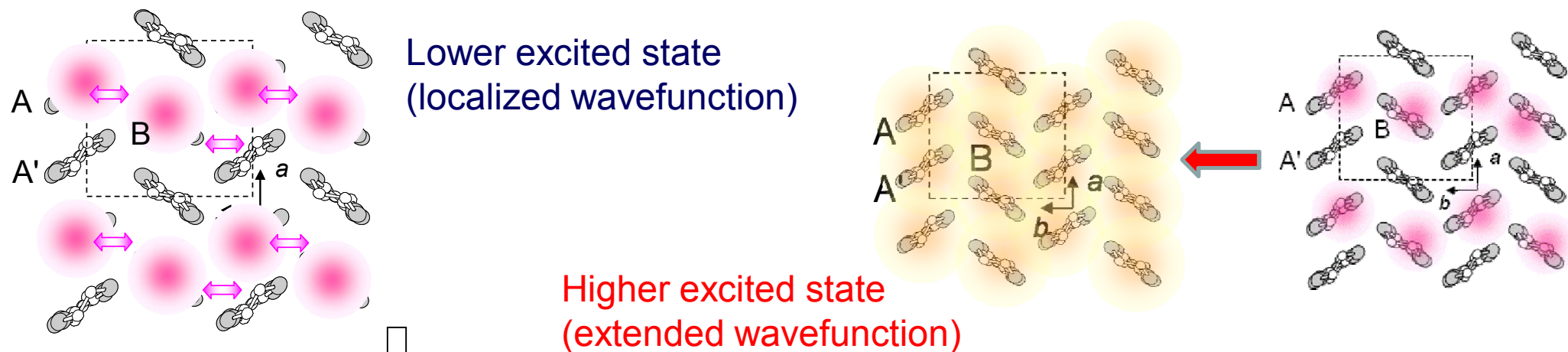


Brida *et al.*, *Opt. Lett* **33**, 741 (2008)

Transform limited
~ 8 fs

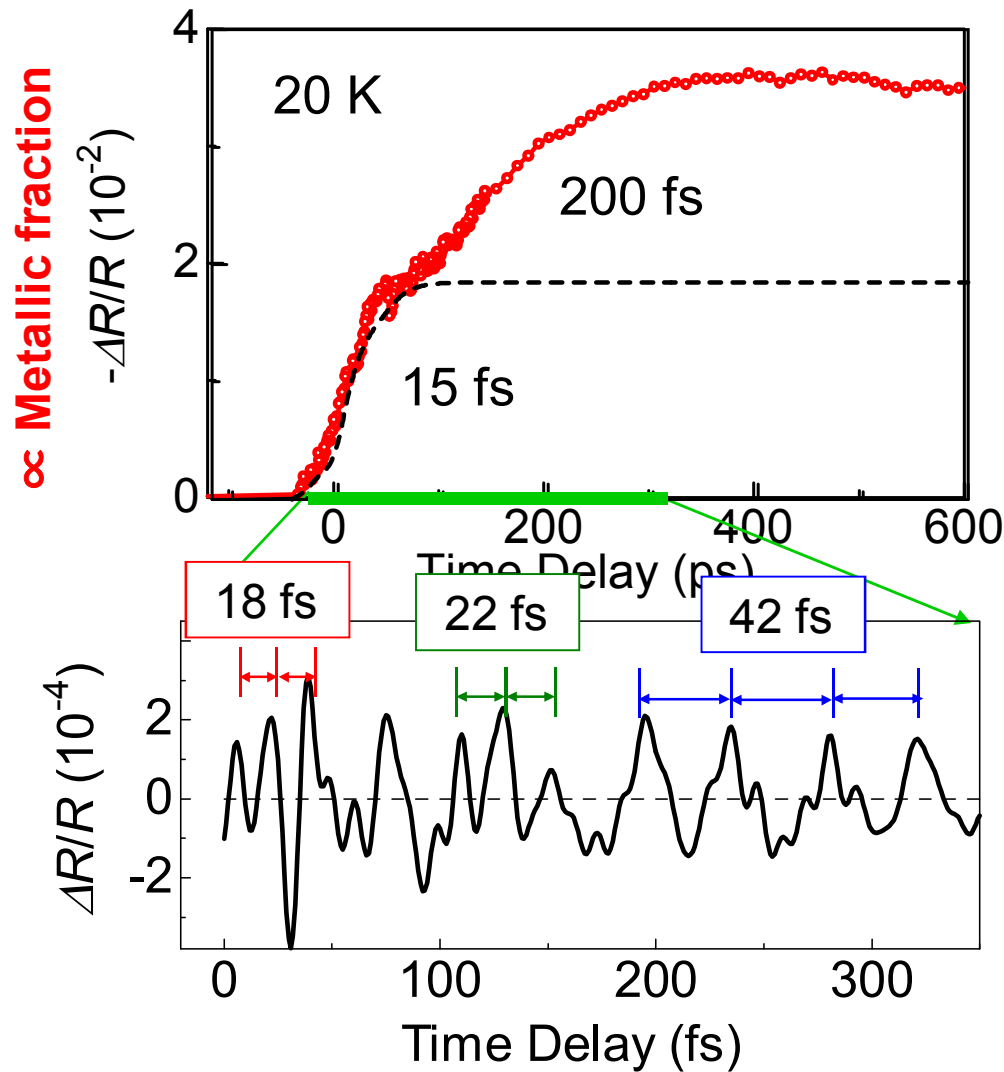


Few-optical cycle spectroscopy of PIMT in α -(BEDT-TTF) $_2$ I $_3$

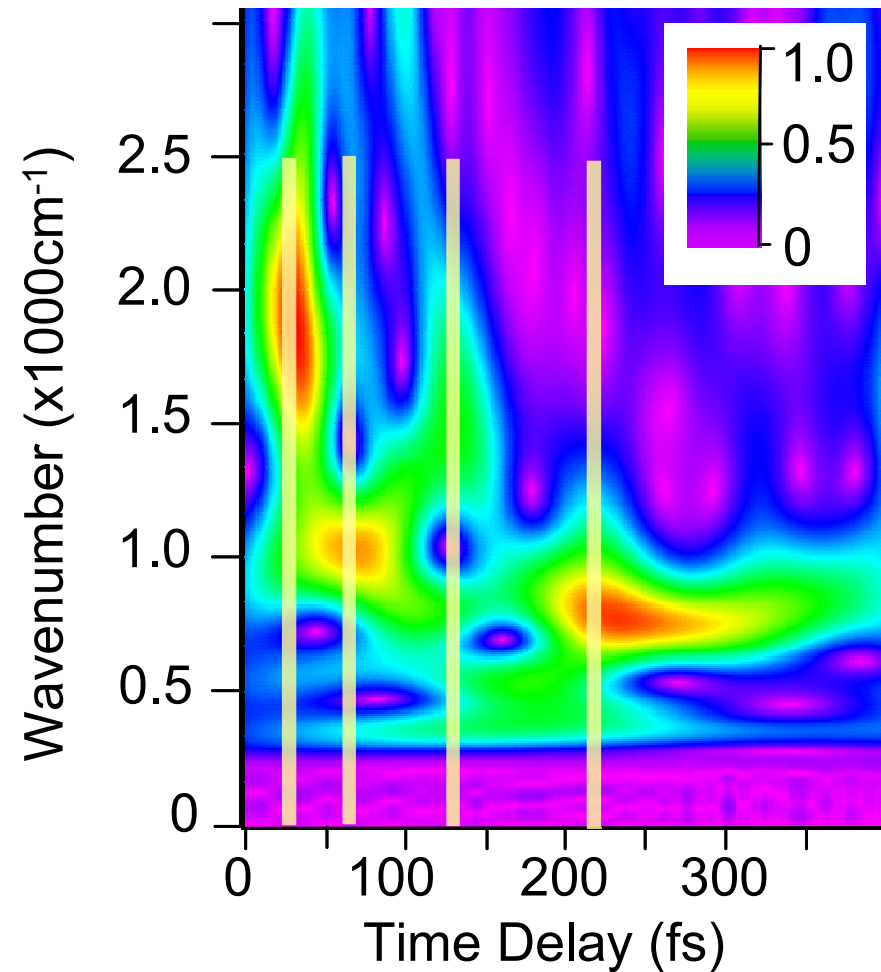


Gomi, Takahashi et al.
JPSJ80, 034709(2011).

High-frequency oscillations



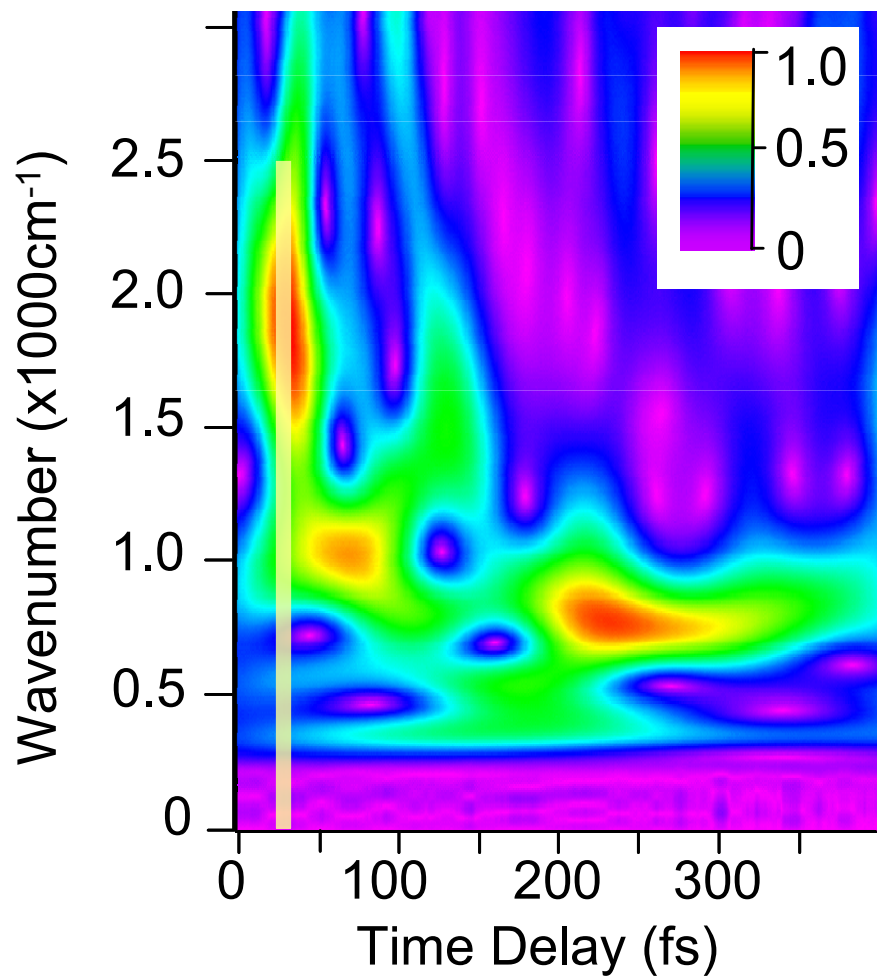
Spectrogram (Wavelet analysis)



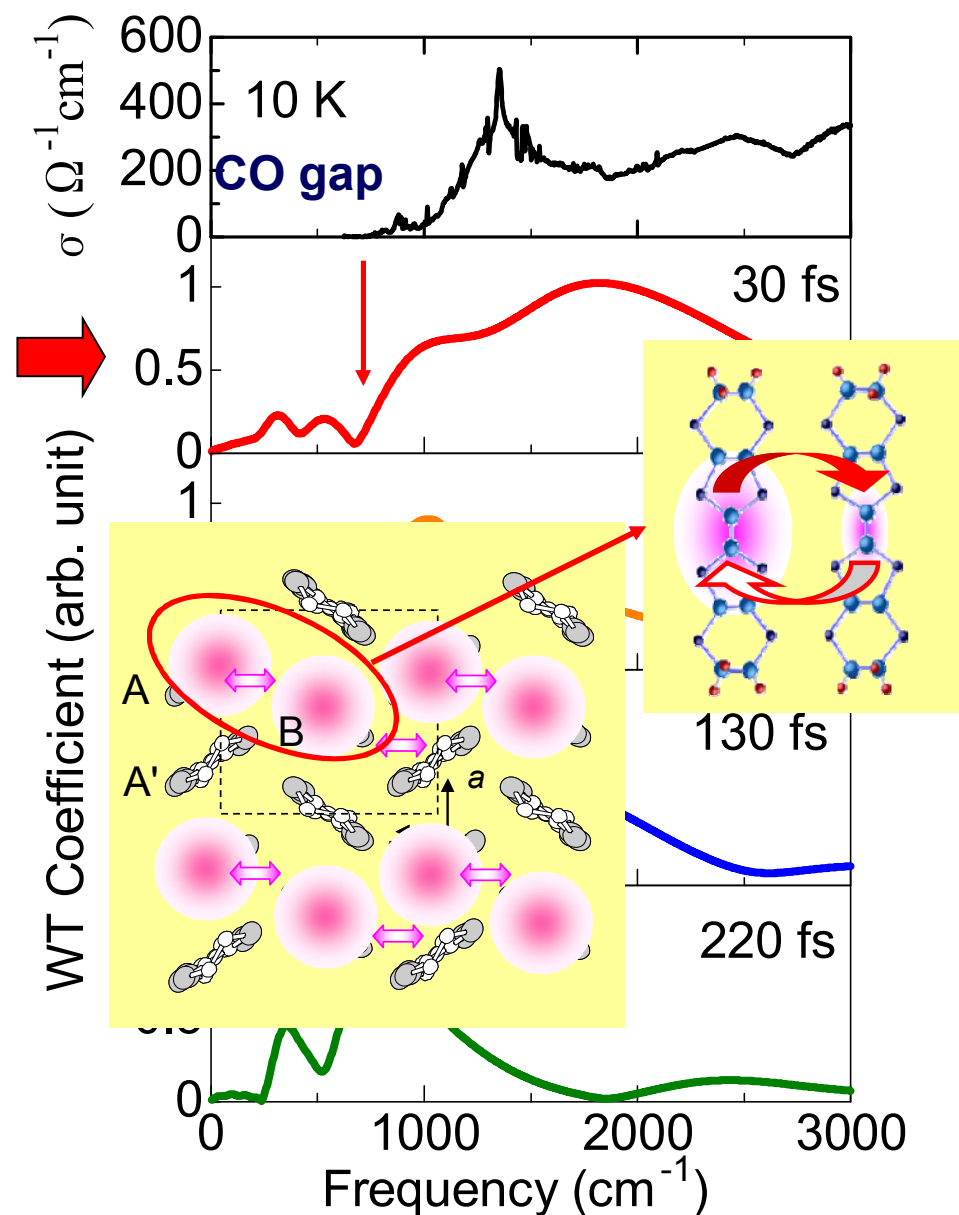
Real-time dynamics of electron and vibrations

< 50 fs Electron oscillation

Spectrogram (wavelet analysis)

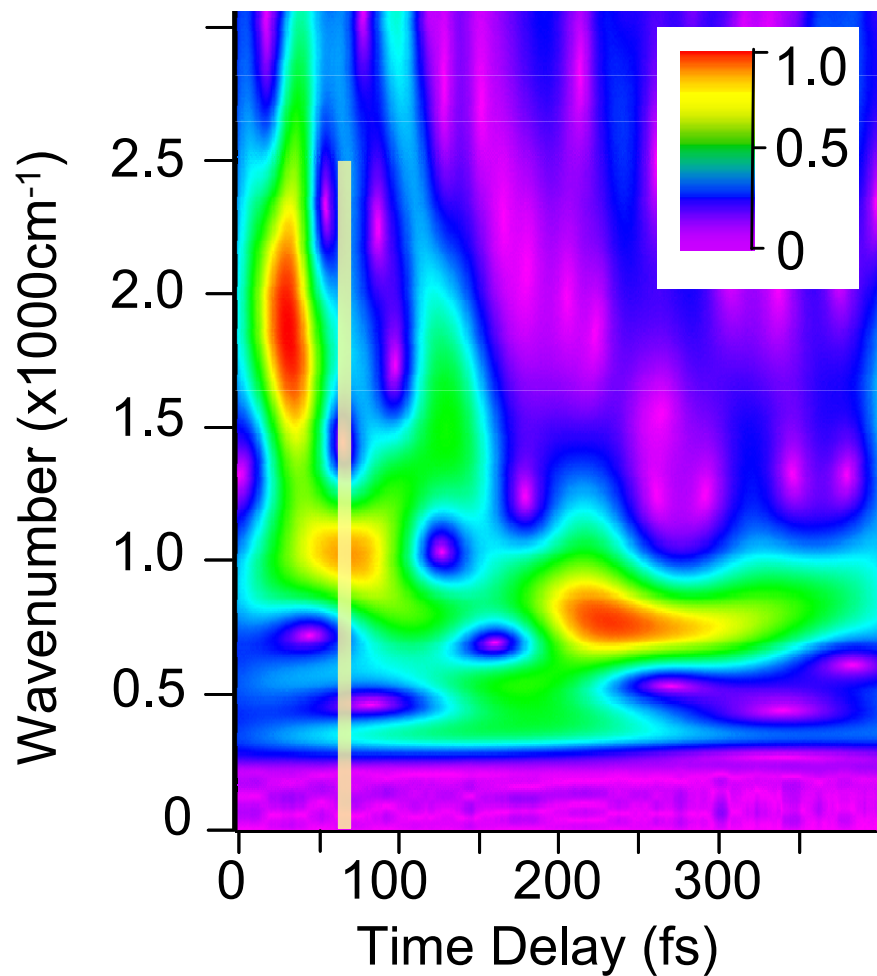


$\sim 1800 \text{ cm}^{-1}$ broad spectrum
Coherent electron oscillation (CO gap)

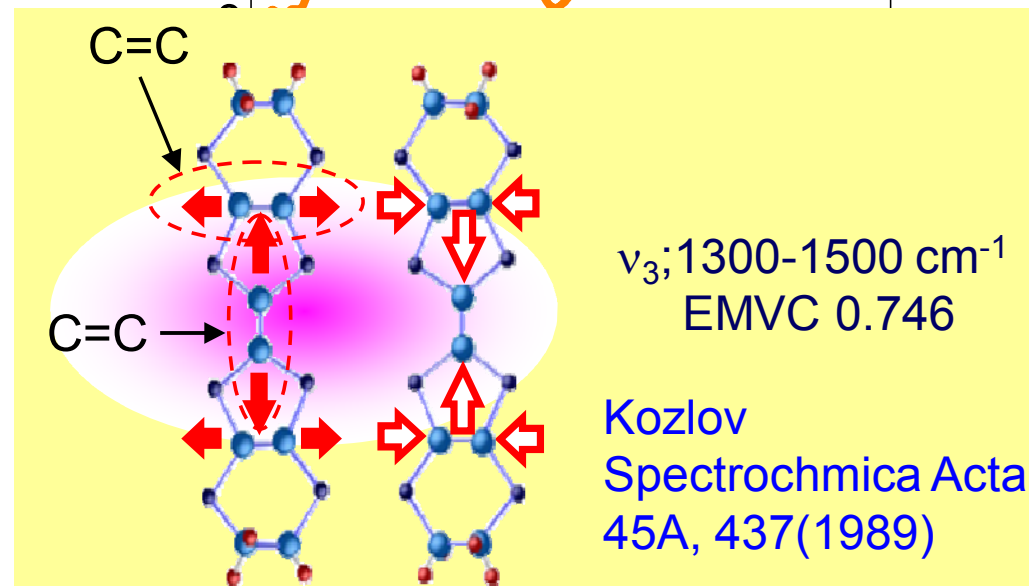
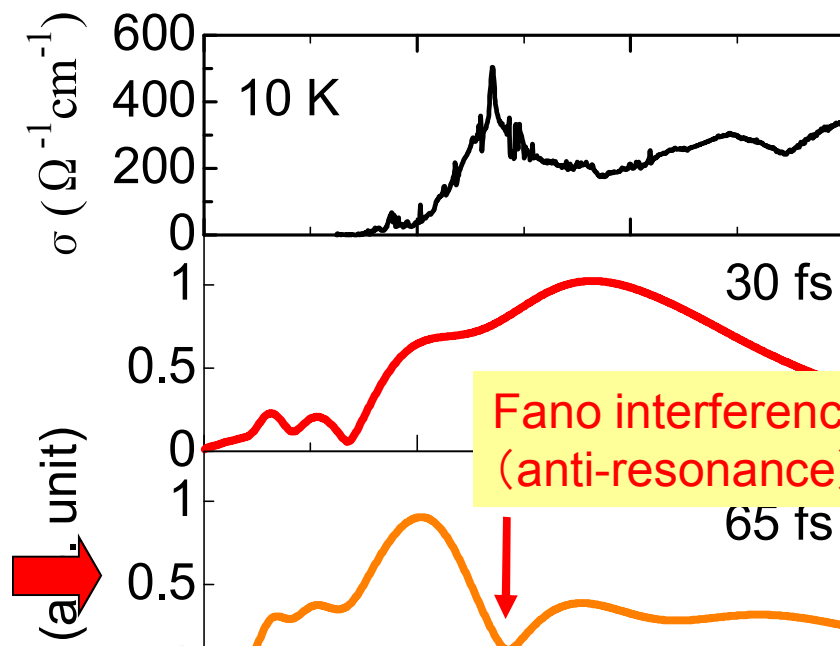


50-100 fs Fano-interference (electron and vibration)

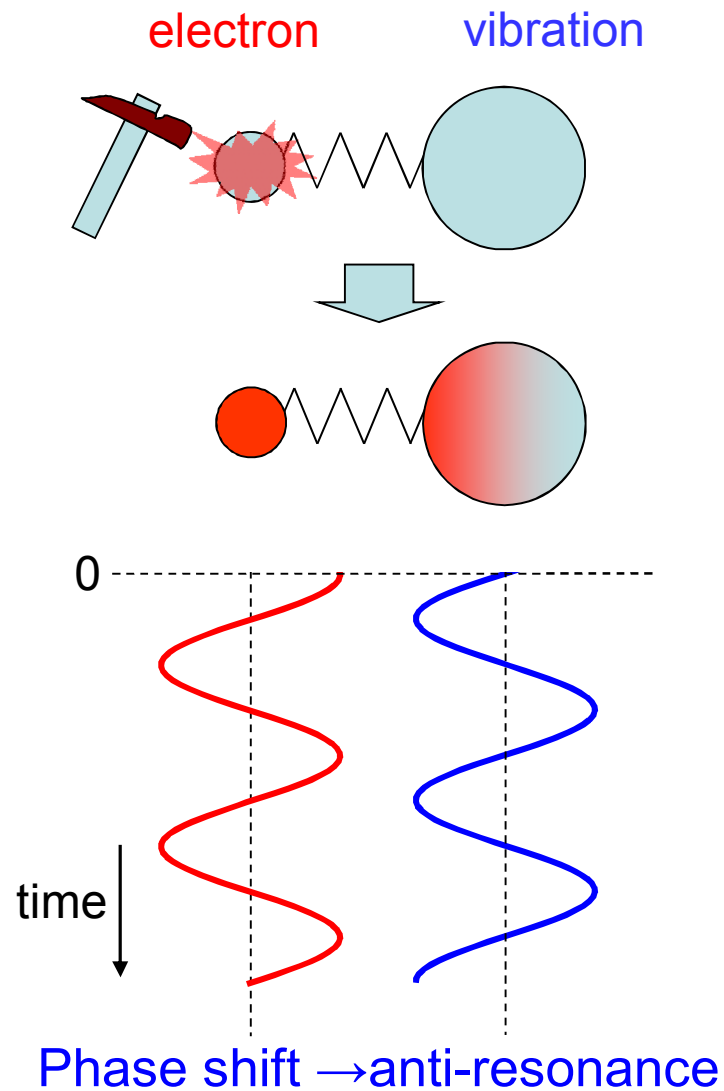
Spectrogram (wavelet analysis)



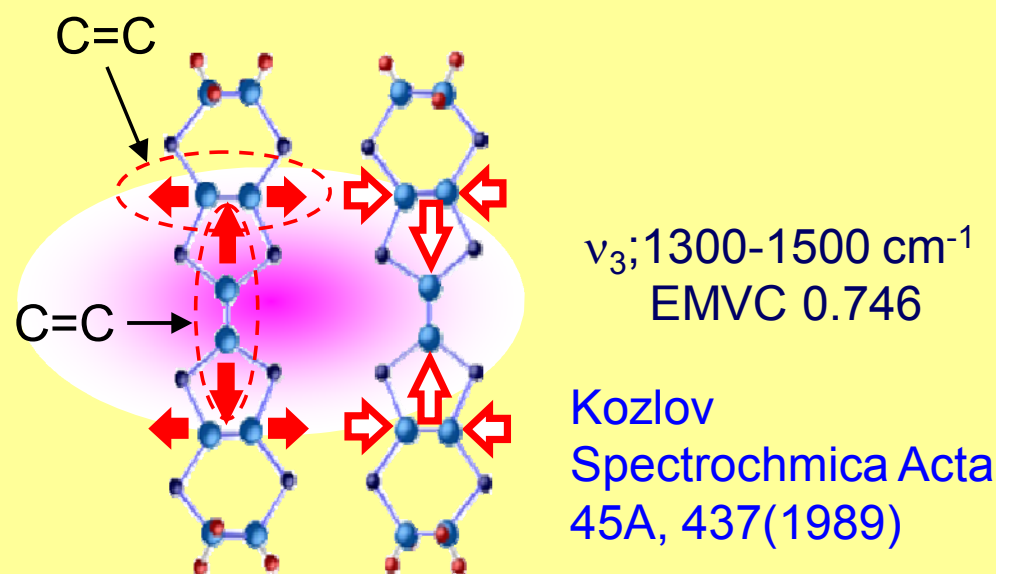
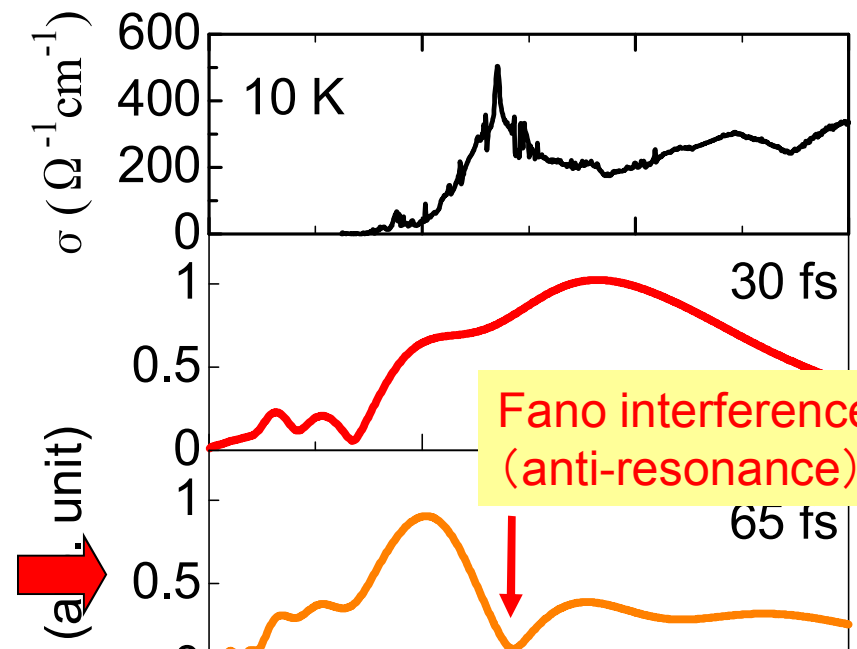
- Fano (anti-resonance)
- C=C stretching vibration



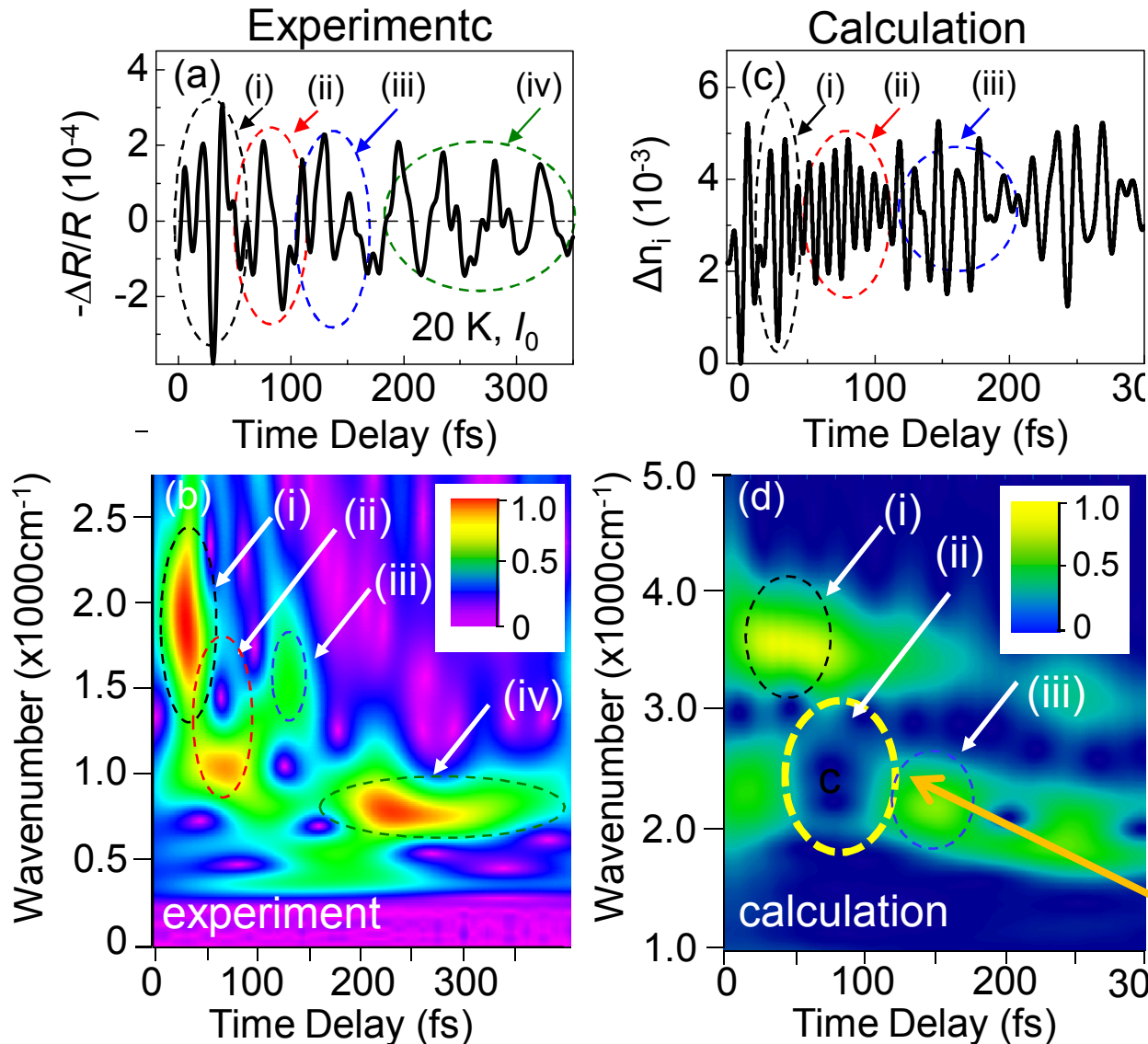
50-100 fs Fano-interference (electron and vibration)



- Fano (anti-resonance)
- C=C stretching vibration



Numerical calculation of time-dependent Schrödinger equation (K. Yonemitsu)



Extended Peierls–Hubbard model

$$\begin{aligned}
 H = & \sum_{(ij)\sigma} [(t_{i,j} \pm \alpha_{i,j} u_{i,j}) e^{i(e/\hbar c) \delta_{i,j} \cdot A(t)} c_{i\sigma}^\dagger c_{j\sigma} + \text{H.c.}] \\
 & + U \sum_i n_{i\uparrow} n_{i\downarrow} + \sum_{(ij)} V_{i,j} n_i n_j + \sum_{(ij)} \frac{K_{i,j}}{2} u_{i,j}^2 \\
 & + \sum_{(ij)} \frac{K_{i,j}}{2\omega_{i,j}^2} \dot{u}_{i,j}^2,
 \end{aligned}$$

Electron;

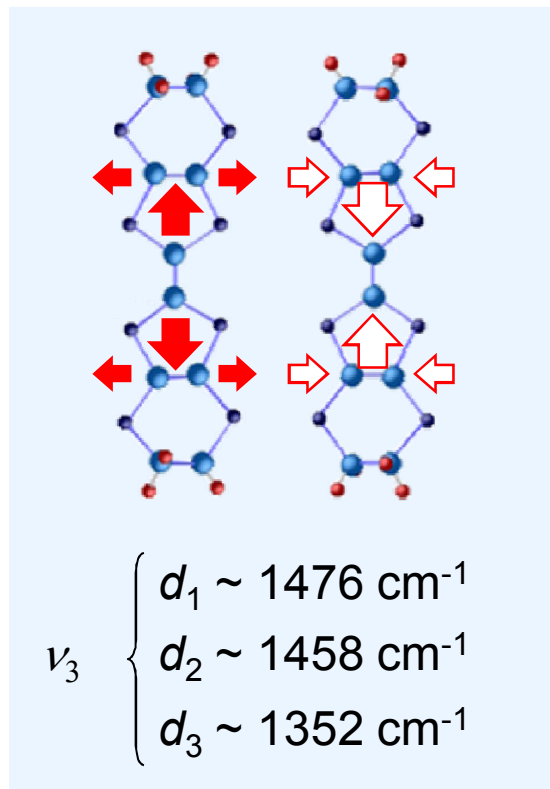
exact many-body wave function

Quantum intramolecular phonon (ν_3 mode)

for 8-site periodic cluster

Destructive interference !

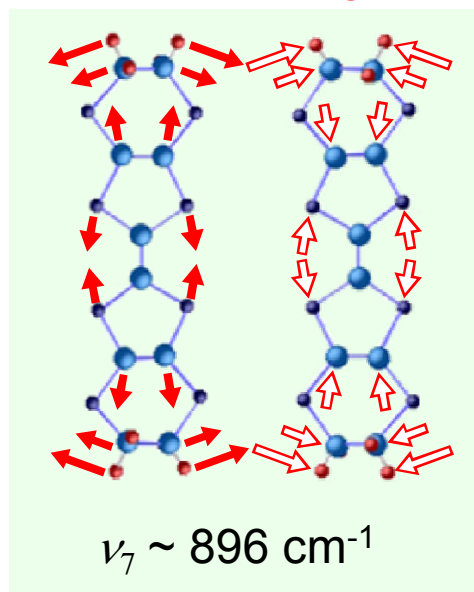
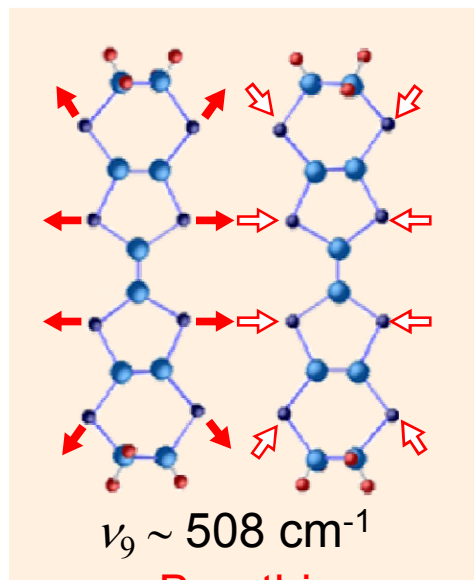
Electron Molecular Vibration (EMV) Coupling



C=C stretching

Wojciechowski et al.
PRB 67, 224105 (2003)

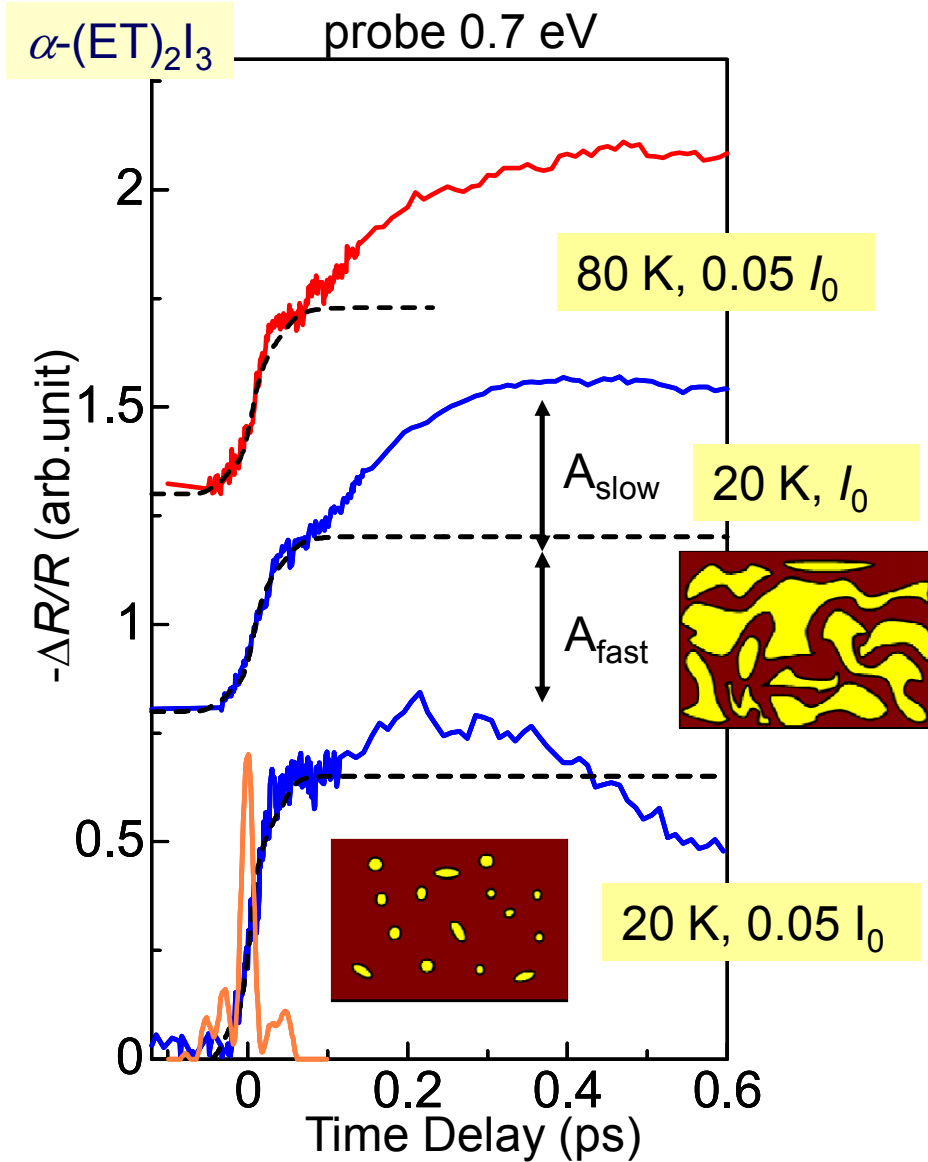
Kozlov et al.
Spectrochim. Acta.
45A, 437 (1989)



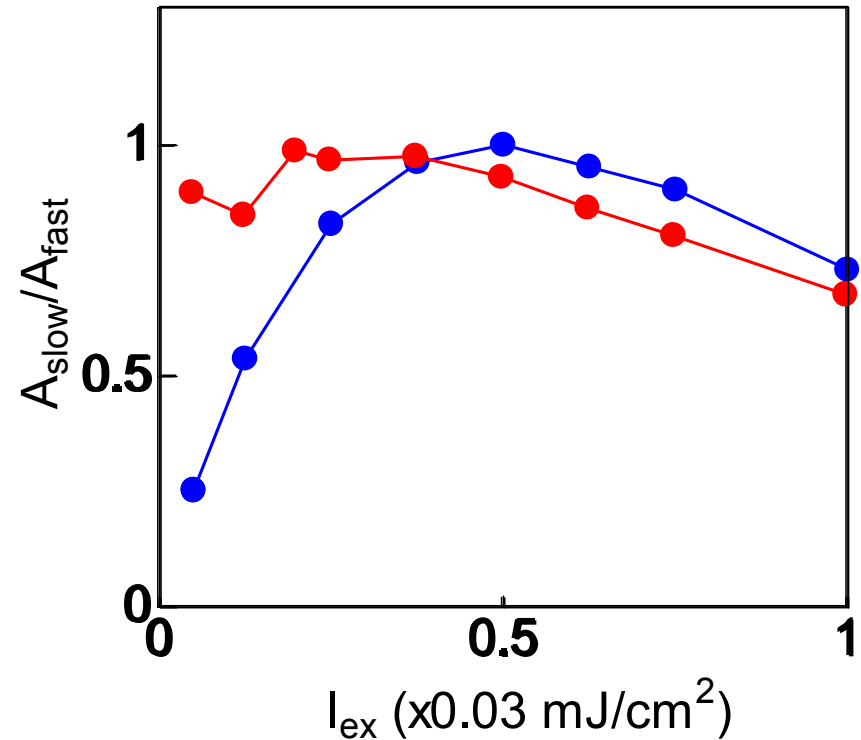
モード	Coupling constant	
ν_3	0.746	大
ν_9	0.476	
ν_8	0.192	
ν_2	0.165	
ν_6	0.140	
ν_7	0.117	
ν_4	0.102	
ν_5	0.063	
ν_{10}	0.050	
ν_{12}	0.041	
ν_{11}	0.025	
ν_1	0.022	小



Excitation intensity (I_{ex}) & temperature dependences



$I_0 = 0.03 \text{ mJ/cm}^2$
1 photon/1500 molecules



20 K; A_{slow}/A_{fast} increases with I_{ex}

80 K; Large A_{slow}/A_{fast} even at small I_{ex}

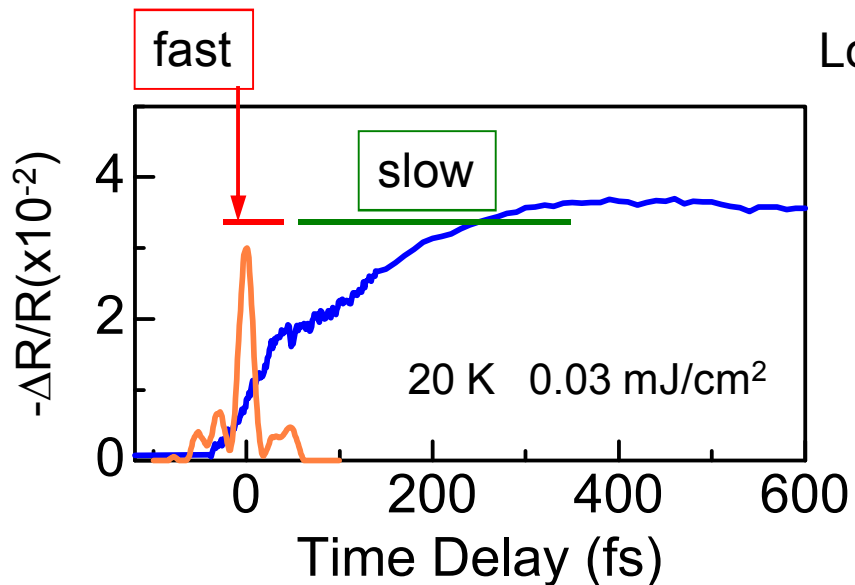
15 fs; ~ time scale of CT

→ electronic melting of CO, nucleation

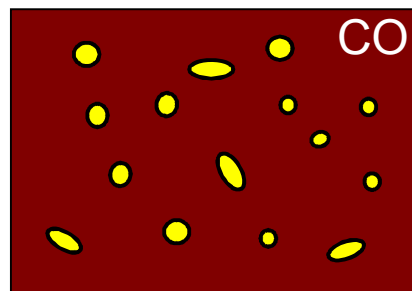
300 fs rise ;

cooperative and critical natures
condensation and multiplication

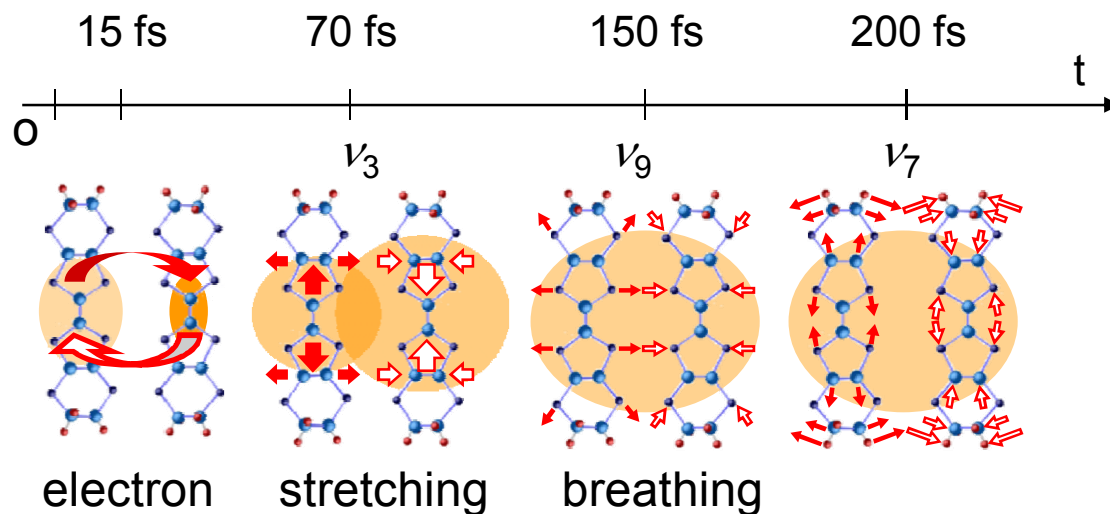
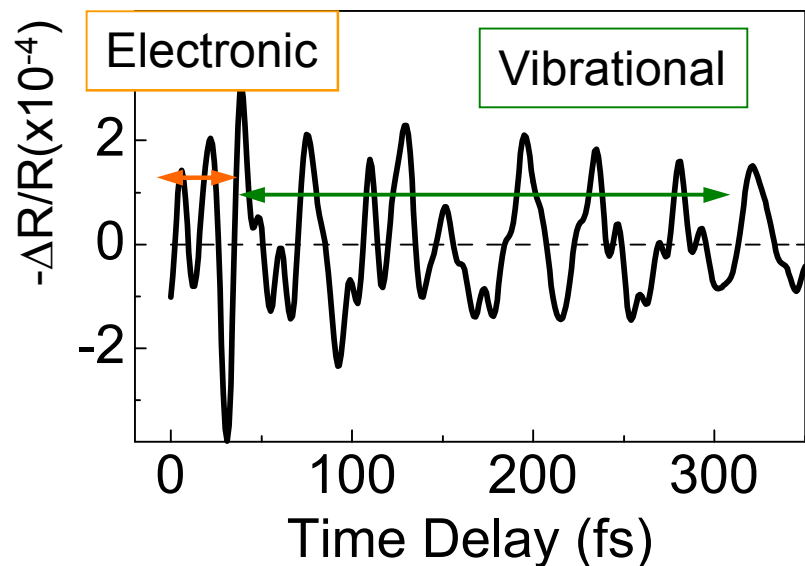
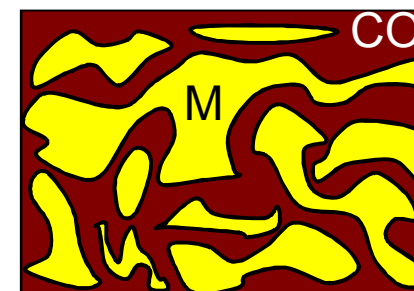
Roles of electronic and vibrational oscillations in PIMT



Local melting of CO
(nucleation) 15 fs

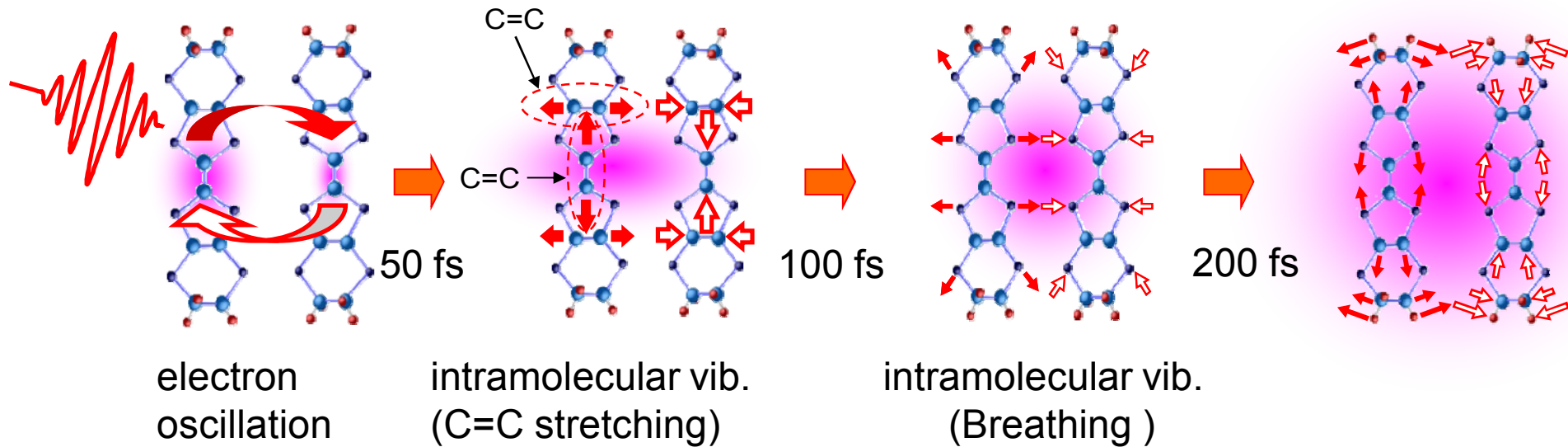


Cooperative condensation
300 fs



15 fs Electronic process; nucleation
 ~ 300 fs interplay with vibrations; condensation

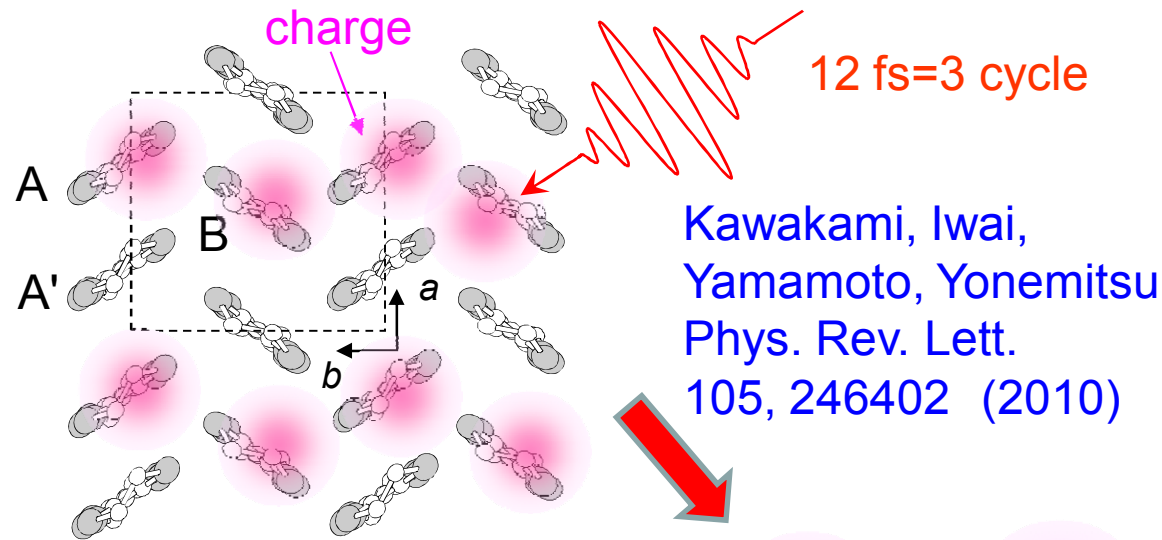
Sequential changes of interacting vibrational modes



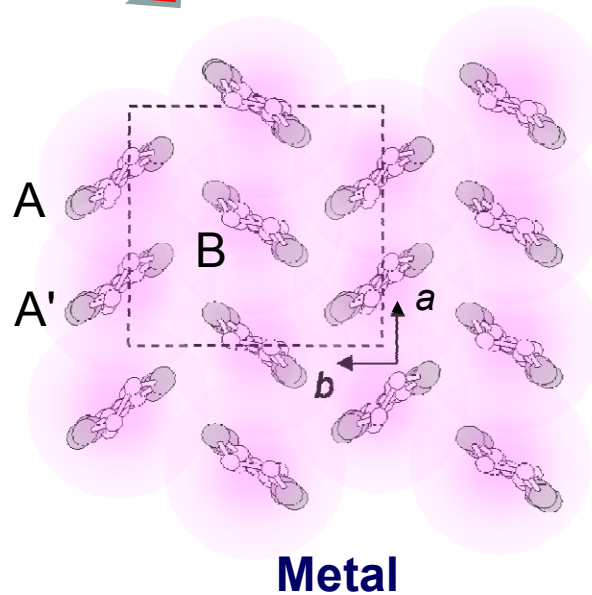
local (ν_3 C=C stretching) \rightarrow delocalized (ν_9 breathing, ν_7)

Local (insulator) \rightarrow delocalized (metal)

Ultrafast snapshot of photoinduced I-M transition



Wigner crystal, Insulator

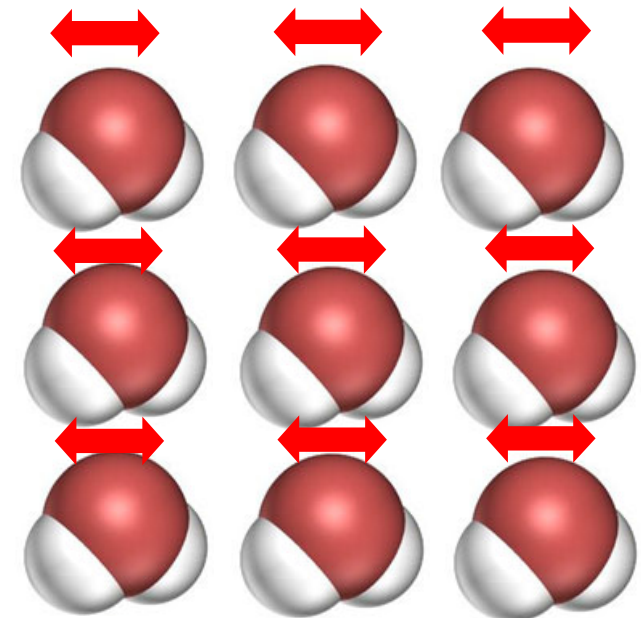


**Melting of CO is initiated by
coherent oscillation of correlated electron !**

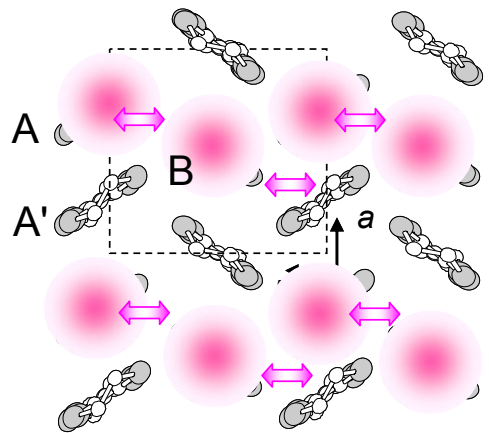
Microwave oven (2.45 GHz)



H₂O



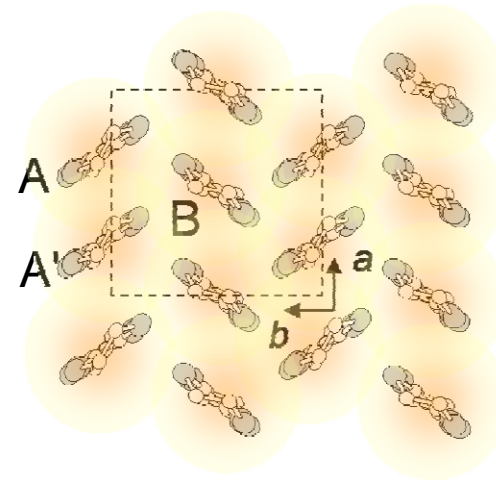
Problem: e-e interaction in photoexcited states



Lower excited state
(localized wavefunction)

correlated electron osc.
~ 18 fs oscillation

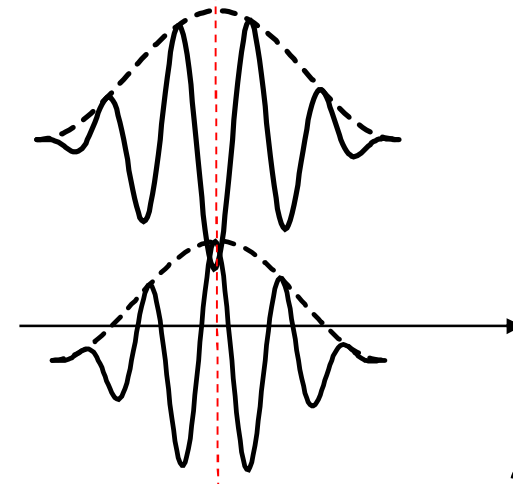
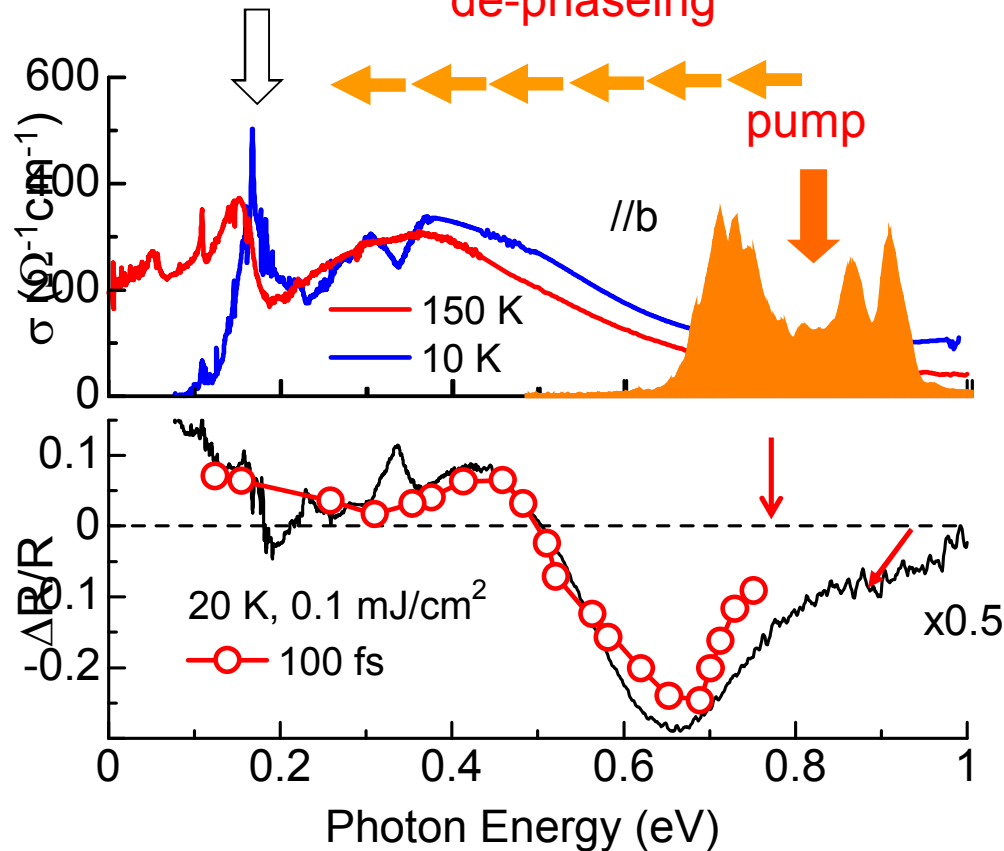
electron relaxation
de-phasing



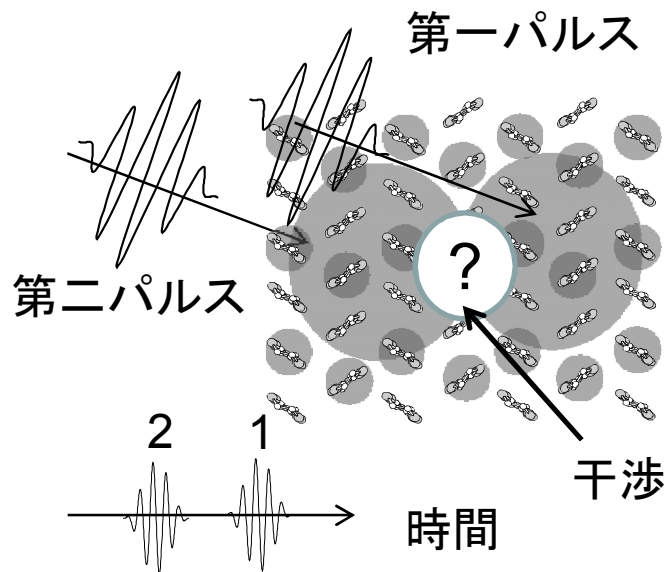
Higher excited state
(extended wavefunction)

electronic polarization
~ 4 fs oscillation

CEP(carrier-envelope phase)



コヒーレント制御; 光誘起相転移から物質の光操作へ モノサイクル化とCEP制御

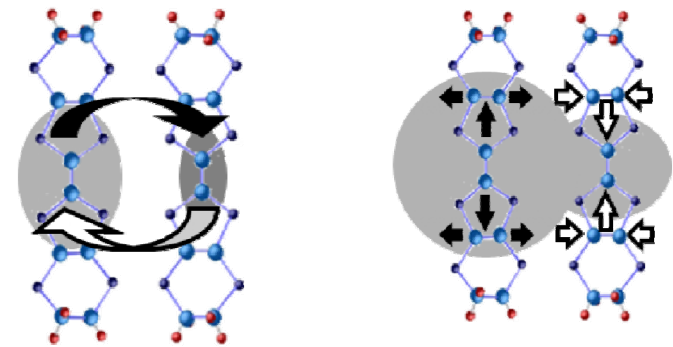


パルス列によって生成した
電子分極、分子／格子振動の干渉



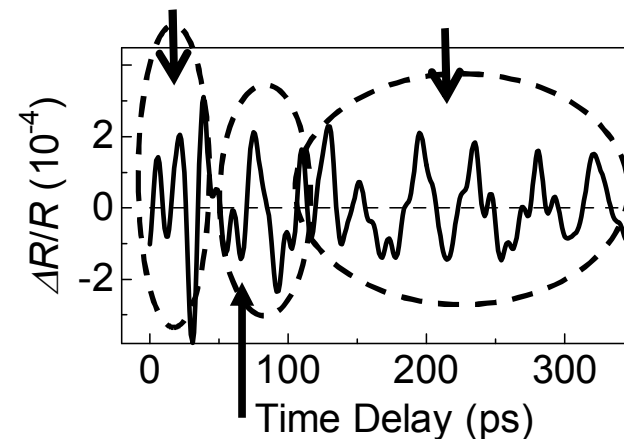
”相互作用モード” (光誘起相転移を駆動)
の増大、抑制

c.f. 少数原子分子系の光反応



電荷の振動
(18 fs)

分子内振動
(22 fs, 40 fs)



電荷と分子内振動の量子干渉
(ファノ干渉)

i) 光による秩序の融解はどのように始まるのか？

極超短パルス光(パルス幅~3光サイクル)によるスナップショット観測

・電荷秩序 α -(ET)₂I₃, θ -(ET)₂RbZn(SCN)₄
電子のコヒーレントダイナミクス

・ダイマーモット絶縁体 κ -(d-ET)₂Cu[N(CN)₂]Br)
電子-格子結合系の非線形ダイナミクス

ii) 光による秩序(揺らぎ)の形成は可能か？

光励起-THzプローブ分光

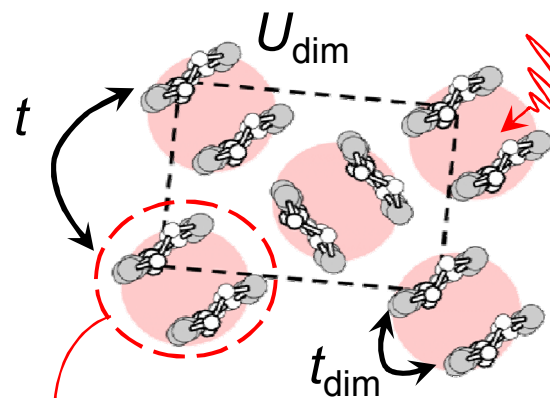
・ダイマーモット絶縁体(電子誘電体) κ -(ET)₂Cu₂(CN)₃

κ -(d-ET)₂[Cu(CN)₂]Brにおける光誘起金属状態の生成過程

ダイマーモット絶縁体

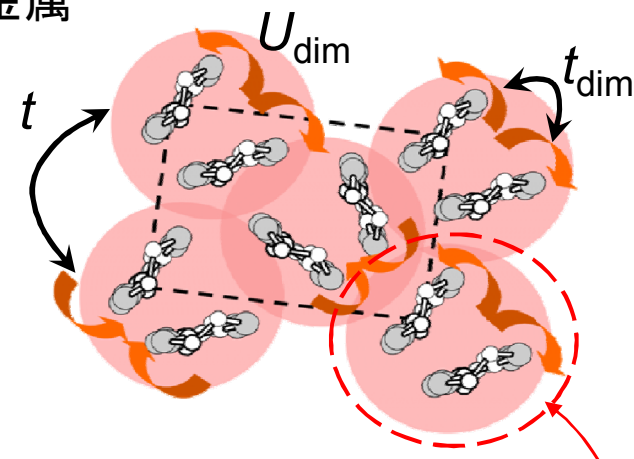
ダイマー内励起
(結合-反結合)

金属



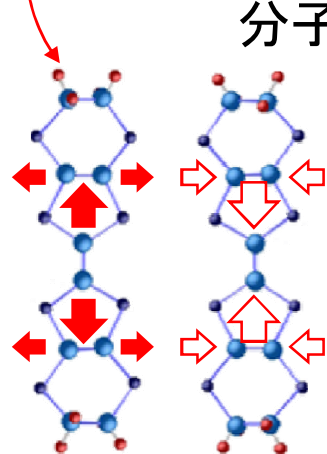
~1 ps

(コヒーレントな)
モード間相互作用

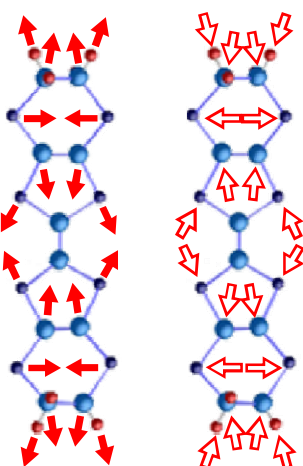


分子内振動

分子間振動



$\nu_3 \sim 1320 \text{ cm}^{-1}$



$\nu_{11} : 318 \text{ cm}^{-1}$

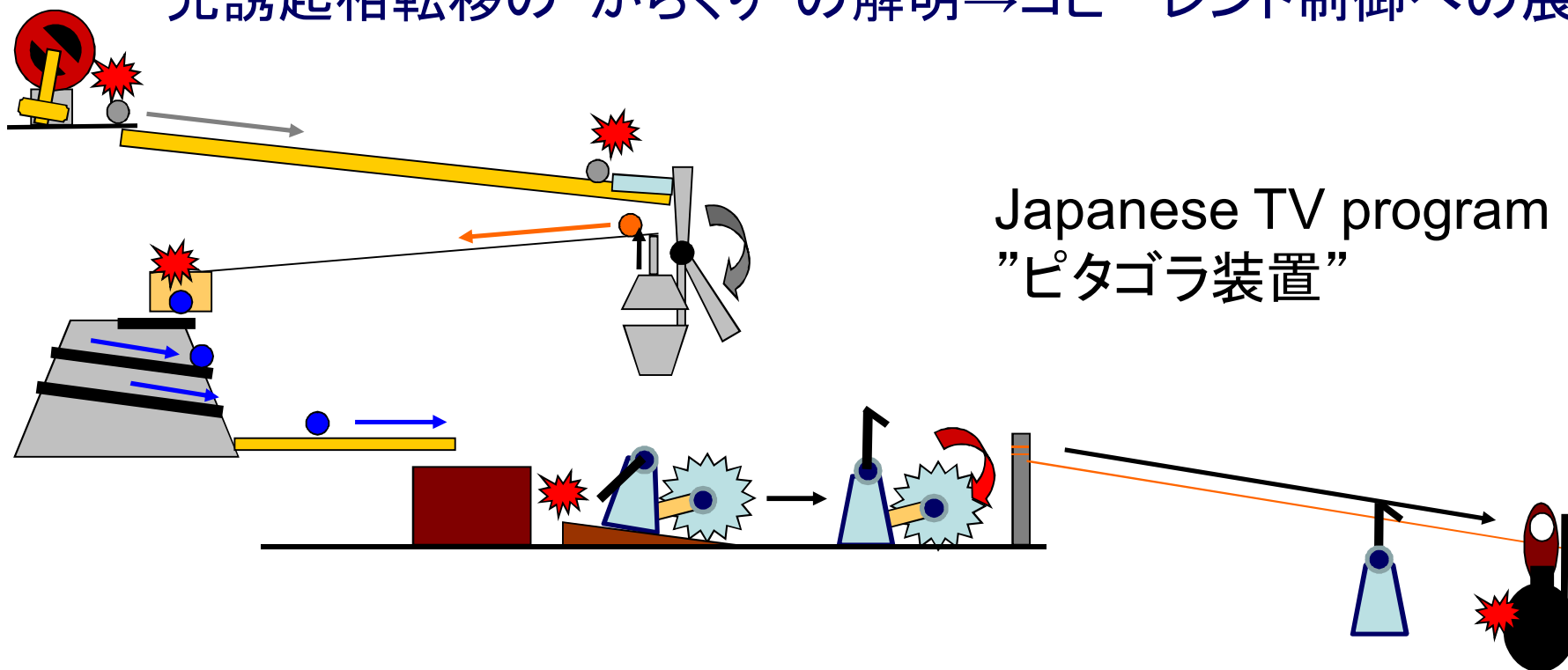
高周波



低周波

分子の内部自由度が重要な役割

光誘起相転移の”からくり”の解明→コヒーレント制御への展開



Japanese TV program
”ピタゴラ装置”

$\alpha\text{-(ET)}_2\text{I}_3$
 電荷移動励起 \implies **電荷のコヒーレント振動** \implies 分子内振動
電荷振動が転移を駆動 (微視的金属状態生成) (微視的金属状態の凝集)

$\kappa\text{-(ET)}_2\text{Cu}[\text{N}(\text{CN})_2]\text{Br}$
 ダイマー内励起 \implies 高周波分子内振動 \implies 低周波分子内、分子間振動 \implies 金属状態
分子内、分子間振動の非線形相互作用

まとめ

光誘起相転移(電荷秩序の融解)の初期過程

赤外12 fs (光電場~3周期) パルスを用いたポンププローブ分光

・ α -(BEDT-TTF)₂I₃

電荷移動励起 \implies 電荷のコヒーレント振動 \implies 分子内振動
(微視的金属状態生成) (微視的金属状態の凝集)

電荷振動が転移を駆動する

Phys. Rev. Lett. 105, 246402 (2010).

・ κ -(BEDT-TTF)₂Cu[N(CN)₂]Br

光励起 \implies 高周波分子内振動 \implies 低周波分子内、
分子間振動 \implies 金属状態

分子内、分子間振動が転移を駆動する

コヒーレント制御(物質の光操作)へ

電子誘電体における光誘起相転移 (分極クラスターの光成長)

2つの秩序相(ダイマーモット相 vs. 電荷秩序相)の競合

ダイマーモット相を不安定化→電荷秩序相の安定化