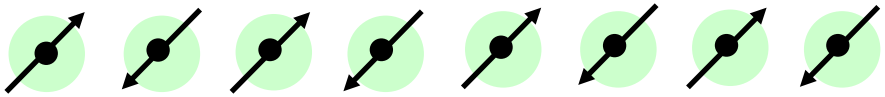
Ultrafast photoinduced phase transitions and large optical nonlinearities in Mott insulators.

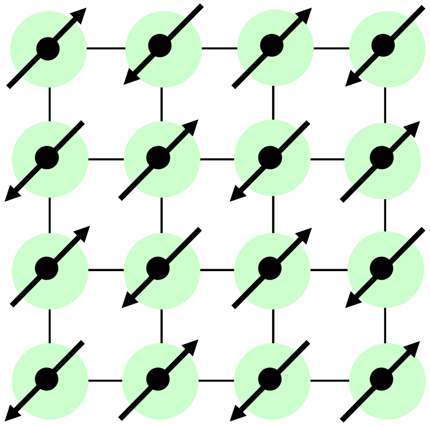
Univ. of Tokyo, Hiroshi Okamoto

Content

1D Mott insulator



2D Mott insulator



1. Introduction
   - Half-filled 1D and 2D Mott insulators
   - Overview of their optical responses

2. Photoinduced Mott-insulator to metal transitions
   - Concept
   - 1D and 2D Mott insulators

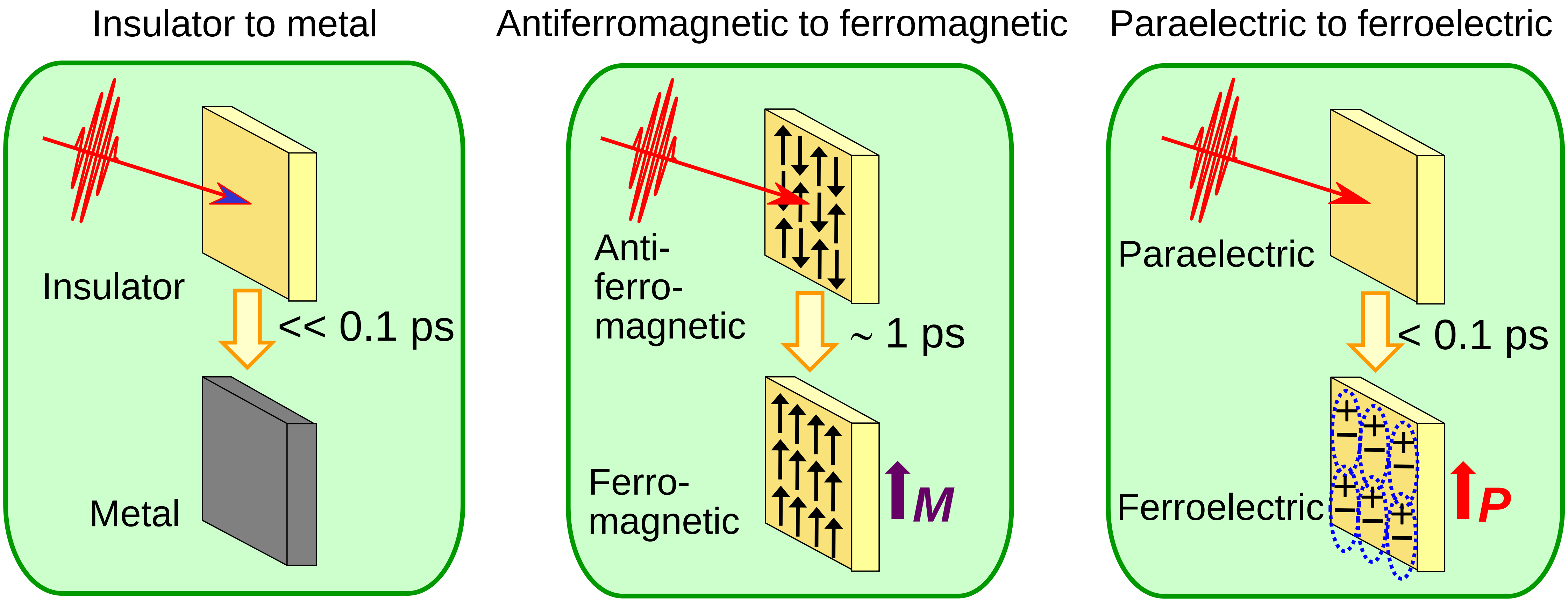
3. Terahertz electric-field induced phase transitions in Mott insulators
   - Mott insulator to metal transition
   - Mott insulator to polar charge-order transition

4. Floquet states formed by a mid-infrared electric field in Mott insulators
   - Photon-dressed Floquet states in 1D Mott insulators
   - Phonon-dressed Floquet states in 1D dimerized Mott insulators
   - Attempts of Floquet engineering

5. Summary

Photoinduced phase transitions (PIPTs) of correlated electron materials

Correlated electron materials :
Photoexcited states change surrounding electron and spin systems through strong e-e interactions → ultrafast photoinduced phase transitions



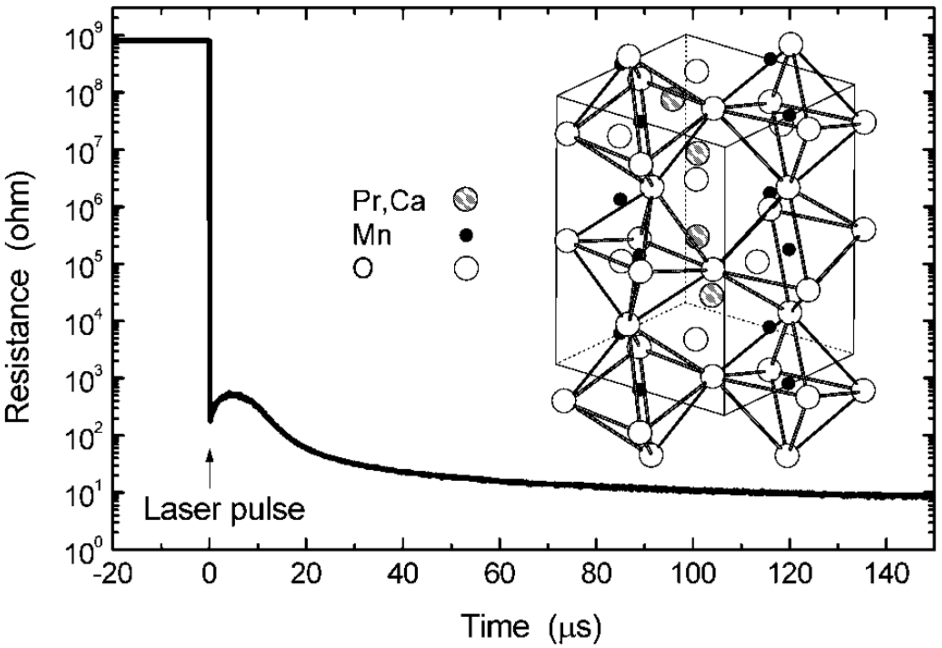
Central research subjects in non-equilibrium quantum physics, a new field of condensed matter

Possible mechanisms for ultrafast optical switching devices

Early stage works of photoinduced insulator-metal transitions

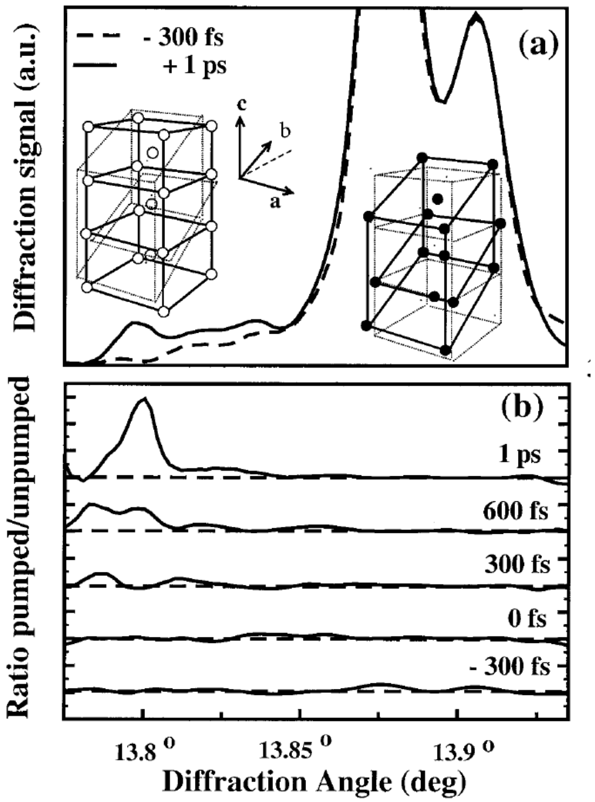
Insulator-metal (IM) transitions are induced via a photoinduced melting of a low-temperature ordered phase such as a charge-order insulator (COI) phase and a Peierls insulator (PI) phase.

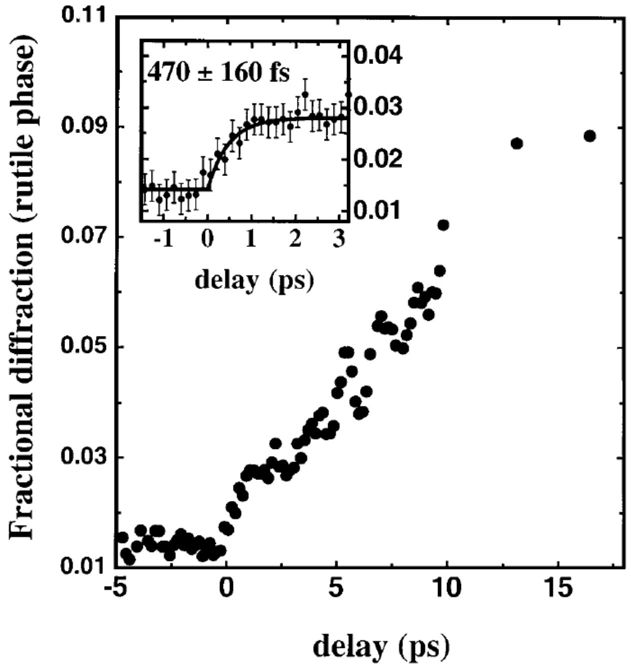
Photoinduced melting of the COI phase in $Pr_{0.7}Ca_{0.3}MO_3$



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

Photoinduced melting of the PI phase in VO_2



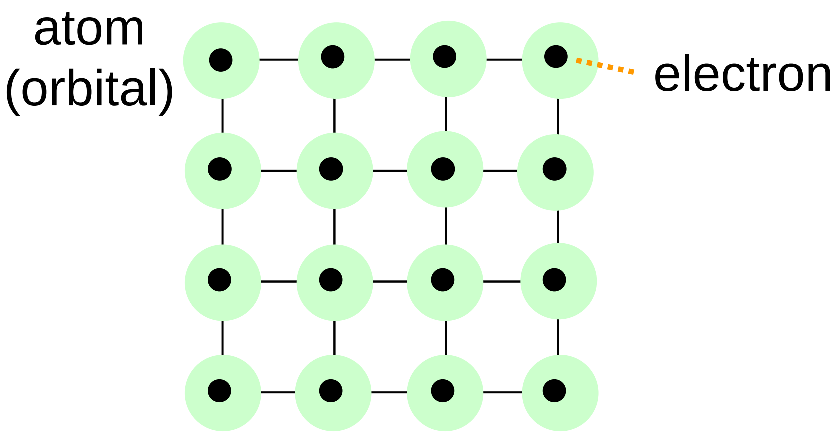


A. Cavalleri *et al.*,
PRL **87**, 237401 (2001)

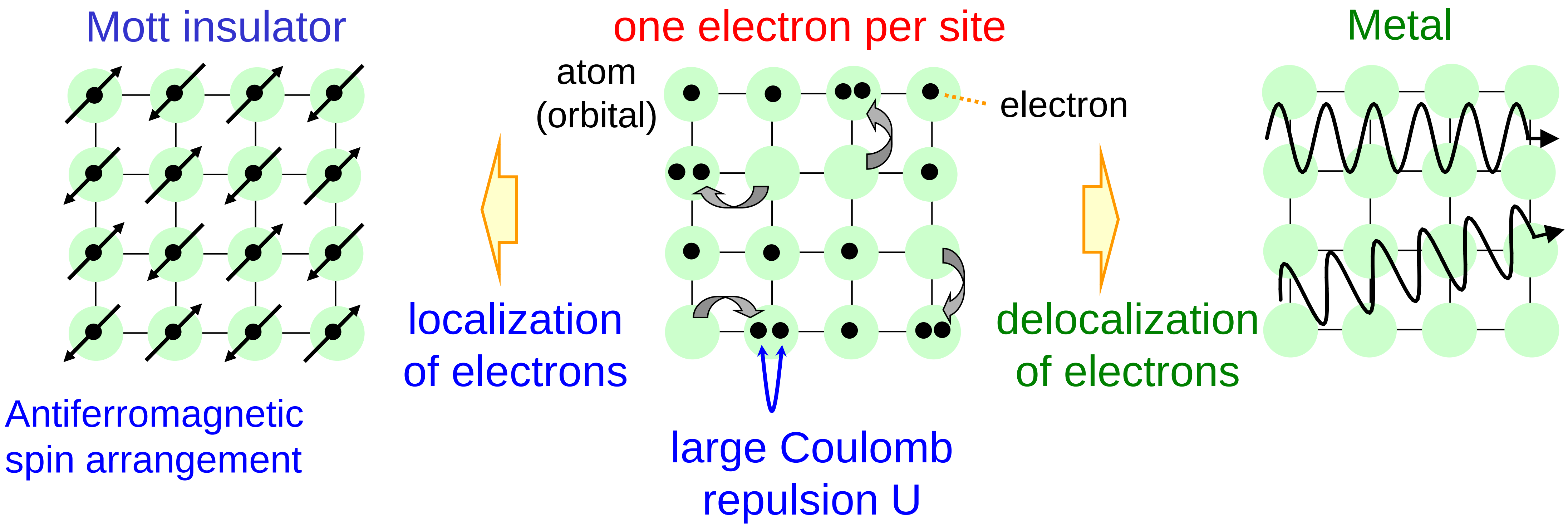
Those phenomena involve charge, spin, lattice, and orbital degrees of freedom. Their dynamics are complicated and depend on specific features of each material.

Half-filled Mott insulators

one electron per site



Half-filled Mott insulators



Mott insulator

one electron per site

Metal

atom
(orbital)

electron

localization
of electrons

delocalization
of electrons

Antiferromagnetic
spin arrangement

large Coulomb
repulsion U

○ The most fundamental insulating state in correlated electron systems

・Good target to study optical responses in quantum many-body system consisting of strongly interacting electrons from both experimental and theoretical viewpoints

ex. Theoretical studies: P. Werner, Y. Murakami, A. Takahashi, etc.

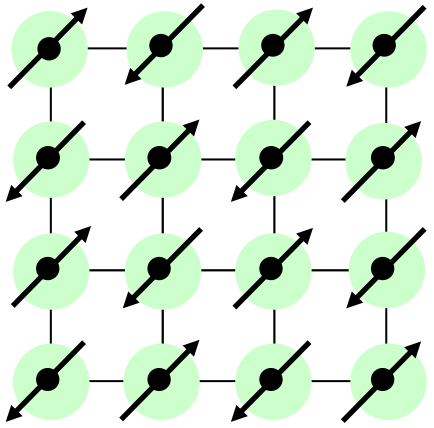
○ Novel responses to lights and electric fields

・Ultrafast metallization

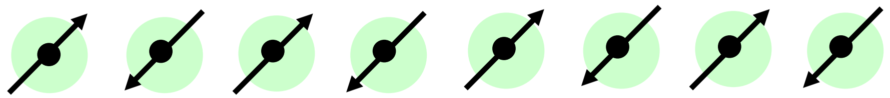
・Large optical nonlinearity

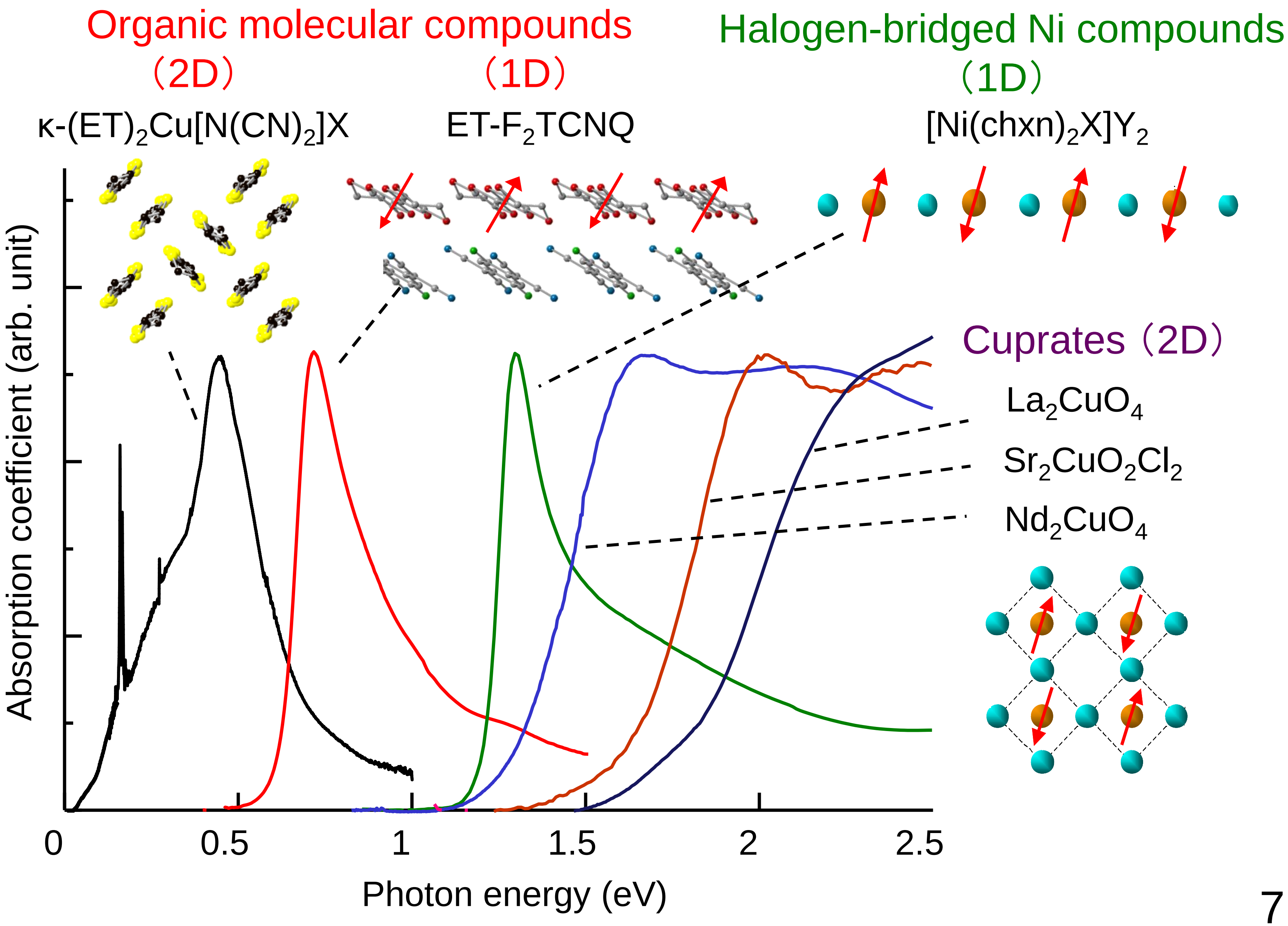
Half-filled 1D and 2D Mott insulators

2D Mott insulator

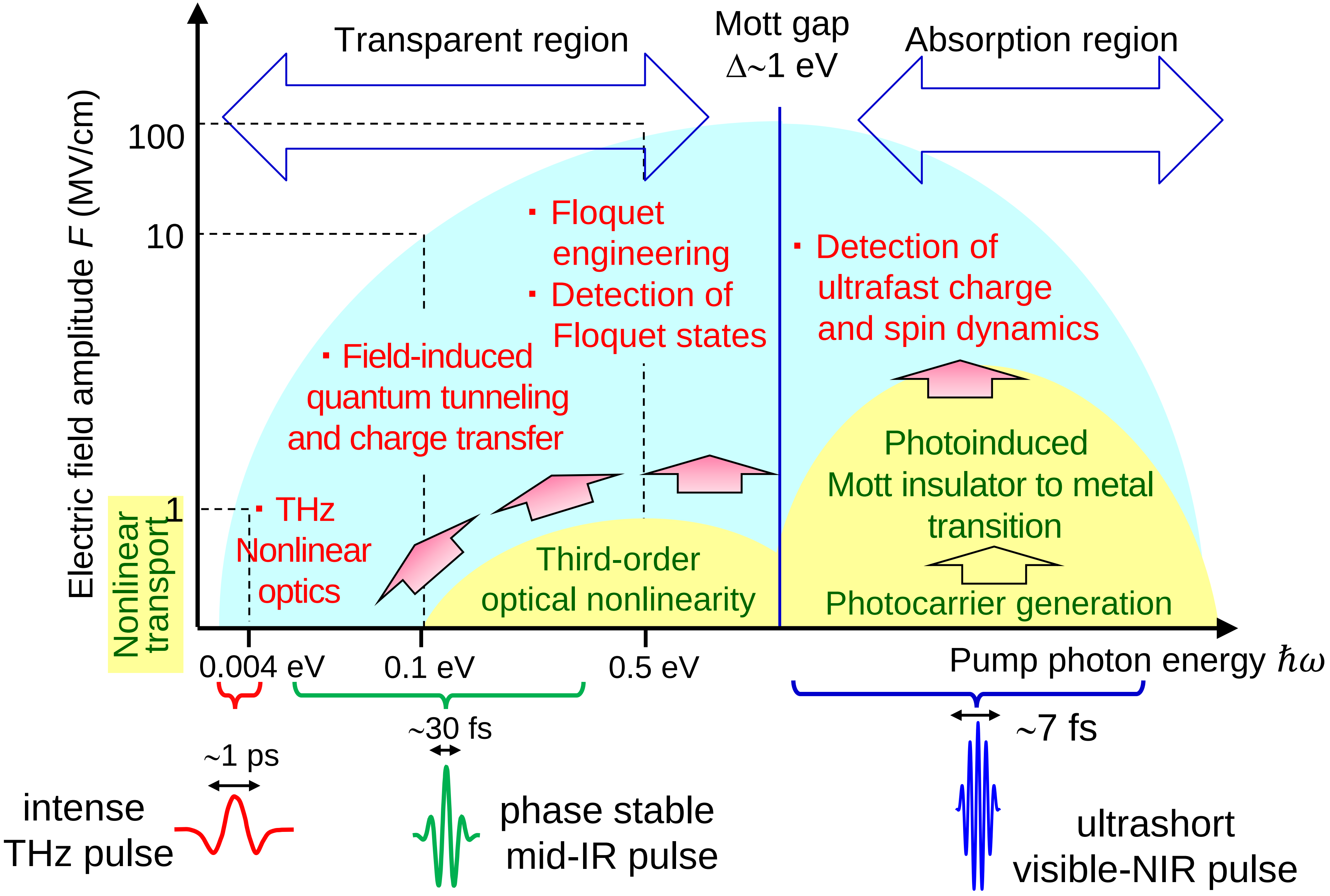


1D Mott insulator





Responses of half-filled Mott insulators to lights and electric fields



Transparent region

Mott gap
Δ~1 eV

Absorption region

- Floquet engineering
- Detection of Floquet states

- Detection of ultrafast charge and spin dynamics

- Field-induced quantum tunneling and charge transfer

- THz Nonlinear optics

Nonlinear transport

Third-order optical nonlinearity

Photoinduced Mott insulator to metal transition

Photocarrier generation

intense THz pulse

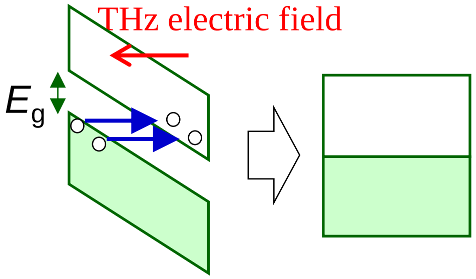
phase stable mid-IR pulse

ultrashort visible-NIR pulse

subcycle spectroscopy

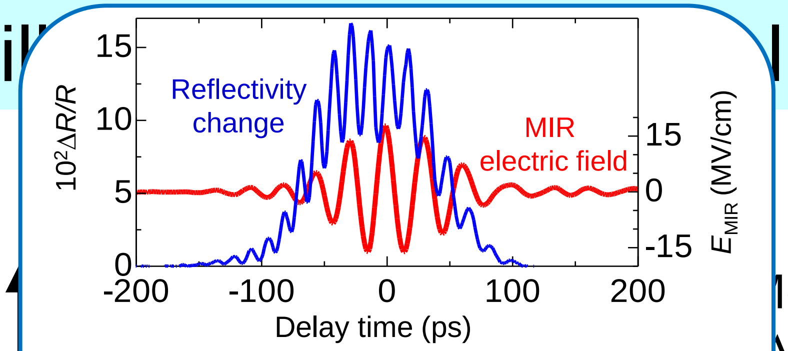
subcycle spectroscopy

high time-resolution (< 10 fs) spectroscopy

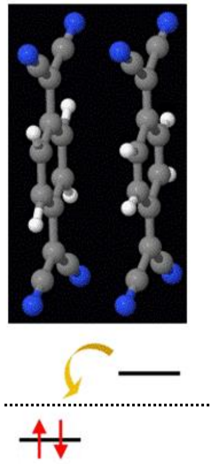


THz field induced
Mott insulator-metal transition
Phase controls via quantum tunneling processes

Nature Materials ***16***, *1100 (2017)*
PRB ***107***, *085147(2023)*



Photon-dressed Floquet states formed by an MIR electric field
New J. Phys. ***25***, *093044 (2023)*



Destabilization of spin-Peierls phase via phonon-dressed Floquet states
Floquet engineering

Commun. Phys. ***5***, *72 (2022)*
Commun. Phys. ***7***, *40 (2024)*

- Floquet engineering
- Detection of Floquet states
- Detection of ultrafast charge and spin dynamics
- Field-induced quantum tunneling and charge transfer
- THz Nonlinear optics

Third-order optical nonlinearity

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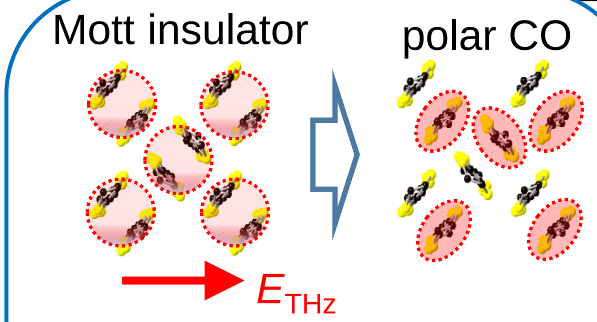
Phot generation

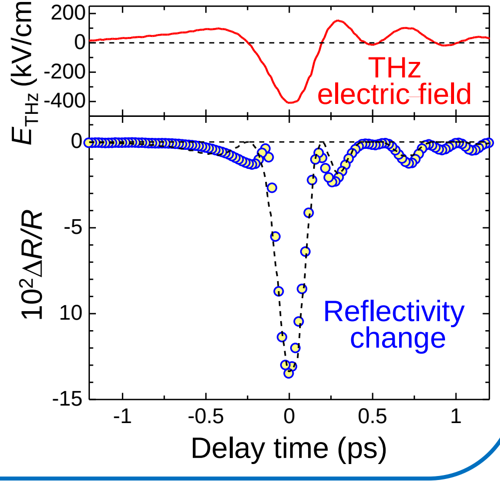


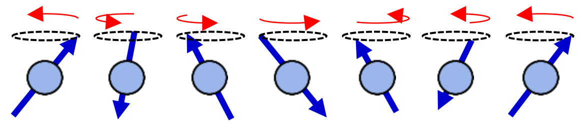
THz field induced
Mott insulator-polar charge order transition
Phase controls via field induced intermolecular charge transfers

Nature Commun. ***16***, *1100 (2017)*
PRB ***104***, *195148(2021)*

THz nonlinear spectroscopy
Science Advances ***5***, *eaav2187 (2019)*

THz generation method
Nature Commun. ***54***, *6229 (2023)*





Magnetic polaron formation and magnon-related dynamics detected using 7 fs pump-probe spectroscopy
charge-spin coupling

Nature Commun. ***9***, *3948 (2018)*

Content

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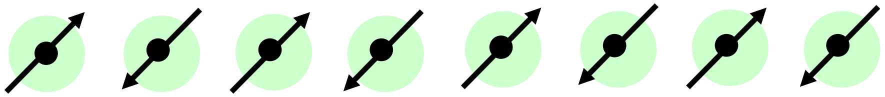
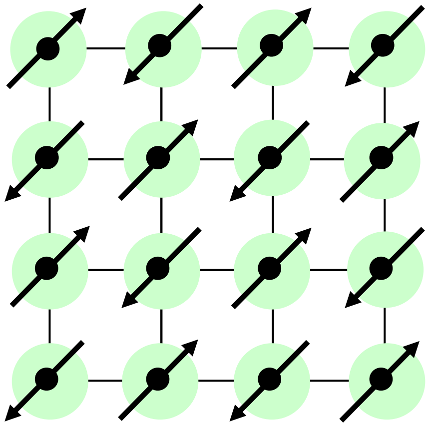


2D Mott insulator



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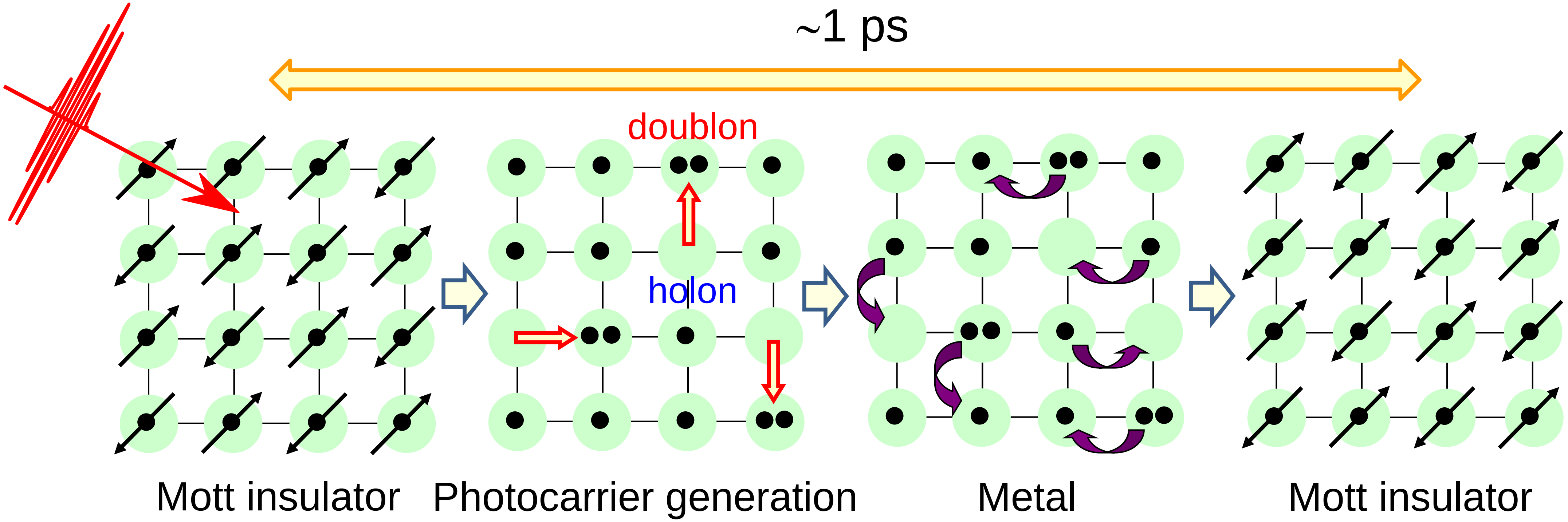
5. Summary

Electronic-state change upon photoexcitation in half-filled Mott insulators

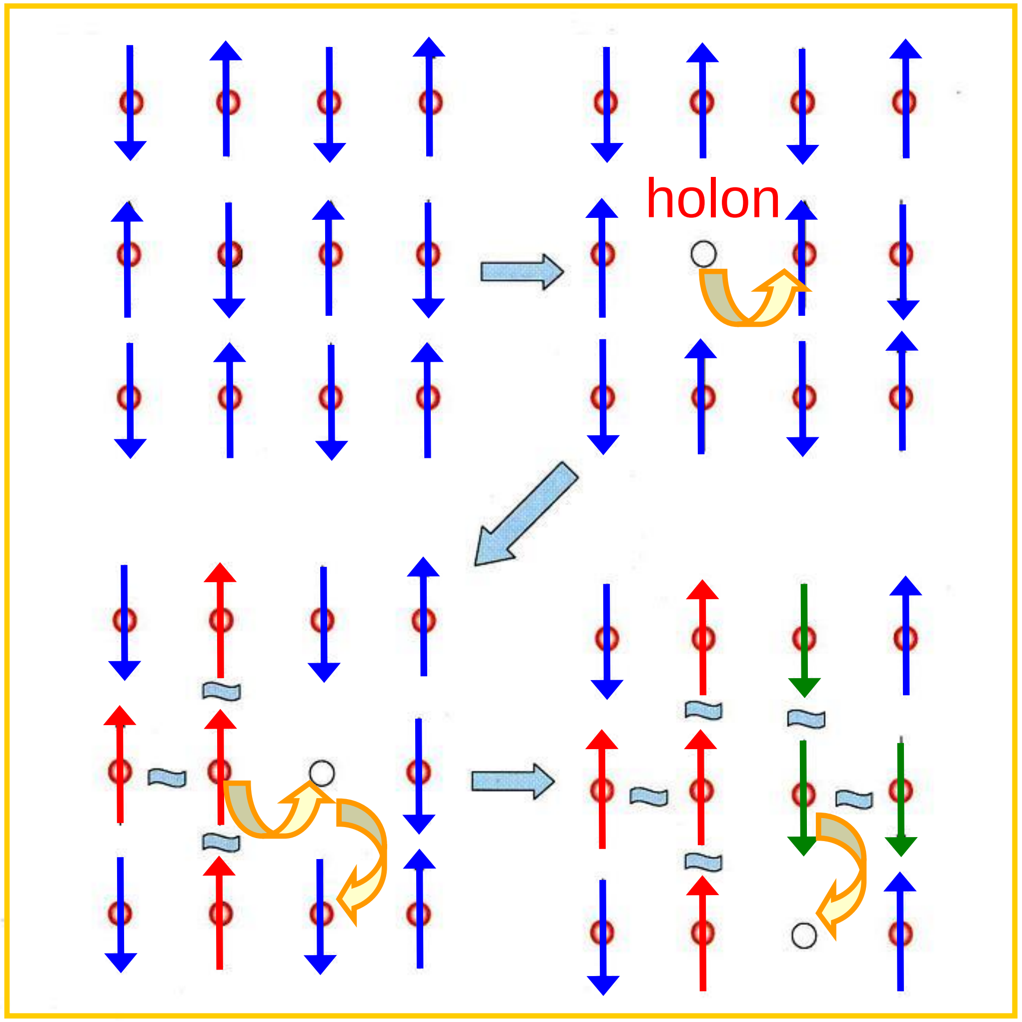


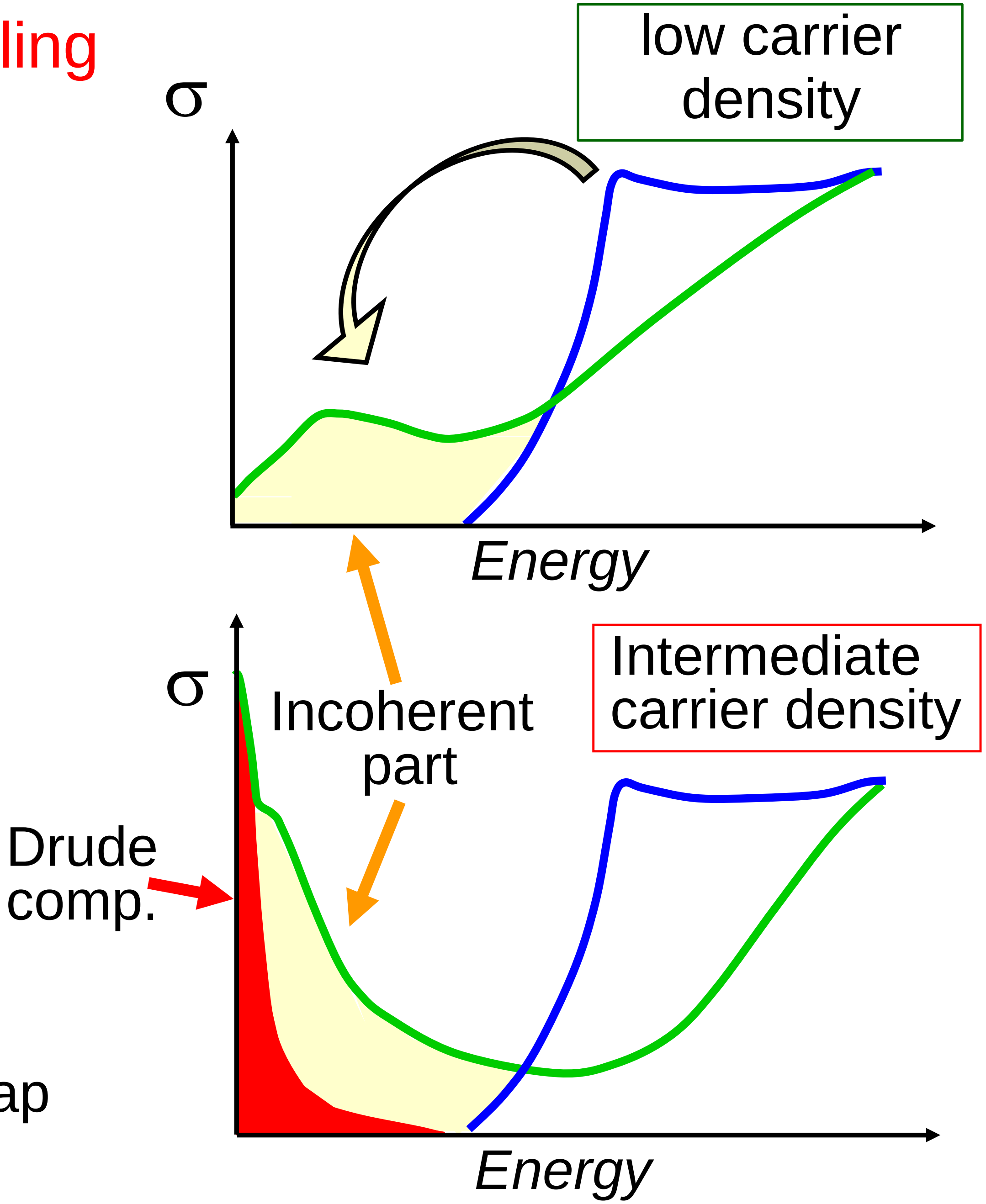
Since this metallization does not change the crystal structure, but change only the electron order, it may occur very fast and return to the original state in the time scale of picosecond.

Coupling of charge and spin degrees of freedom in 2D Mott insulators

2D MI (large U)

spin-charge coupling





Introductions of carriers produce midgap absorption (incoherent part).

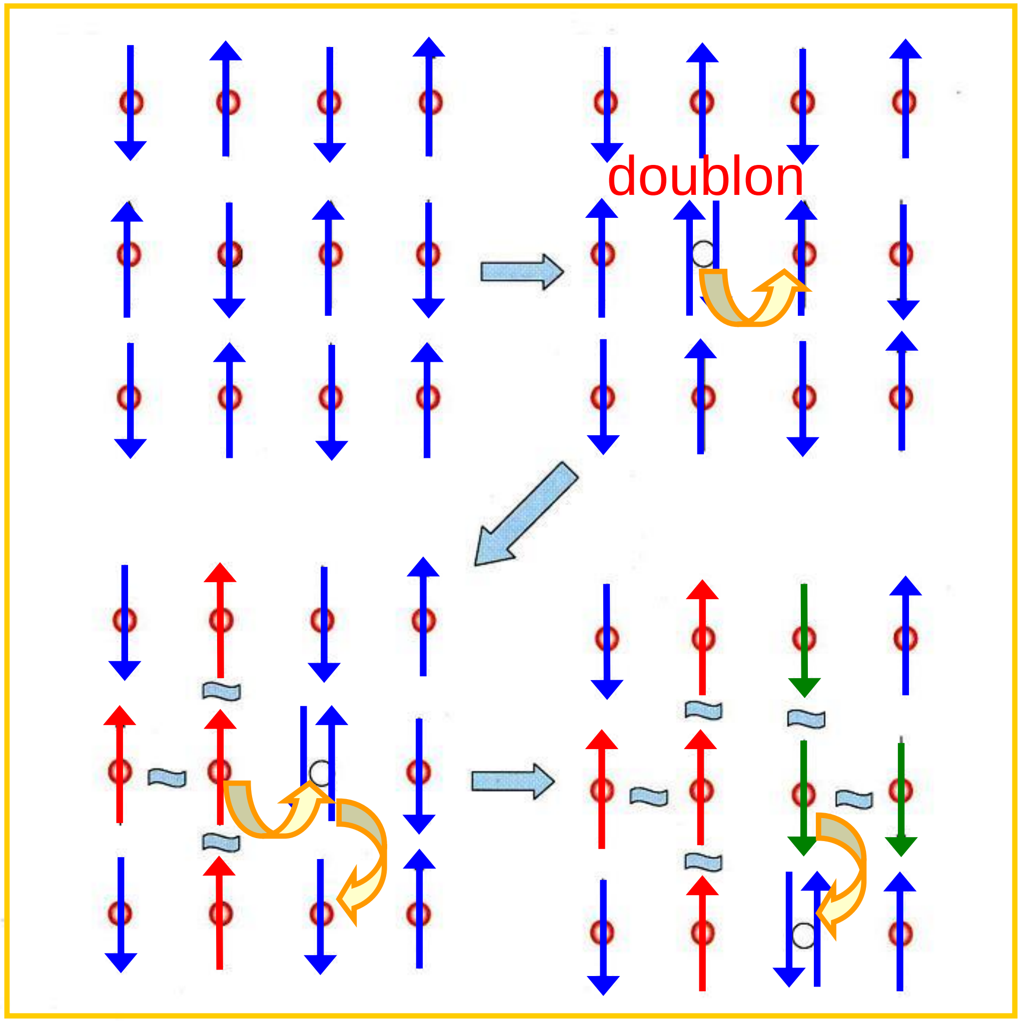
Drude weight is small as compared to the incoherent part.

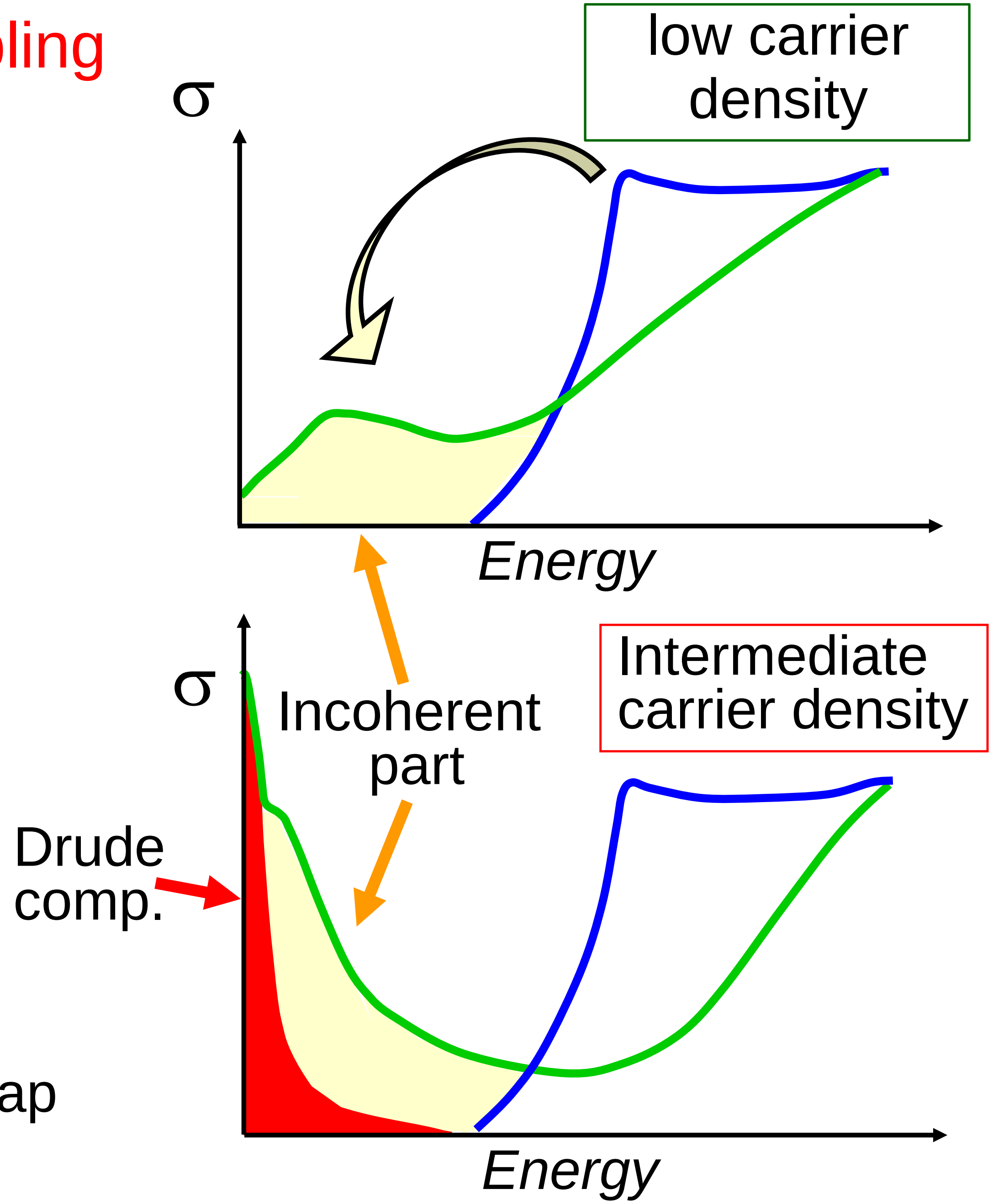
ex. Chemical carrier doping in cuprates such as LSCO and NCCO

Coupling of charge and spin degrees of freedom in 2D Mott insulators

2D MI (large U)

spin-charge coupling





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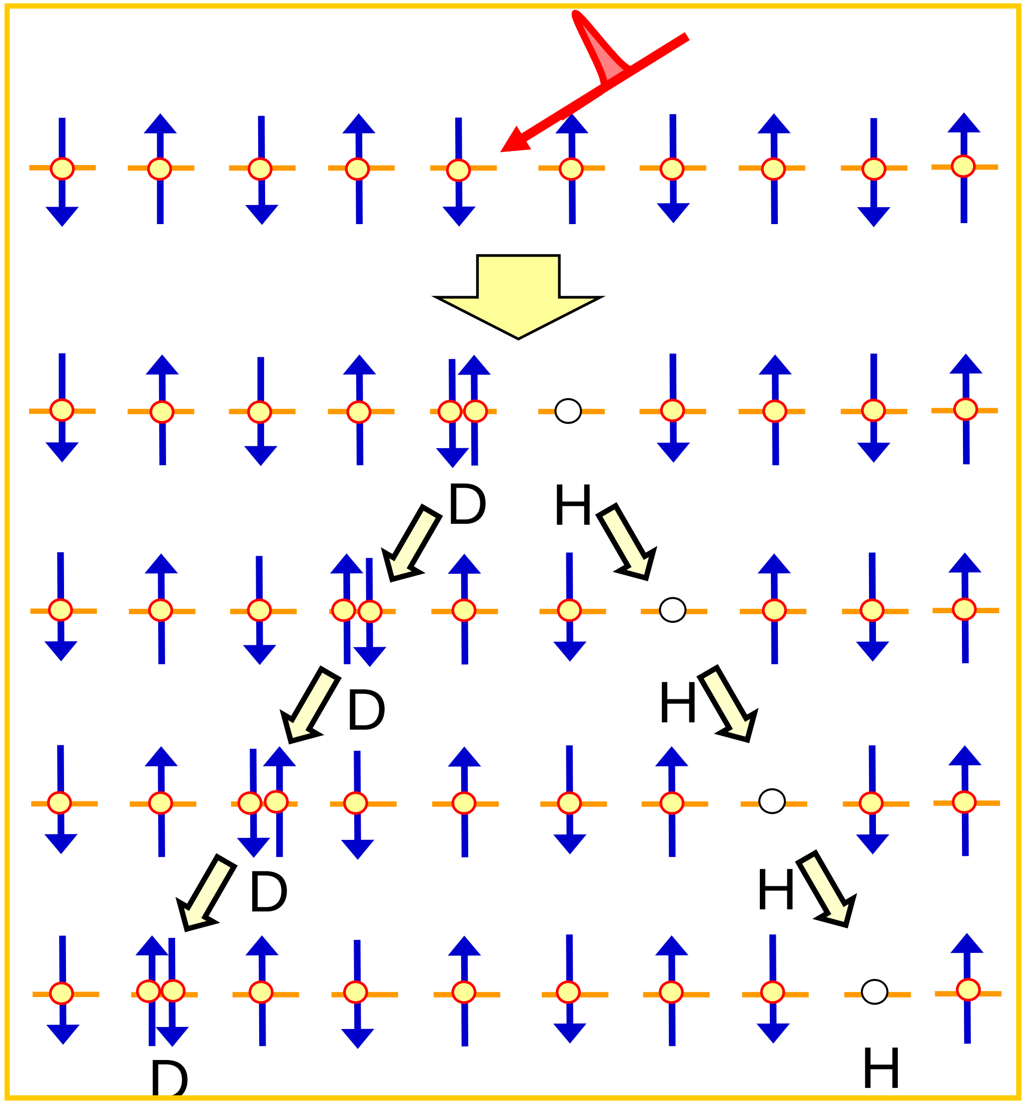
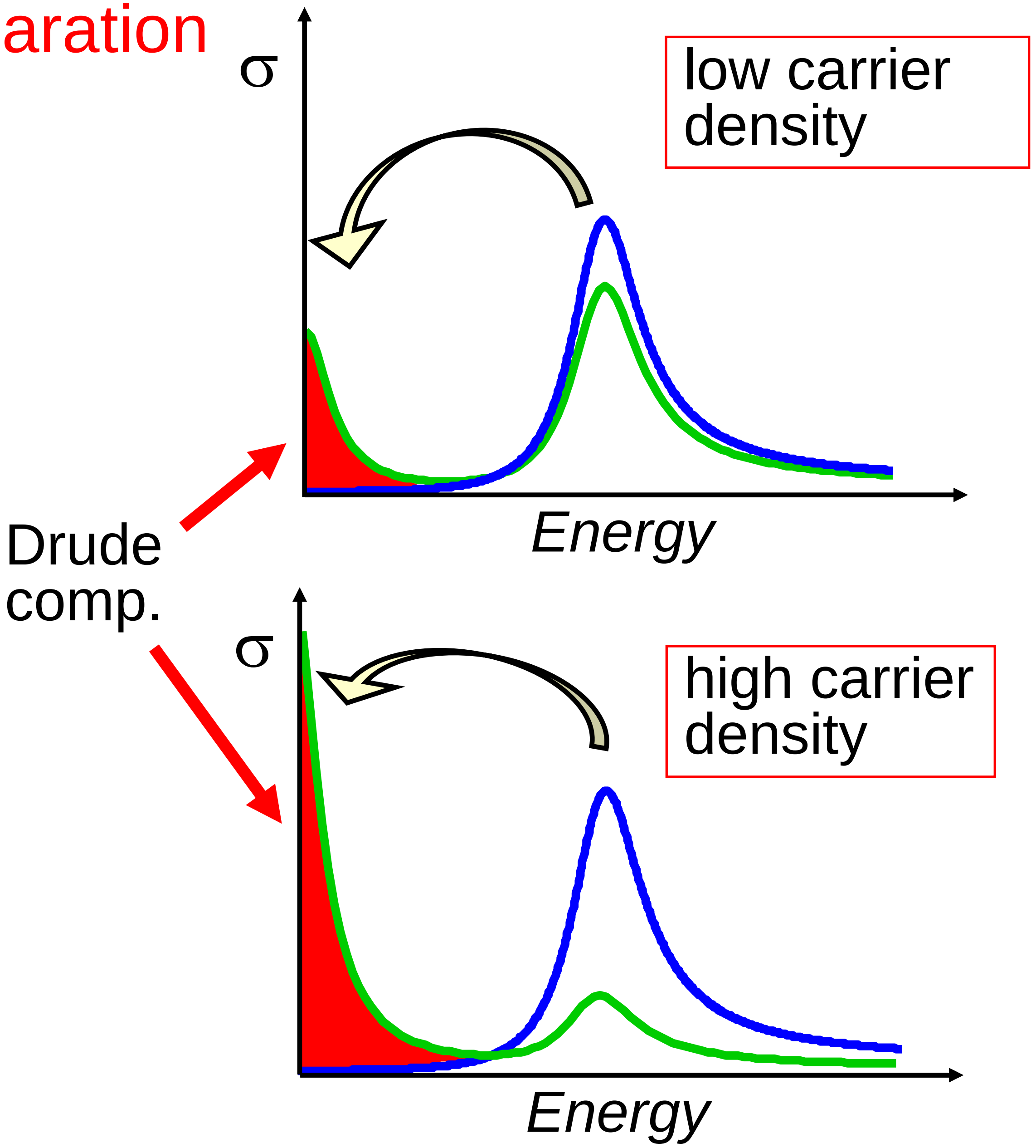
Decoupling of charge and spin degrees of freedom in 1D Mott insulators

1D MI (large U)

spin-charge separation





low carrier density

high carrier density

Drude comp.

By a photocarrier doping, the spectral weight of the gap transition is expected to be transferred to the Drude component, irrespective of carrier density.

M. Ogata and H. Shiba, PRB ***41****, 2326 (1990).*

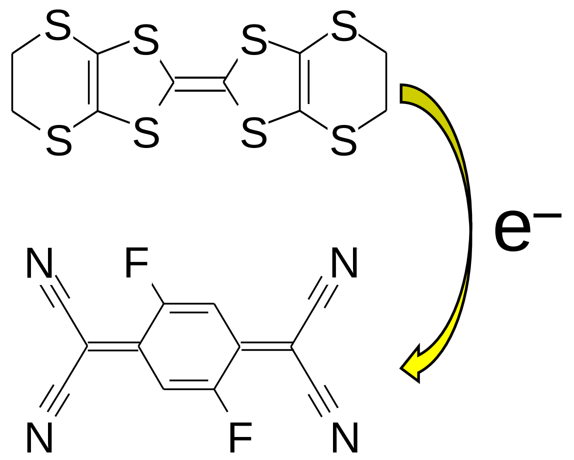
H. Eskes and A.M. Oles, PRL ***77****, 1279 (1994).*

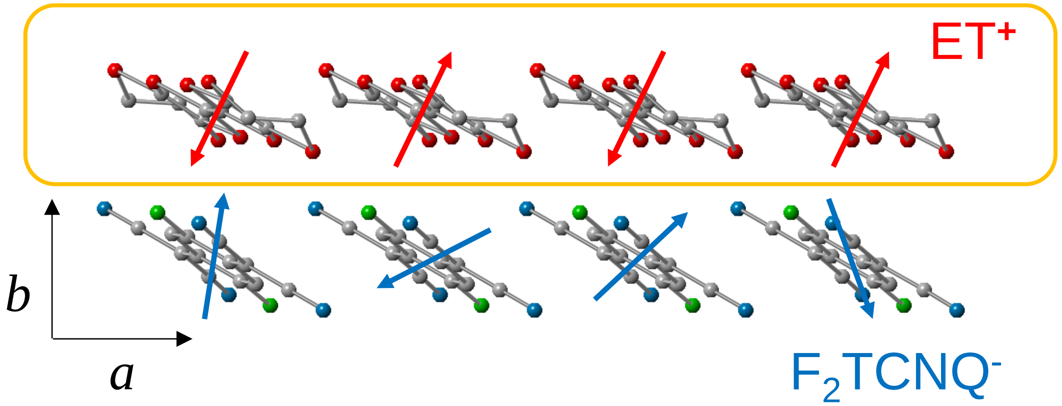
Half-filled 1D Mott insulator : ET-F_2TCNQ

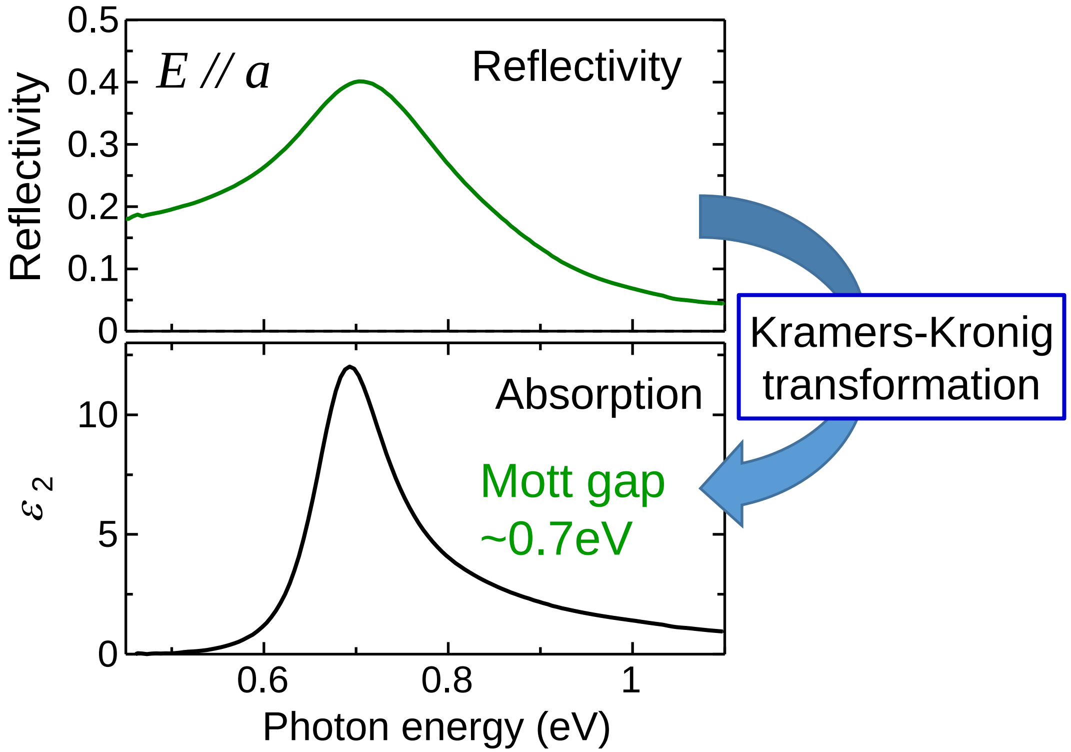
Organic molecular compound

ET(BEDT-TTF)
[Donor]

F_2TCNQ
[Acceptor]

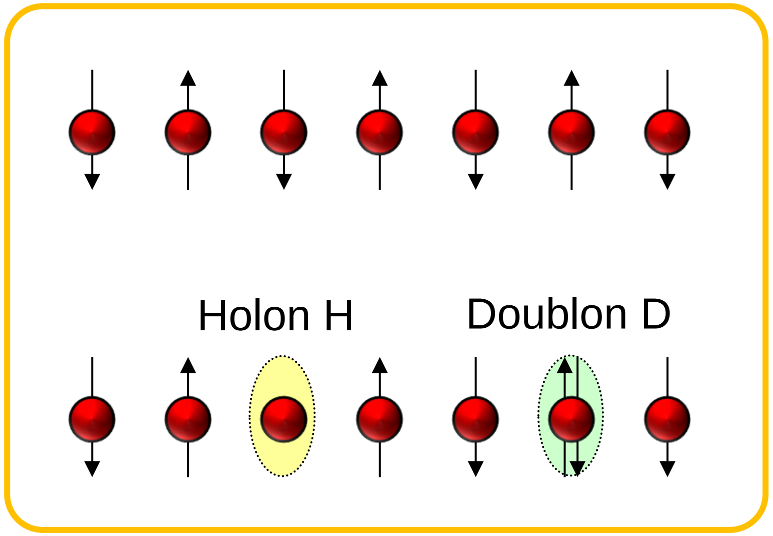






○ ET stacks → 1D half-filled band
○ large on-site Coulomb repulsion U on ET

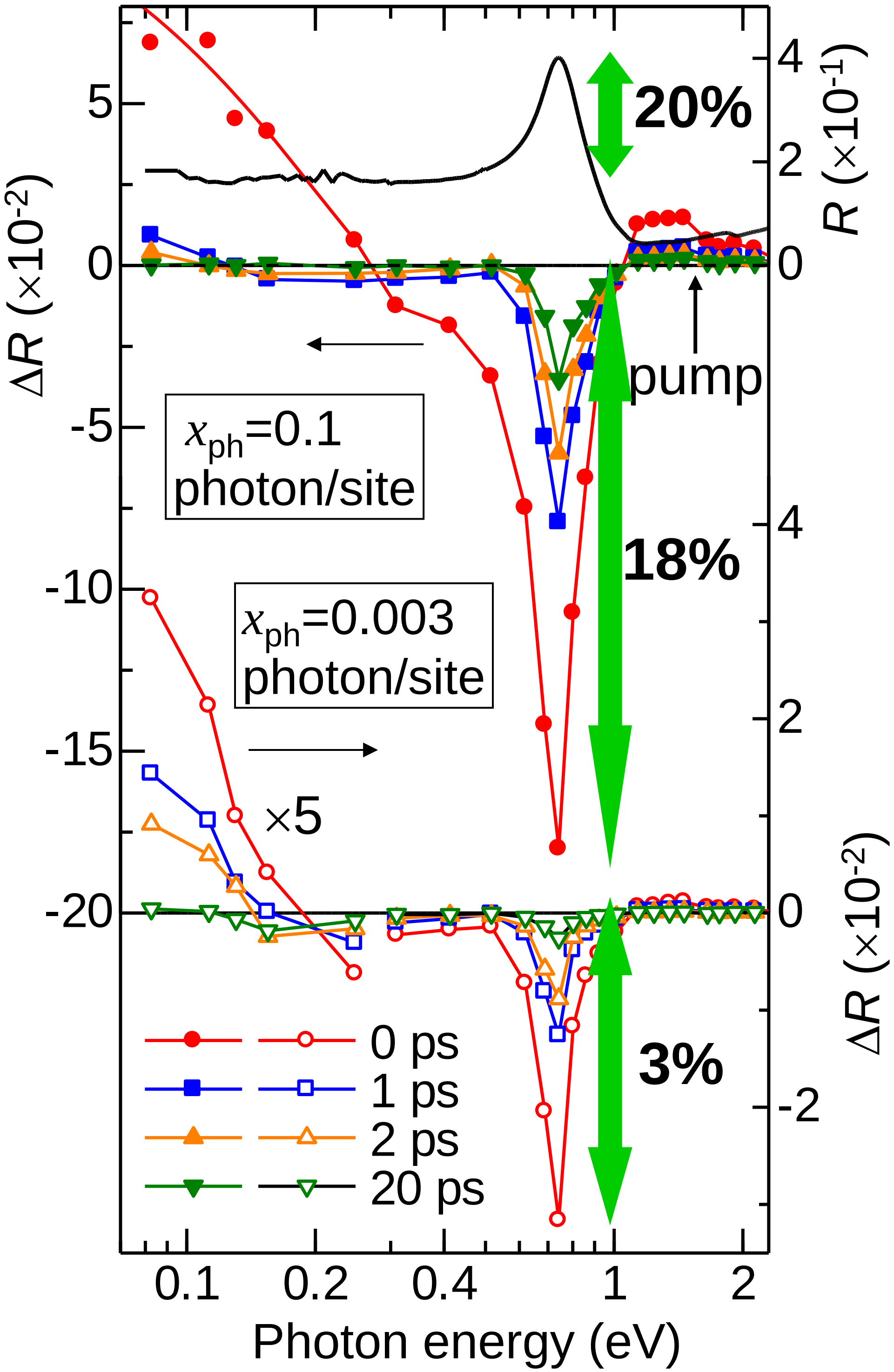
Half-filled 1D Mott insulator



T. Hasegawa et al,
Solid State Commun. ***103****, 489 (1997).*

T. Miyamoto et al., Communications Phys. ***2****, 131 (2019)*
S. Ohmura, H.O. et al., Phys. Rev. B ***100****, 235134 (2019)*

Transient reflectivity changes in (BEDT-TTF)(F_2TCNQ) (Time resolution: 180 fs)



1.55-eV excitation

Spectral weight of the gap transition is transferred to the inner gap region.

● By the strong excitation (x_{ph}=0.1 ph/site), the optical gap almost disappears.

Photoinduced Mott insulator to metal transition

● By the weak excitation (x_{ph}=0.003 ph/site), ΔR monotonically increases with decrease of energy and the spectral weight exists in the lower energy region.

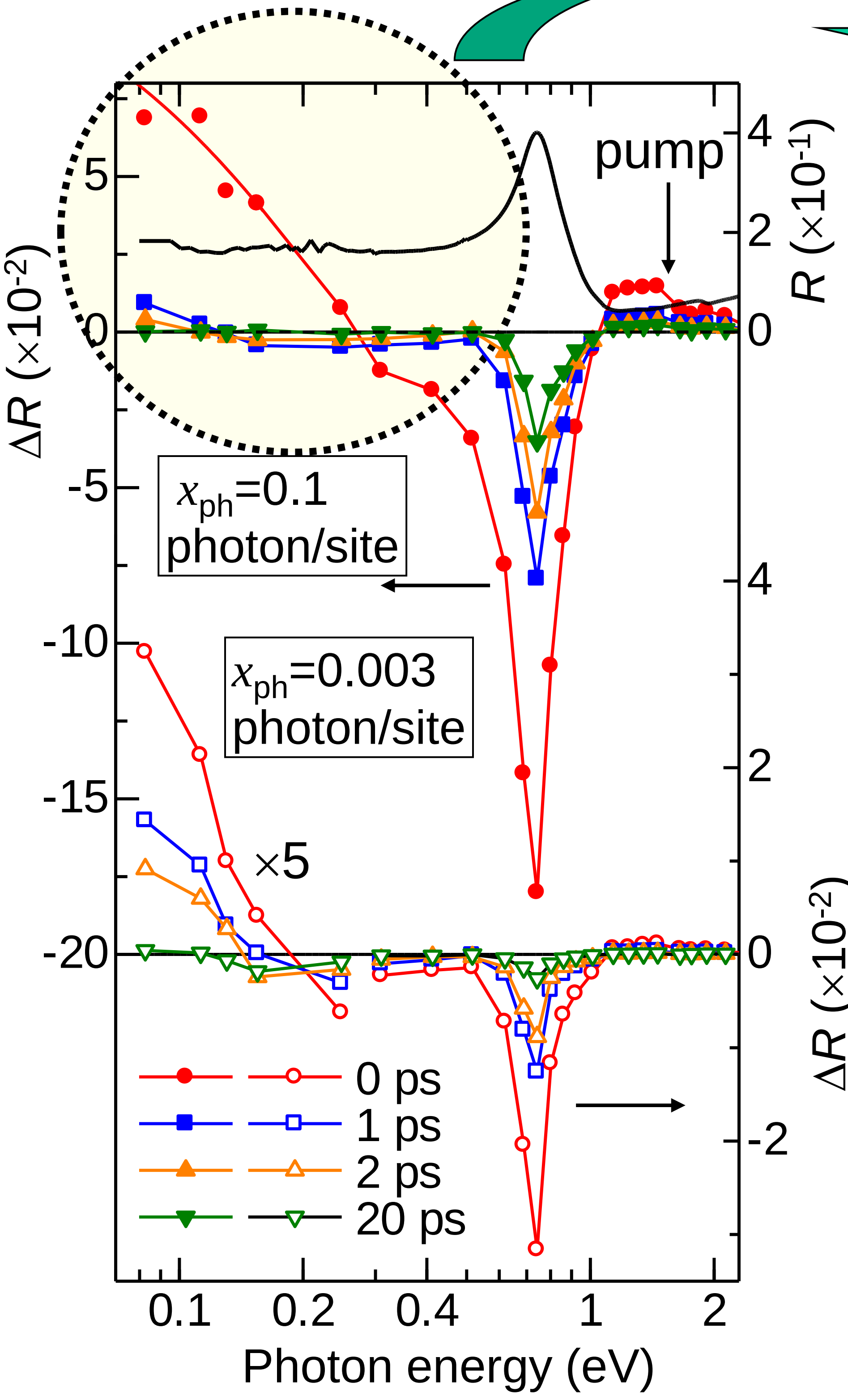
Simple Drude response

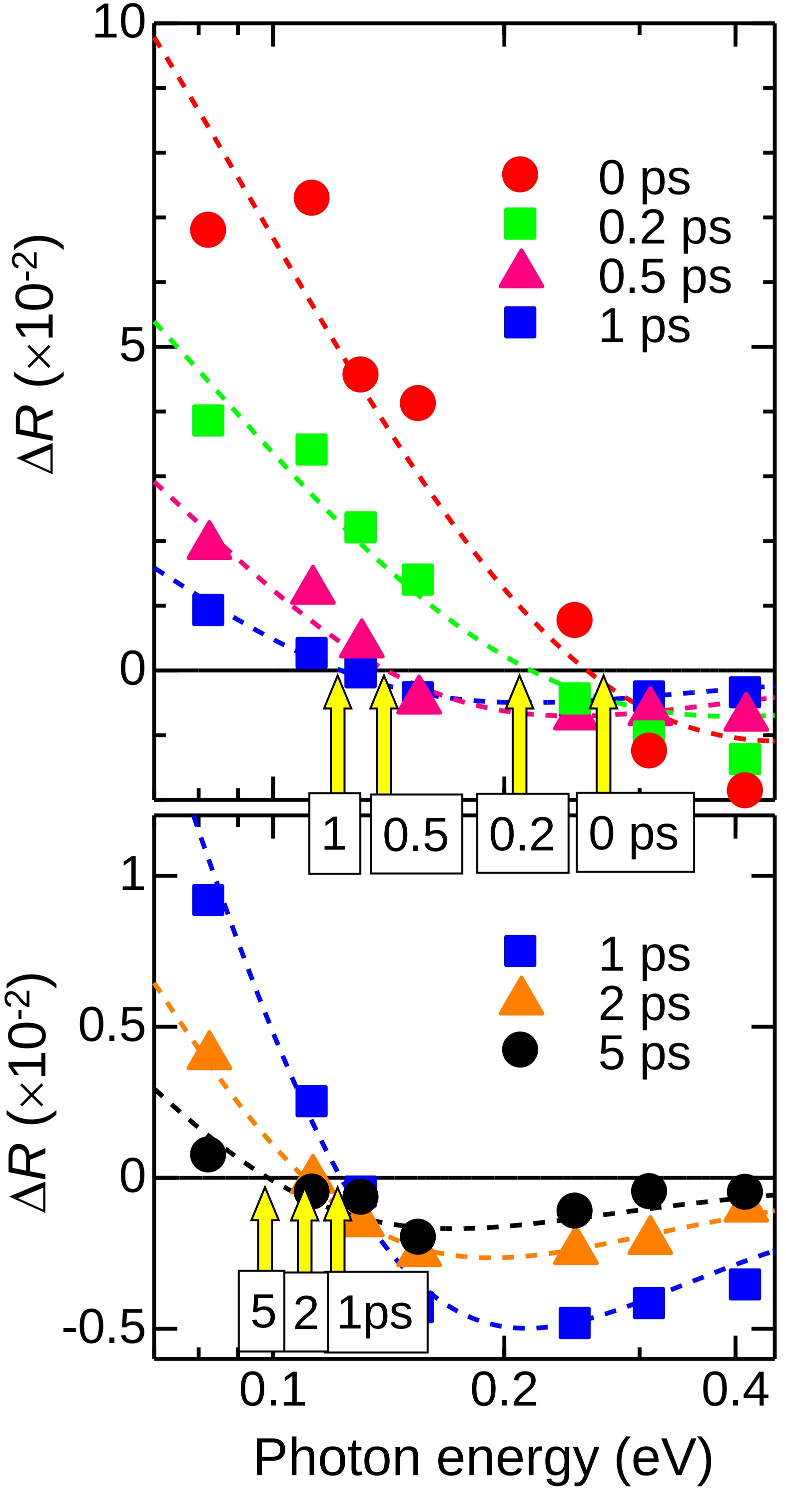
Spin-charge separation characteristic of 1D MI

H.O. et al., PRL ***98****, 037401 (2007)*

T. Miyamoto et al., Commun. Phys. ***2****, 131 (2019)*

The crossing positions for ΔR=0 shift to the lower energy with time.



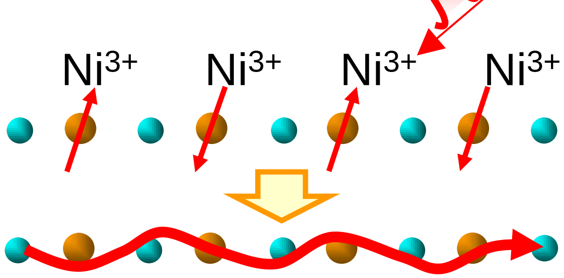


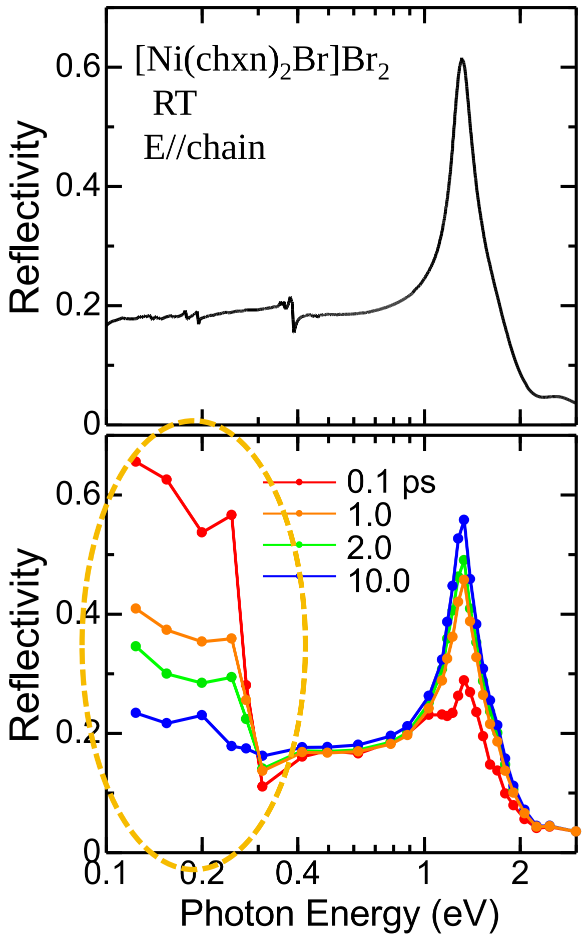
Drude model (broken lines)

spin-charge separation predicted in 1D MI

Drude responses in photoinduced Mott insulator to metal transitions of 1D systems

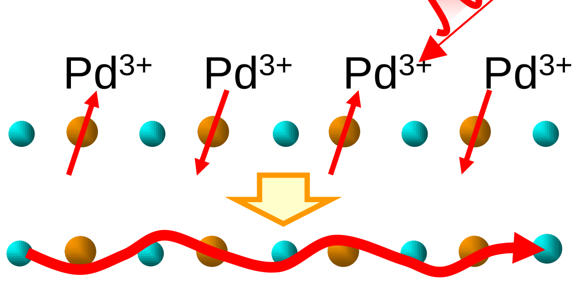
$[Ni(chxn)_2Br]Br_2$

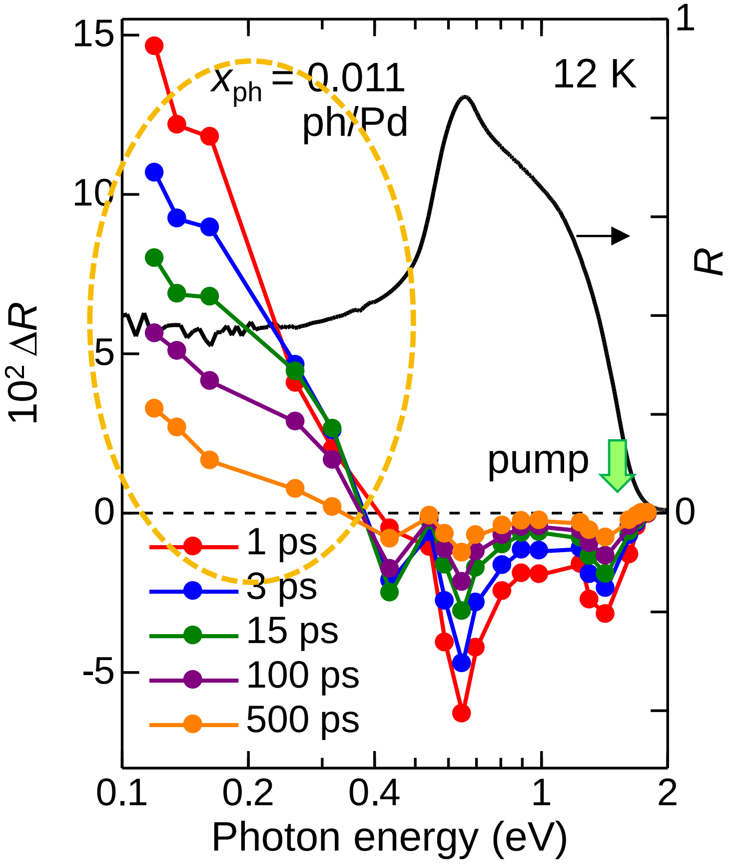




S. Iwai, et al.,
PRL ***91****, 57401 (2003).*

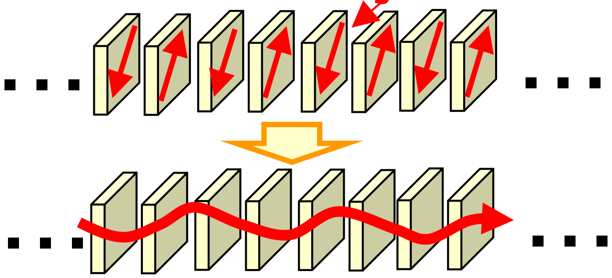
$[Pd(en)_2Br](C_5\text{-}Y)_2$

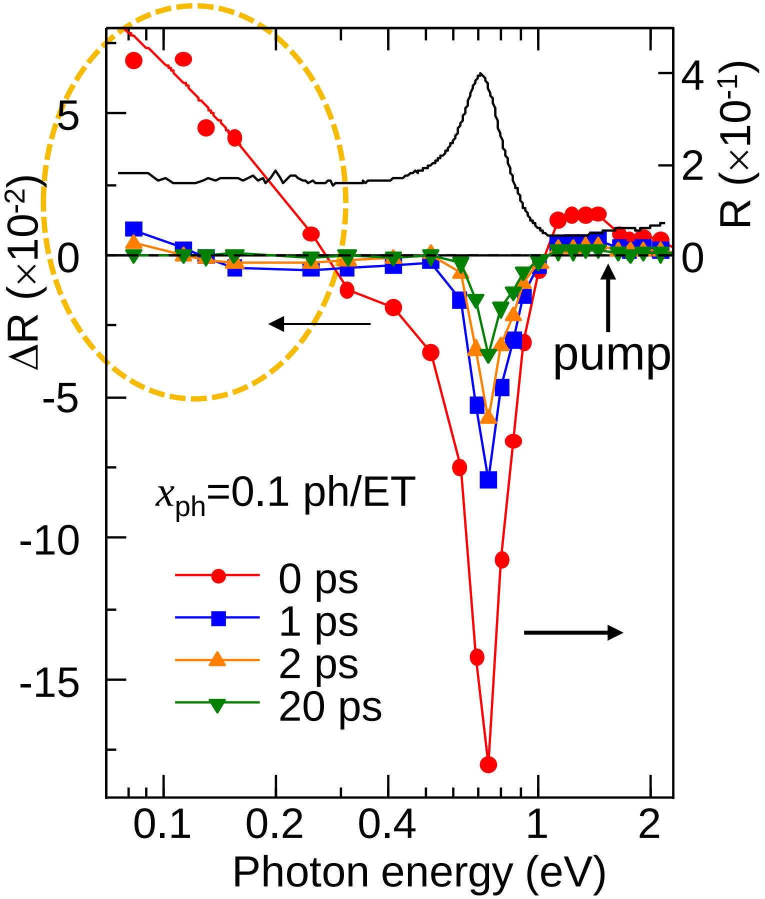




H. Matsuzaki et al.,
PRL ***113****, 096403 (2014).*

ET-F_2TCNQ



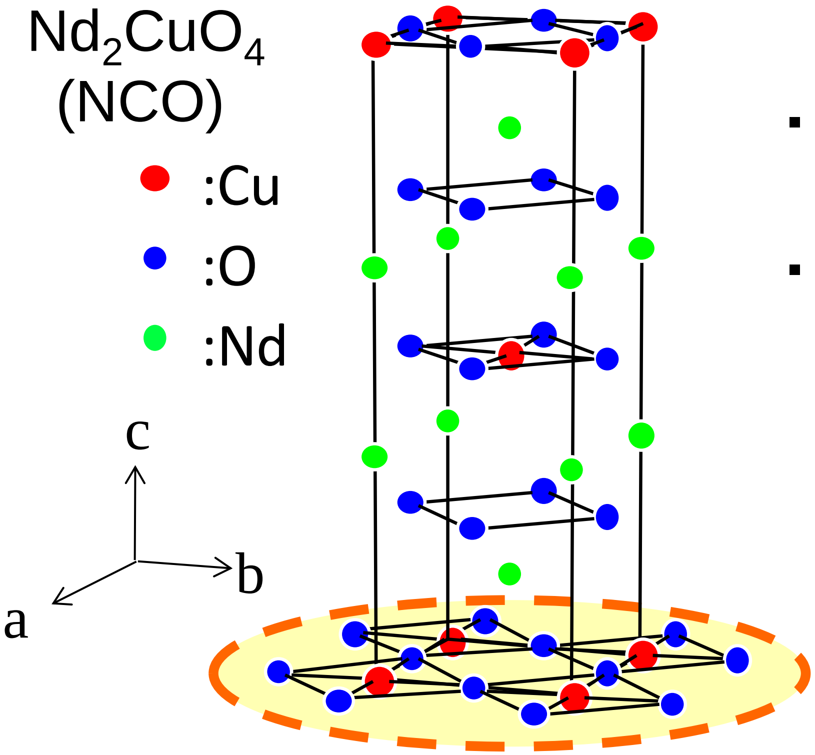


H. Okamoto et al.,
PRL ***98****, 037401 (2007).*

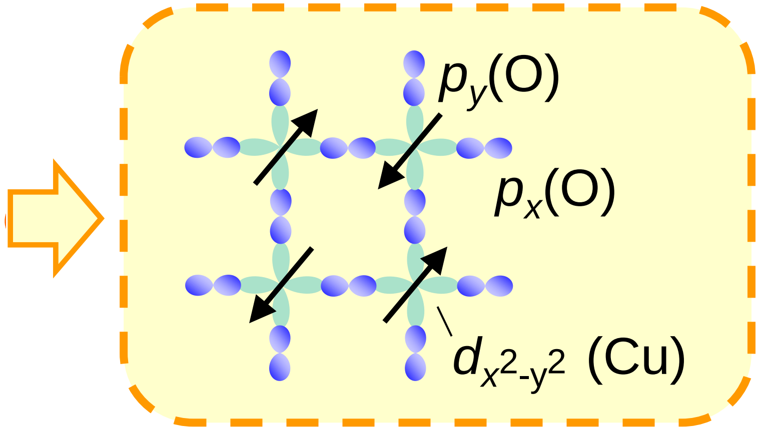
Photoinduced Mott-insulator to metal transition in Nd_2CuO_4 (180 fs res.)

*H. Okamoto et al., PRB **82**, 060513R (2010), PRB **83**, 125102 (2011).*

2D Mott insulator



- A parent compound of an electron-doped superconducting cuprate
- A typical 2D Mott insulator



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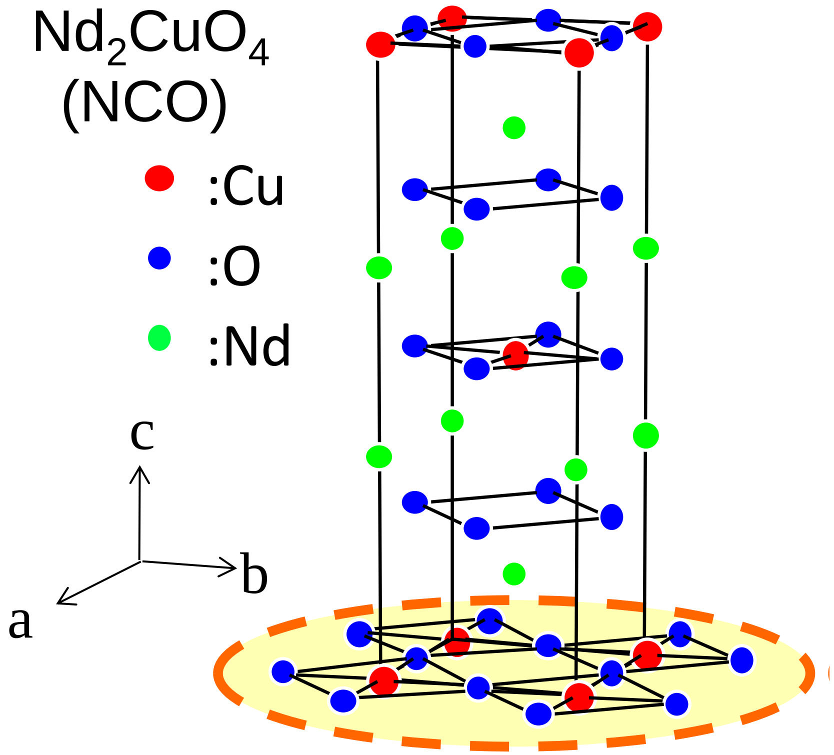

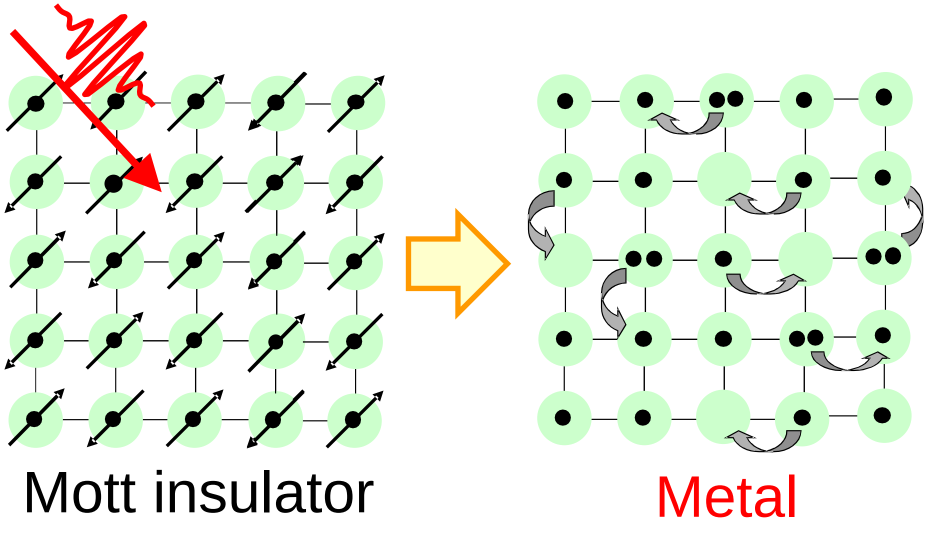

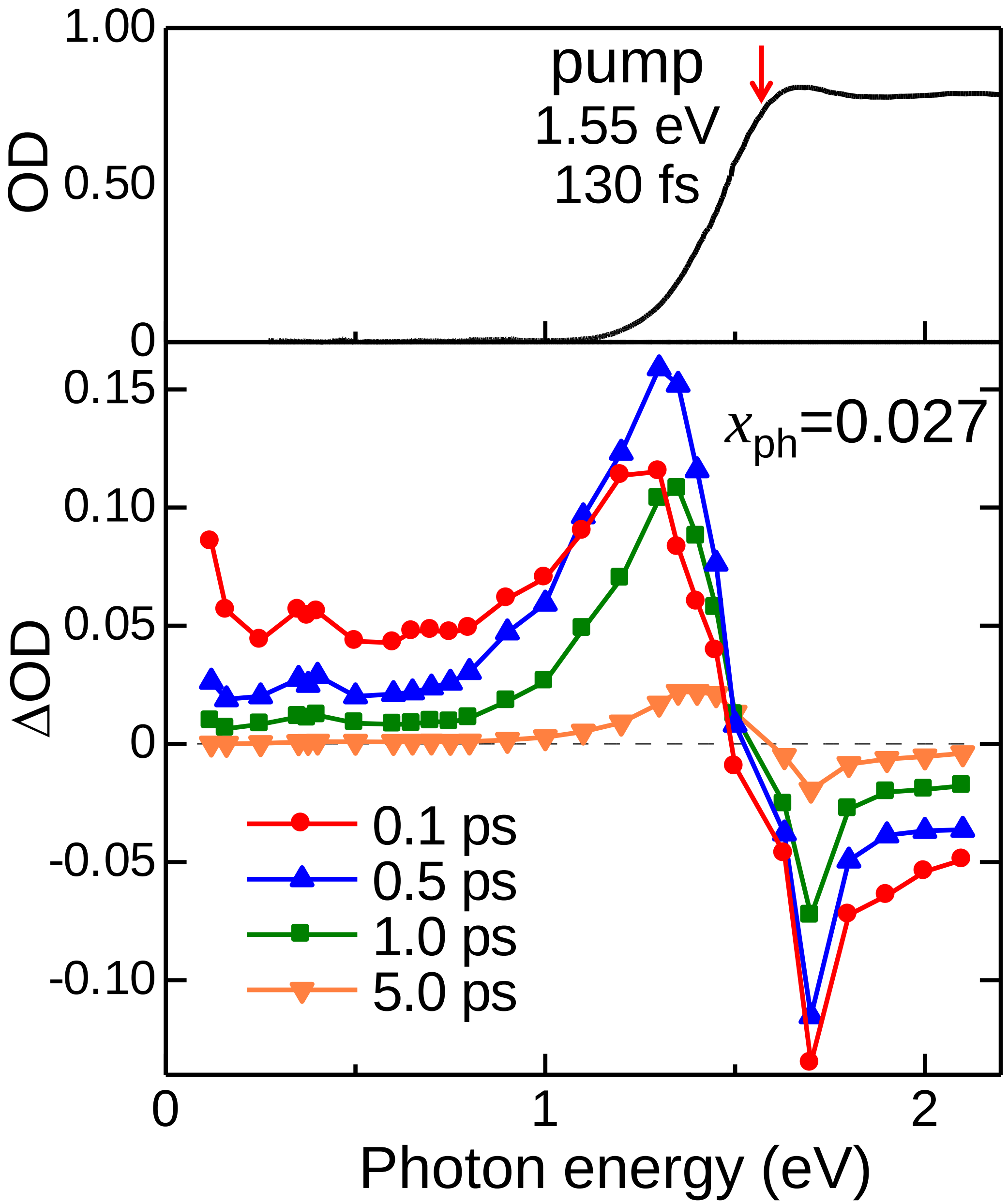

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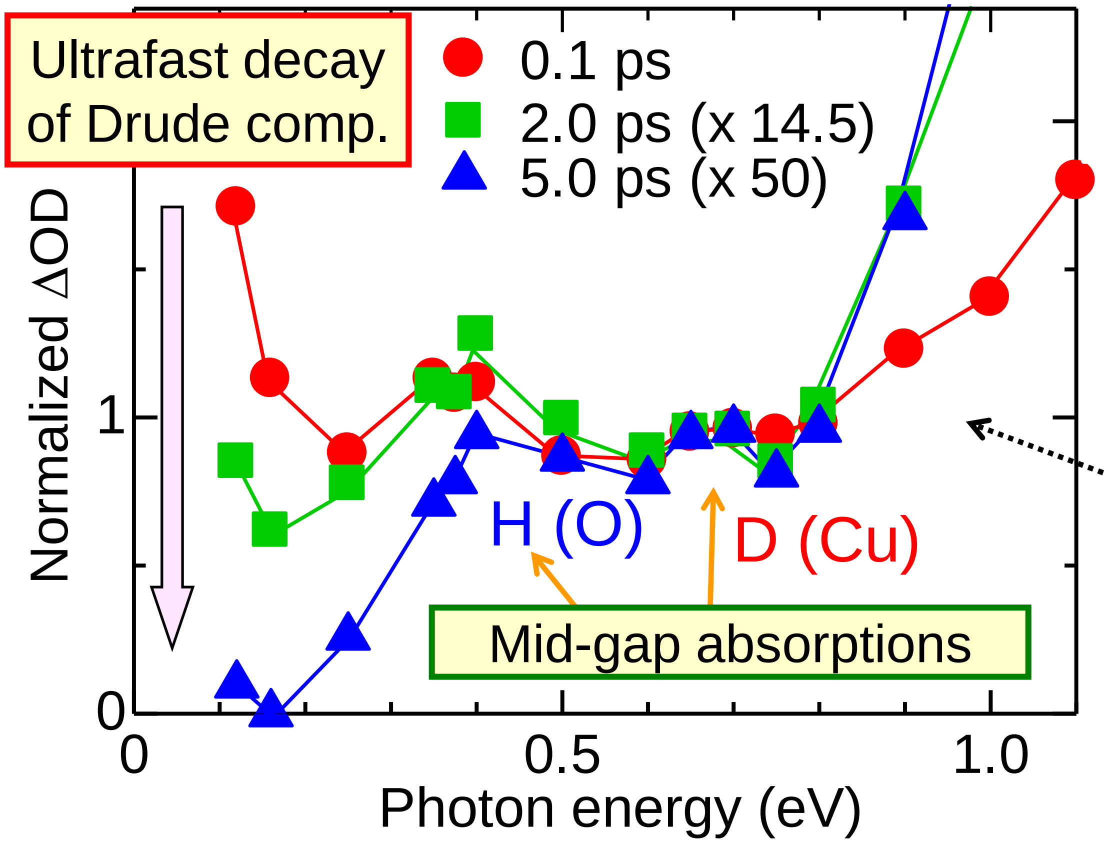

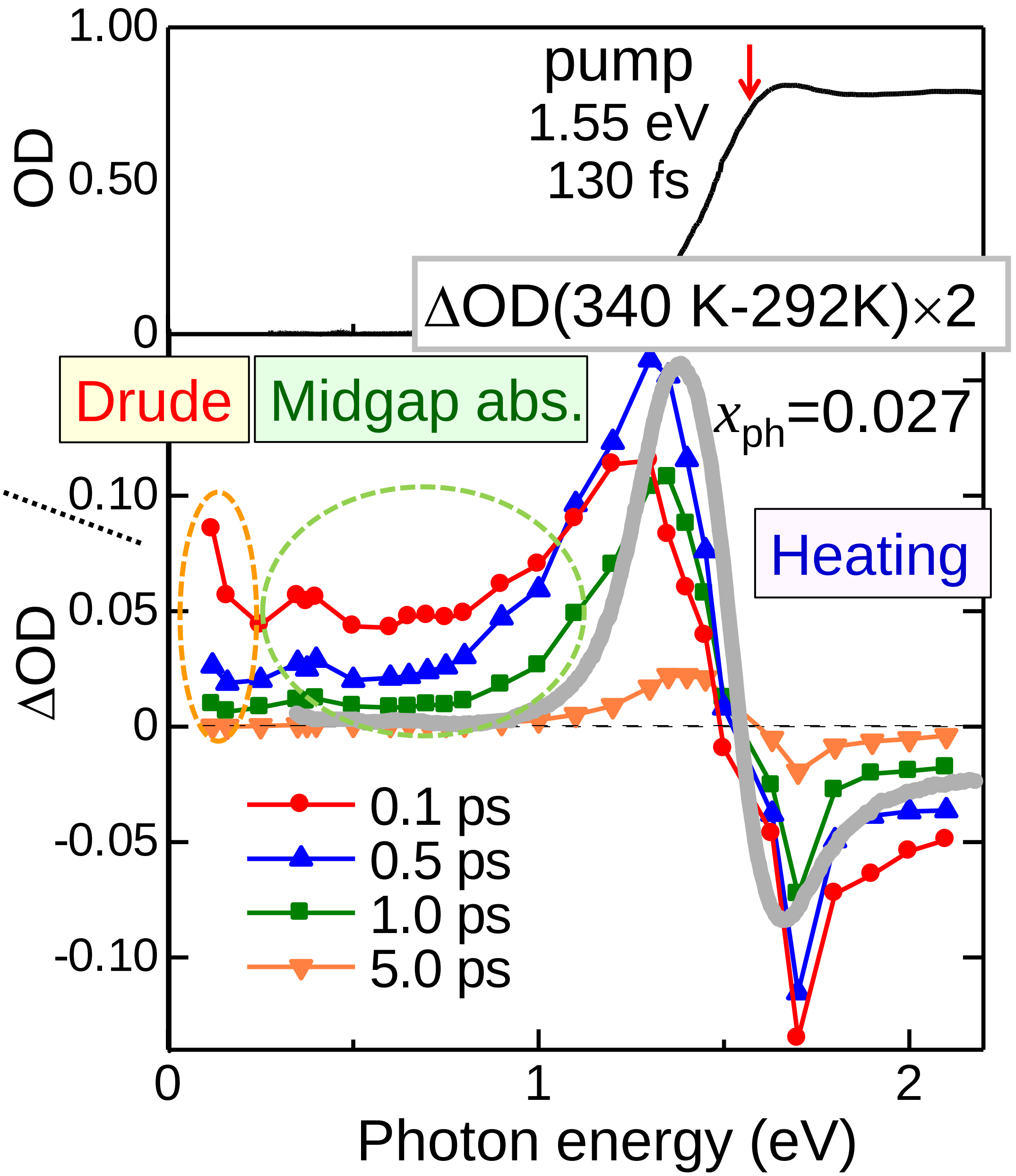

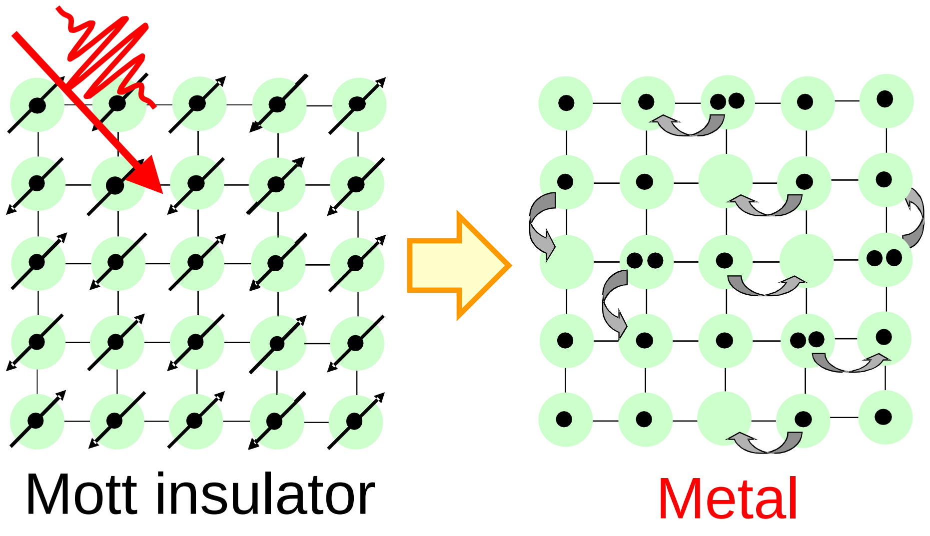

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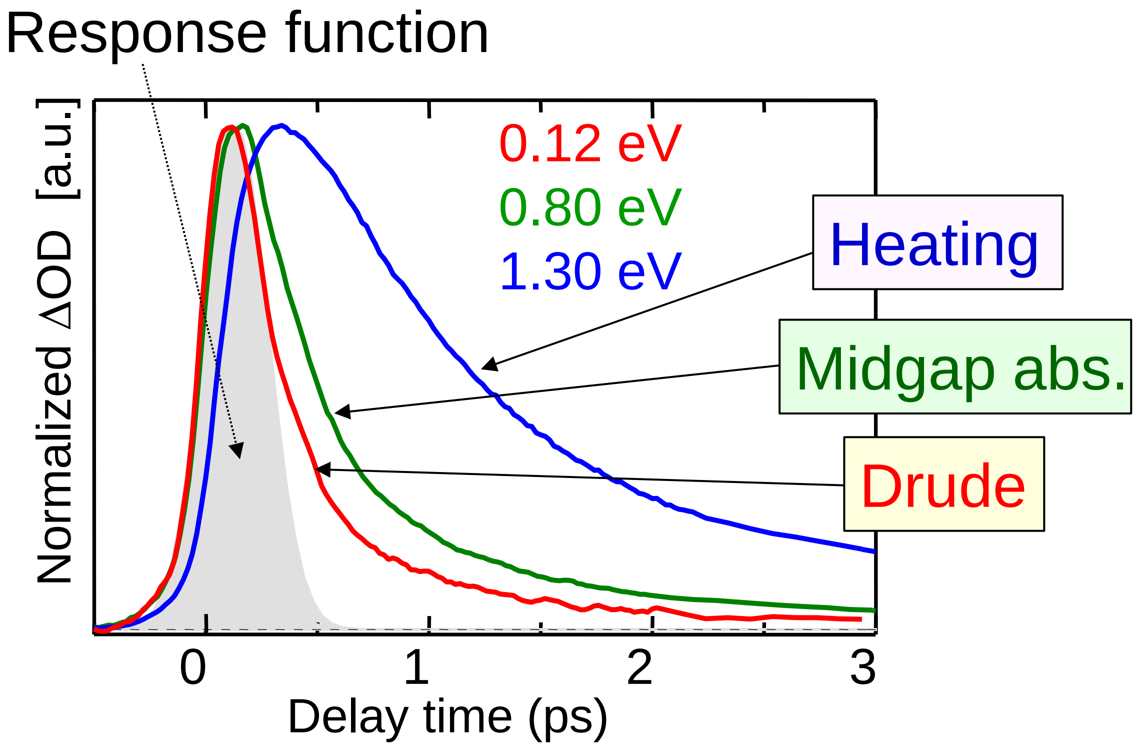

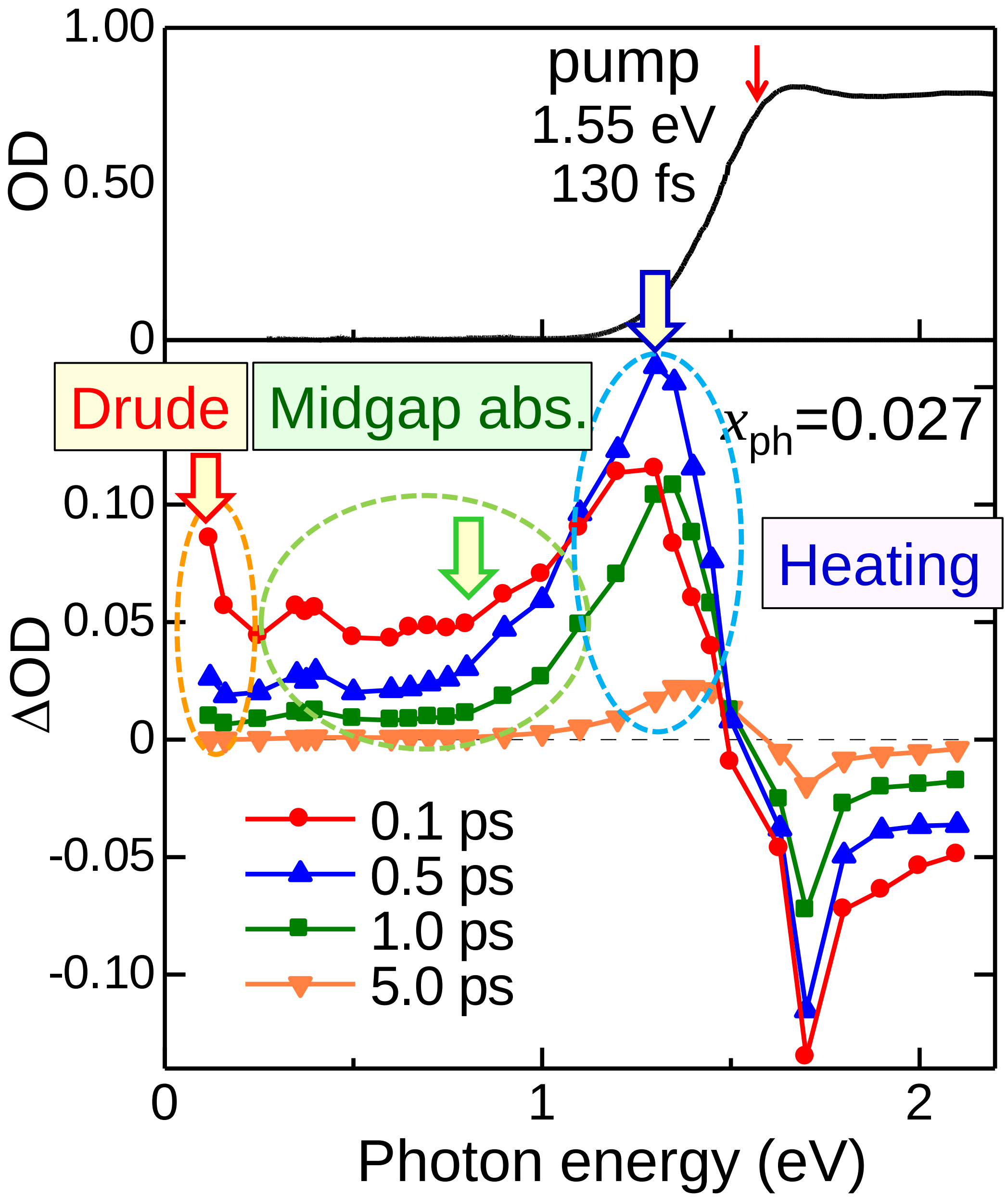

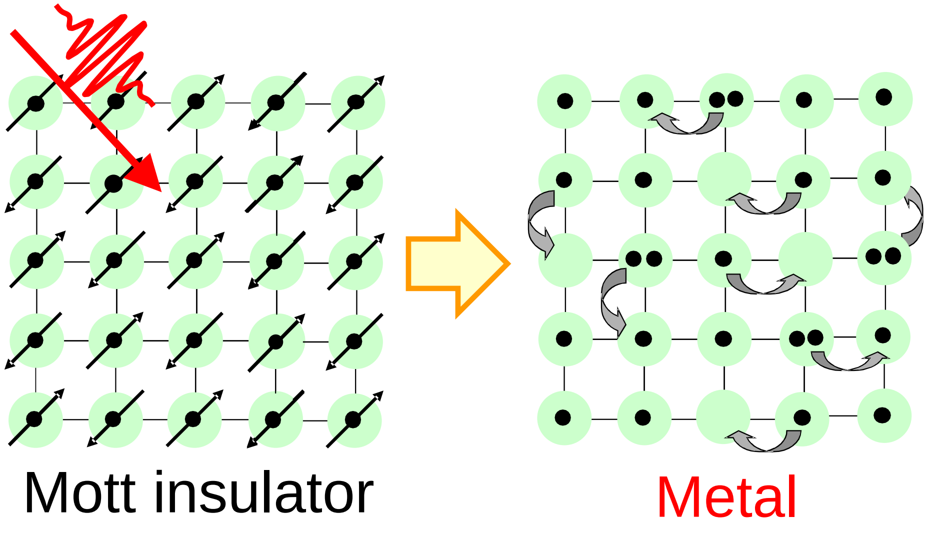

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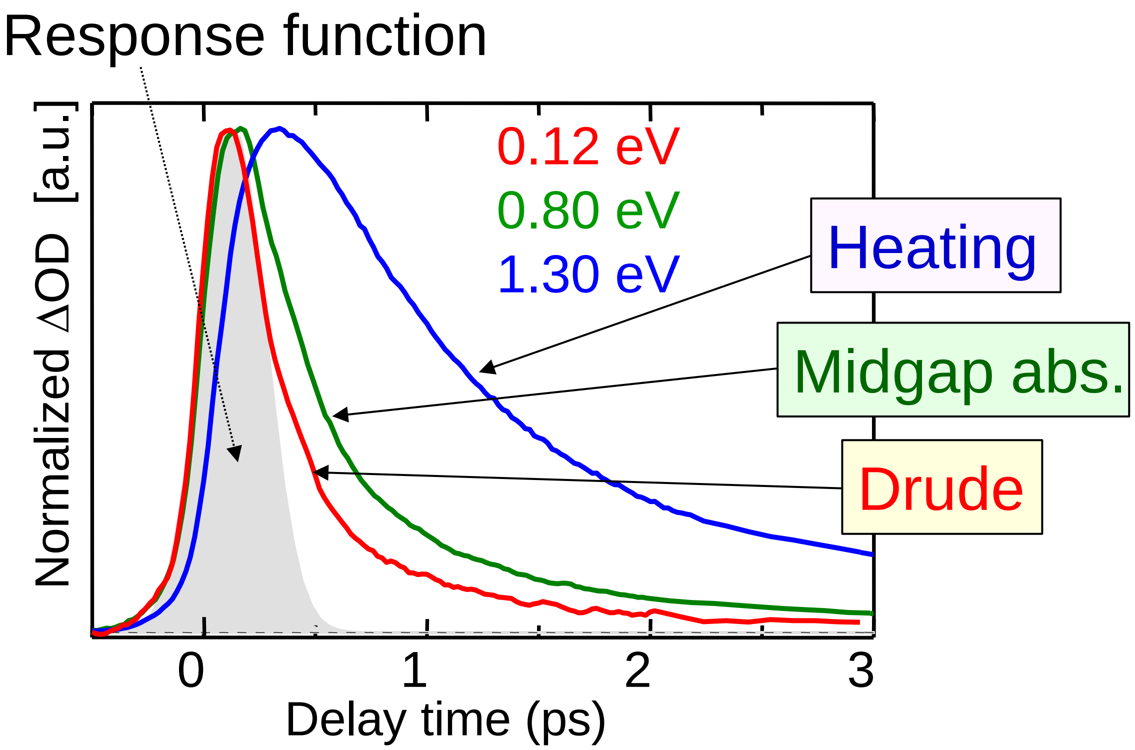
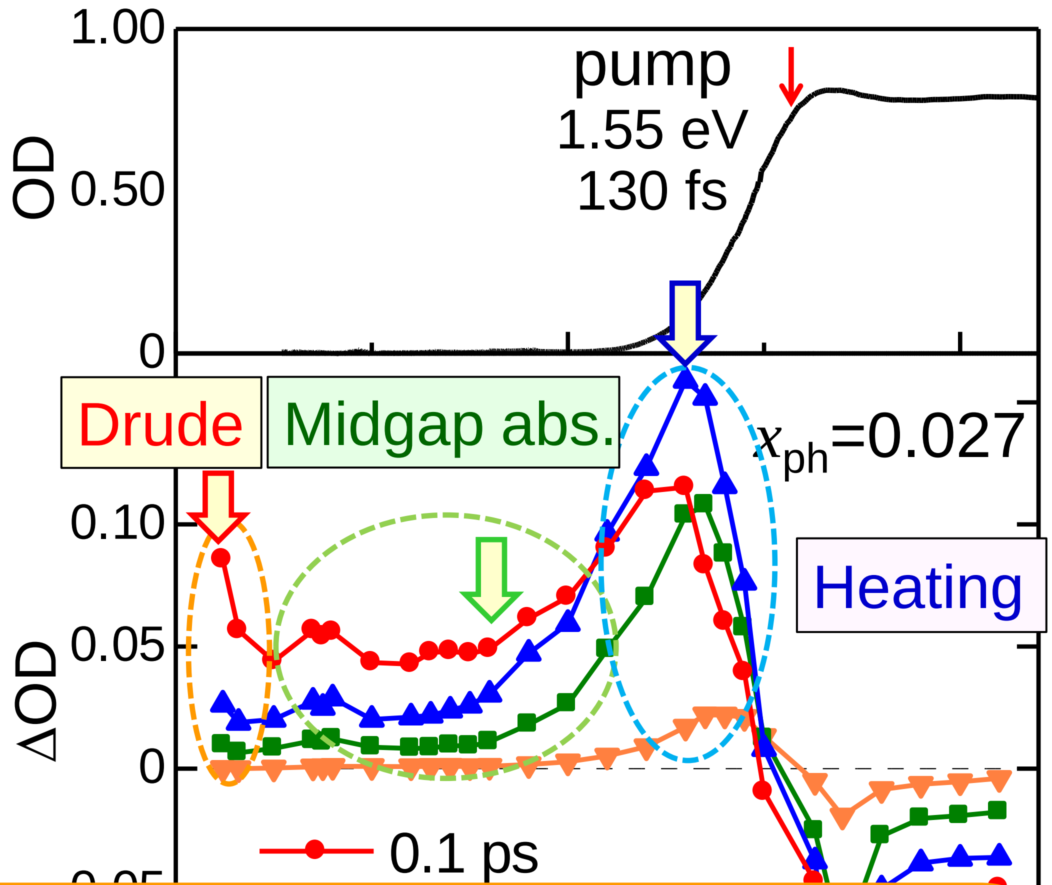
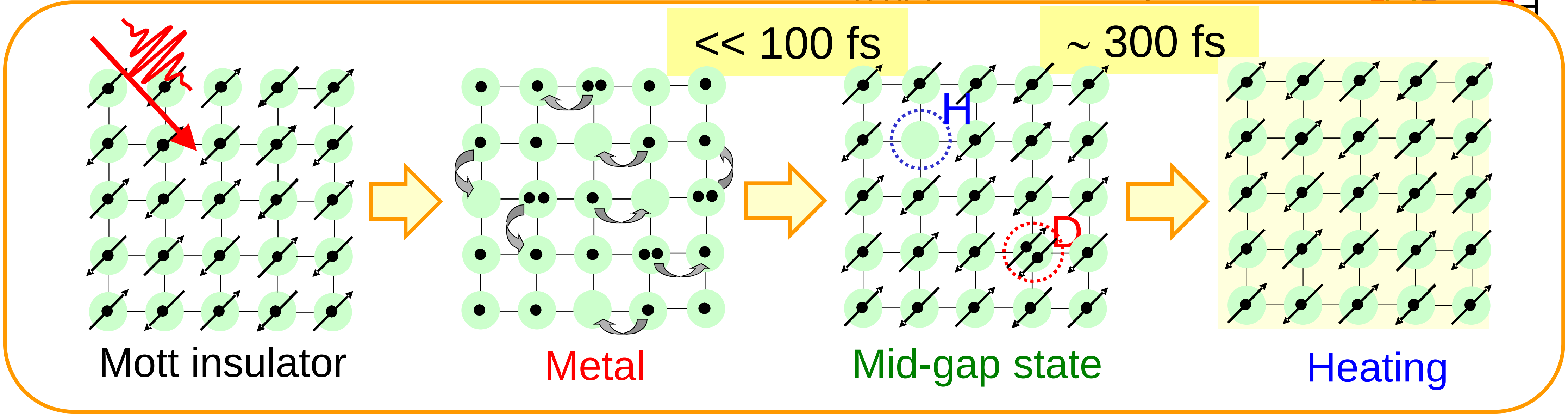
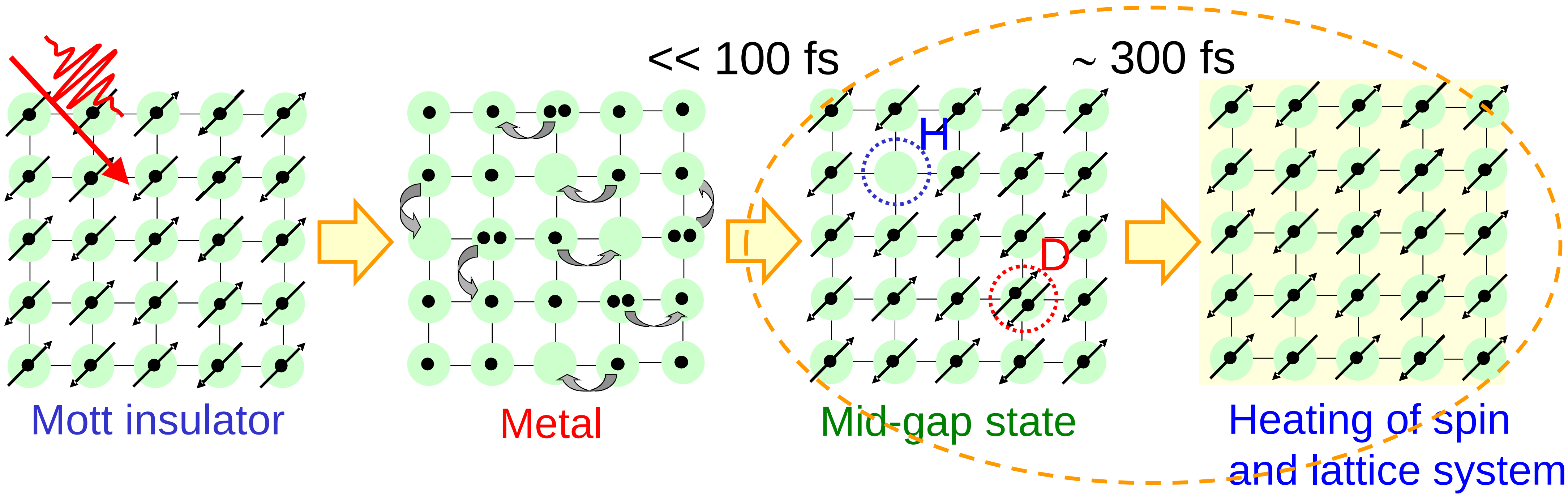
*H. Okamoto et al., PRB **82**, 060513R (2010), PRB **83**, 125102 (2011).*







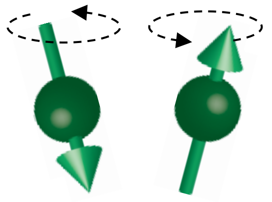
Photoinduced Mott-insulator to metal transition in Nd$_2$CuO$_4$ (180 fs res.)



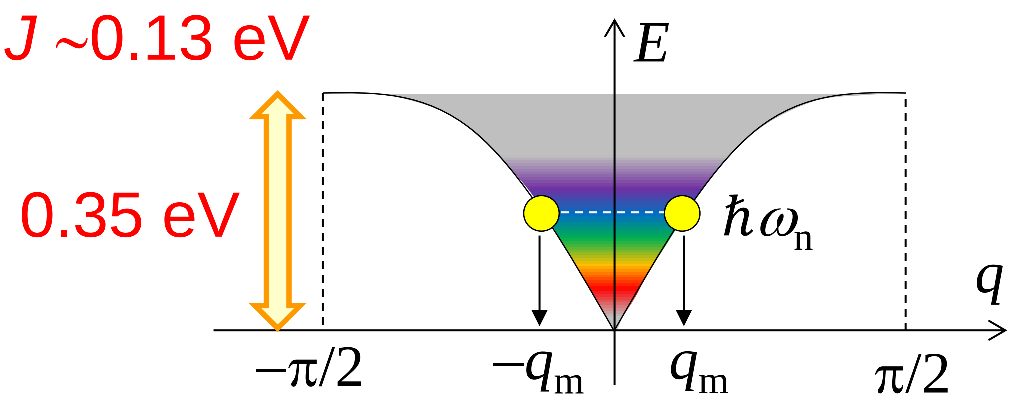
Fast recombination of a D-H pair ~300 fs ⇔ energy transfer to the spin system

Theory :

- *A. Takahashi, H. Gomi, and M. Aihara, PRL **89**, 206402 (2002)*
- *L. Vidmar, J. Bonca, T. Tohyama, and S. Maekawa, PRL **107**, 246404 (2011)*
- *Z. Lenarcic and P. Prelovsek, PRL **111**, 016401 (2013)*
- *E. Iyoda and S. Ishihara, PRB **89**, 125126 (2014)*

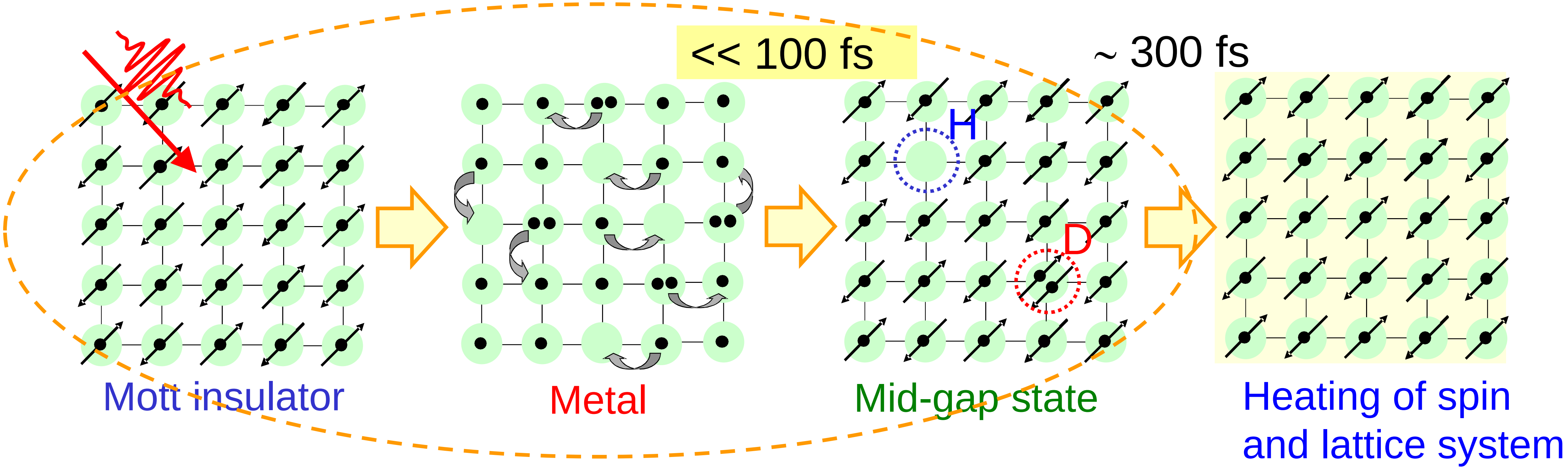


Magnon-dispersion



*K. Ishii et al., Nat. Commun. **5**, 3714 (2014)*

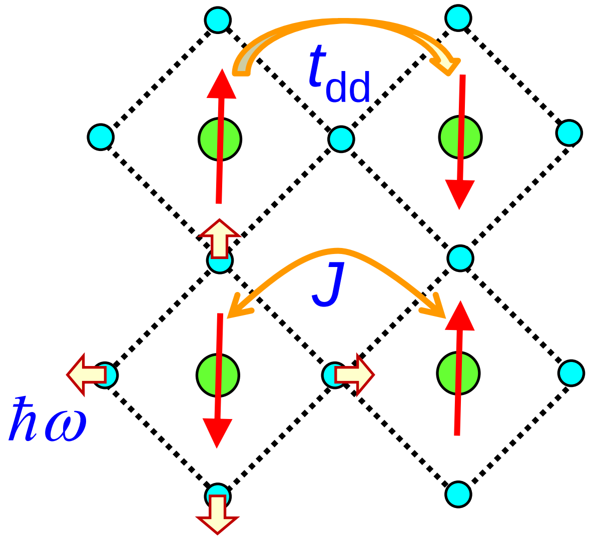
Photoinduced Mott-insulator to metal transition in Nd_2CuO_4 (180 fs res.)



Fast recombination of a D-H pair ~300 fs ⇔ energy transfer to the spin system

Photoniduced metallization and relaxation processes << 100 fs ⇔ ????

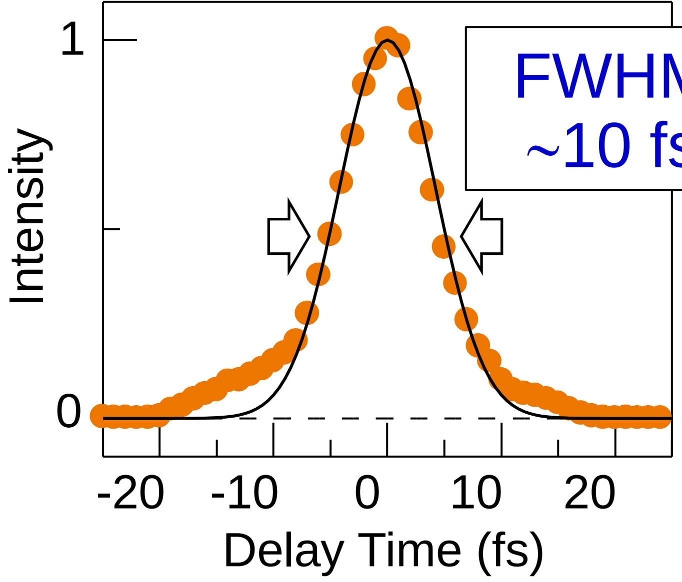
Transfer energy	t_{dd} , t_{pp} ~ 0.4 eV →	~ 10 fs
Exchange interaction	J ~ 0.13 eV →	~ 30 fs
Phonon frequency	$\hbar\omega$ ~ 500 cm^{-1} → ~ 0.06 eV	~ 60 fs



Time resolution of 10 fs is necessary.

Reflection-type pump-probe system using 7 fs pulses (time res. 10 fs）

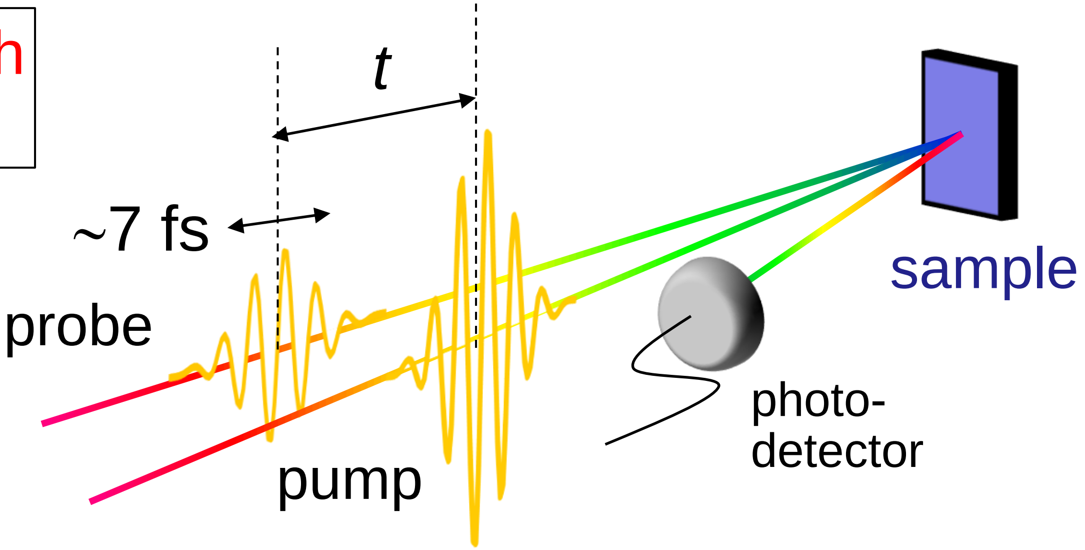
Cross correlation profile



FWHM
~10 fs

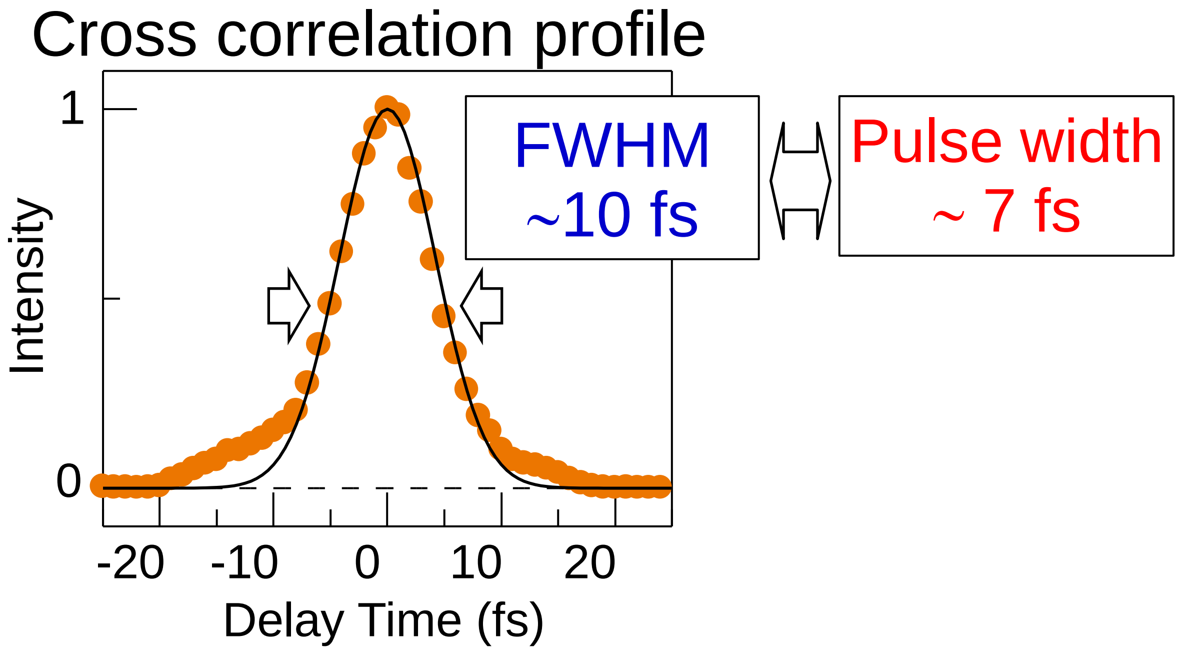
⟺

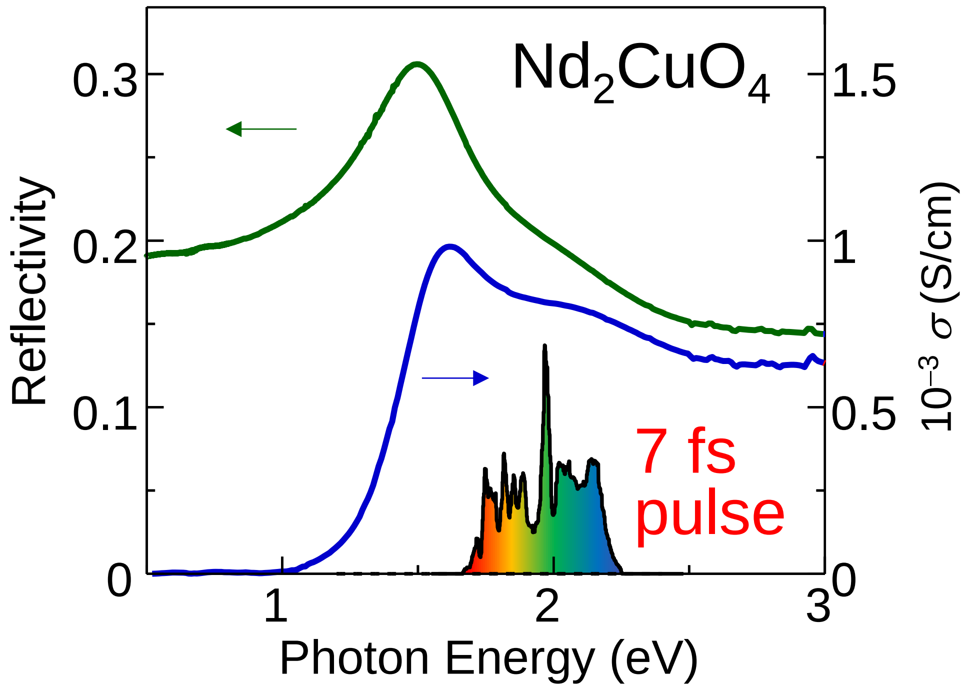
Pulse width
~ 7 fs



PP experiments with the time resolution of 10 fs on NCO

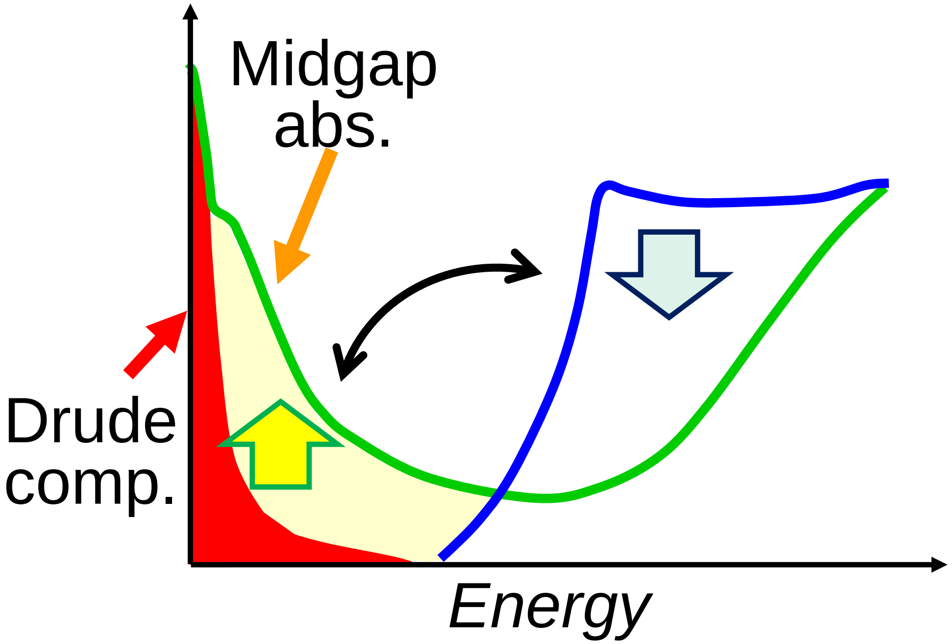
Reflection-type pump-probe system using 7 fs pulses (time res. 10 fs）



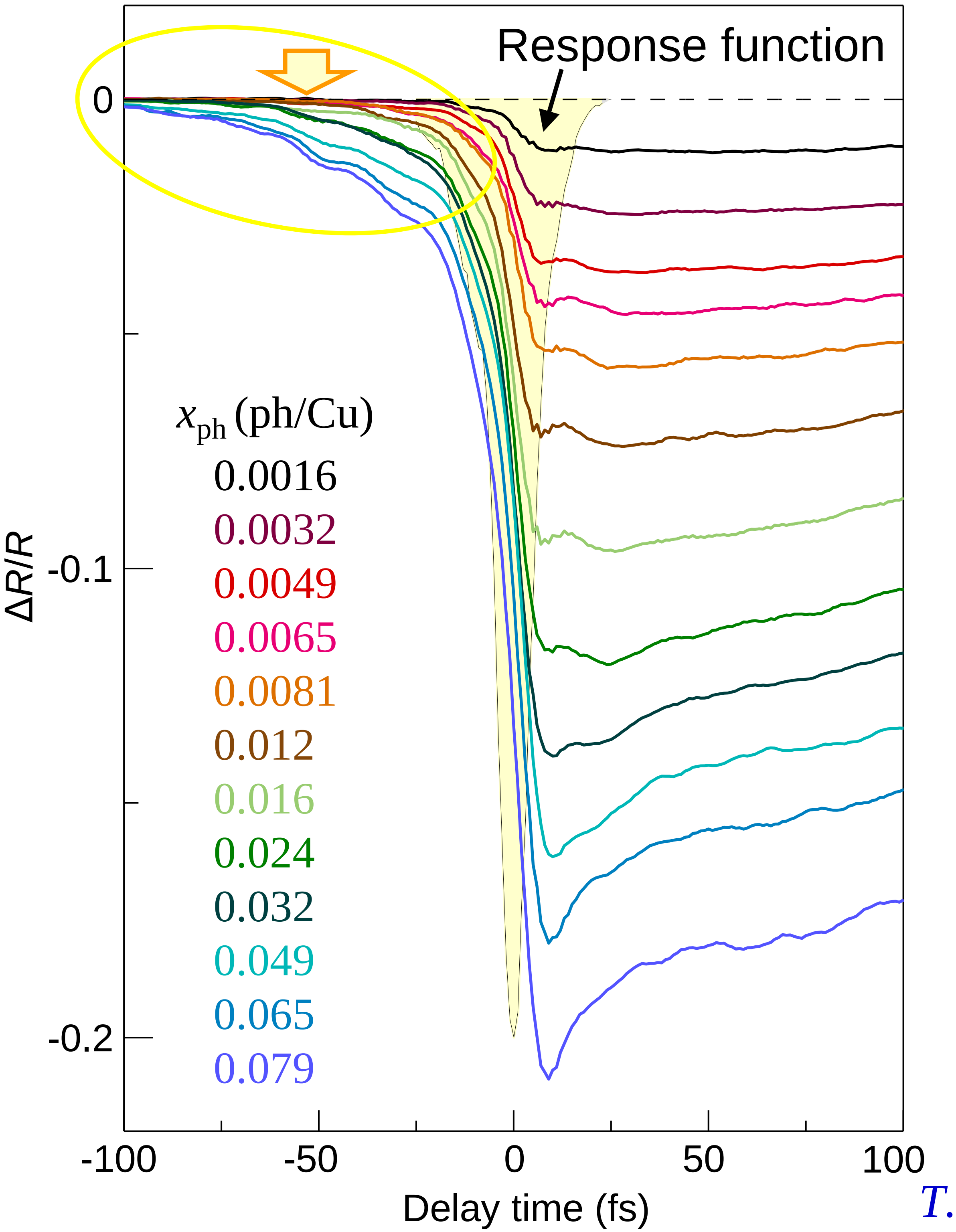


PP experiments with the time resolution of 10 fs on NCO

- ○ The spectral weight of the Mott gap transition should be transferred to the inner gap region.
- ○ Time evolutions of bleaching signals → detection of the dynamics of both metallic states and mid-gap states



Time evolutions of bleaching signals of the Mott-gap transition

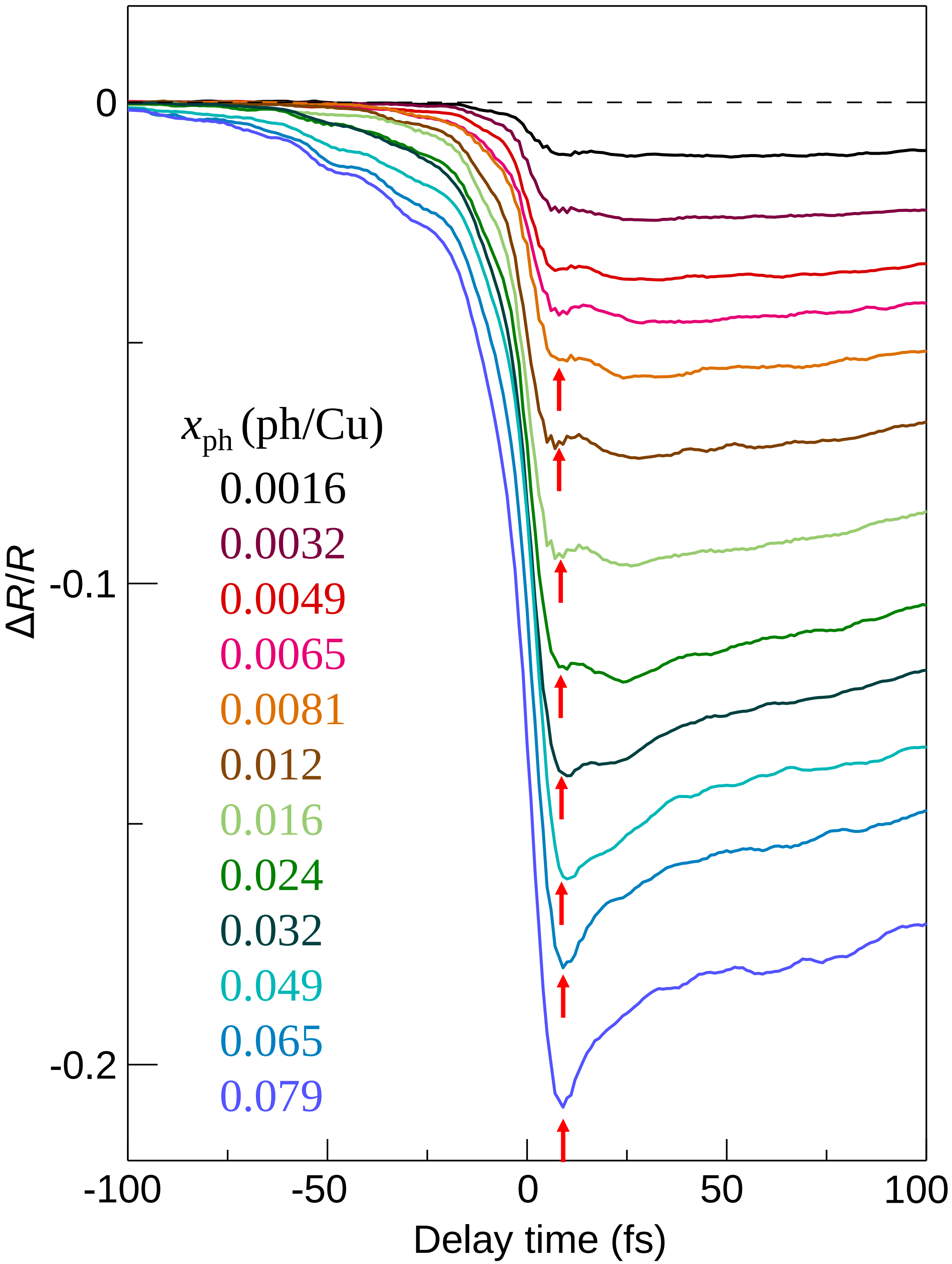


Perturbed free induction decay of probe-pulse induced polarization

C.H. Brito Cruz et. al.,
IEEE J. Quantum Electron. ***24*** *261 (1988)*

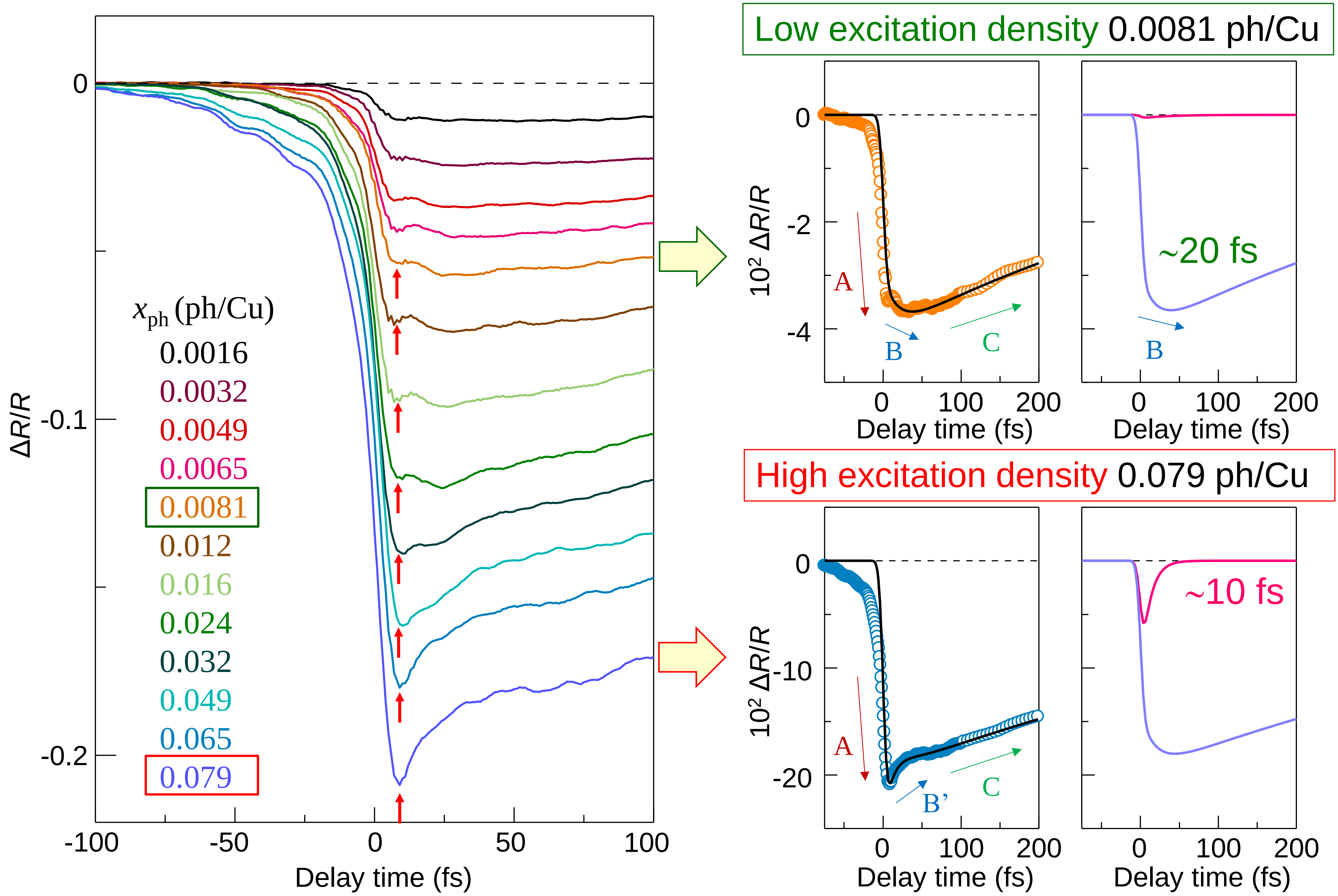
T. Miyamoto et al., Nat. Commun. ***9****, 3948 (2018)*

Time evolutions of bleaching signals of the Mott-gap transition



- Ultrafast dip structures
  → photoinduced metallic state
- Residual slow components
  → mid-gap states.

Time evolutions of bleaching signals for various excitation densities



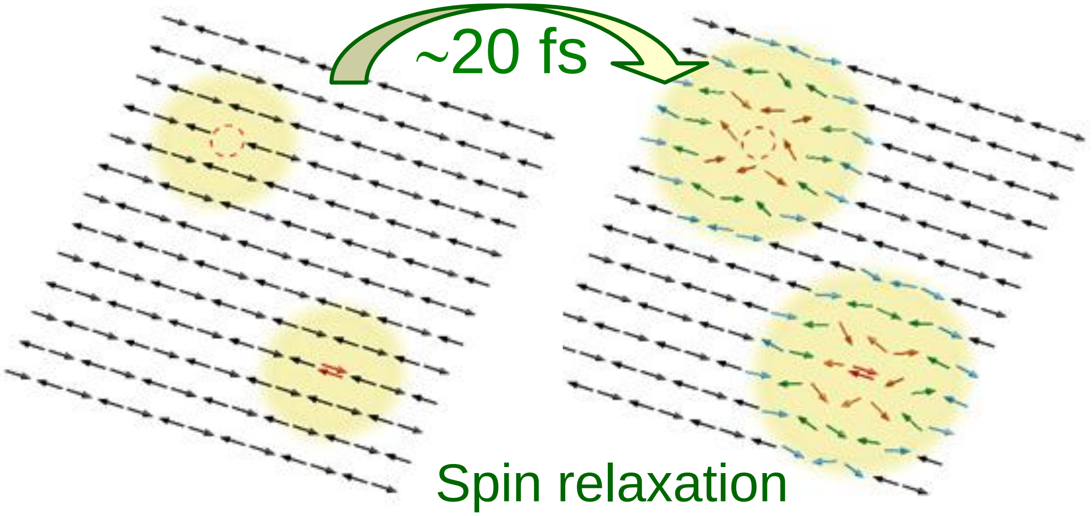
Low excitation density 0.0081 ph/Cu

High excitation density 0.079 ph/Cu

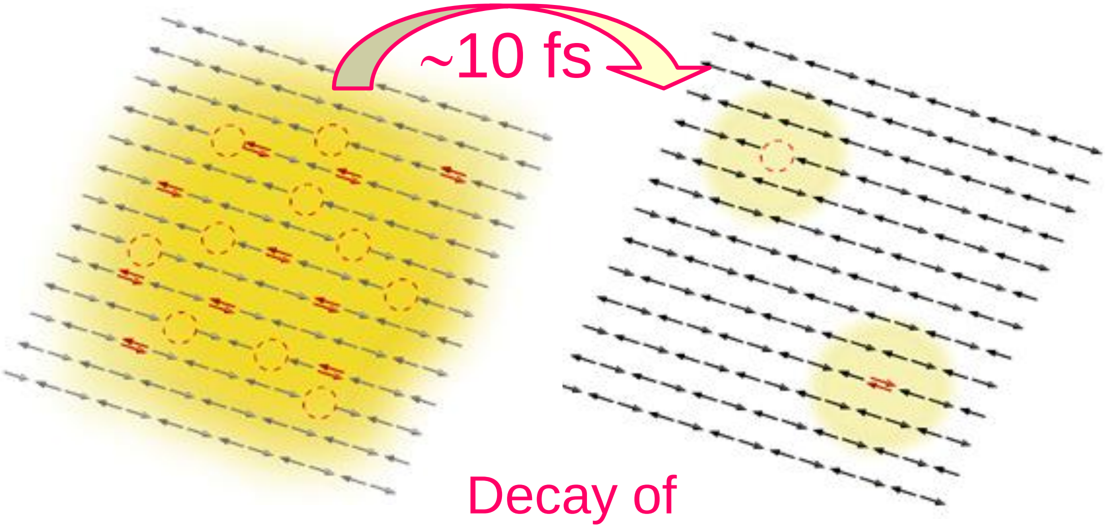
Time evolutions of bleaching signals of the Mott-gap transition

Time scale of phonon : $\hbar\omega$ ~500 cm^{-1} ⇔ 60 fs

Time scale of spin : J ~ 0.13 eV ⇔ 30 fs

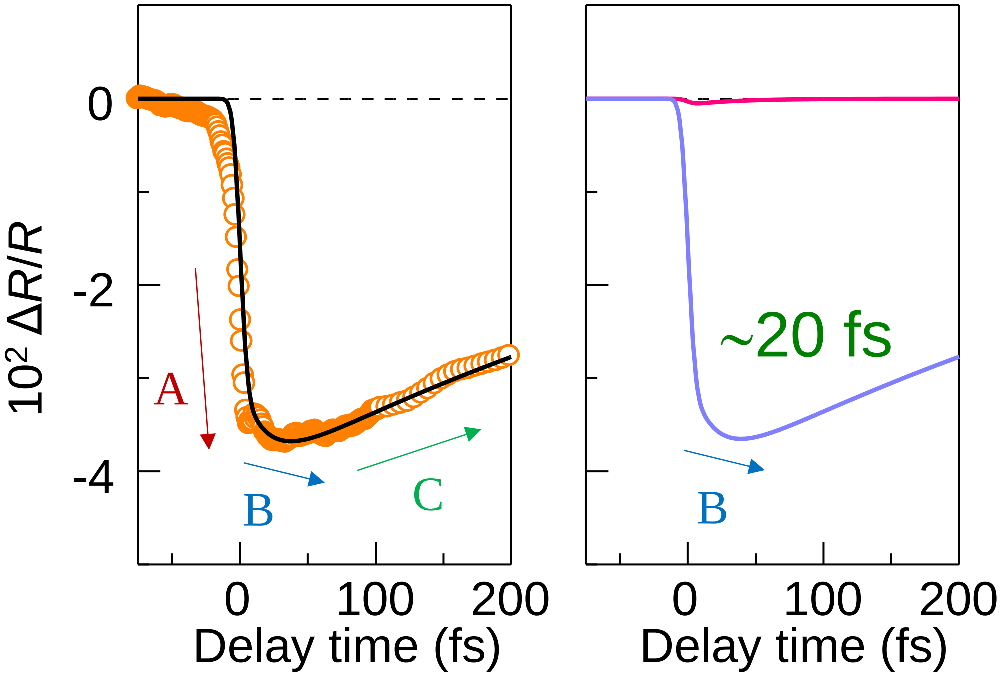


Spin relaxation
(magnetic polaron formation)

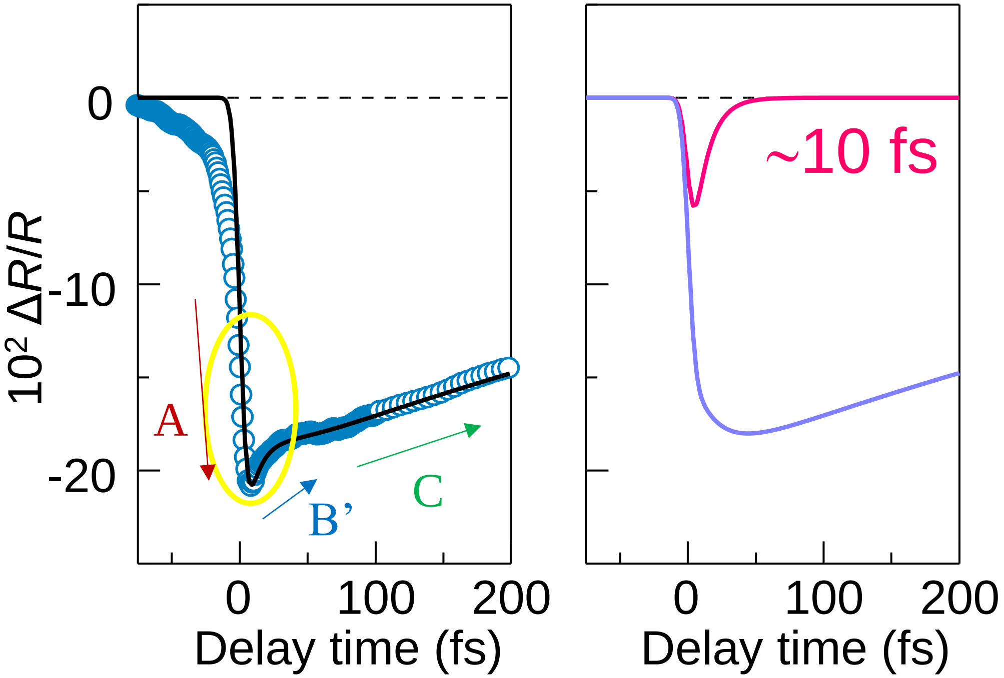


Decay of
metallic state

Low excitation density 0.0081 ph/Cu



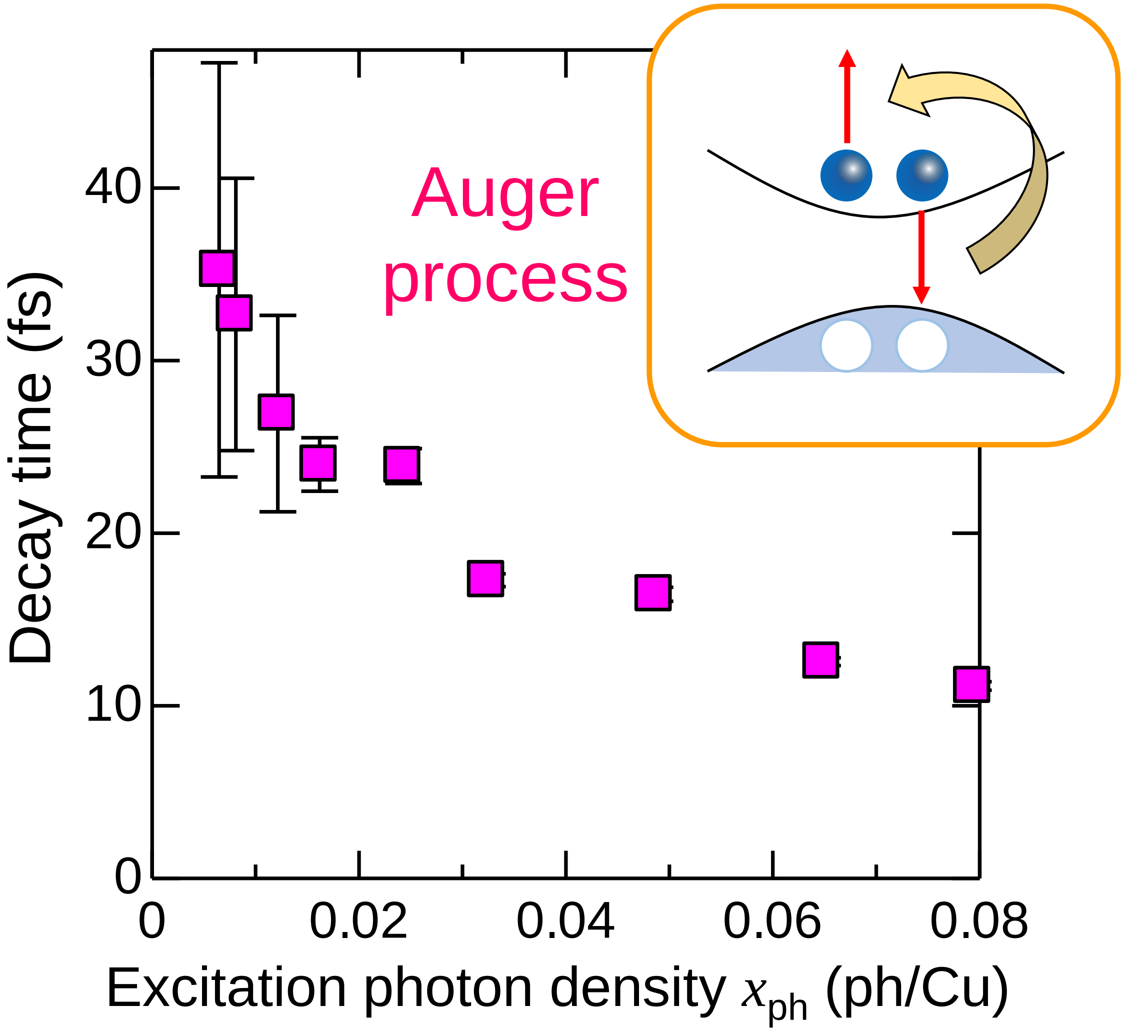
High excitation density 0.079 ph/Cu



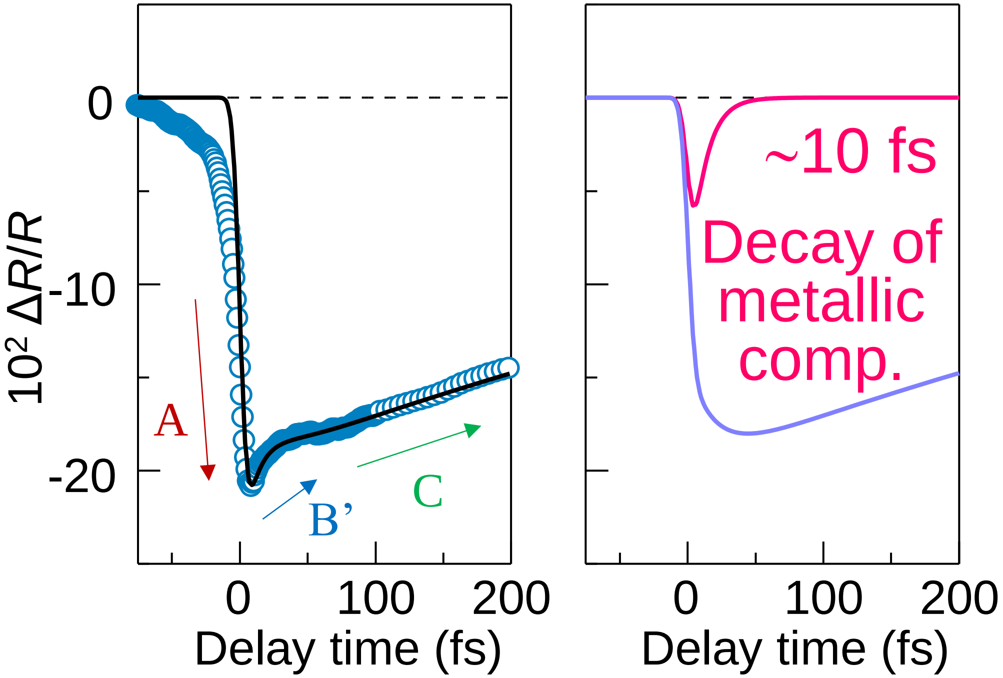
Excitation density dependence of the decay time of photoinduced metallic states

Time scale of phonon : $\hbar\omega \sim 500\ \mathrm{cm}^{-1}$ ⇔ 60 fs
Time scale of spin : $J \sim 0.13$ eV ⇔ 30 fs

Decay time of the ultrafast components reflecting the metallic states



High excitation density 0.079 ph/Cu



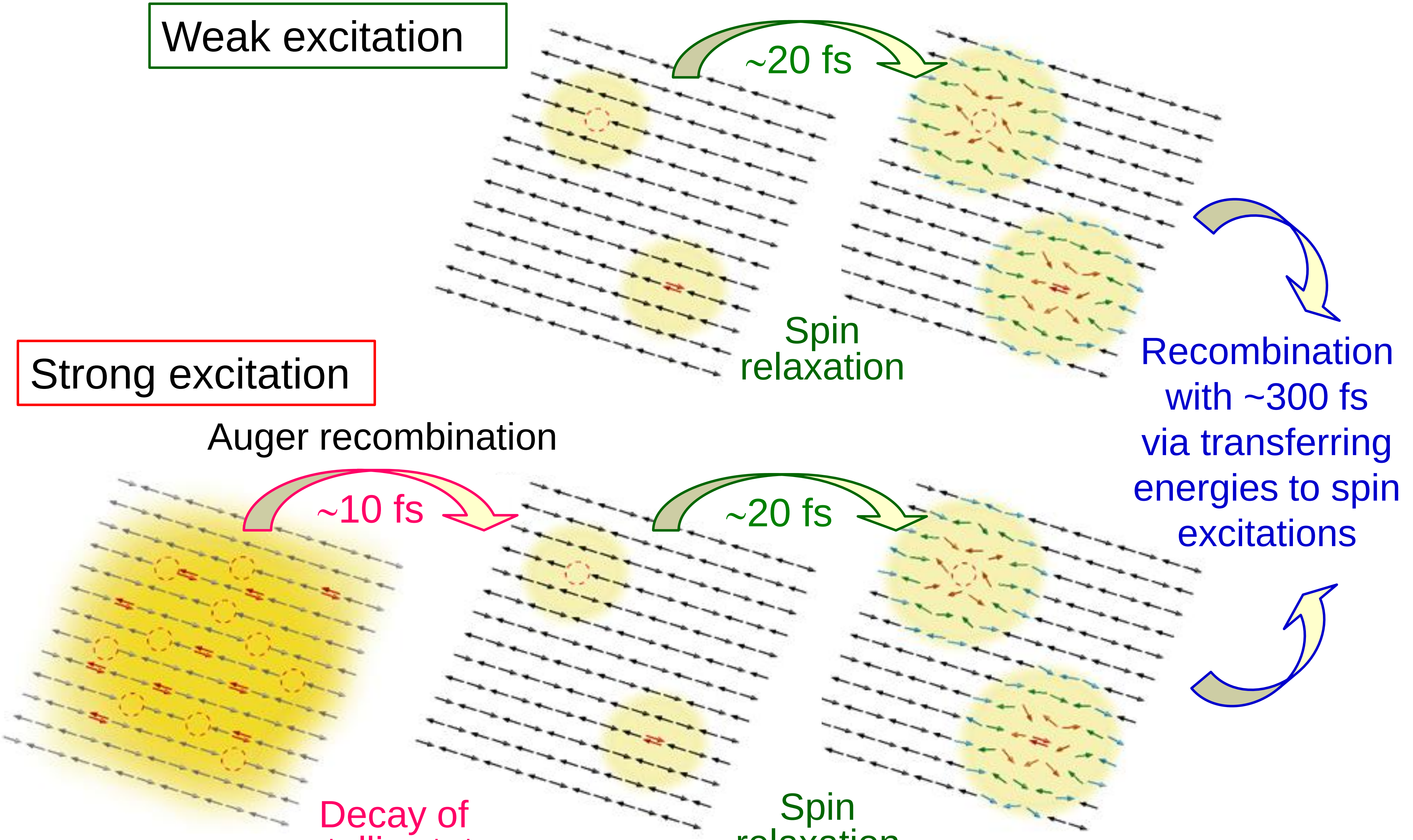
Decrease in the decay time
with increase of the excitation density

Auger recombination of carriers,
where a D-H pair recombines by
transferring its energy to other carriers

Efficient carrier scatterings specific to
correlated electron systems

T. Miyamoto et al., Nat. Commun. **9**, *3948 (2018)*

Summary 1: Overall photoinduced metallization and relaxation dynamics



Weak excitation

~20 fs

Spin
relaxation

Recombination
with ~300 fs
via transferring
energies to spin
excitations

Strong excitation

Auger recombination

~10 fs

~20 fs

Decay of
metallic states

Spin
relaxation
(magnetic polarons)
weakening the antiferromagnetic spin arrangements

Content

1. Introduction
   - Half-filled 1D and 2D Mott insulators
   - Overview of their optical responses

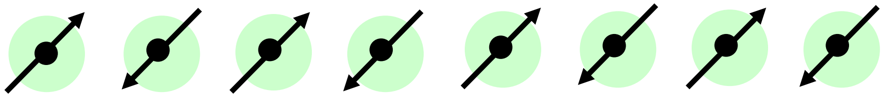
2. Photoinduced Mott-insulator to metal transitions
   - Concept
   - 1D and 2D Mott insulators

3. Terahertz electric-field induced phase transitions
   - Mott insulator to metal transition
   - Mott insulator to polar charge-order transition

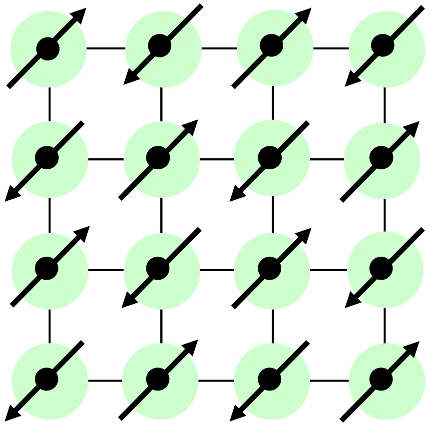
4. Floquet states formed by a mid-infrared electric field in Mott insulators
   - Photon-dressed Floquet states in 1D Mott insulators
   - Phonon-dressed Floquet states in 1D dimerized Mott insulators
   - Attempts of Floquet engineering

5. Summary

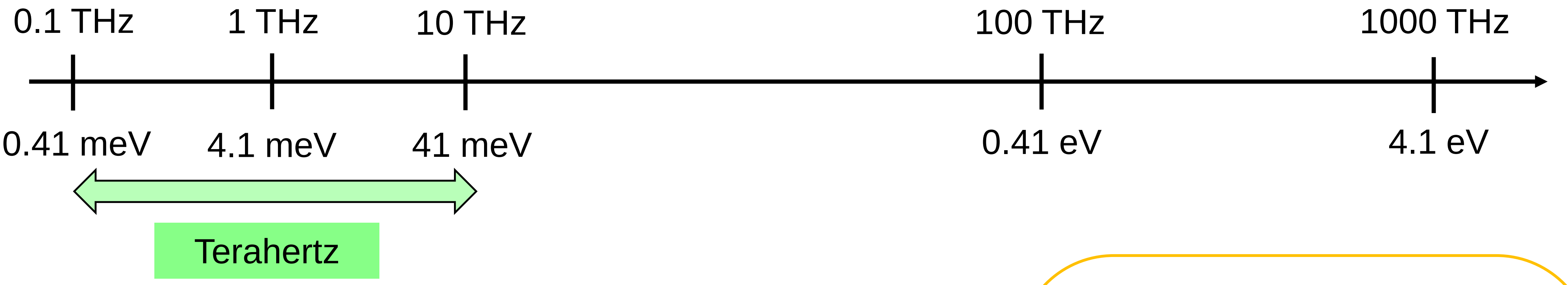
1D Mott insulator

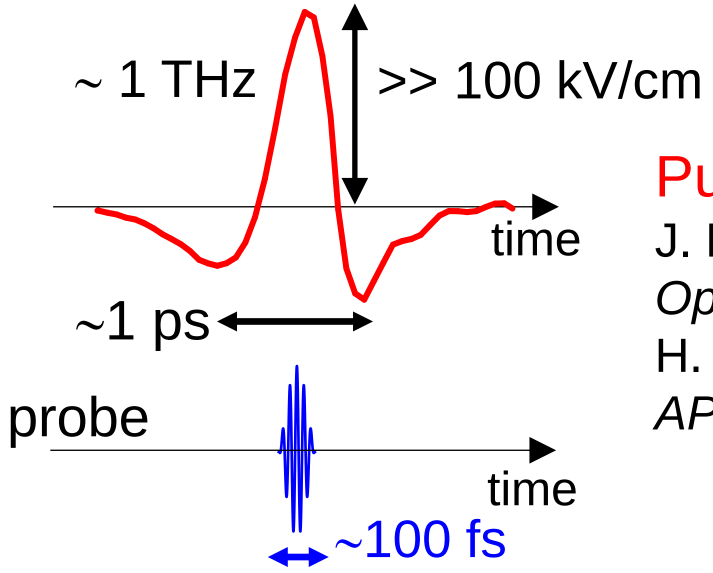


2D Mott insulator



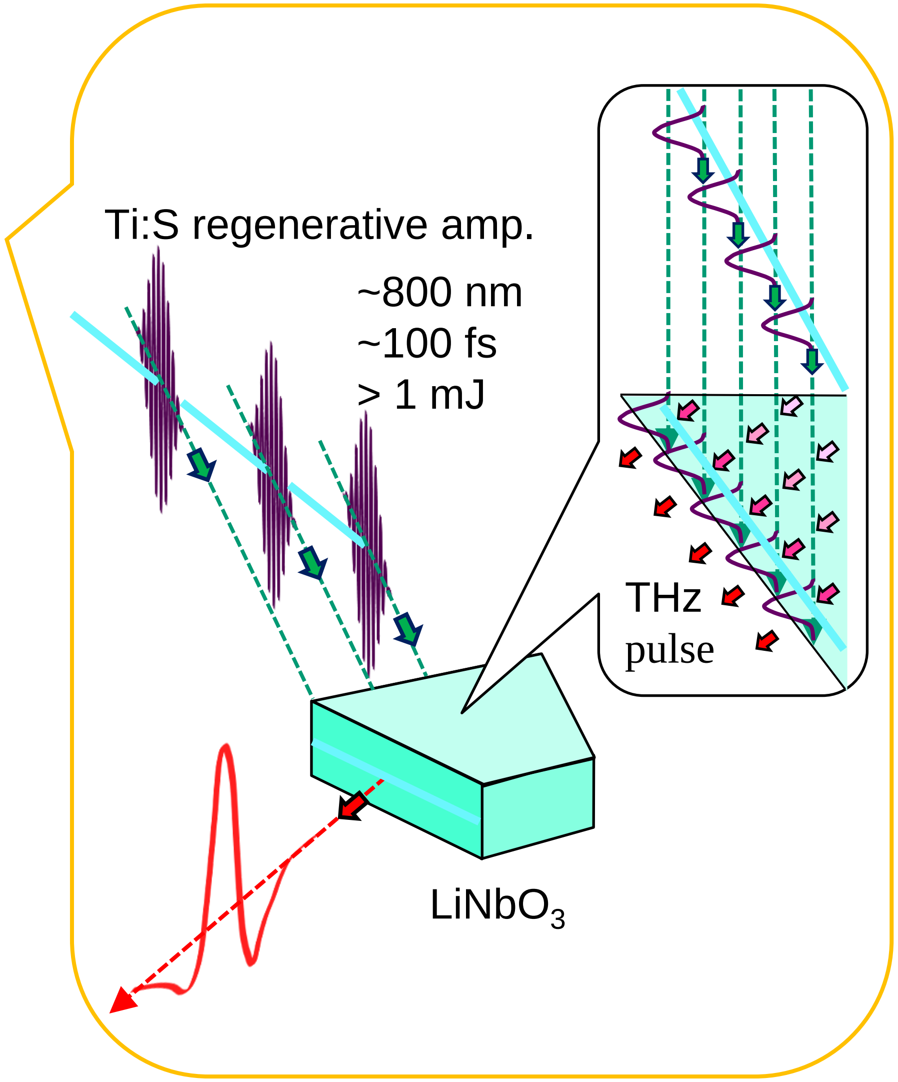
Electronic-state controls by an intense terahertz pulse





Pulse-front tilting method:

J. Hebling *et al*.,
Opt. Express **10**, 1161 (2002).
H. Hirori *et al*.,
APL **98**, 091106 (2011).



✓ A strong electric field (>>100 kV/cm) can be applied in a specific direction.
→ electric-field induced phase transitions

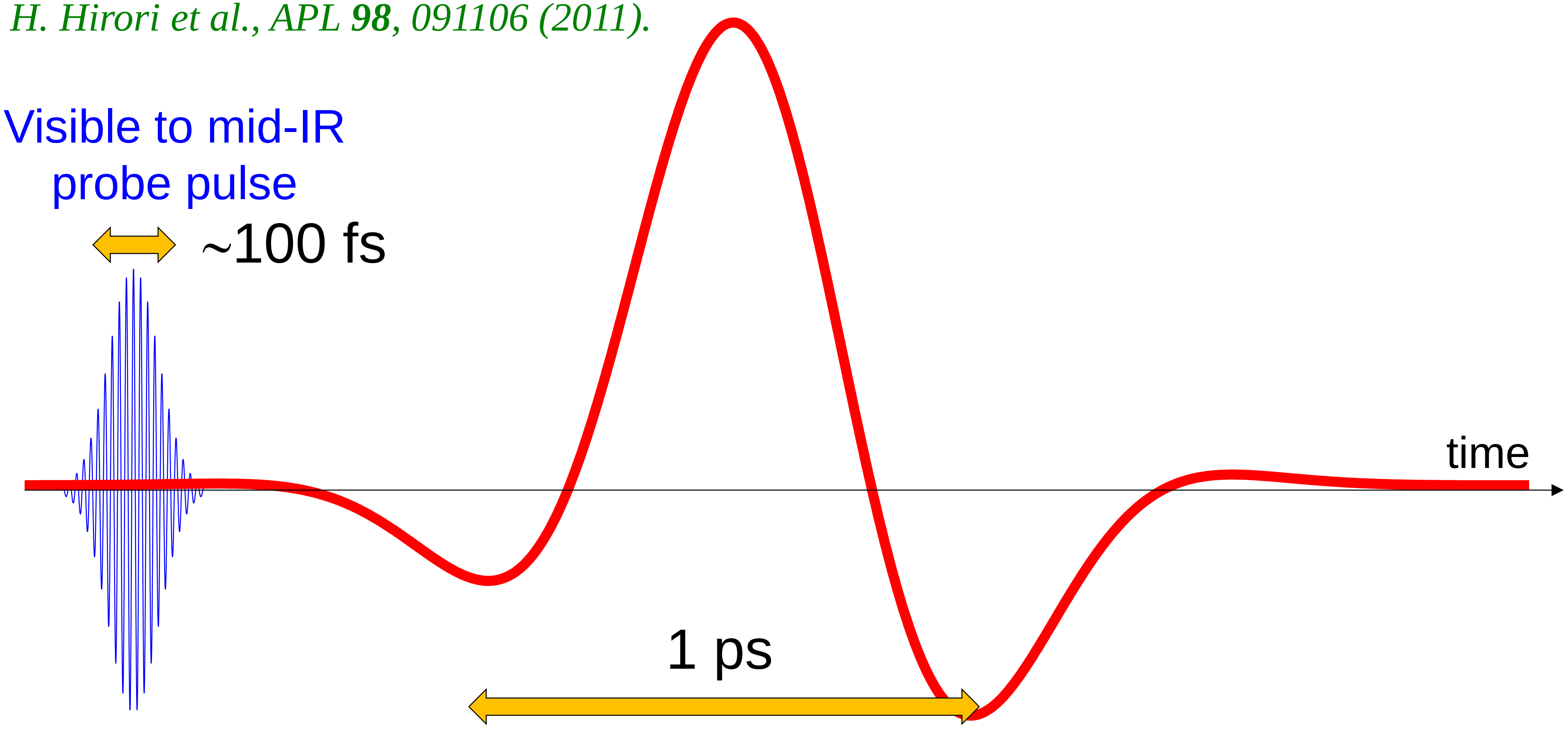
✓ By using a probe pulse with a time width of ~ 100 fs, electronic state changes along the electro-magnetic field can be detected.
→ sub-cycle spectroscopy

Sub-cycle spectroscopy using a strong THz pulse

Pulse front tilting

J. Hebling et al., Opt. Express ***10****, 1161 (2002).*

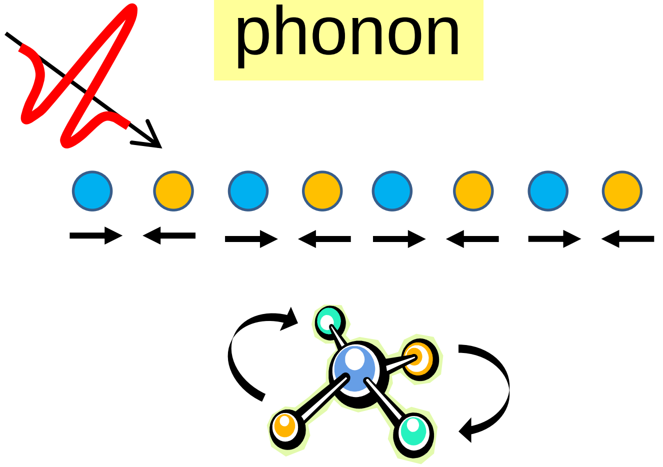
H. Hirori et al., APL ***98****, 091106 (2011).*



By using a probe pulse with a time width of ~ 100 fs, electronic state changes along the electro-magnetic field can be detected.

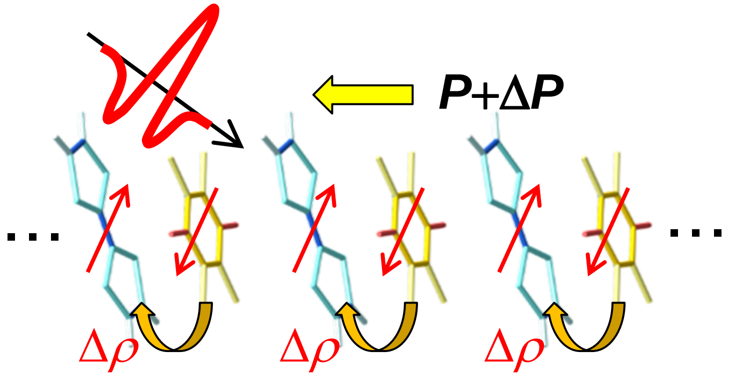
Attempts to control physical properties using a strong THz pulse

phonon



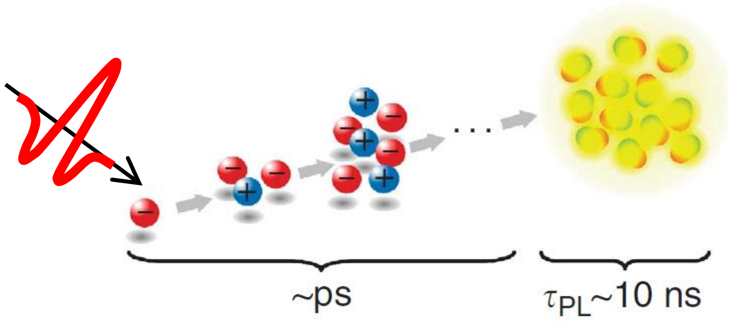
I. Katayama et al., *PRL* (2012)

polarization



T. Miyamoto *et al*.,
Nat. Commun. (2013)

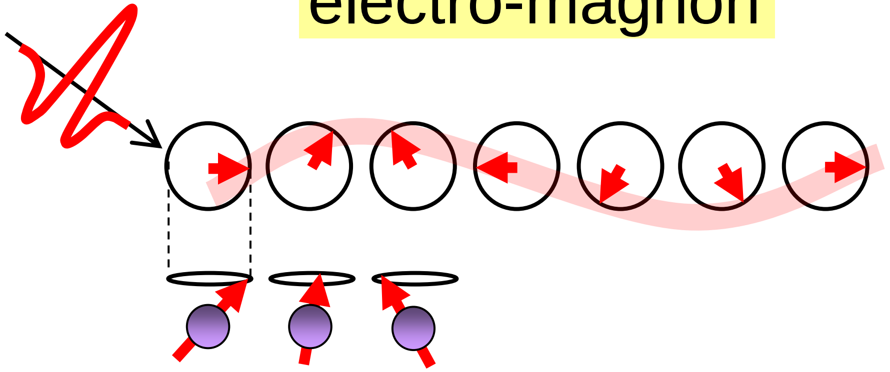
carrier number



M. C. Hoffmann *et al*., *PRB* (2009)
H. Hirori et al., *Nat. Commun*. (2013)

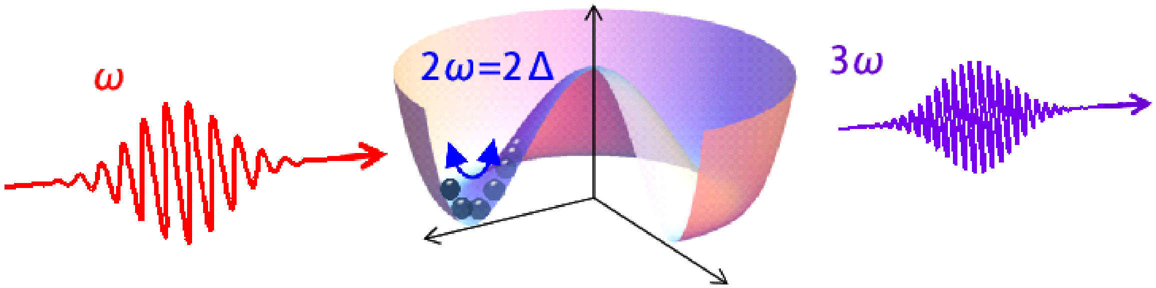
magnon

electro-magnon



T. Kampfrath et al.,
Nature Photonics (2010)
T. Kubacka *et al*., *Science* (2014)

superconducting order parameter

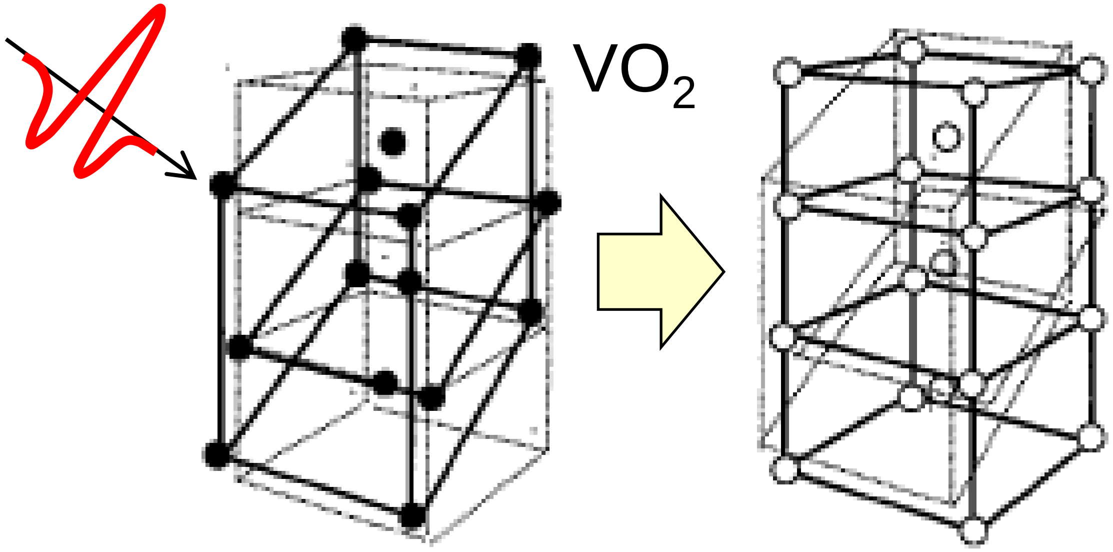


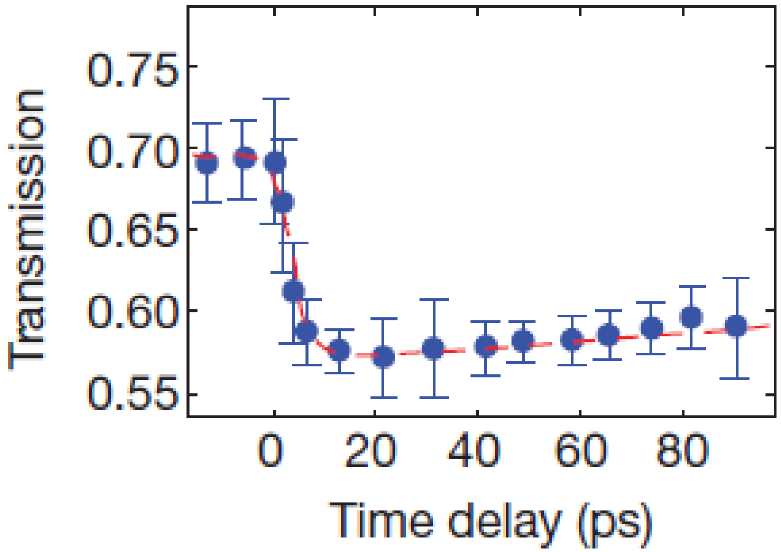
R. Matsunaga, N. Tsuji, R. Shimano *et al*.,
Science (2014)

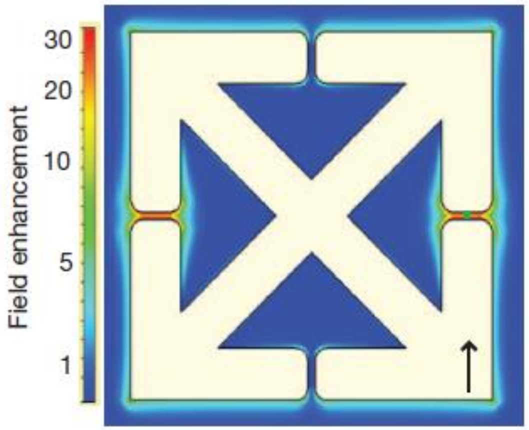
Attempts to drive a phase transition by a strong THz pulse

insulator-metal transition

M. Liu, R. Averitt, K.A. Nelson *et al.*, *Nature* (2012)





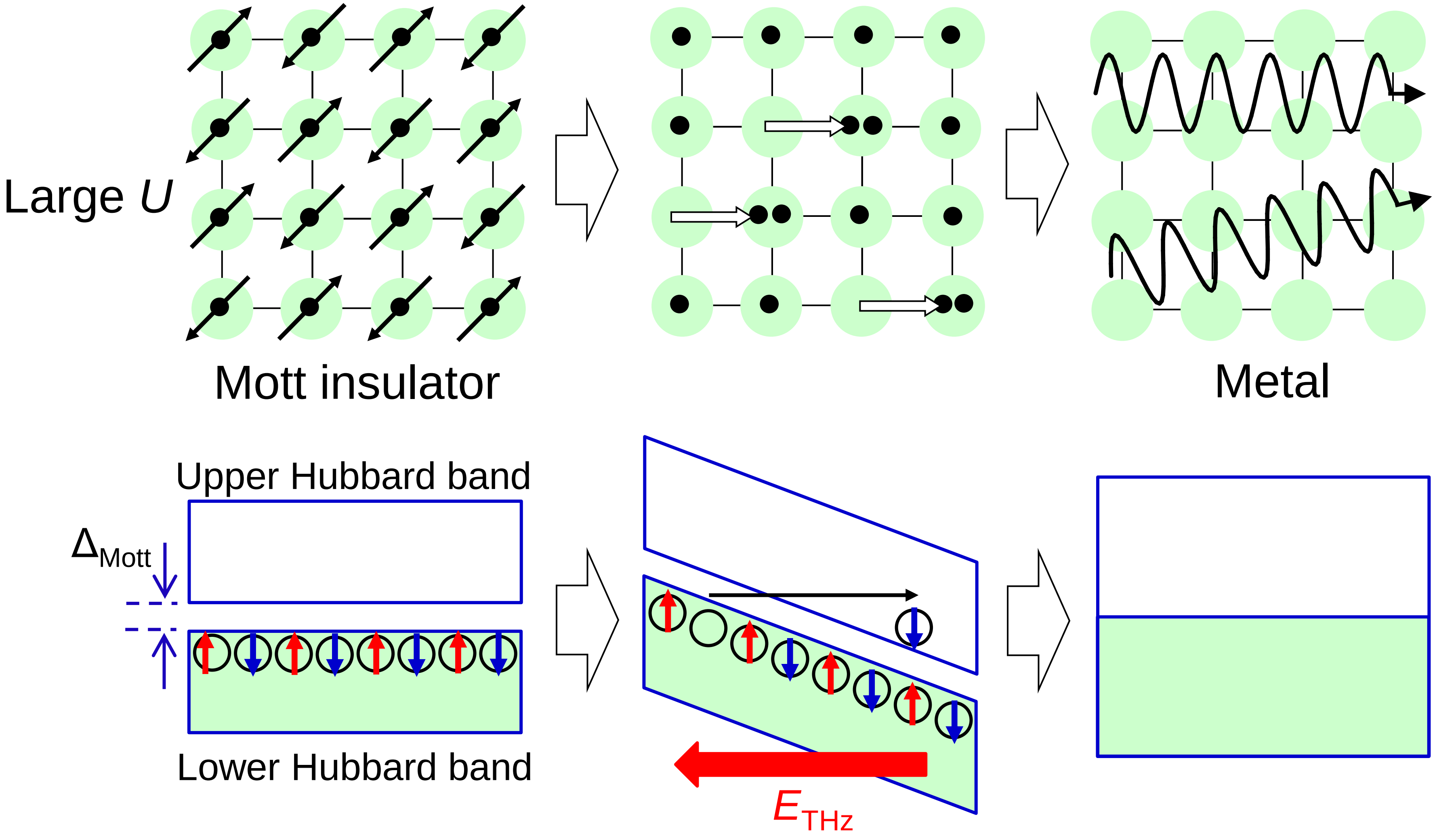


An insulator to metal transition was induced by a terahertz electric field enhanced to ~2 MV/cm in a metamaterial resonator.

- Heating due to accelerations of carriers
- Large structural change
- Slow transition dynamics >> 1 ps

To achieve an ultrafast phase control in a sub-picosecond time scale, focus on electronic phase transitions without large structural changes.

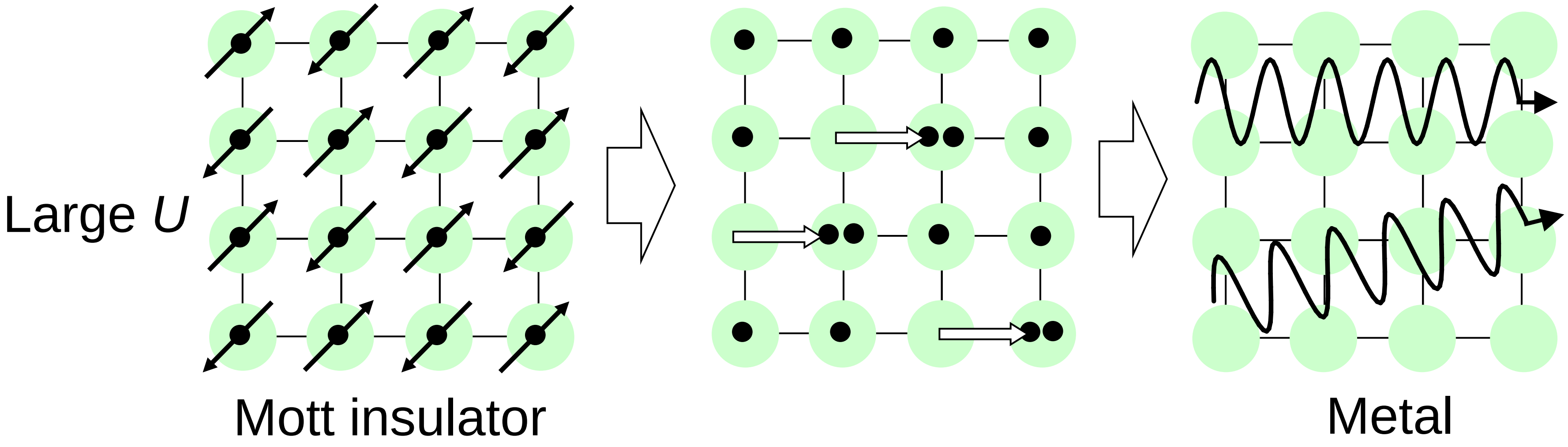
Electric-field induced Mott insulator to metal transition

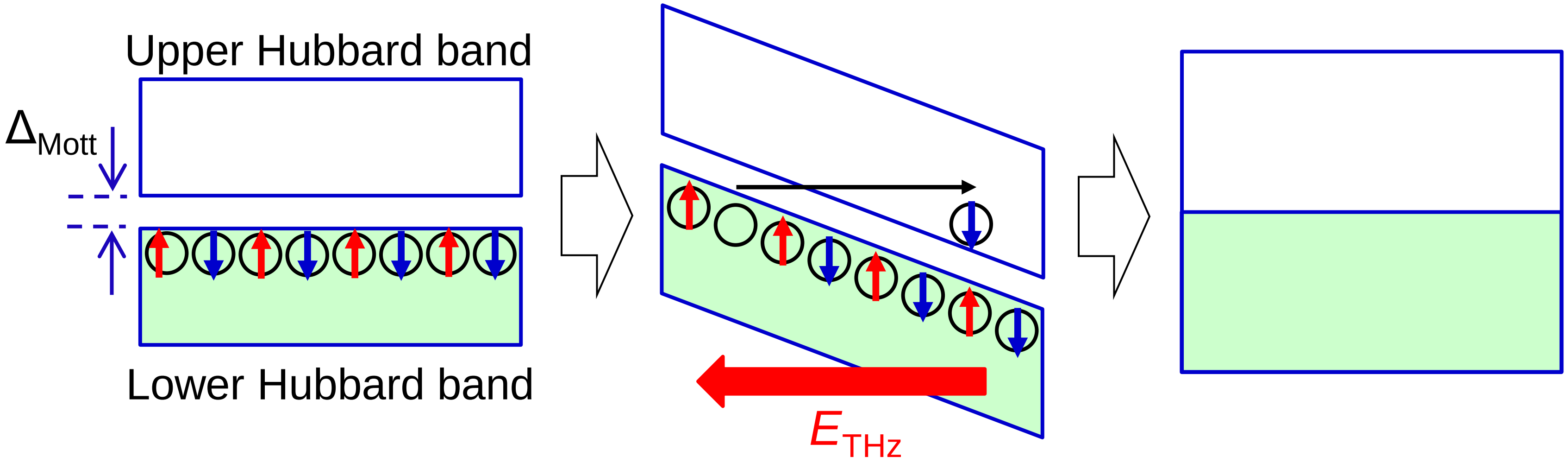


Carrier generations
through quantum tunneling
(Zener tunneling)

T. Oka, Phys. Rev. B ***86****, 075148 (2012)*

Electric-field induced Mott insulator to metal transition





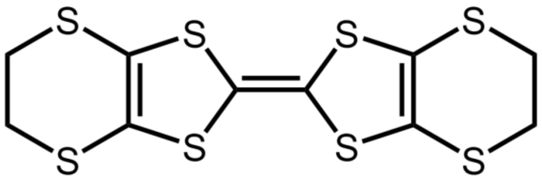
Theory	Δ_{Mott} (eV)	E_{th} (MV/cm)
ET-F_2TCNQ	0.7	3
Sr_2CuO_3	1.5	9

To drive a transition
by a lower electric field,
a narrow-gap Mott insulator
is advantageous.

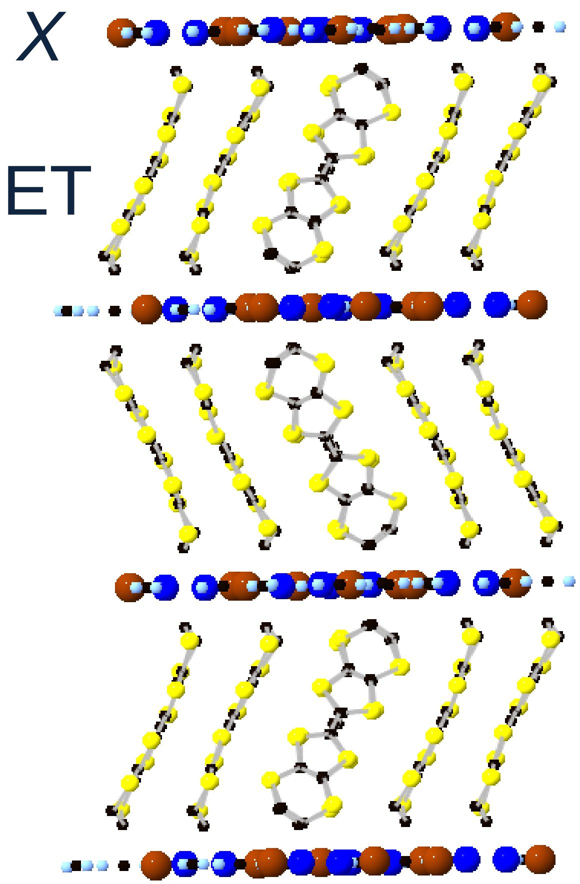
T. Oka, Phys. Rev. B ***86****, 075148 (2012)*

Insulator-metal transition in κ-$(ET)_2X$

ET

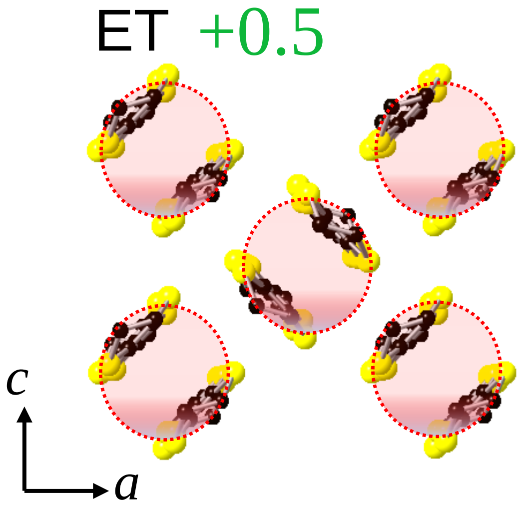


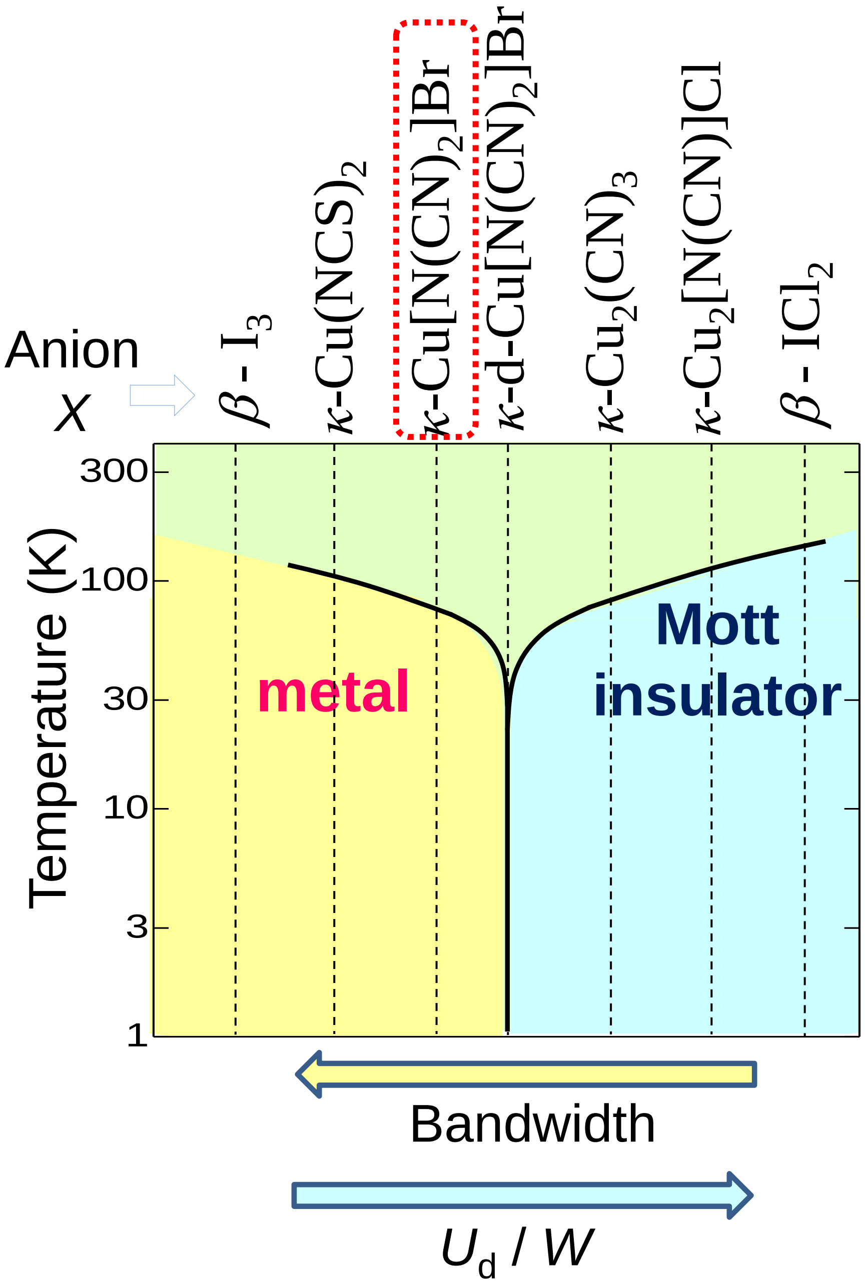
$(ET)_2^+X^-$



A unit is an ET dimer.
The nominal valence of each ET is +0.5.
Each dimer has one hole.

2D half-filled band

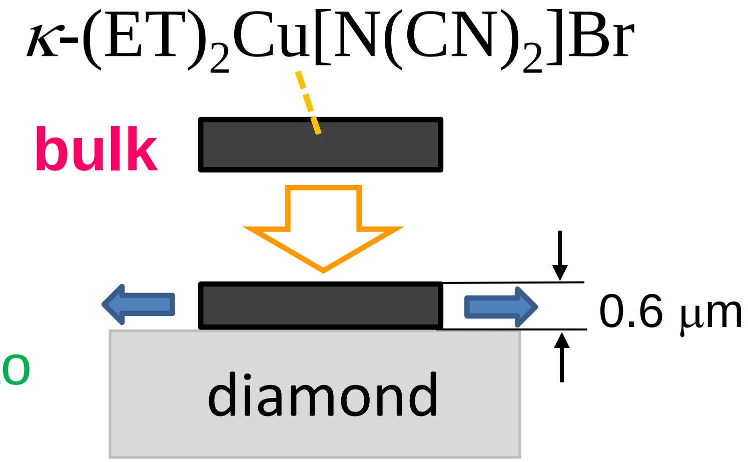




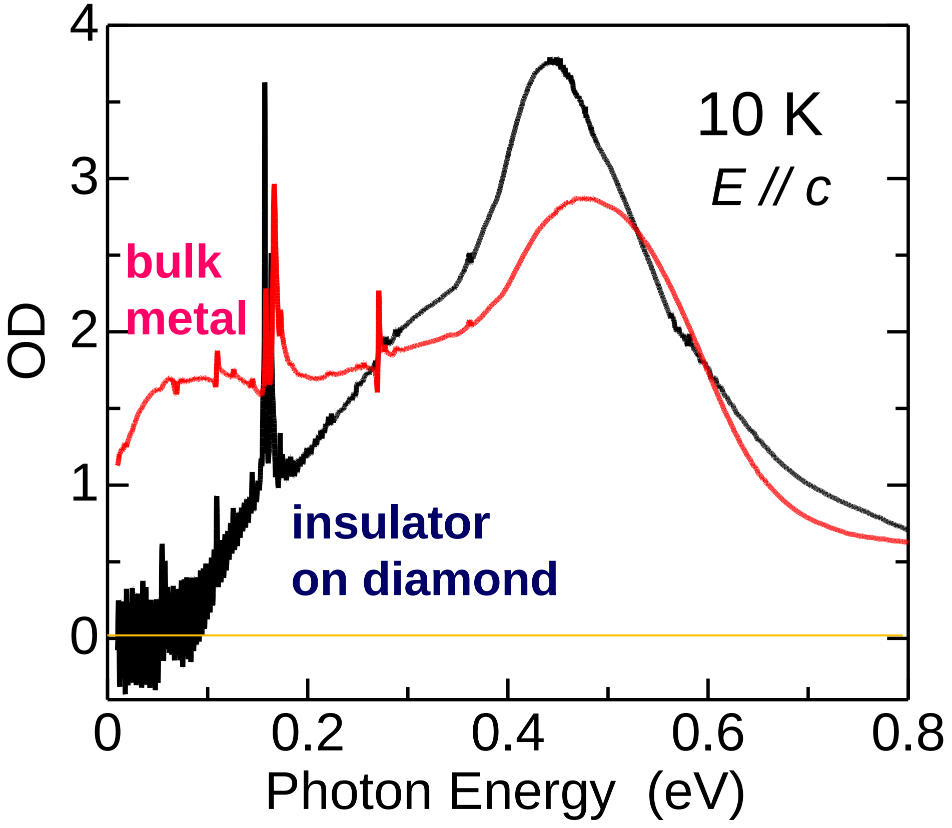
K. Kanoda, JPSJ **75**, 051007 (2006)

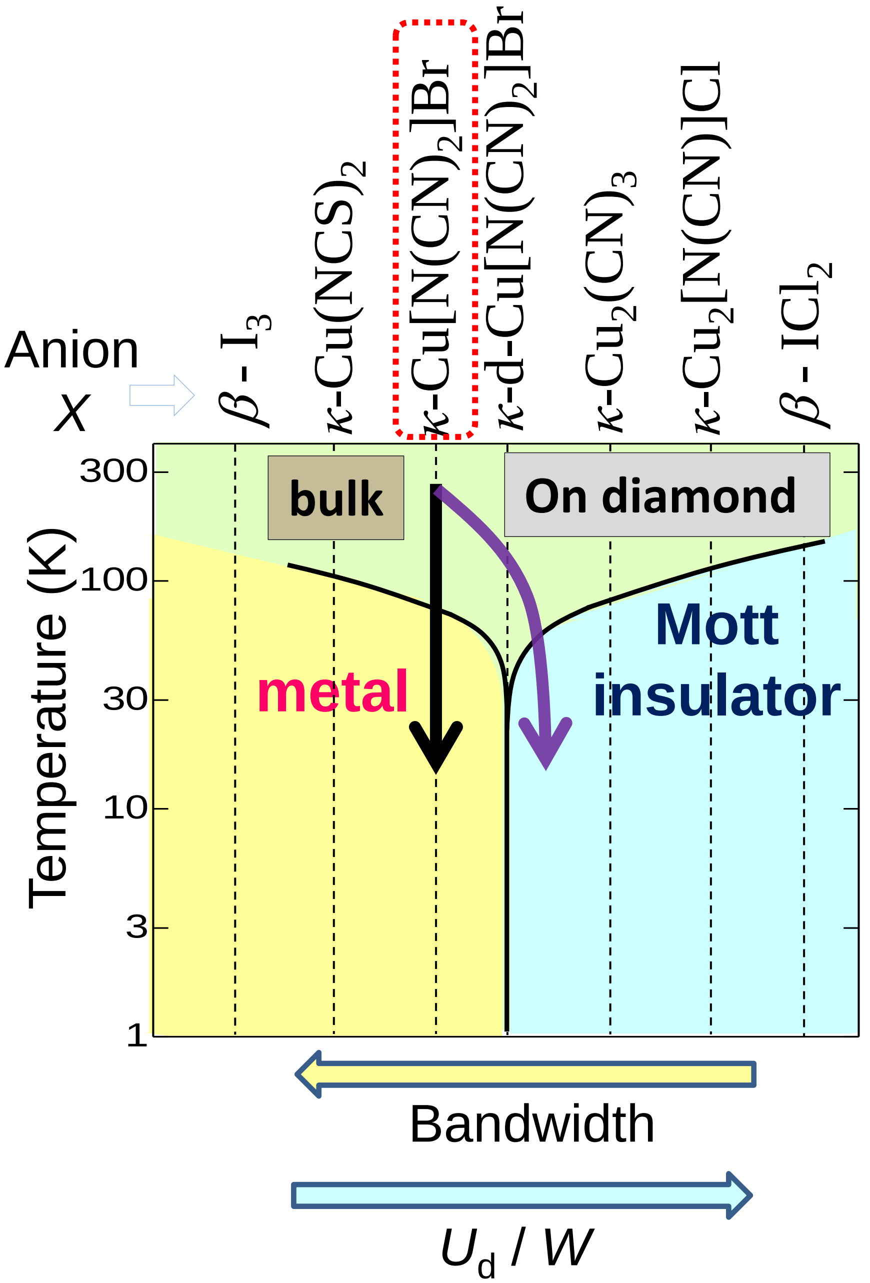
Insulator-metal transition in κ-$(ET)_2X$

Suda, Yamamoto (IMS)



Absorption (OD: optical density) spectra



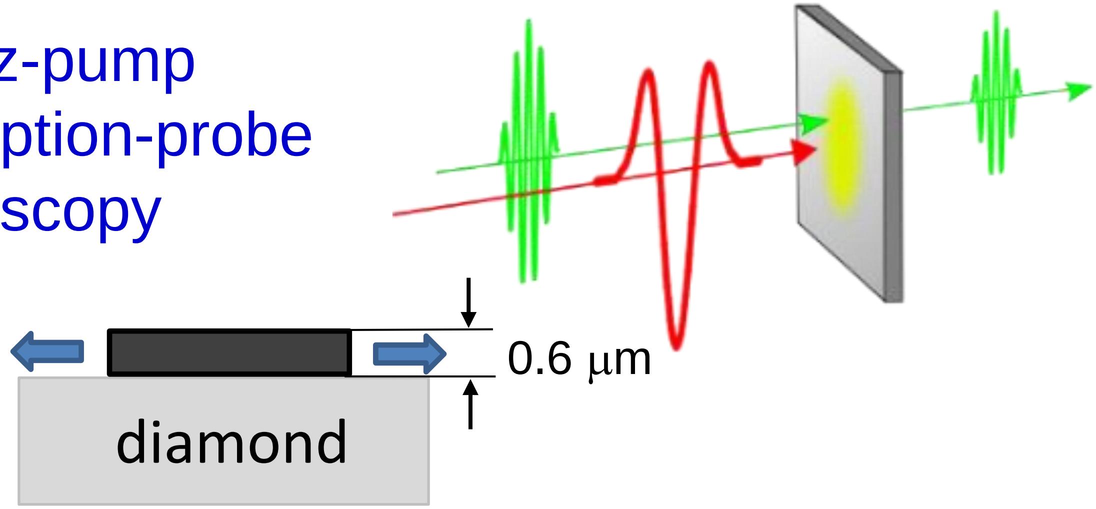


K. Kanoda, JPSJ **75**, 051007 (2006)

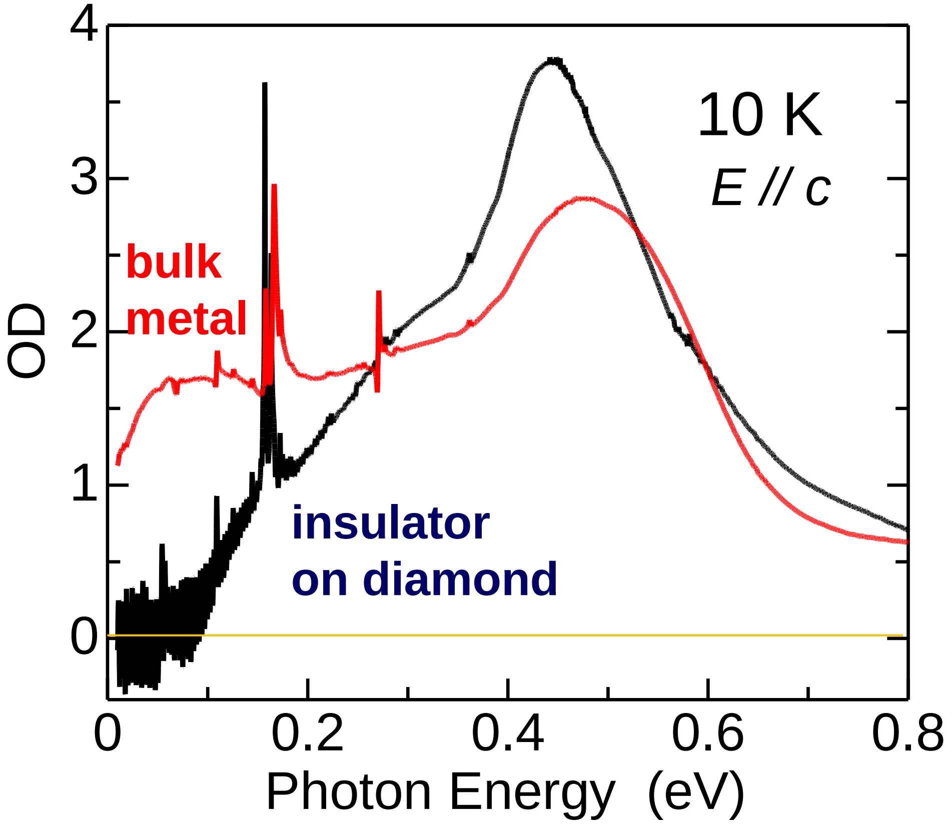
Insulator-metal transition in κ-$(ET)_2X$

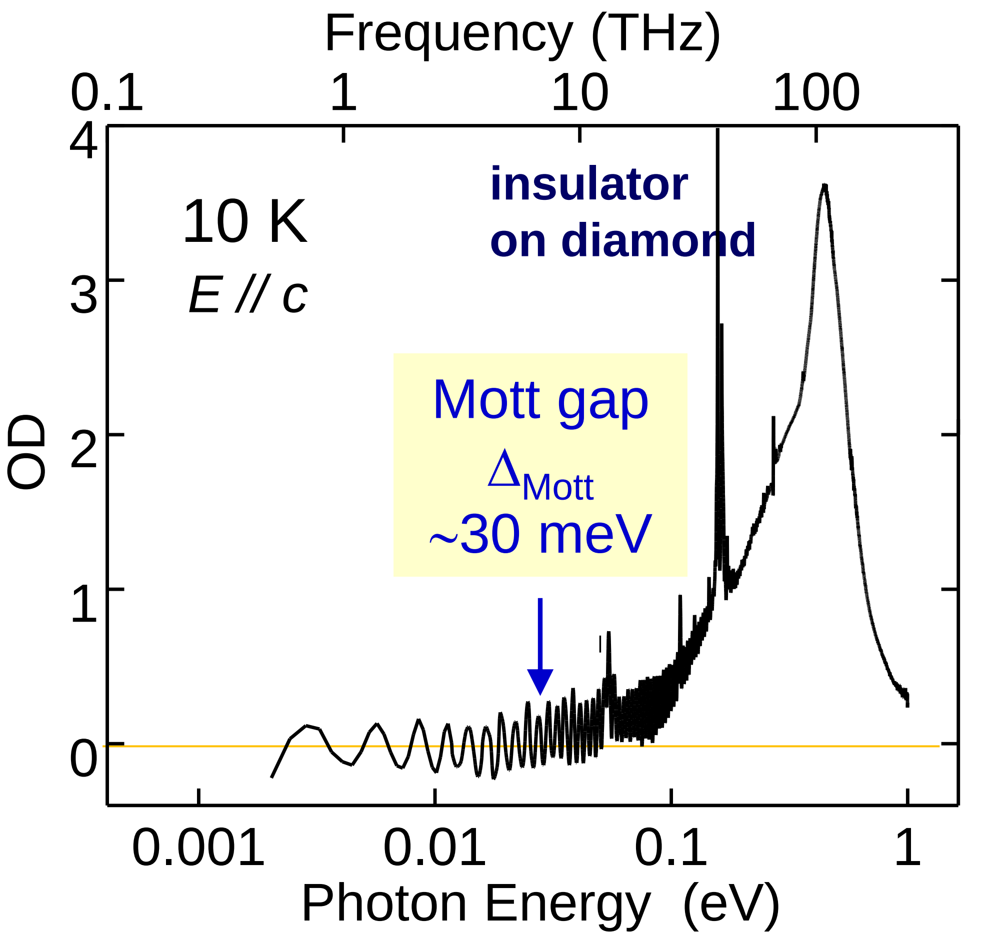
Terahertz-pump
optical-absorption-probe
spectroscopy

Suda,
Yamamoto
(IMS)



Absorption (OD: optical density) spectra

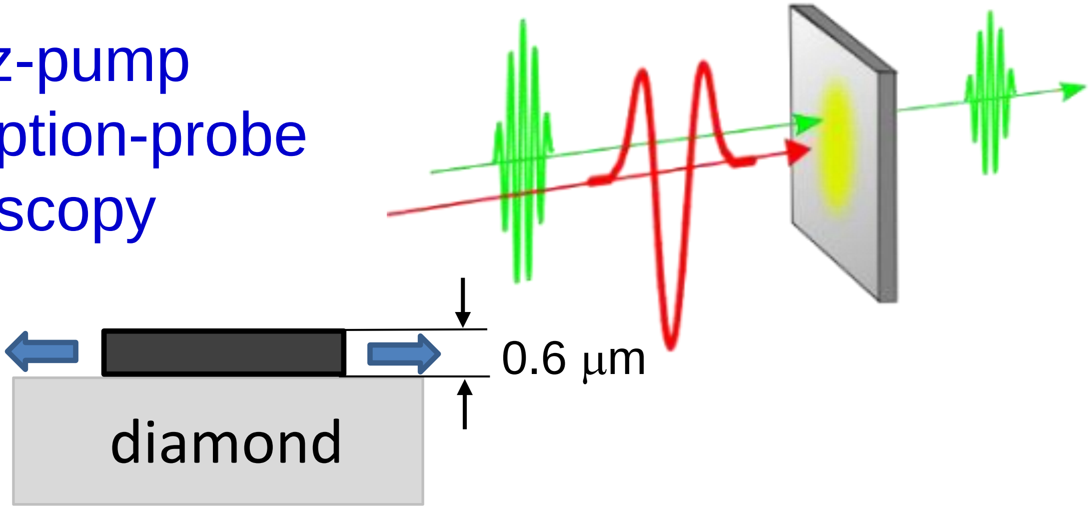


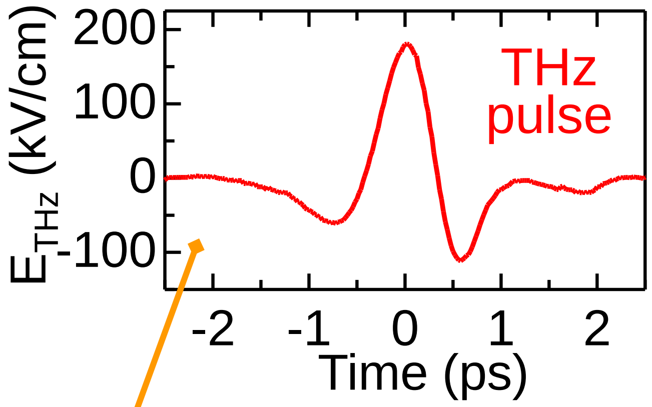


Insulator-metal transition in κ-(ET)$_2X$

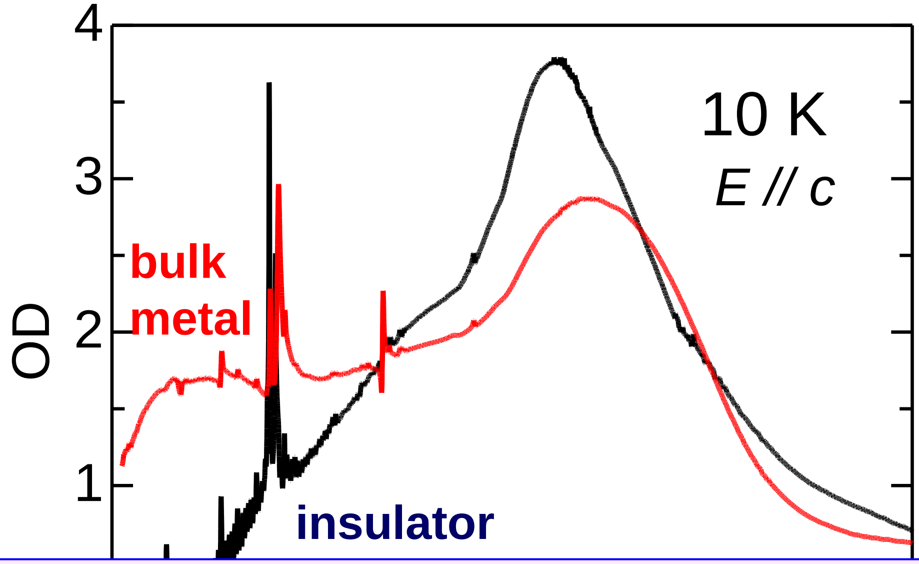
Terahertz-pump
optical-absorption-probe
spectroscopy

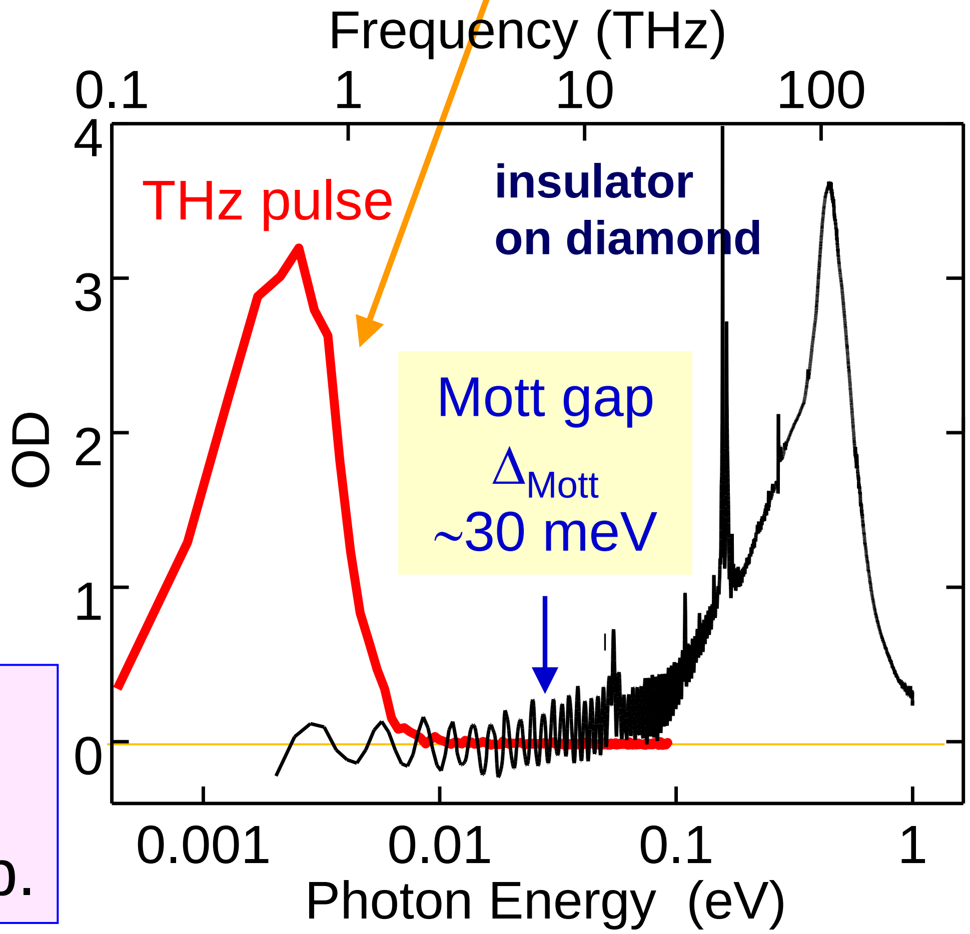
Suda,
Yamamoto
(IMS)





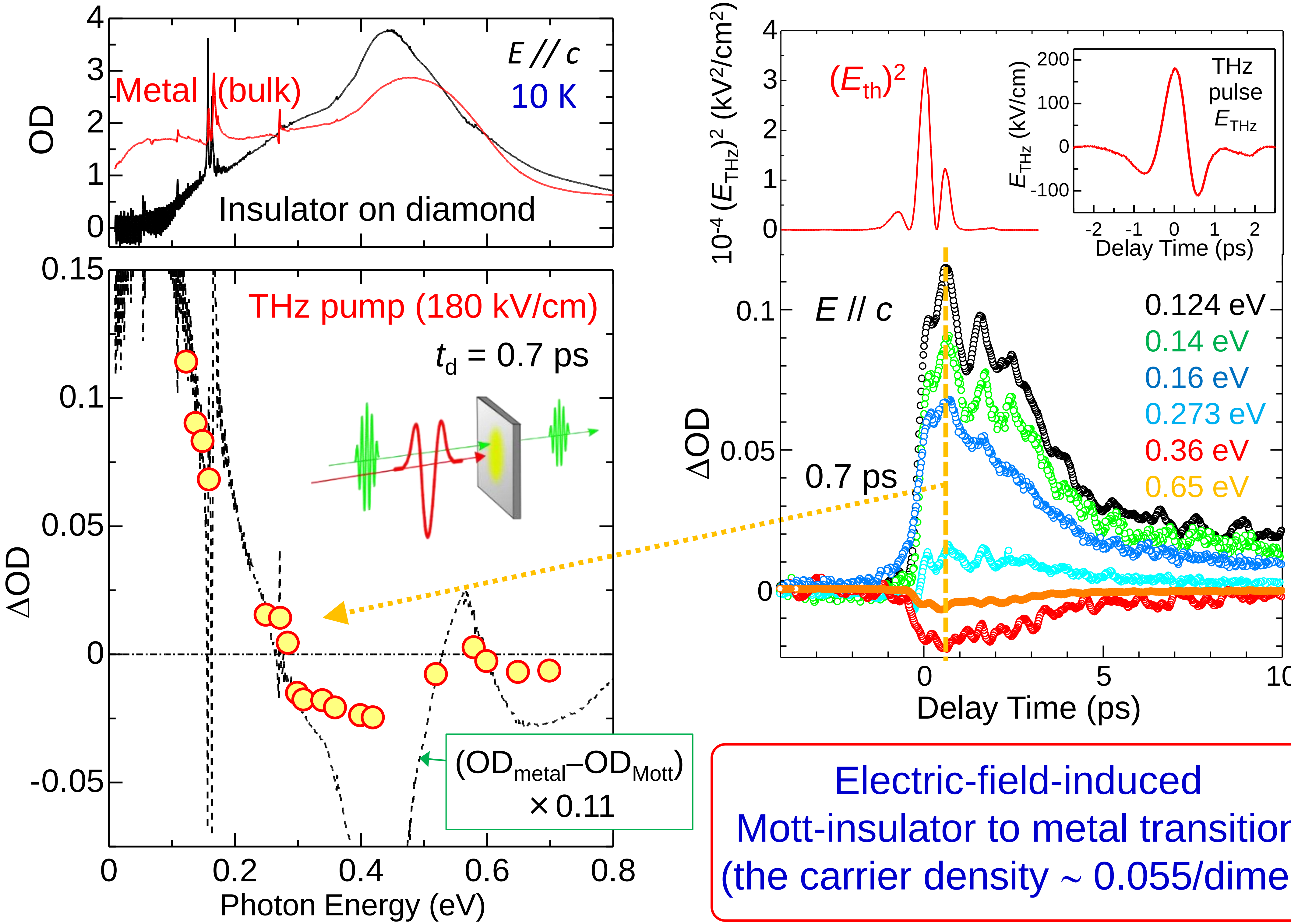
Absorption (OD: optical density) spectra





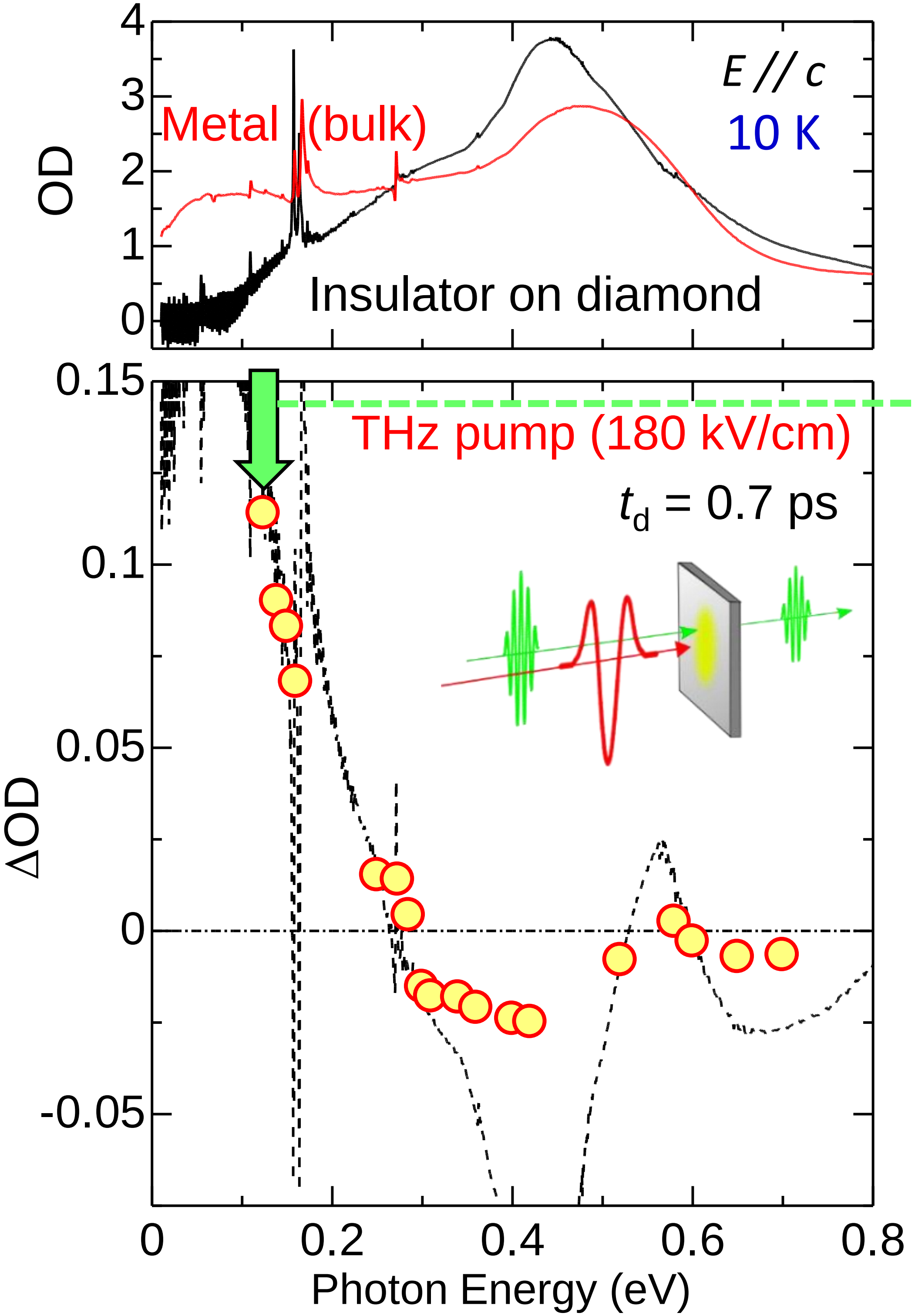
The sample is transparent
to the THz pulse.
No carriers are excited beyond the gap.

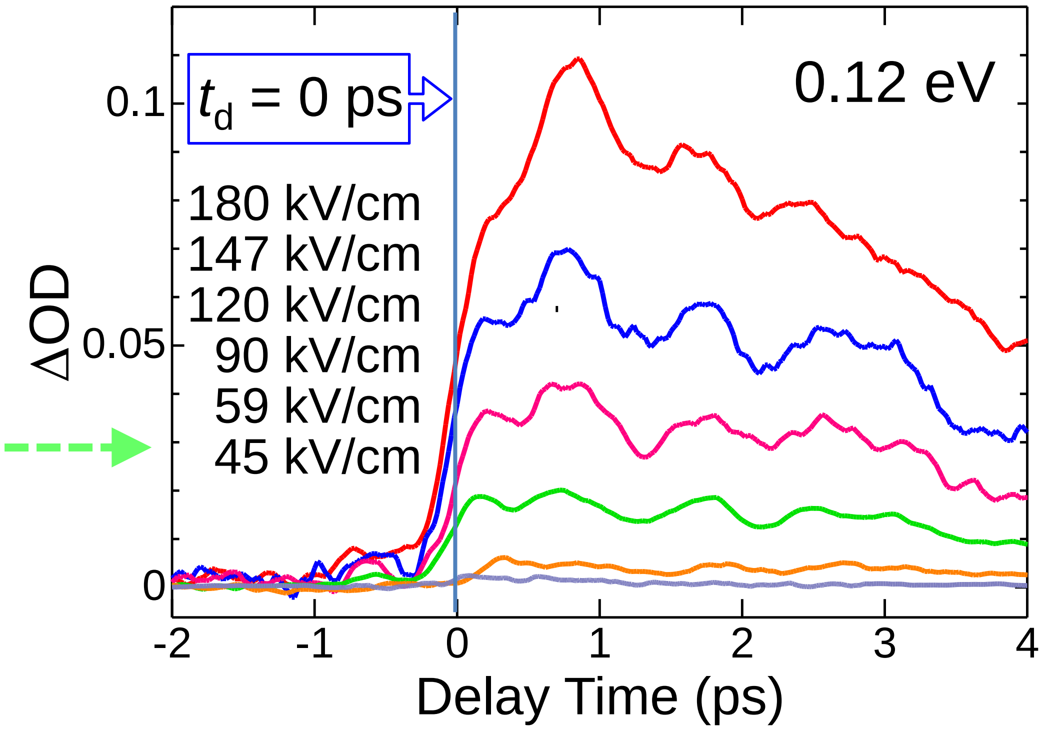
THz-pump optical-absorption-probe spectroscopy (180 kV/cm)

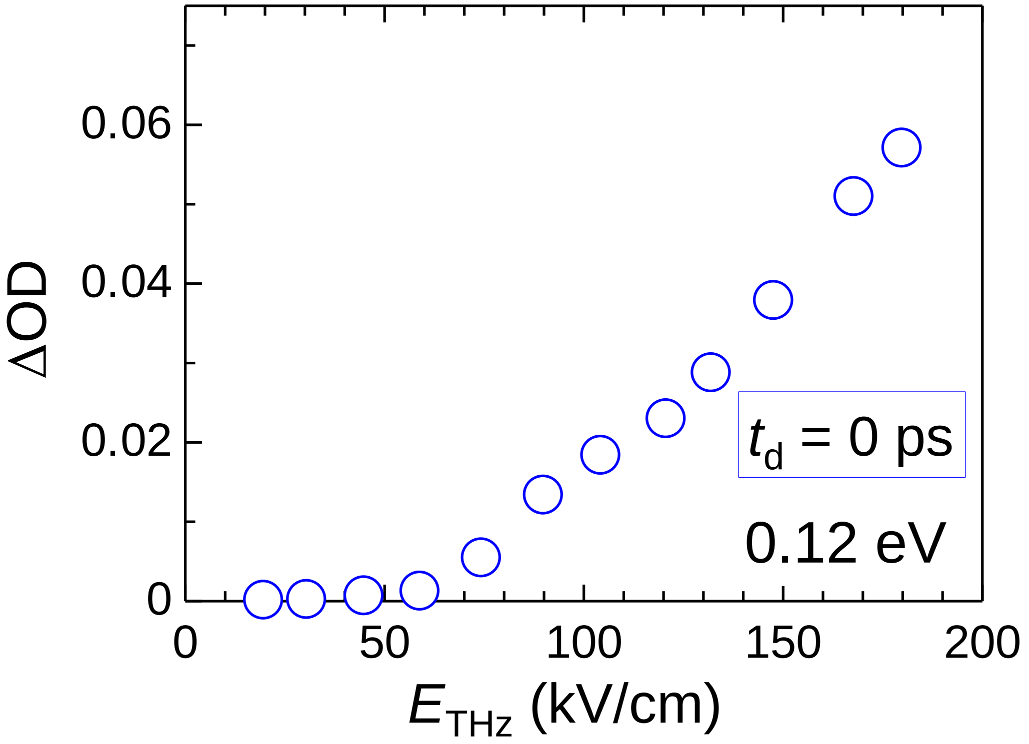


Electric-field-induced
Mott-insulator to metal transition
(the carrier density ~ 0.055/dimer)

THz electric-field dependence of absorption changes in IR region

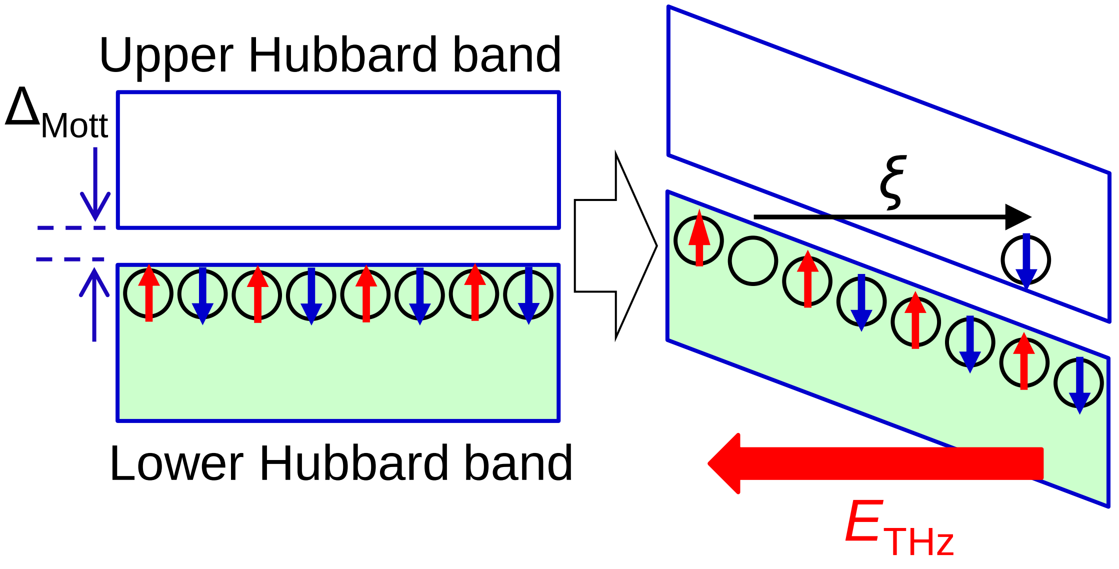


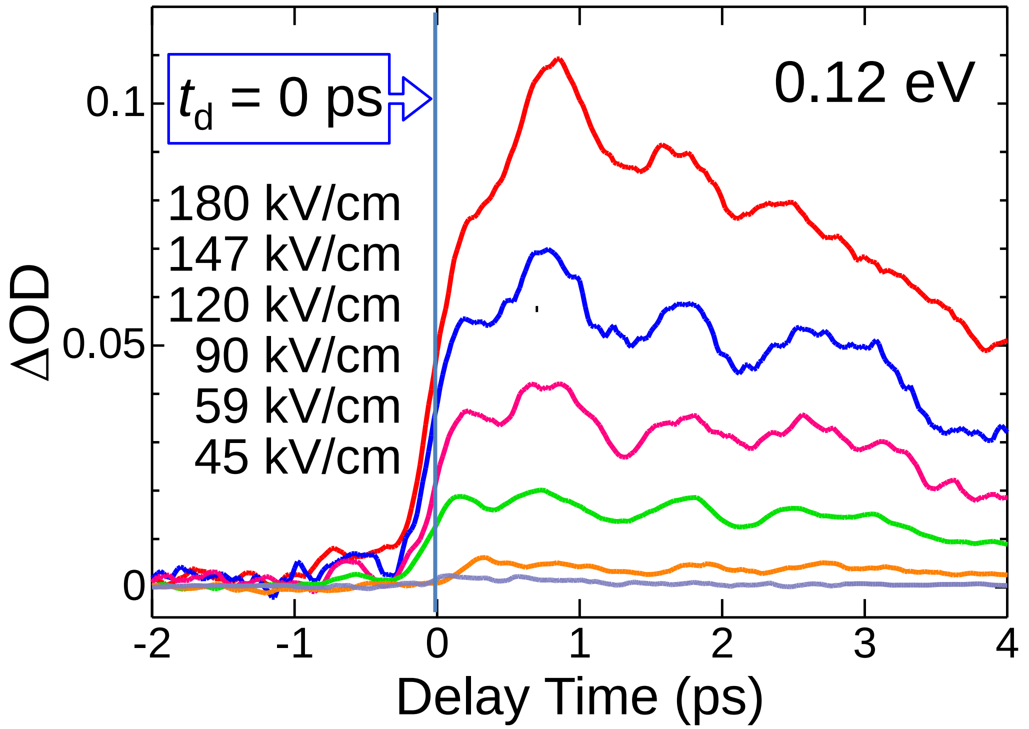




THz electric-field dependence of absorption changes in IR region

Carrier generation via quantum tunneling





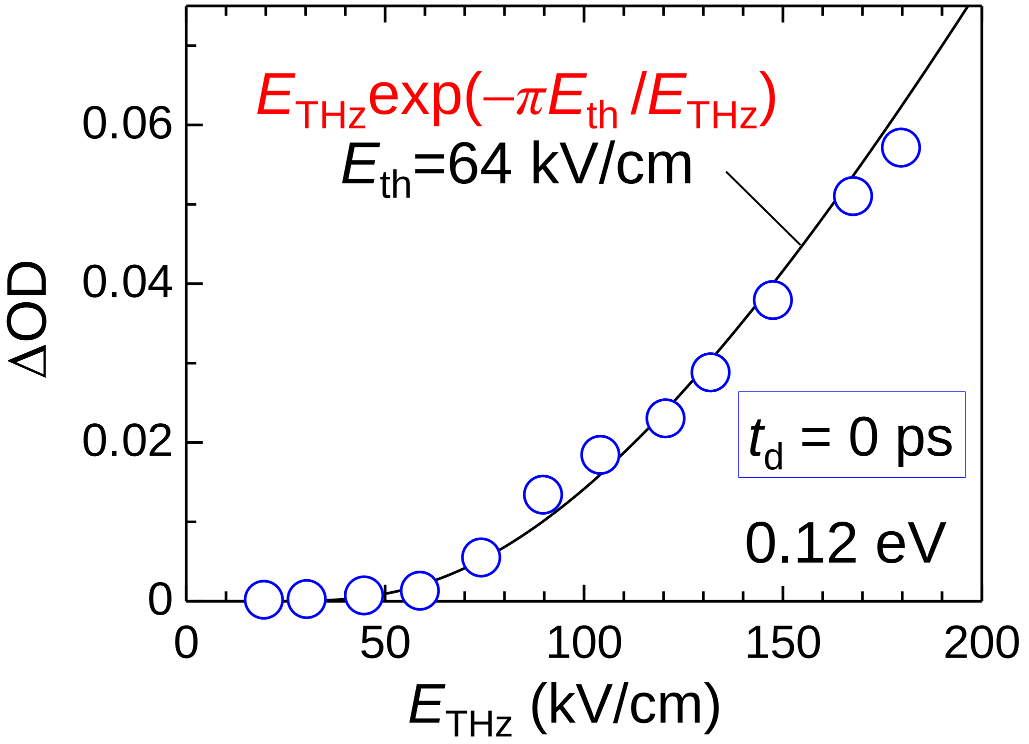
Probability of quantum tunneling

$E_{\mathrm{THz}}\exp(-\pi E_{\mathrm{th}}/E_{\mathrm{THz}}) \Leftrightarrow \Delta\mathrm{OD}$

T. Oka, Phys. Rev. B ***86****, 075148 (2012)*

⇩

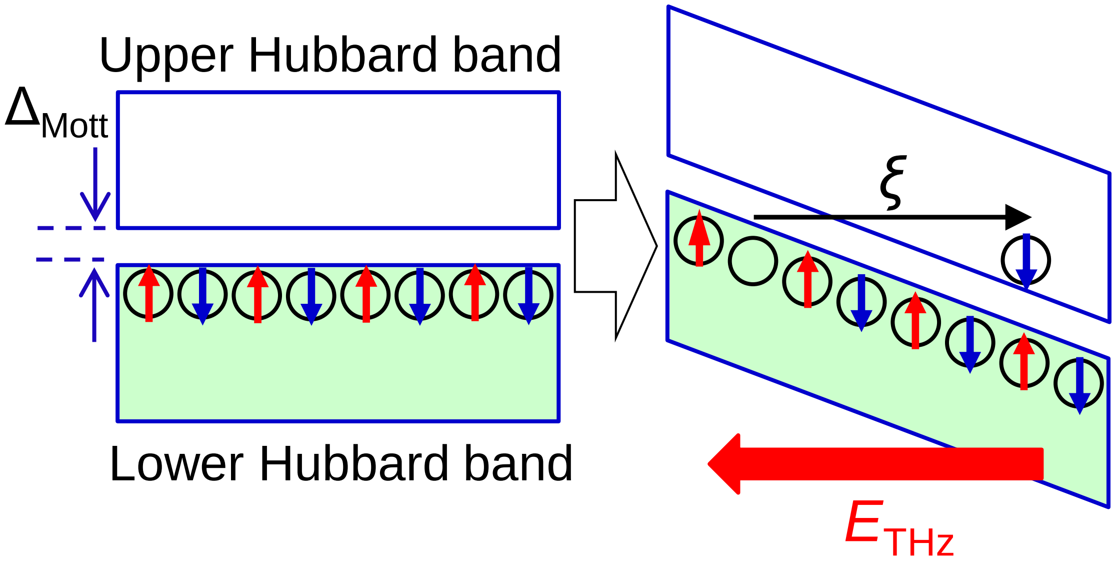
The I-M transition is driven by carrier generations via the quantum tunneling mechanism.

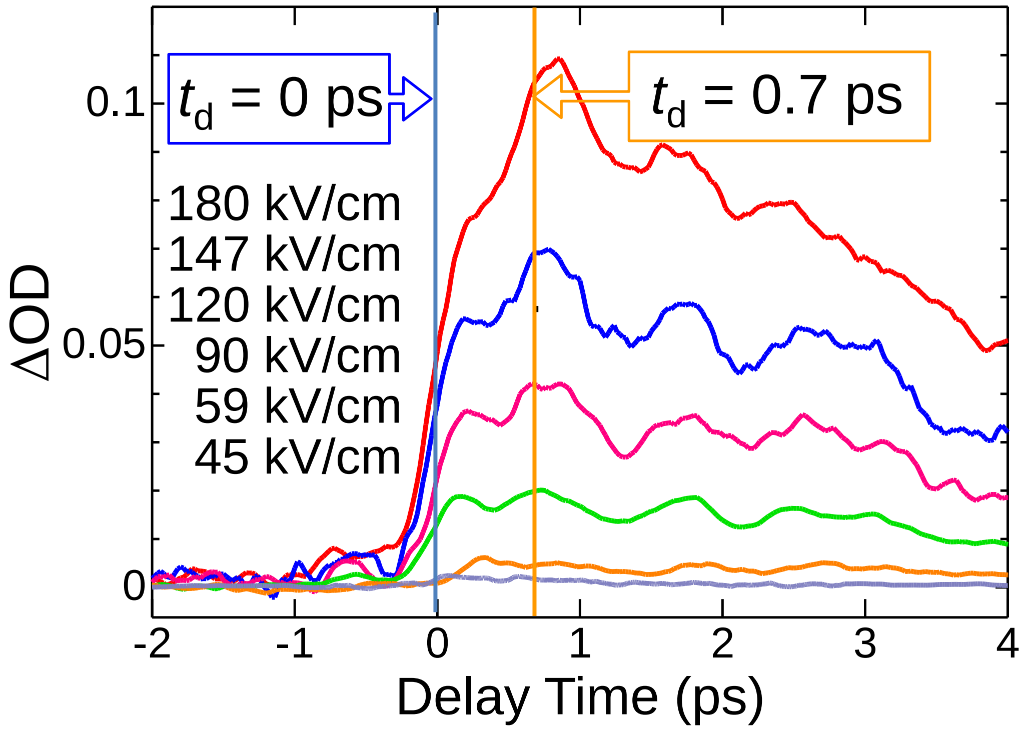


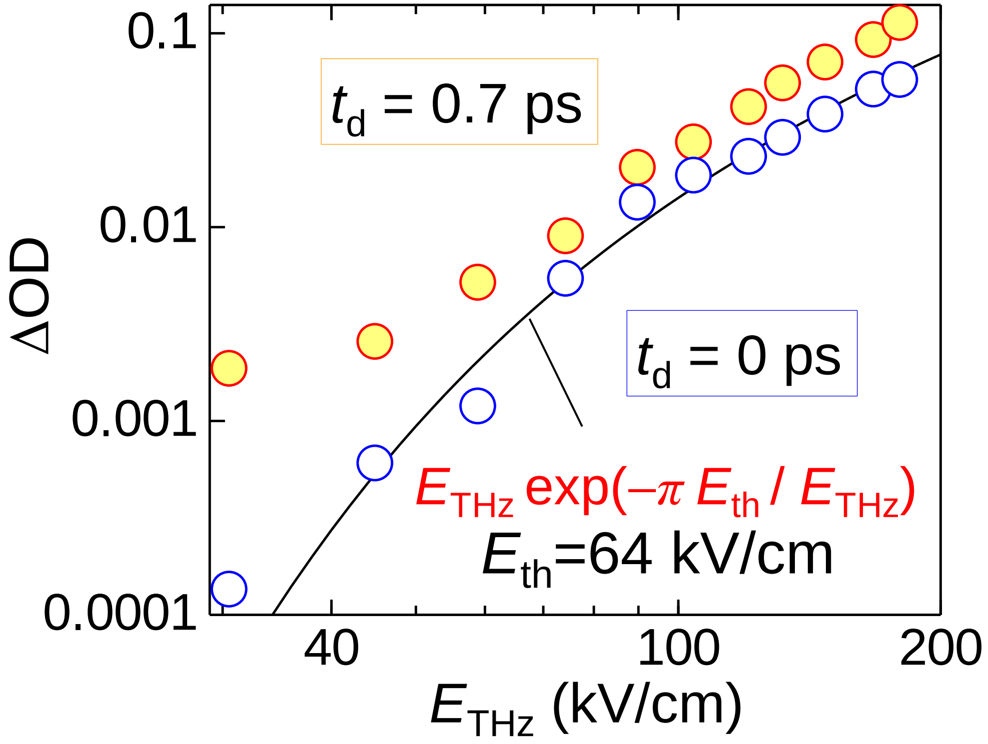
H. Yamakawa et al.,
Nature Materials ***16****, 1100 (2017)*

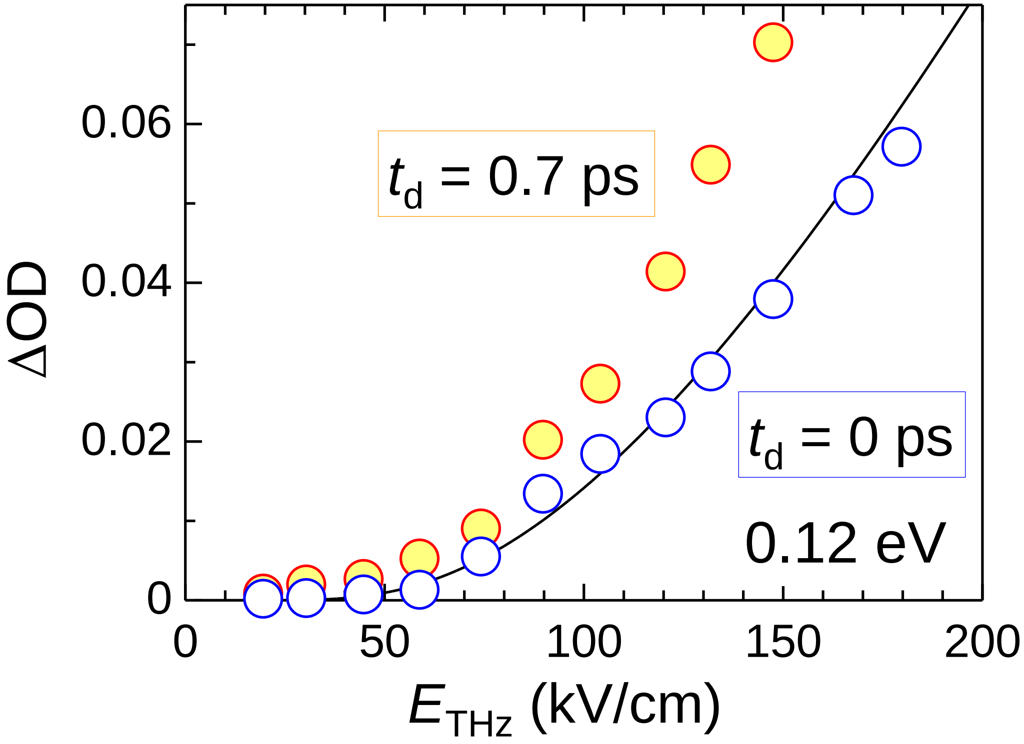
Dynamical property of THz electric-field-induced Mott transition

Carrier generation via quantum tunneling



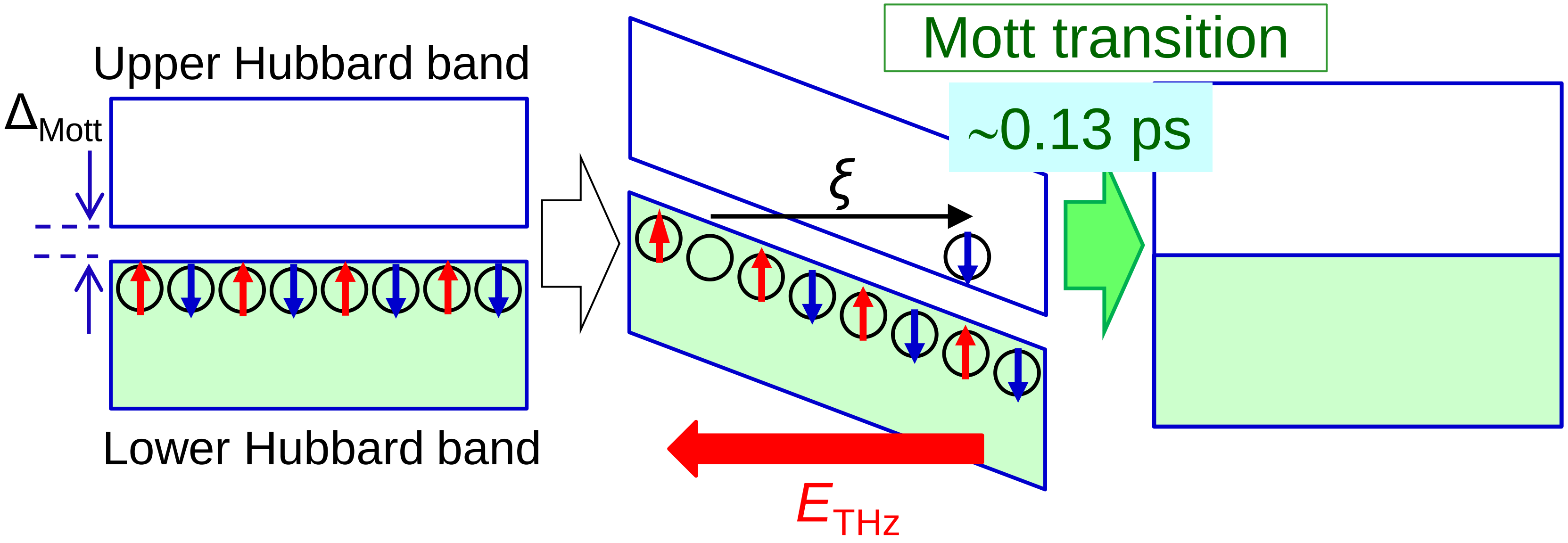




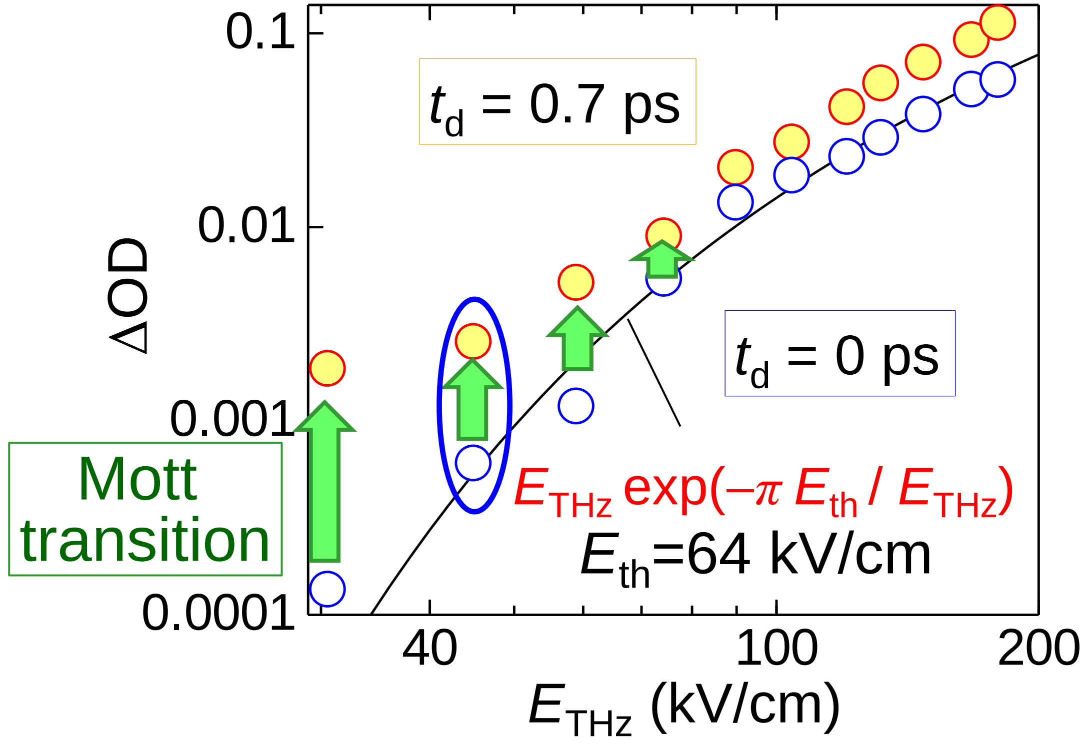


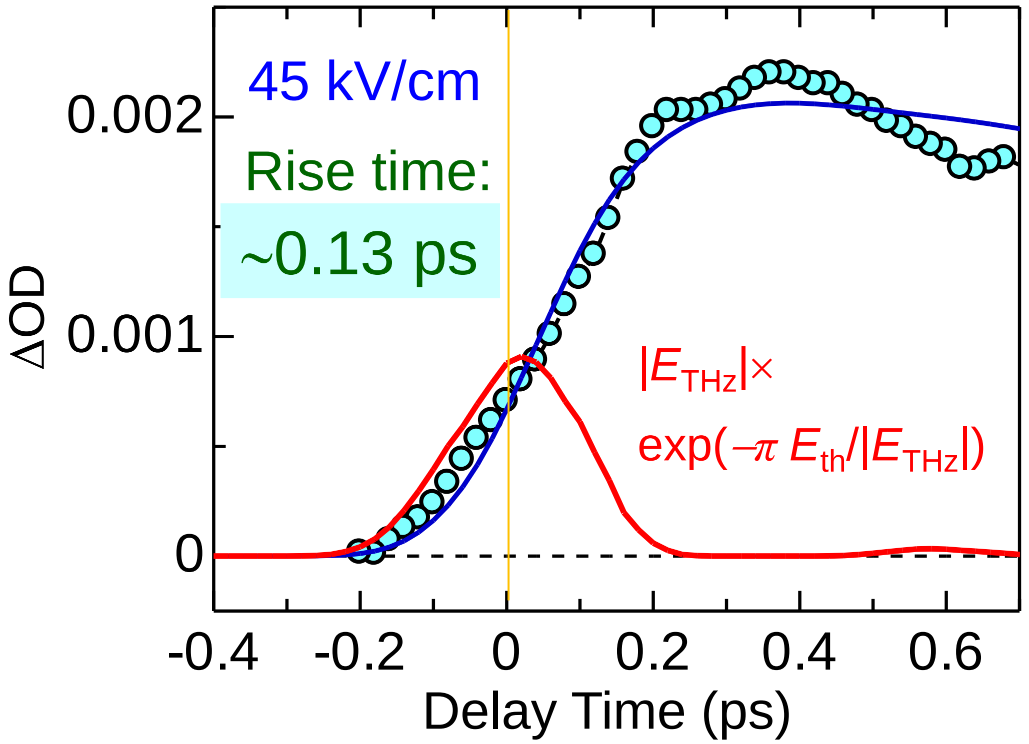
Dynamical property of THz electric-field-induced Mott transition

Carrier generation via quantum tunneling



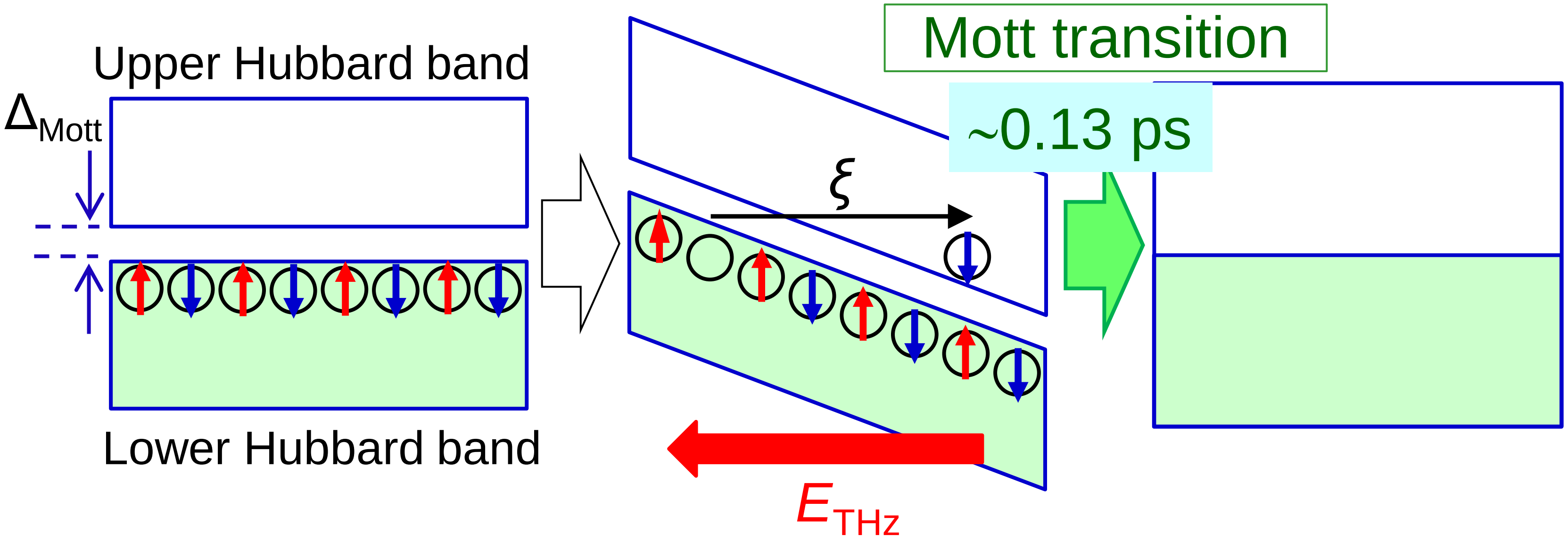
Rise time ~0.13 ps is the characteristic time of the Mott transition.





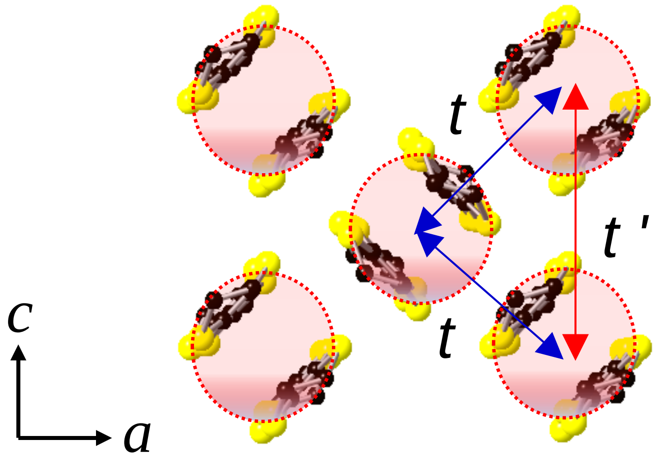
Dynamical property of THz electric-field-induced Mott transition

Carrier generation via quantum tunneling



Rise time ~0.13 ps is the characteristic time of the Mott transition.

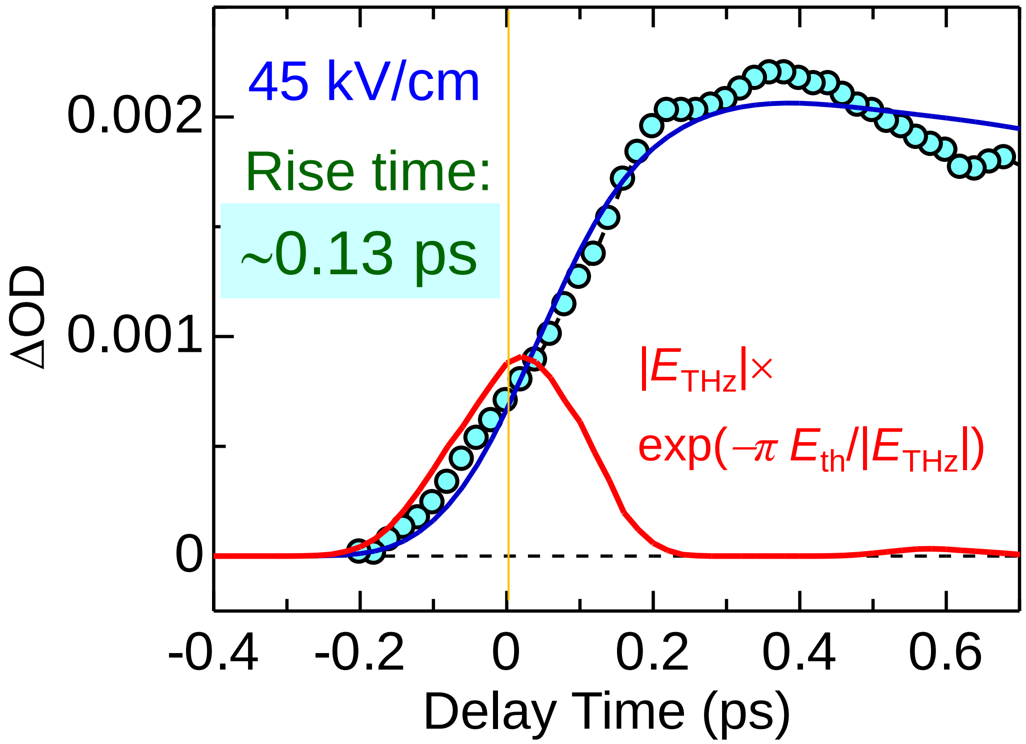
The electronic-state change takes a finite time determined by the transfer energy.



t = 78 meV ⇔ 0.051 ps

t' = 33 meV ⇔ 0.12 ps

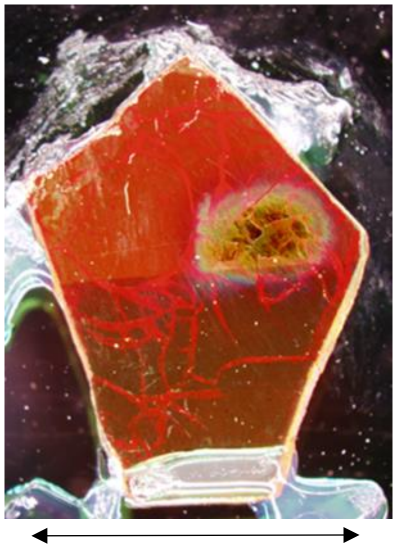
The values of parameters
*K. Sedlmeier et al., PRB **86**, 245103 (2012).*

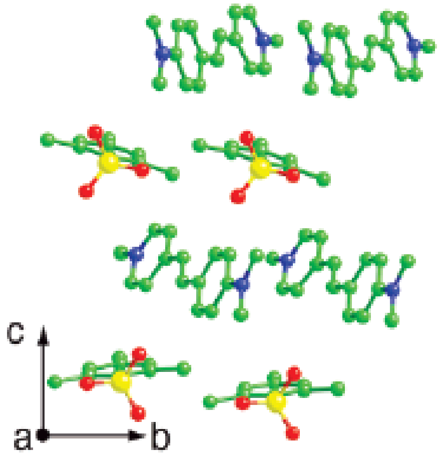


Organic nonlinear optical crystal : DSTMS

DSTMS

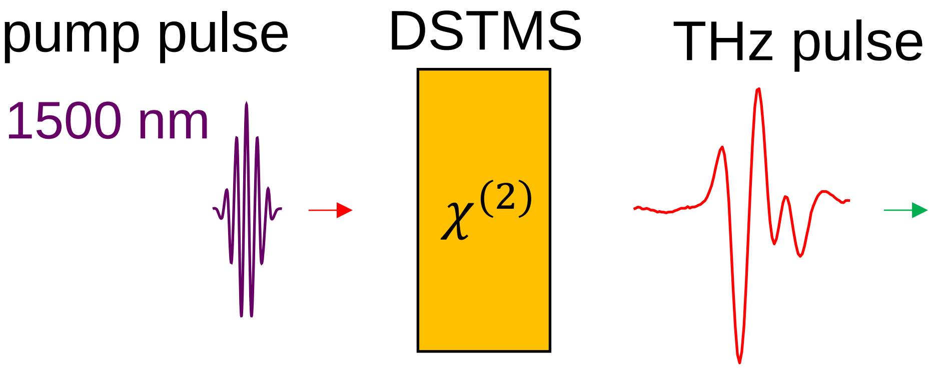
4-N,N-dimethylamino-4'-N'-methyl-stilbazolium
2,4,6-trimethylbenzenesulfonate





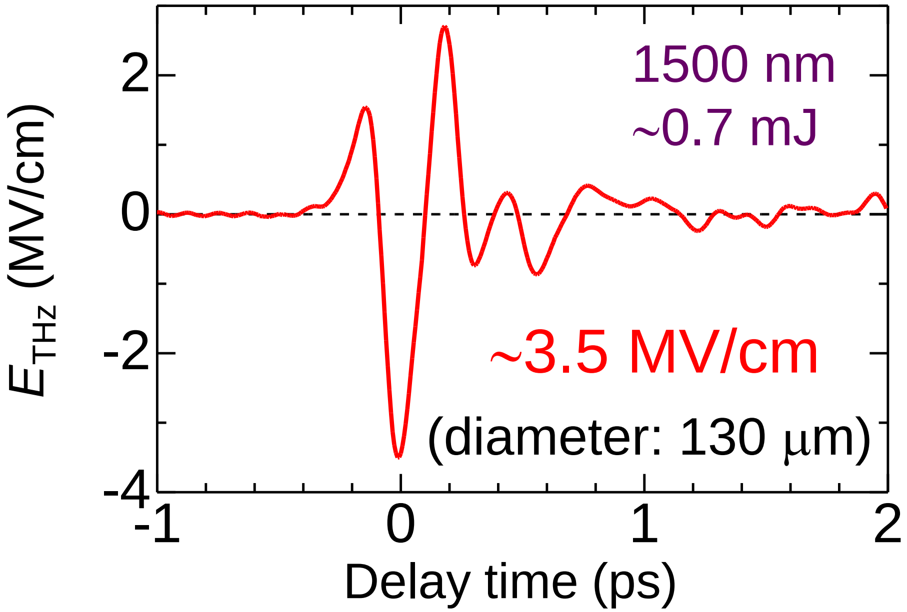
Z. Yang et al.,
Chem. Mater. ***19****, 3512 (2007).*

Terahertz radiation via optical rectification

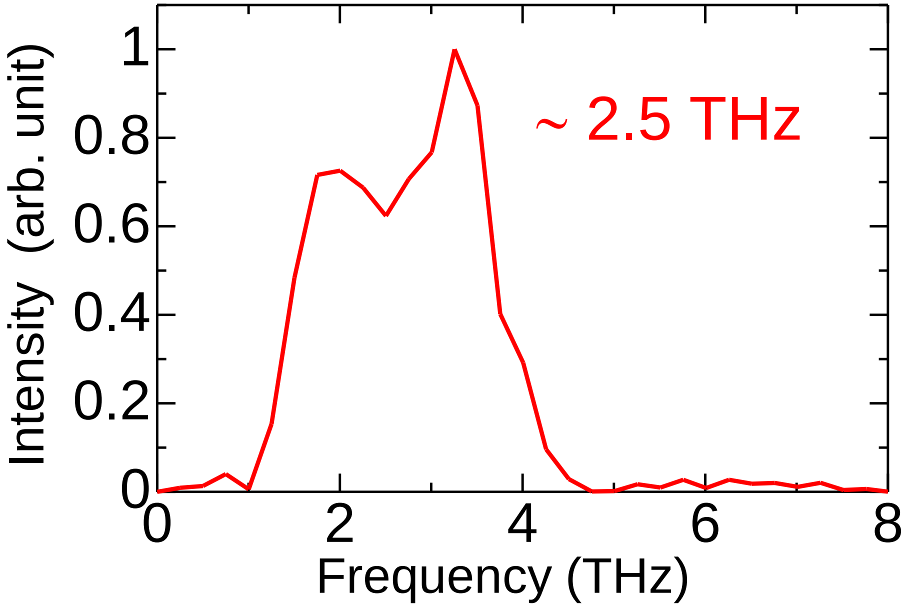


C. Ruchert et al., Phys. Rev. Lett. 110, 123902 (2013).

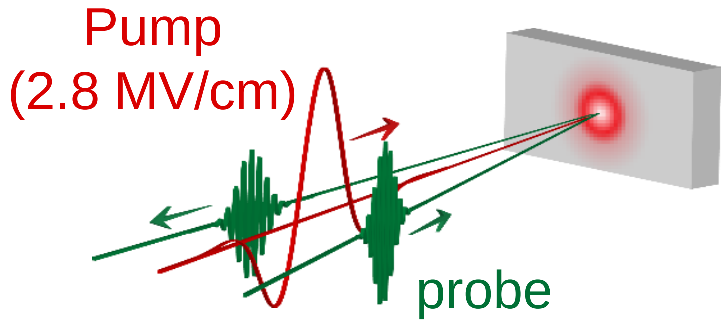
Electric-field waveform (this work)

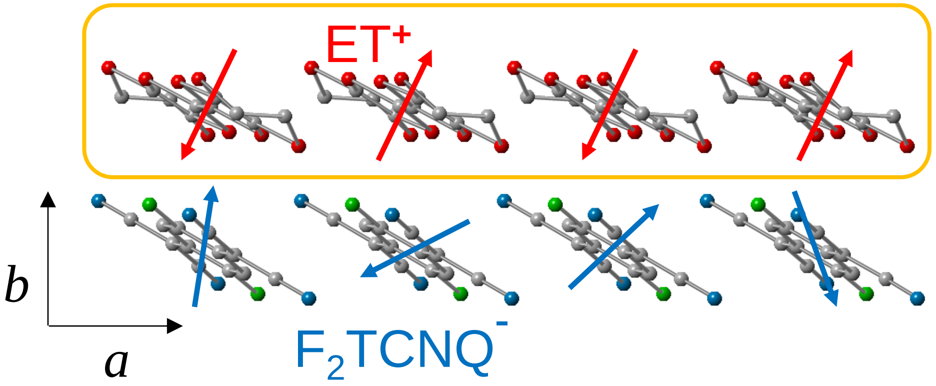


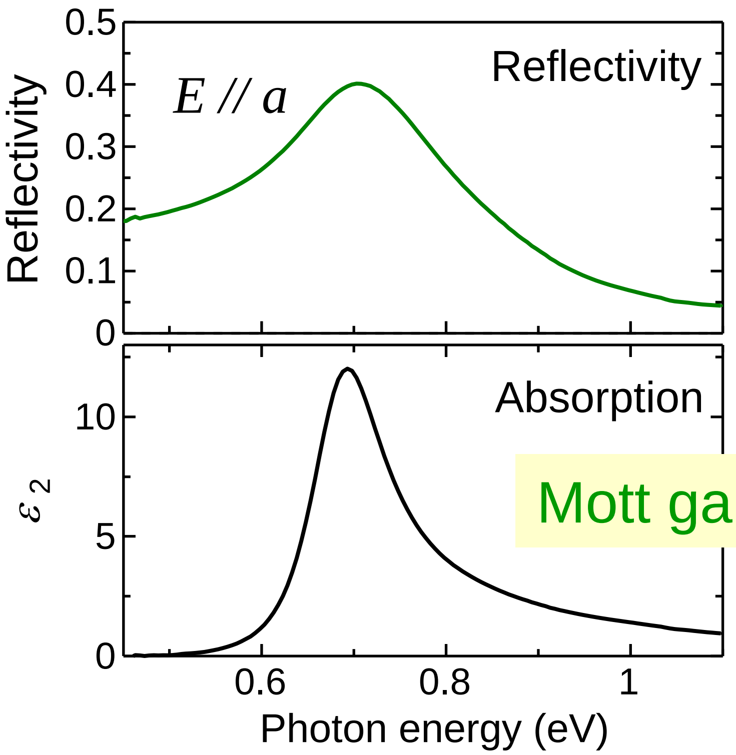
Spectrum (this work)



Metallization of a Mott insulator with a larger Mott gap: ET-F$_2$TCNQ

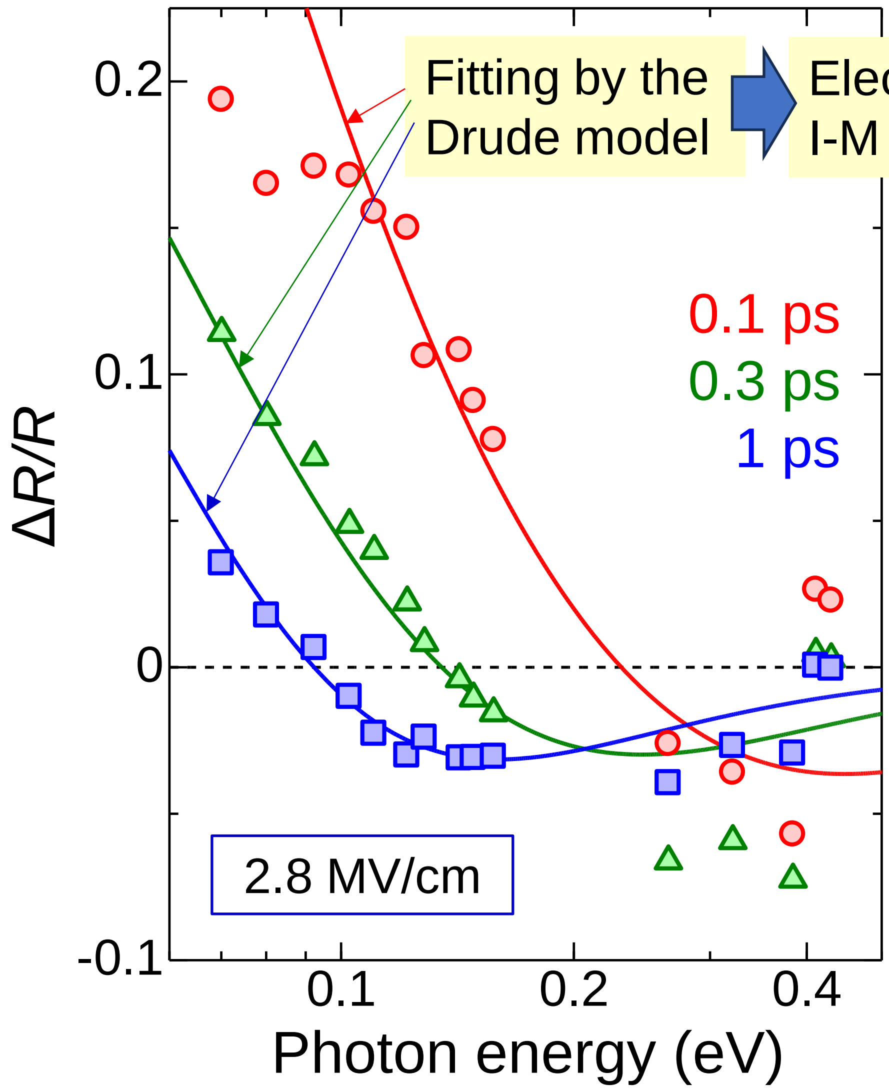






Mott gap ~ 0.7eV

Fitting by the Drude model → Electric-field induced I-M transition



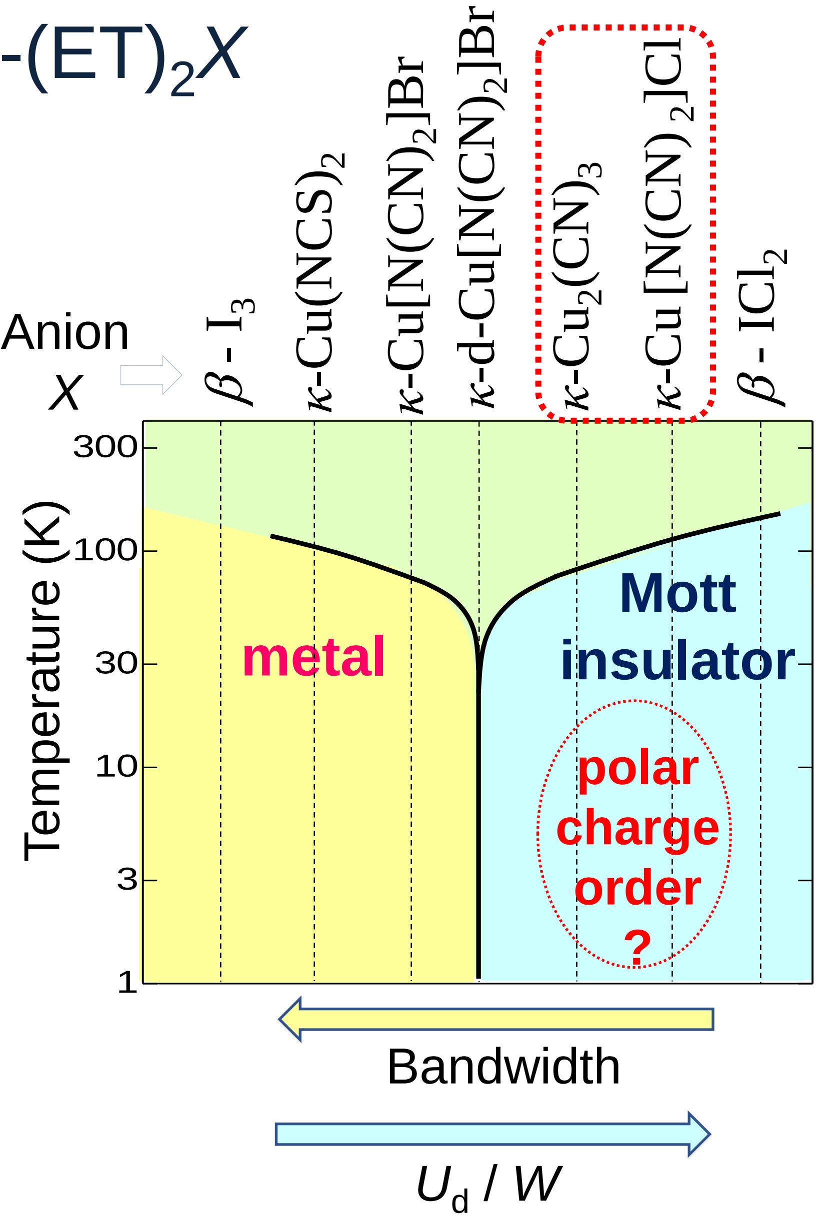
$$\varepsilon(z) = \varepsilon_s - \frac{\omega_p^2}{\omega^2+\gamma^2}\left(1 - i\frac{\gamma}{\omega}\right) e^{-\frac{z}{l}}$$

$$\omega_p^2 = \frac{e^2 N_c(0)}{\varepsilon_0 m^*}$$

N. Takamura et al., Phys. Rev. B ***107****, 085147 (2023)*

Instability of Mott insulator to polar charge-order in κ-(ET)$_2X$

κ-(ET)$_2X$



K. Kanoda, JPSJ **75**, 051007 (2006)

κ-(ET)$_2$Cu$_2$(CN)$_3$ (κ-CN)

Dielectric anomaly below 60 K

*M. Abdel-Jawad, T. Sasaki et al, PRB **82**, 125119 (2010)*

Theory: Instability to a polar charge order

*C. Hotta, PRB **82**, 241104(R) (2010)*

*M. Naka and S. Ishihara, JPSJ **79**, 063707 (2010)*

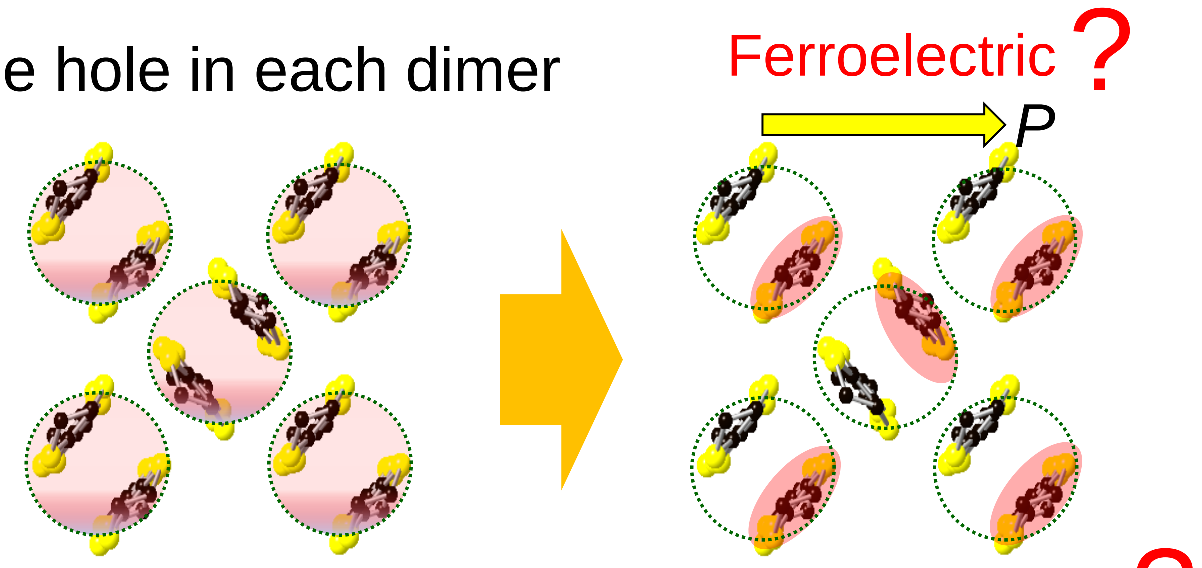
κ-(ET)$_2$Cu[N(CN)$_2$]Cl (κ-Cl)

Hysteresis behavior in P-E curve at 25 K

*P. Lunkenheimer et al , Nature Mater. **11**, 755 (2012)*

One hole in each dimer

Ferroelectric ?

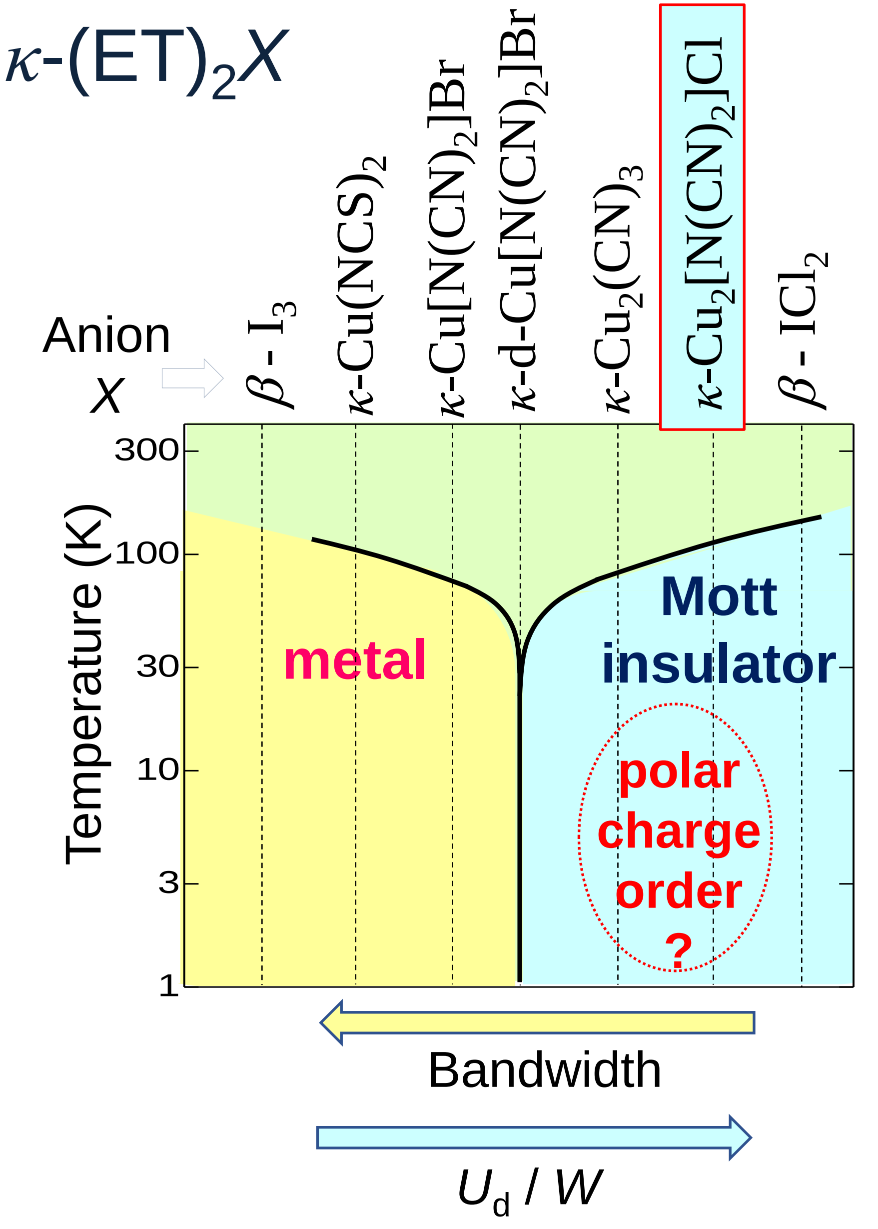


Mott insulator

Polar charge order?

Instability to a polar charge order phase?

Instability of Mott insulator to polar charge-order in κ-(ET)$_2X$



K. Kanoda, JPSJ **75**, 051007 (2006)

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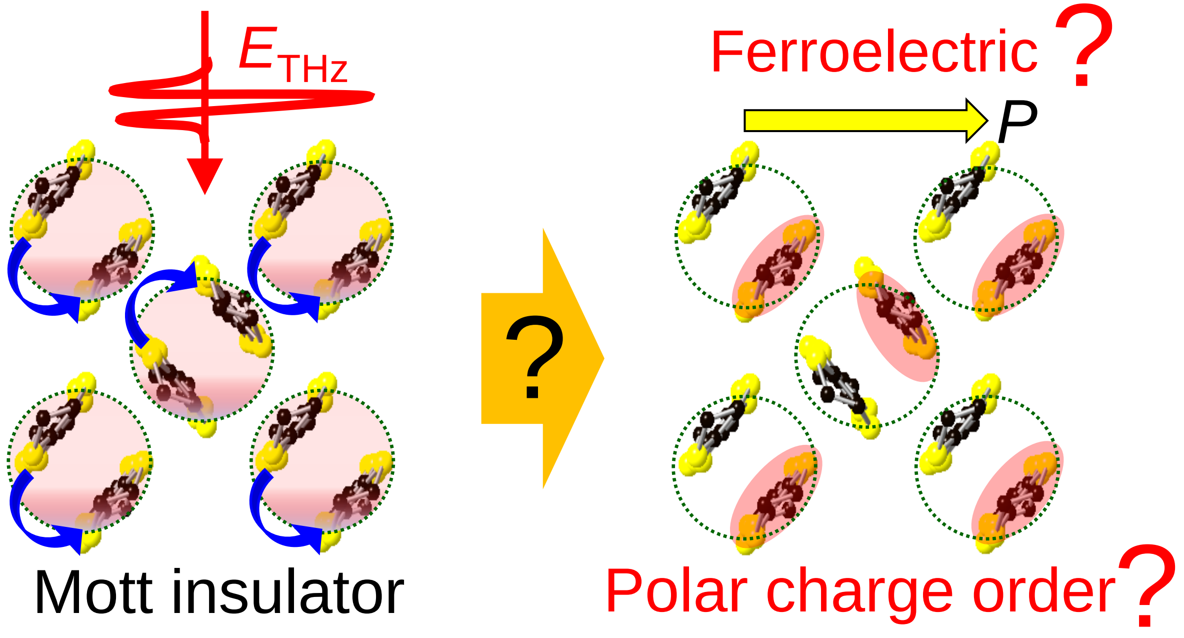
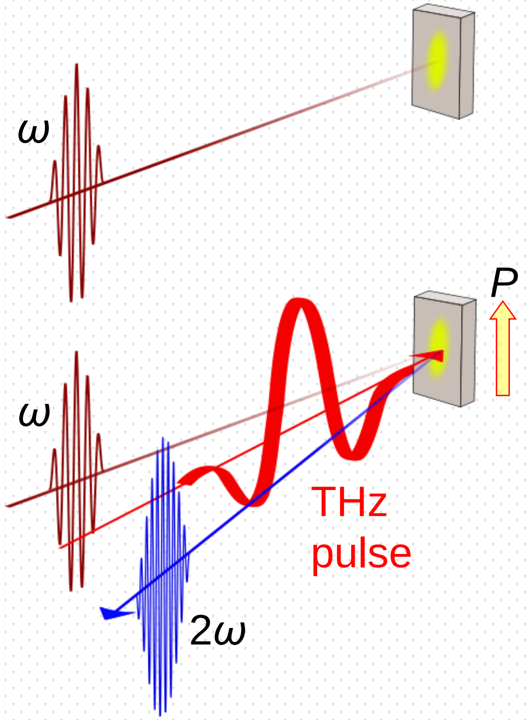
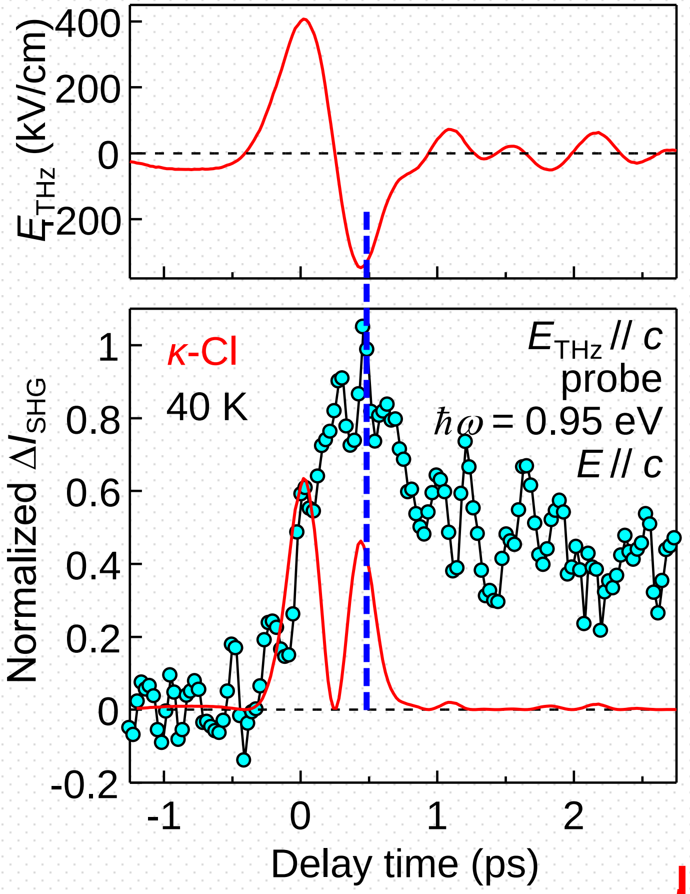


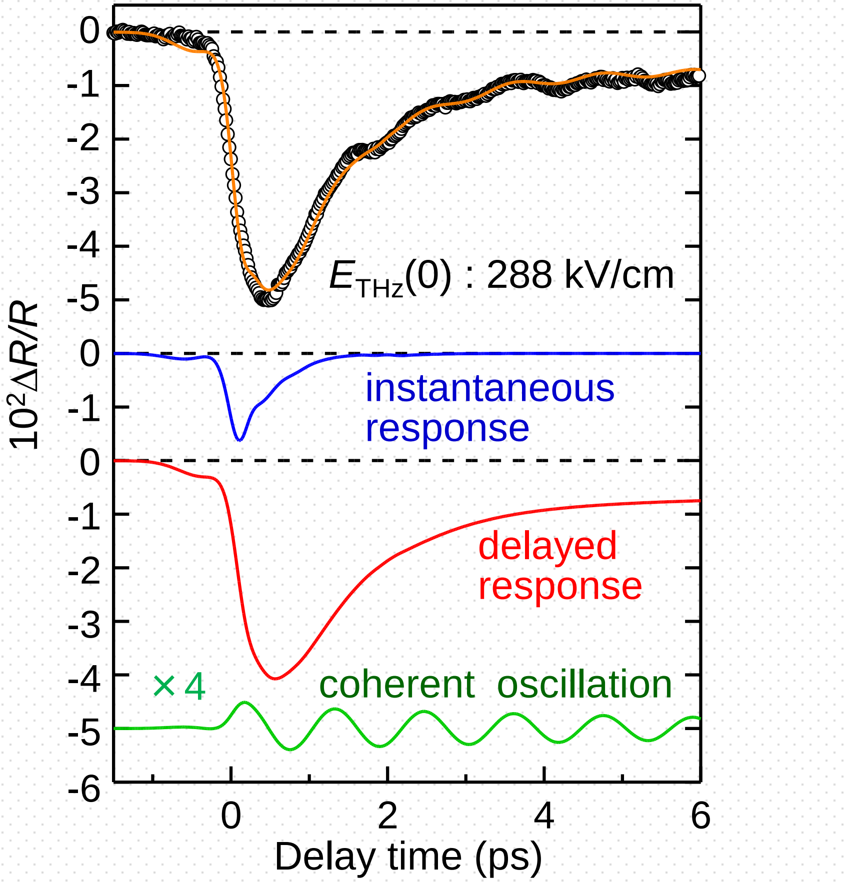
Terahertz field induced polar charge order in κ-$(ET)_2Cu[N(CN)_2]Cl$

THz electric-field induced SHG



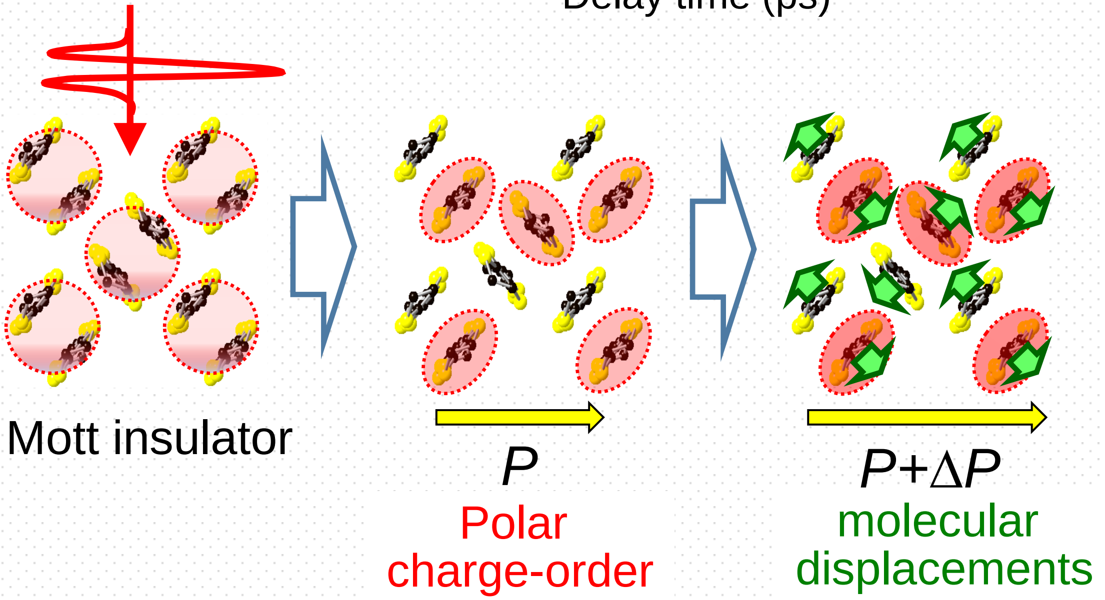


THz electric-field induced *R* changes



An SH signal rises up following $(E_{THz})^2$.
→ A polar charge order state is produced.

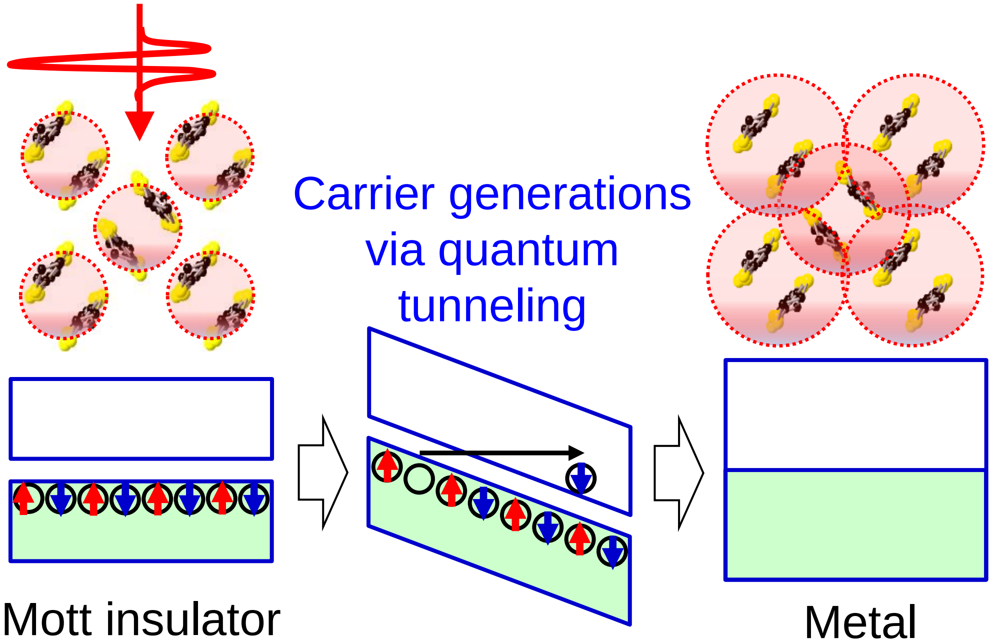
The SH signal does not decrease by a reverse electric field, and it remains after E_{THz} diminishes.
→ A polar charge order state is metastable.



H. Yamakawa et al., Nature Commun. ***12****, 953 (2021)*

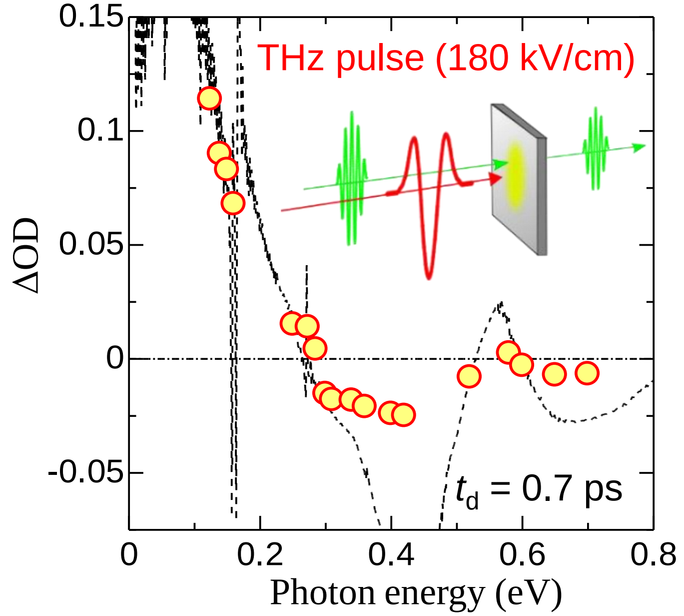
Summary 2 : THz electric-field induced phase transitions in Mott insulators

○ Mott insulator to metal transition


Carrier generations via quantum tunneling

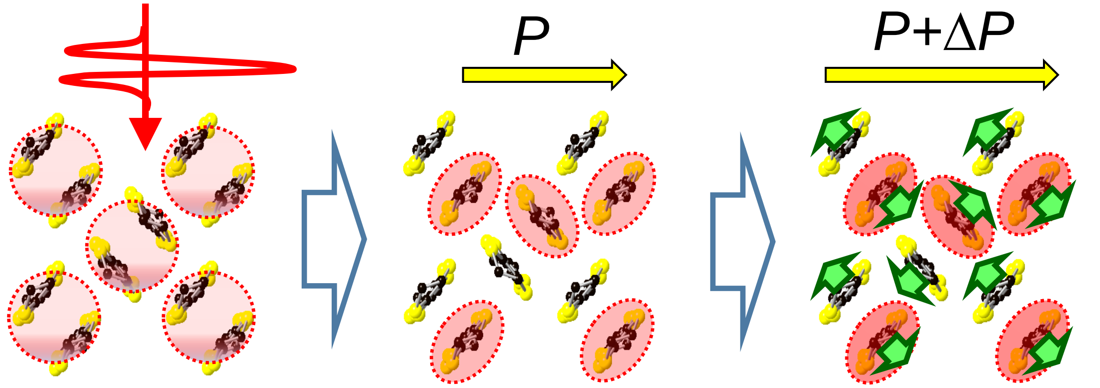
Mott insulator

Metal



*H. Yamakawa et al., Nature Materials **16**, 1100 (2017)*
*N. Takamura, PRB **107**, 085147(2023)*

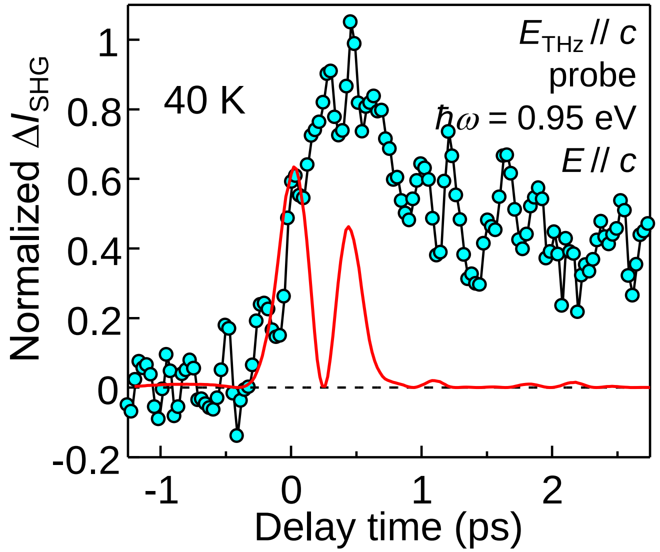
○ Mott insulator to polar CO transition



Mott insulator

Polar charge-order

Stabilization by molecular displacements



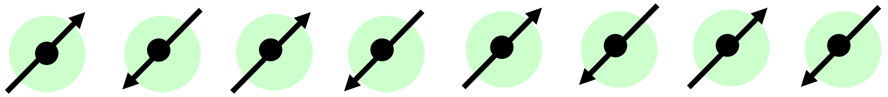
*H. Yamakawa et al., Nature Commun. **12**, 953 (2021)*

A terahertz electric-field pulse is a powerful source to melt an ordered state and, also to create a more ordered state or a lower-symmetry state.

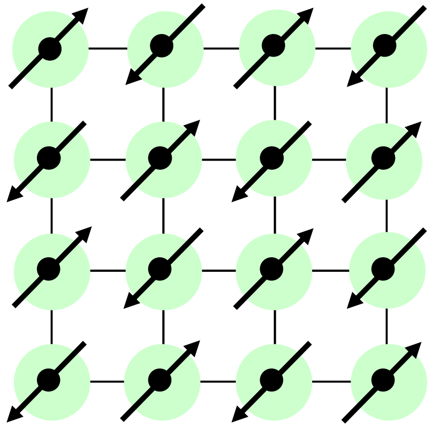
Content

1. Introduction
   - Half-filled 1D and 2D Mott insulators
   - Overview of their optical responses
2. Photoinduced Mott-insulator to metal transitions
   - Concept
   - 1D and 2D Mott insulators
3. Terahertz electric-field induced phase transitions
   - Mott insulator to metal transition
   - Mott insulator to polar charge-order transition
4. Floquet states formed by a mid-infrared electric field in Mott insulators
   - Photon-dressed Floquet states in 1D Mott insulators
   - Phonon-dressed Floquet states in 1D dimerized Mott insulators
   - Attempts of Floquet engineering
5. Summary

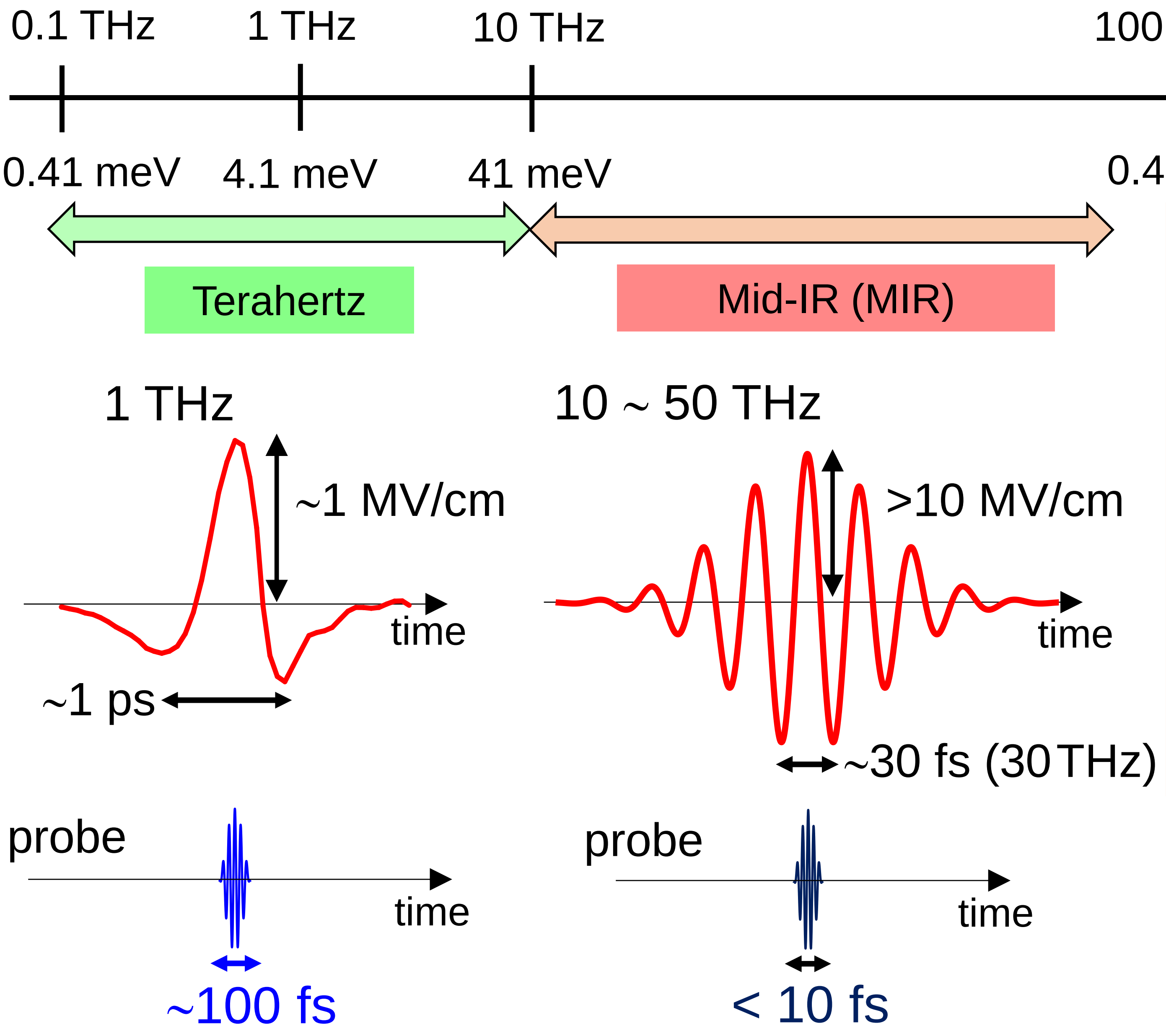
1D Mott insulator



2D Mott insulator

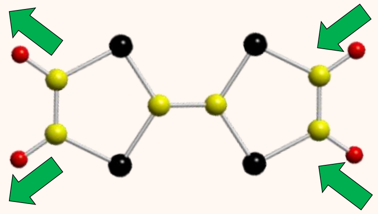


Electronic-state controls by a mid-IR (MIR) electric field



○ Application of a high electric-field ~10 MV/cm

○ Resonant phonon excitation
molecular vibration
lattice vibration



○ Multi-cycle pulse

+

Sub-cycle spectroscopy using a probe pulse with a time width shorter than 10 fs

These features of mid-infrared pulses enable to create novel electronic states such as Floquet states and investigate related electronic state changes.

Dressed states under a periodic electric field of light: Floquet picture

Under a light electric field that varies with frequency Ω, new levels are created around an original level at intervals of ℏΩ.

Experiments:

Y. H. Wang *et al.*, *Science* **342**, 453 (2013)

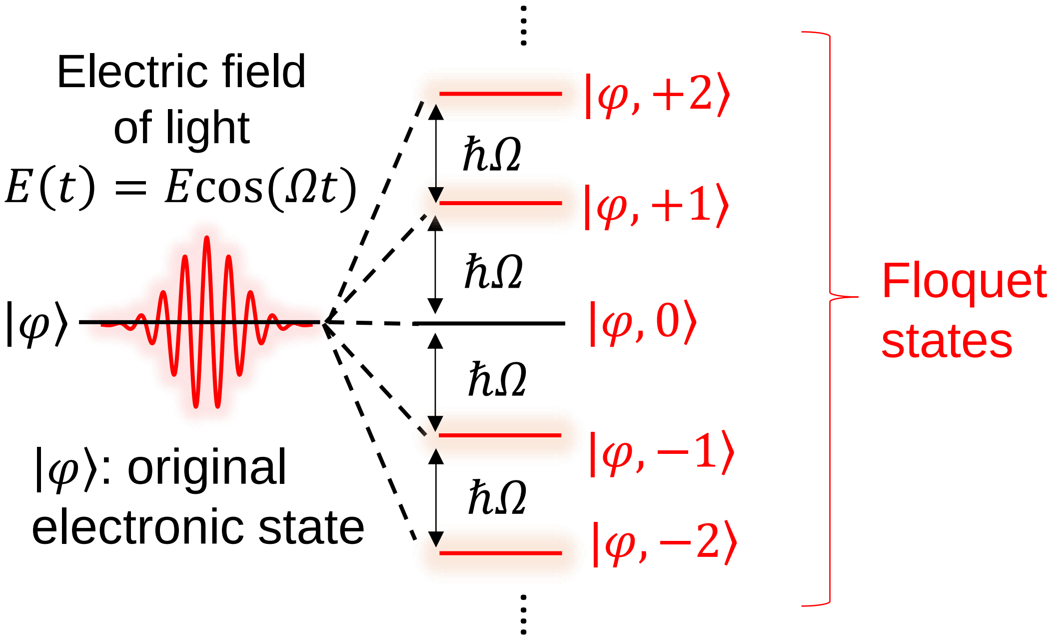
F. Mahmood *et al.*, *Nat. Phys.* **12**, 306 (2016).

⋮

Theory:

T. Oka *et al.*, *Annu. Rev. Condens. Matter Phys.* **10**, 387 (2019).

cf. Yesterday's Talk by A. Sentef



Electric field of light $E(t) = E\cos(\Omega t)$

$|\varphi\rangle$: original electronic state

Schrodinger equation

$$i\hbar\frac{\partial}{\partial t}|\psi(t)\rangle = \hat{H}(t)|\psi(t)\rangle$$

Hamiltonian has a period $T = 2\pi/\Omega$.

$$\hat{H}(t) = \hat{H}_0 + \hat{H}_\Omega(t),$$

$$\hat{H}(t+T) = \hat{H}(t)$$

Floquet theorem

Floquet pseudo energy

$$|\psi(t)\rangle = \sum_{\alpha} c_\alpha \exp\left(-i\frac{\epsilon_\alpha}{\hbar}t\right)|\Phi_\alpha(t)\rangle$$

dressed state

$$|\Phi_\alpha(t+T)\rangle = |\Phi_\alpha(t)\rangle$$

Fourier series expansions

n-photon dressed state

$$\hat{H}(t) = \sum_{m=-\infty}^{\infty} \exp(-im\Omega t)\,\hat{H}_m\,,\quad |\Phi_\alpha(t)\rangle = \sum_{n=-\infty}^{\infty} \exp(-in\Omega t)\,|\varphi_\alpha, n\rangle$$

$$\sum_{m=-\infty}^{\infty}\left(\hat{H}_{n-m} - m\Omega\delta_{mn}\right)|\varphi_\alpha, m\rangle = \epsilon_\alpha|\varphi_\alpha, m\rangle$$

$$\hat{\mathcal{H}}_{\mathrm{F}}|\Phi_\alpha\} = \epsilon_\alpha|\Phi_\alpha\}$$

$$\hat{\mathcal{H}}_{\mathrm{F}} = \begin{bmatrix} \ddots & & & \\ & \hat{H}_0 + \hbar\Omega & \hat{H}_{-1} & \hat{H}_{-2} \\ & \hat{H}_{+1} & \hat{H}_0 & \hat{H}_{-1} \\ & \hat{H}_{+2} & \hat{H}_{+1} & \hat{H}_0 - \hbar\Omega \\ & & & \ddots \end{bmatrix}, |\Phi_\alpha\} = \begin{bmatrix} \vdots \\ |\varphi_\alpha, -1\rangle \\ |\varphi_\alpha, 0\rangle \\ |\varphi_\alpha, +1\rangle \\ \vdots \end{bmatrix}$$

Time-independent eigenvalue problem for Floquet Hamiltonian $\hat{\mathcal{H}}_{\mathrm{F}}$, which yields the eigenstate consisting of *n*-photon dressed states.

Subcycle spectroscopy on 1D Mott insulators to investigate Floquet states formed by a mid-IR pulse

○ Photon-dressed Floquet state in 1D Mott insulators

T. Yamakawa et al., New J. Phys. ***25****, 093044 (2023)*

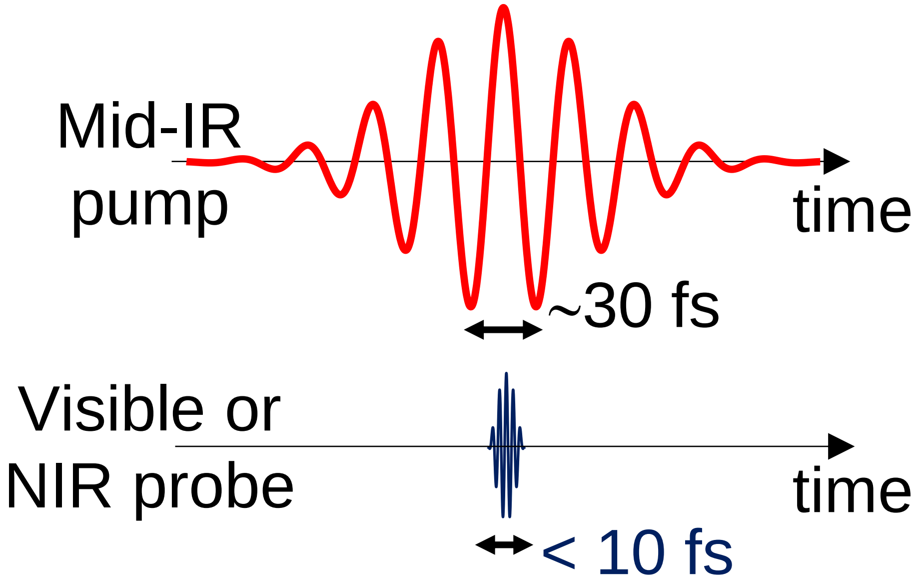
○ Phonon-dressed Floquet state in 1D dimerized Mott insulators

N. Sono et al., Commun. Phys. ***5****, 72 (2022)*

○ Destabilization of a spin-Peierls phase via phonon-dressed Floquet states
: Floquet engineering

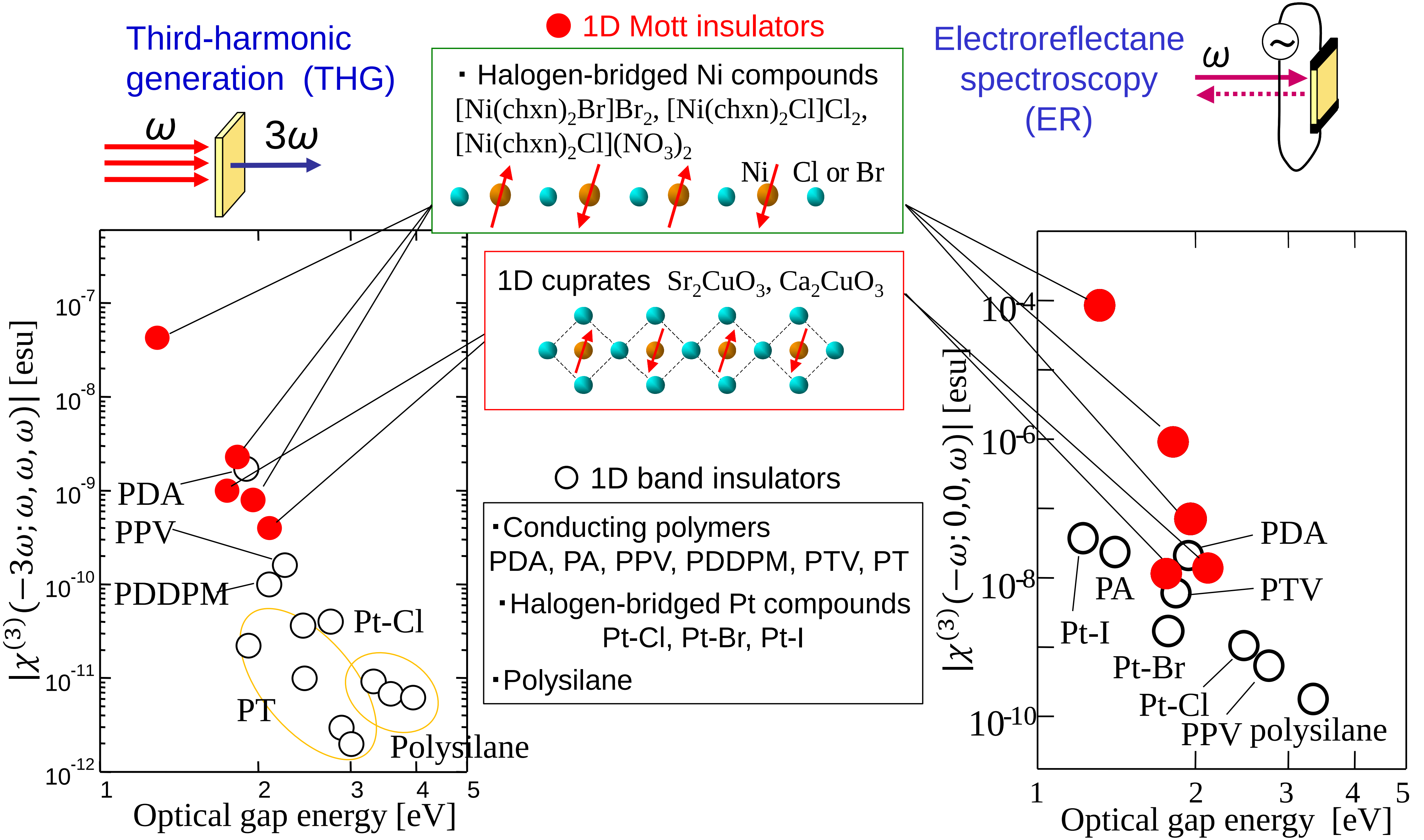
D. Sakai et al., Commun. Phys. ***7****, 40 (2024)*

Mid-infrared pump visible sub-cycle probe spectroscopy



Large third-order optical nonlinearity in 1D Mott insulators

$P = \varepsilon_0\left(\chi^{(1)}E + \chi^{(3)}EEE + \cdots\right)$ $\chi^{(3)}$: third-order nonlinear susceptibility



Third-harmonic generation (THG)

● 1D Mott insulators

- Halogen-bridged Ni compounds

$[Ni(chxn)_2Br]Br_2$, $[Ni(chxn)_2Cl]Cl_2$, $[Ni(chxn)_2Cl](NO_3)_2$

1D cuprates Sr_2CuO_3, Ca_2CuO_3

○ 1D band insulators

- Conducting polymers
  PDA, PA, PPV, PDDPM, PTV, PT
- Halogen-bridged Pt compounds
  Pt-Cl, Pt-Br, Pt-I
- Polysilane

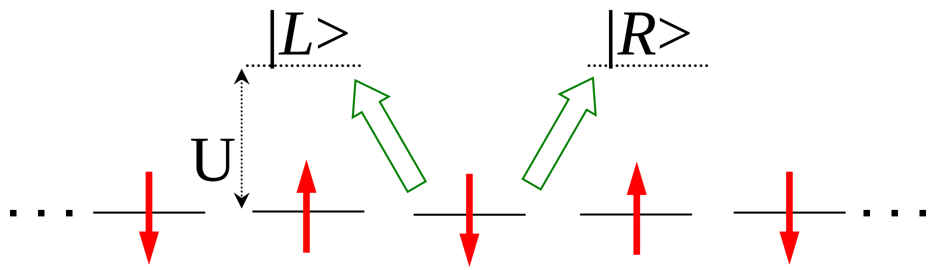
Electroreflectane spectroscopy (ER)

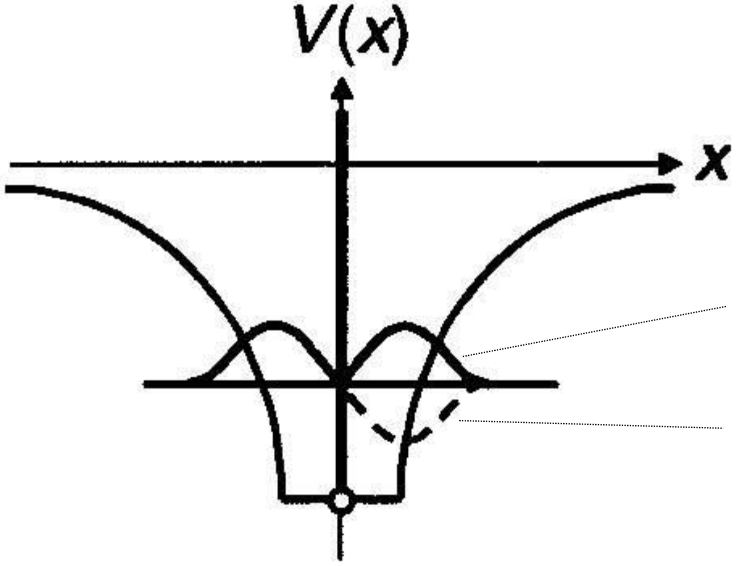
Kishida *et al.*, *PRL* **87**, 177401 (2001), Ono et al, *PRL* **95**, 087401 (2005)

Kishida *et al.*, *Nature* **405**, 929 (2000)

Large third-order optical nonlinearity in 1D Mott insulators

Lowest excited state





1-photon forbidden excitonic state with even-parity

$$|2\rangle = \frac{1}{\sqrt{2}}(|L\rangle + |R\rangle)$$

$$|1\rangle = \frac{1}{\sqrt{2}}(|L\rangle - |R\rangle)$$

1-photon allowed excitonic state with odd-parity

Two excited states are almost degenerate and have similar wavefunctions except for their phases. $\langle 1|x|2\rangle$ becomes large and enhances $\chi^{(3)}$.

⇩

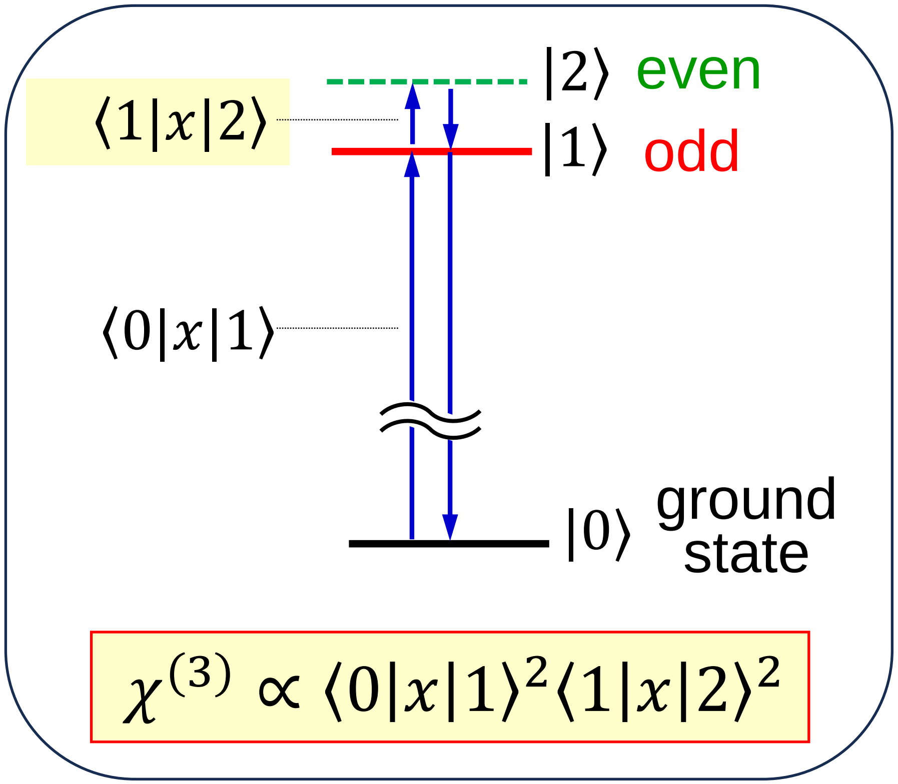
Observation of photon-dressed Floquet states

Third-order nonlinear optical response

$$P = P^{(1)} + \underline{\underline{P^{(3)}}} + \cdots\cdots$$
$$= \varepsilon_0\left(\chi^{(1)}E + \underline{\underline{\chi^{(3)}}}EEE + \cdots\cdots\right)$$

Third-order nonlinear susceptibility

Three-level model

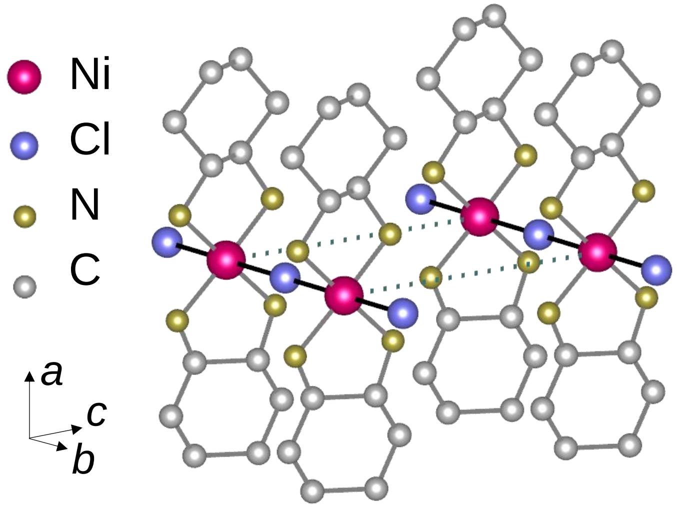


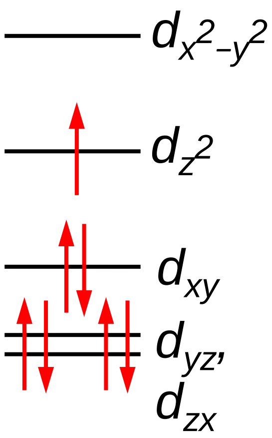
$$\chi^{(3)} \propto \langle 0|x|1\rangle^2 \langle 1|x|2\rangle^2$$

H. Kishida *et al.*, *Nature* **405**, 929 (2000)
Y. Mizuno *et al.*, *Phys. Rev. B* **62**, 4769(R) (2000)
M. Ono *et al.*, *Phys. Rev. B* **70**, 085101 (2004)

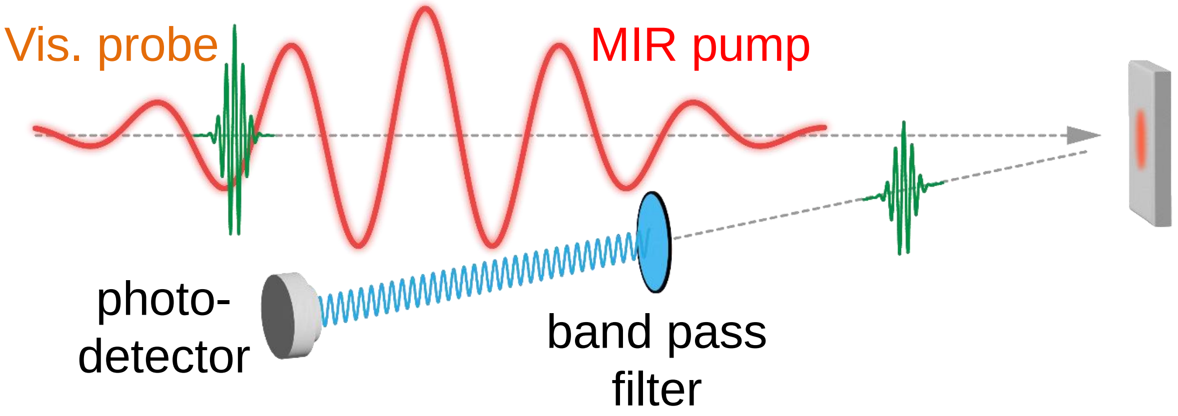
Subcycle spectroscopy of photon-dressed Floquet states in 1D Mott insulators

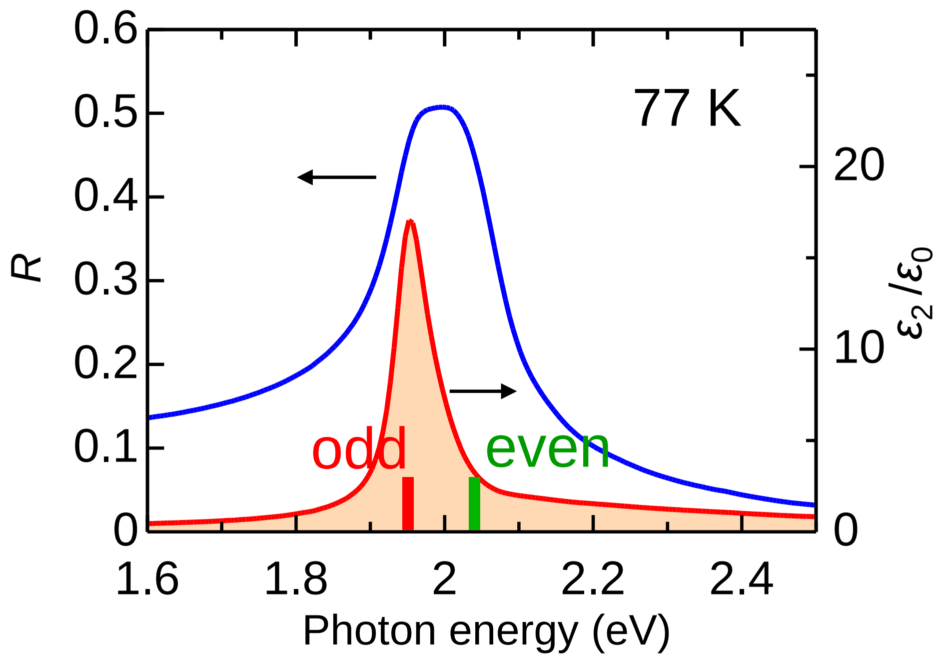
Chlorine-bridged Ni-chain compound : $[\mathrm{Ni(chxn)_2Cl}](\mathrm{NO_3})_2$

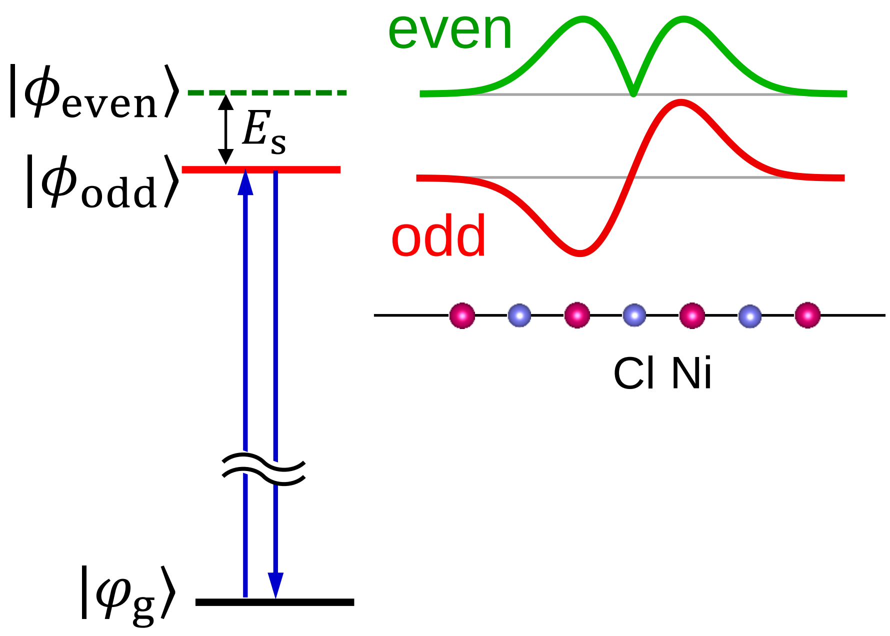




Mid-IR pump visible subcycle probe spectroscopy
in a reflection configuration



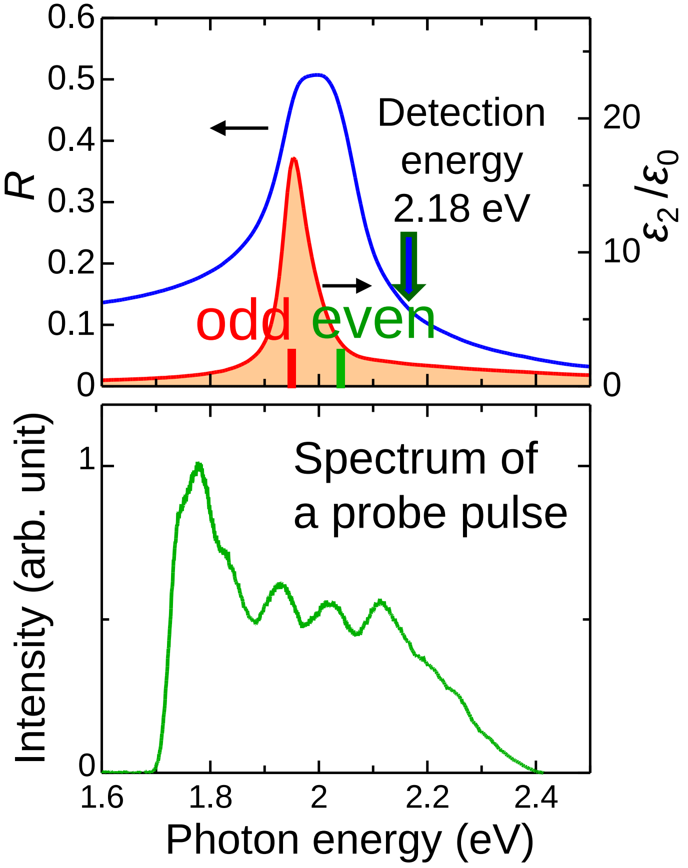


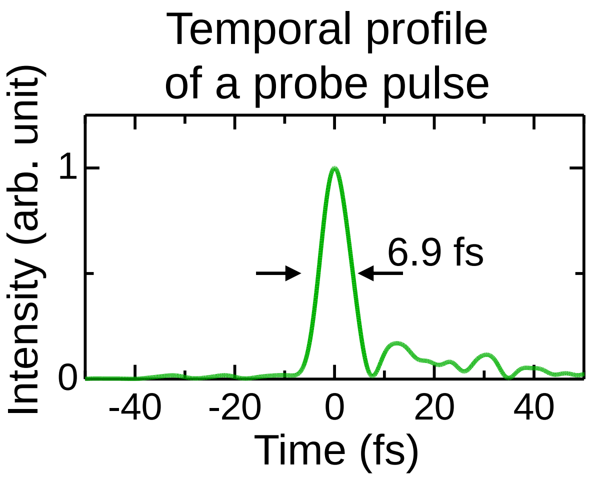


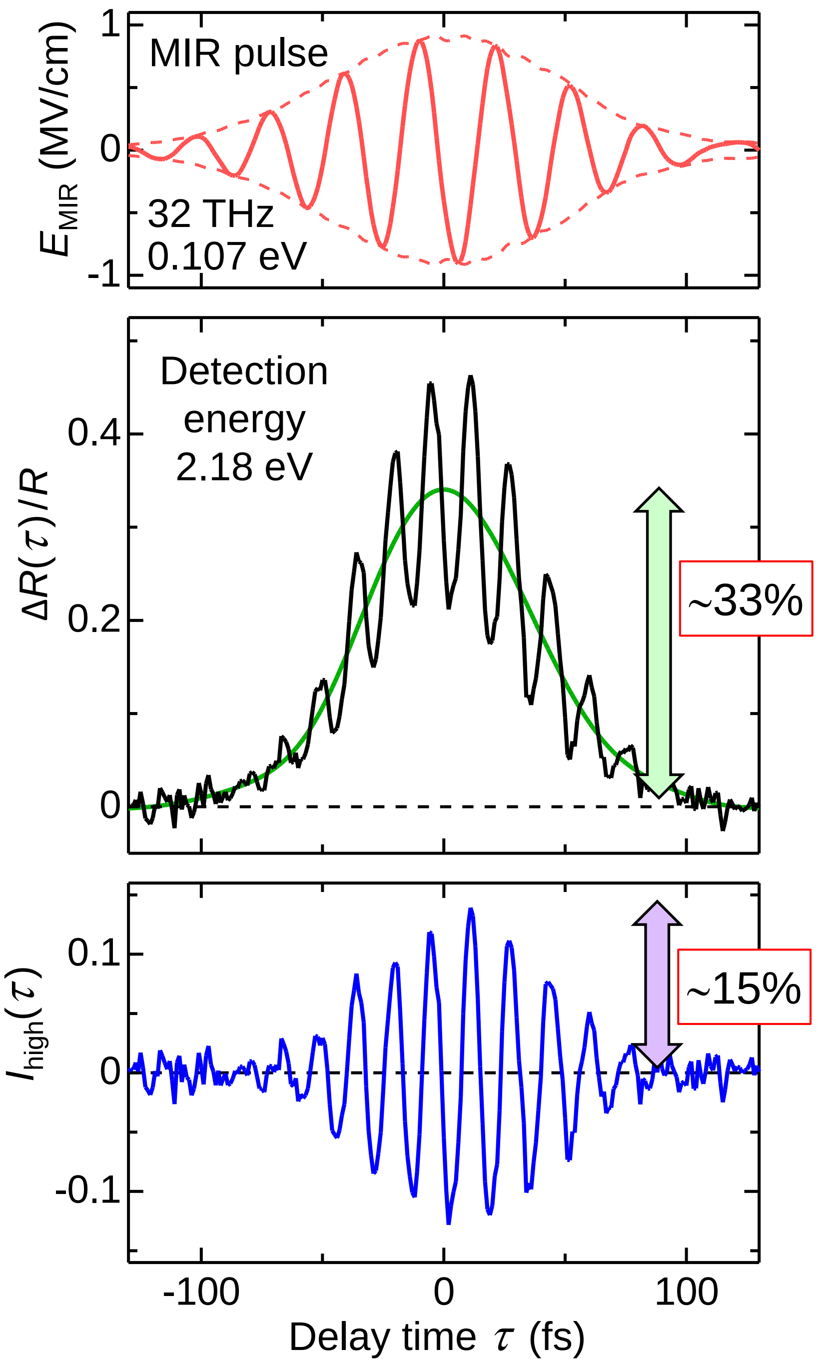
H. Kishida *et al.*, *Nature* **405**, 929 (2000)
M. Ono *et al.*, *Phys. Rev. B* **70**, 085101 (2004)

Gigantic photo-responses of photon-dressed Floquet states in 1D Mott insulators

$[Ni(chxn)_2Cl](NO_3)_2$

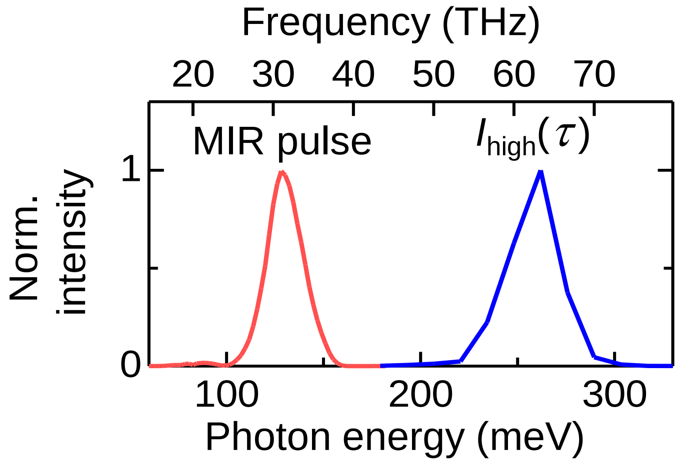






MIR pulse (32 THz, ~0.1 eV) with an amplitude of 1 MV/cm

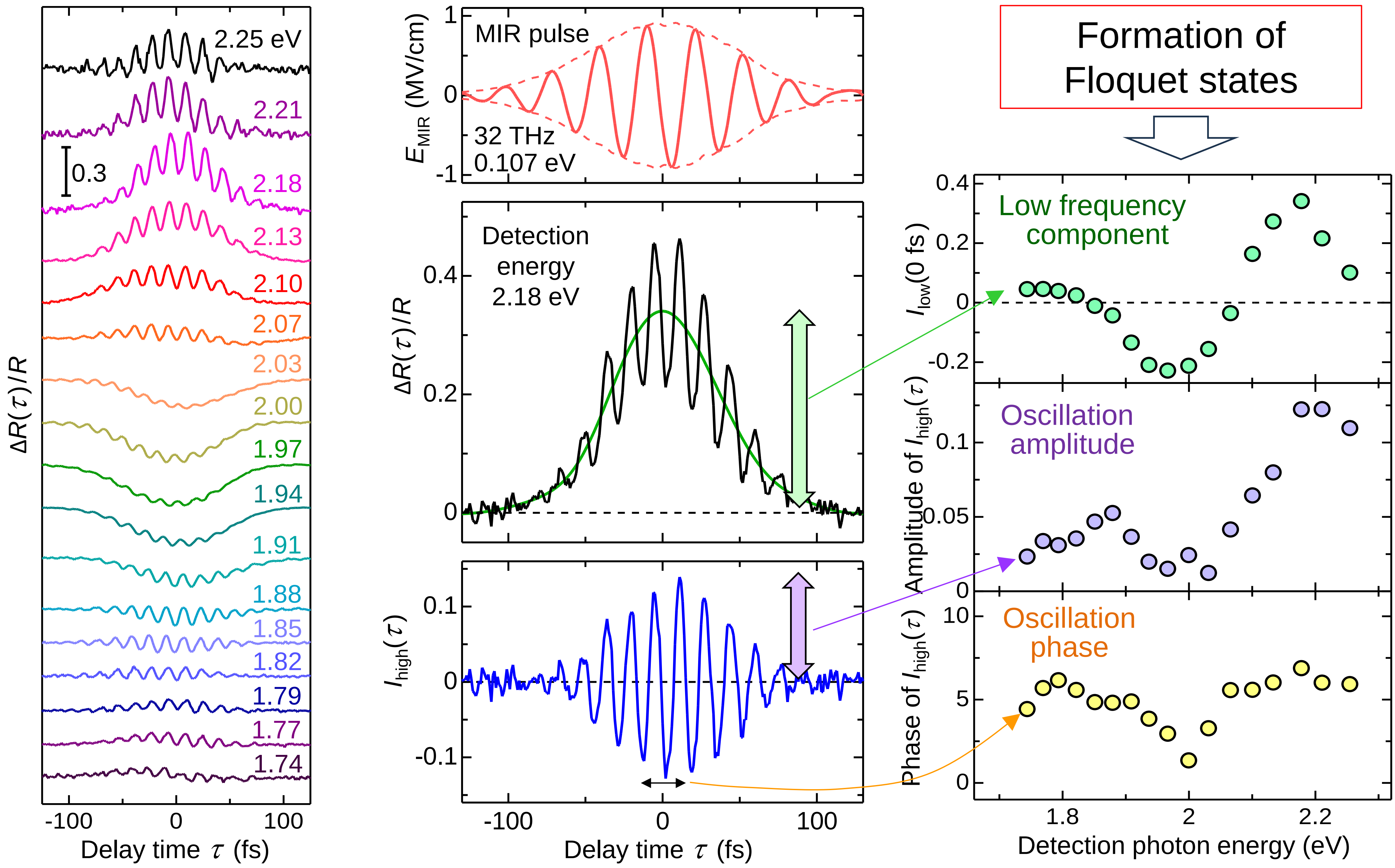
- A low frequency reflectivity change exceeding 30 %.
- An oscillatory component has twice the MIR frequency



T. Yamakawa et al., New J. Phys. ***25****, 093044 (2023)*

Probe energy dependence of reflectivity changes associated with Floquet states

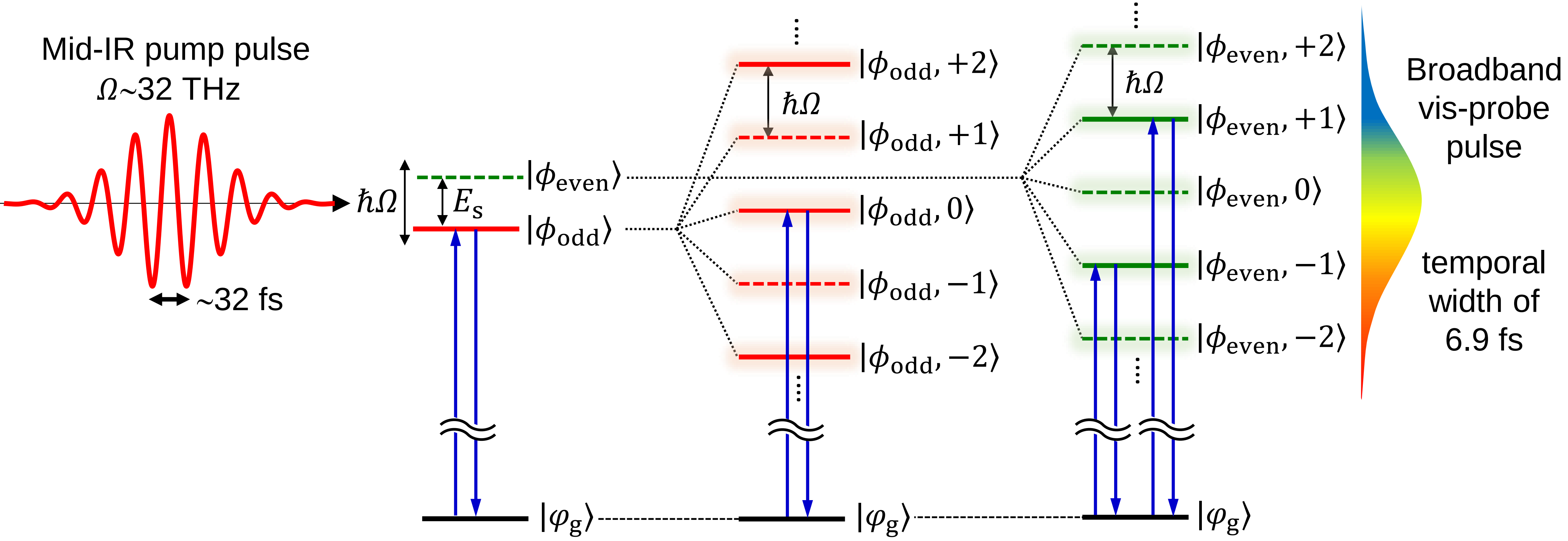
$[Ni(chxn)_2Cl](NO_3)_2$



Formation of Floquet states

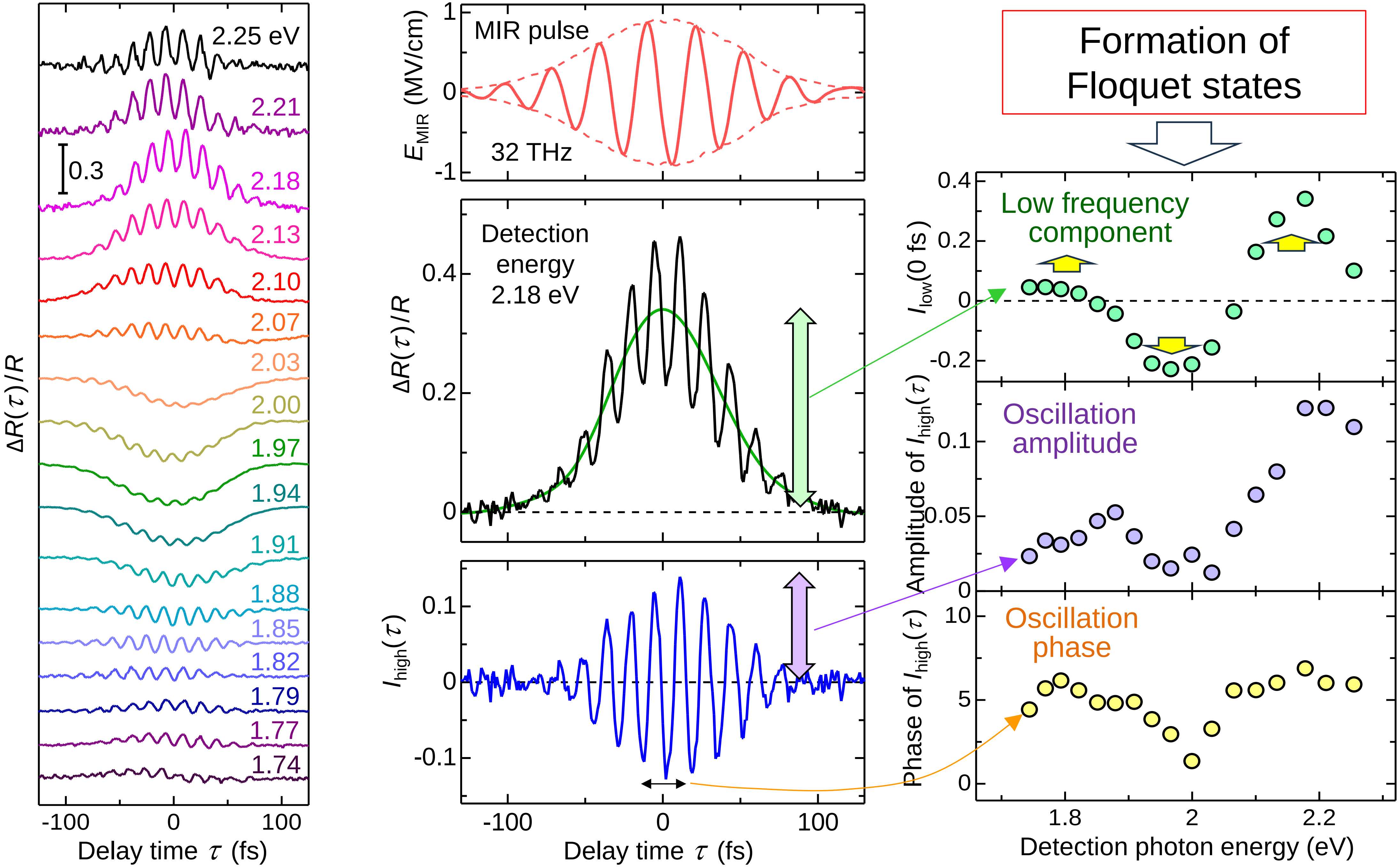
T. Yamakawa et al., New J. Phys. ***25****, 093044 (2023)*

Formation of n-photon side bands by an MIR pulse and related optical responses



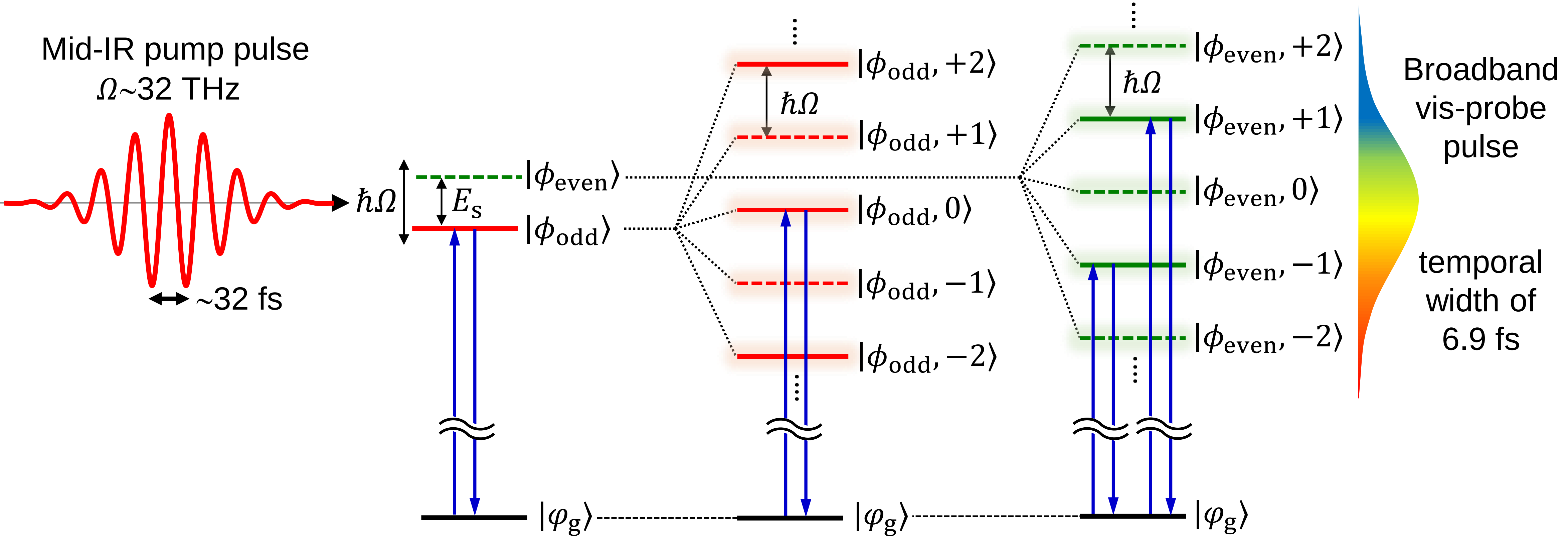
- The original transition to the one-photon allowed state shifts and loses its intensity.
- The transitions to the one-photon allowed side bands gain intensities.

Probe energy dependence of low-frequency components and oscillations

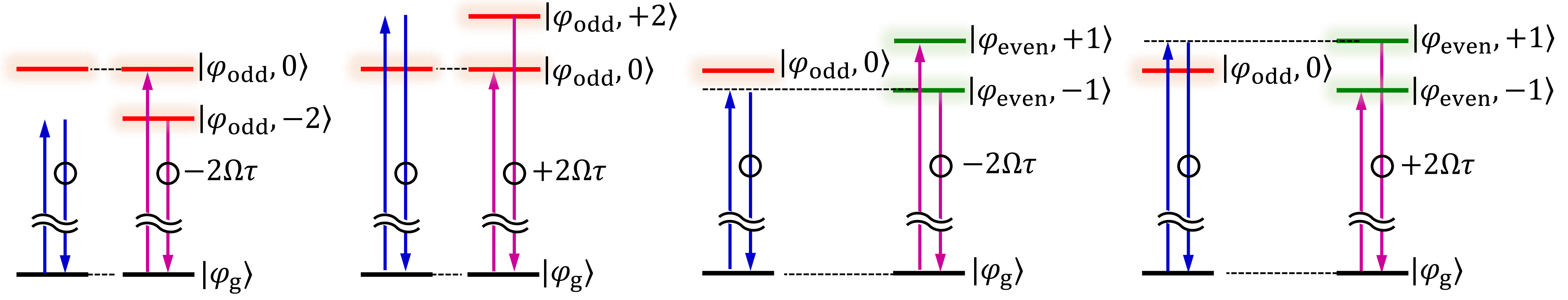


T. Yamakawa et al., New J. Phys. ***25****, 093044 (2023)*

Formation of n-photon side bands by an MIR pulse and related optical responses

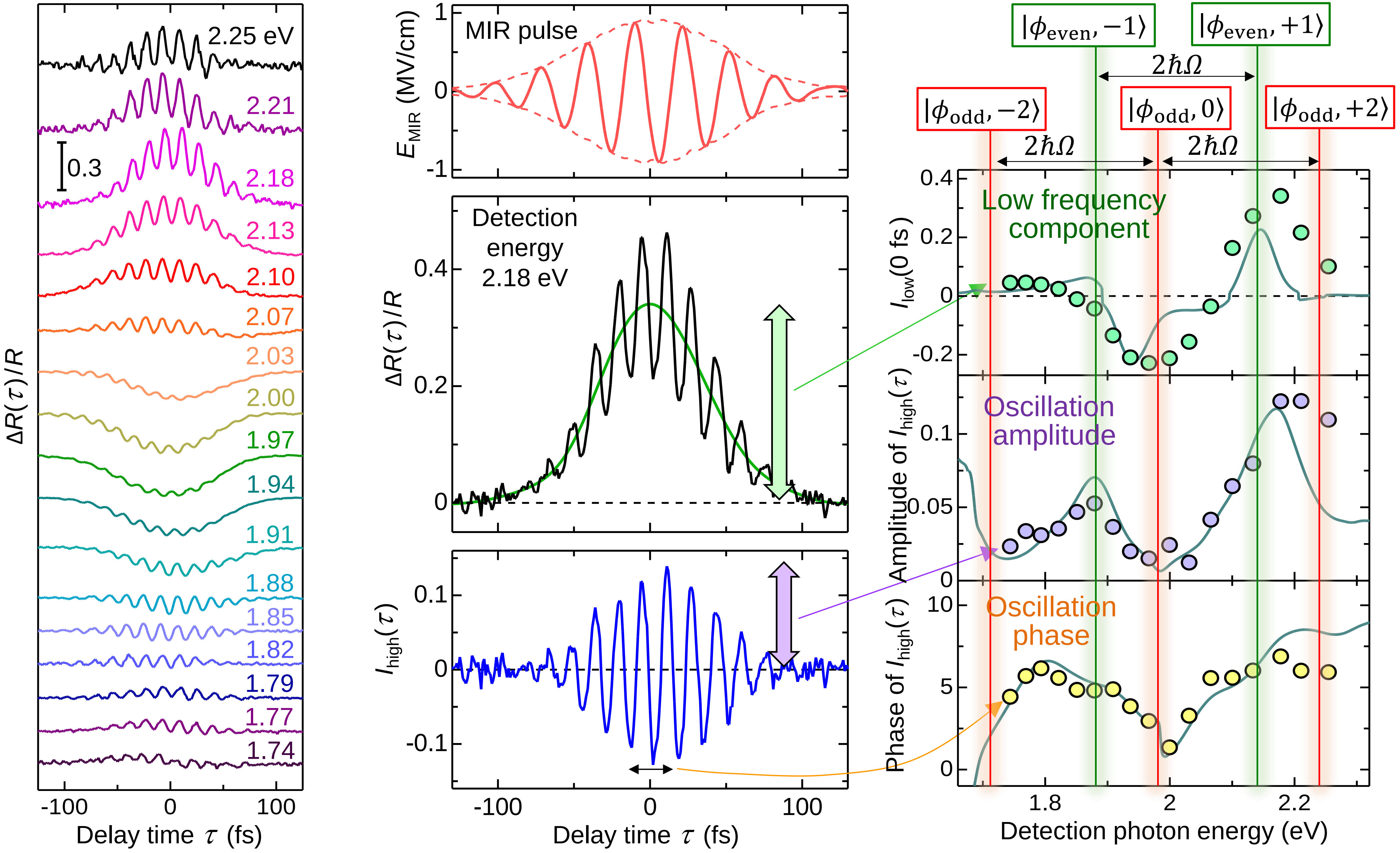


Various scattering processes associated with n-photon side bands occur and interfere with the linear optical processes.



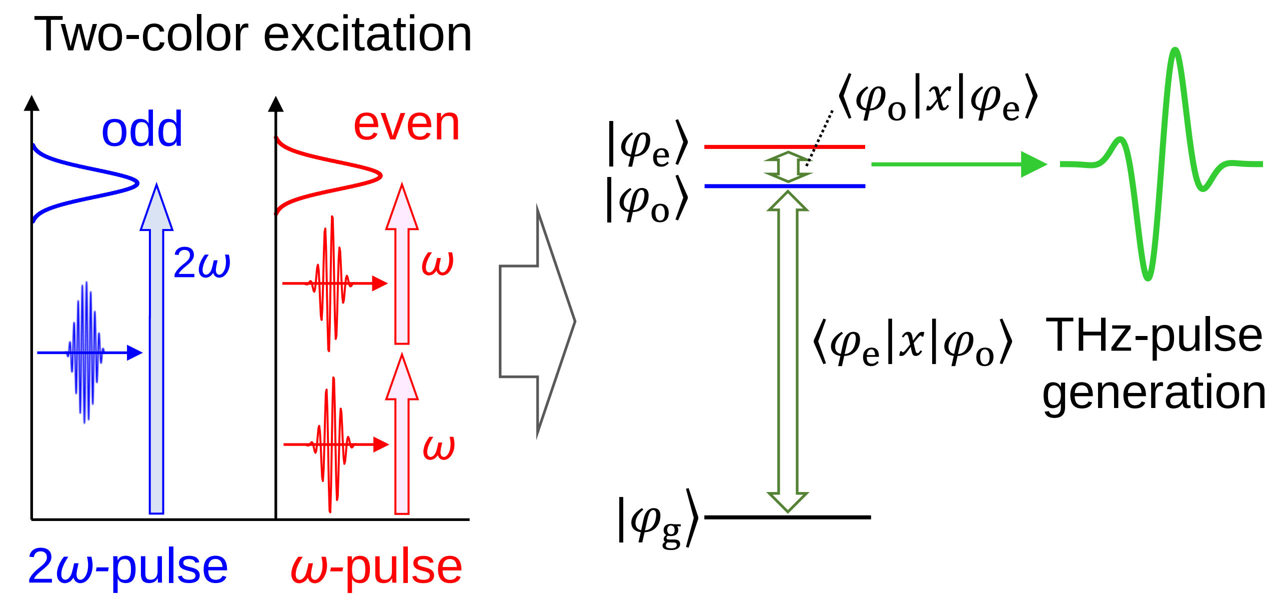
Phases of scattering lights change by $\pm 2\Omega\tau$ which causes an oscillation with twice the MIR freq.

Analyses of photon-dressed Floquet states considering n-photon side band states

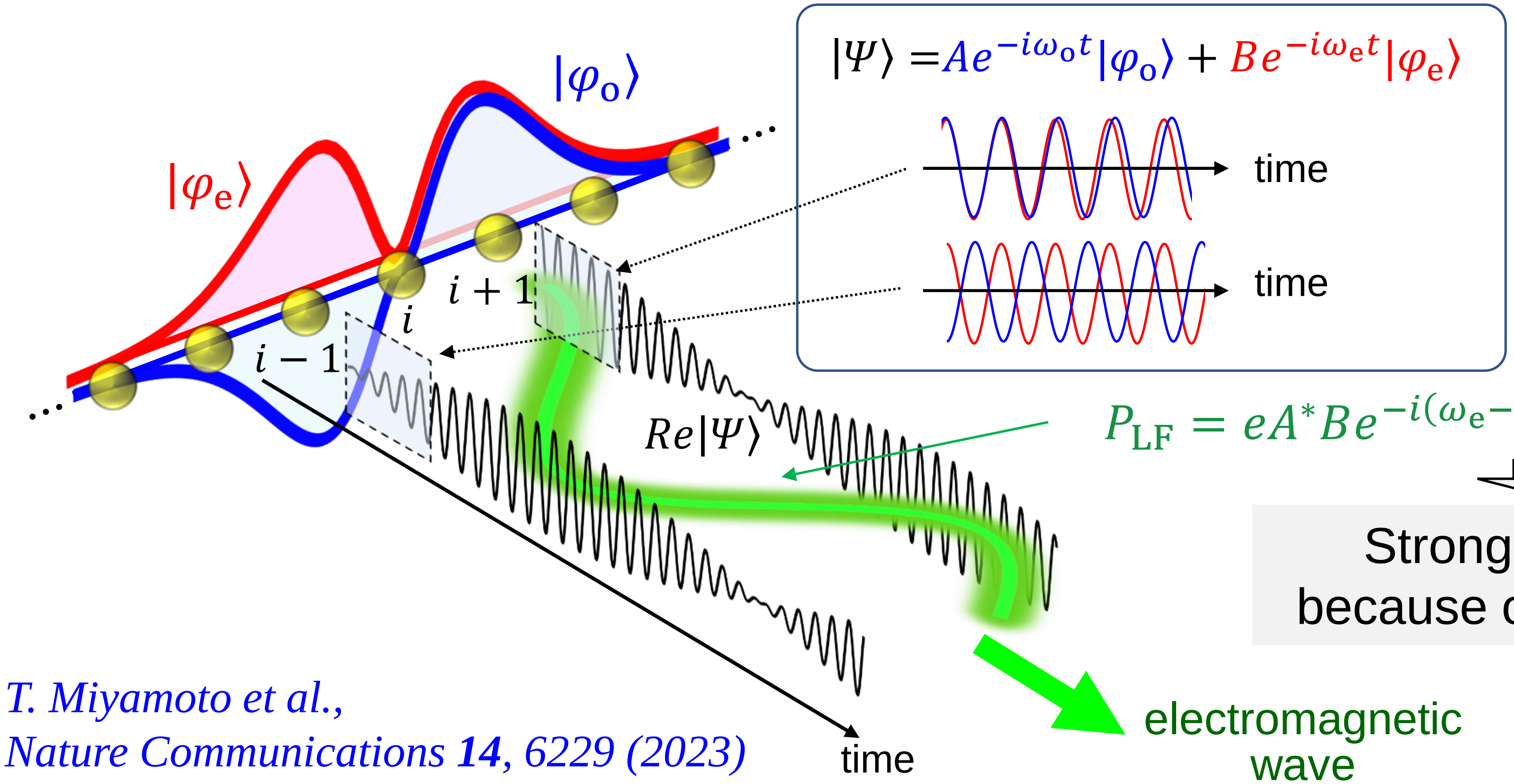


T. Yamakawa et al., New J. Phys. ***25****, 093044 (2023)*

THz nonlinear optics : phase and amplitude controllable THz radiation



When odd-parity and even-parity excitons are simultaneously excited, a THz pulse having a difference frequency between two excitonic states can be generated via their interferences.



$$|\Psi\rangle = Ae^{-i\omega_\mathrm{o}t}|\varphi_\mathrm{o}\rangle + Be^{-i\omega_\mathrm{e}t}|\varphi_\mathrm{e}\rangle$$

$$P_\mathrm{LF} = eA^*Be^{-i(\omega_\mathrm{e}-\omega_\mathrm{o})t}\langle\varphi_o|x|\varphi_e\rangle + \mathrm{c.c.}$$

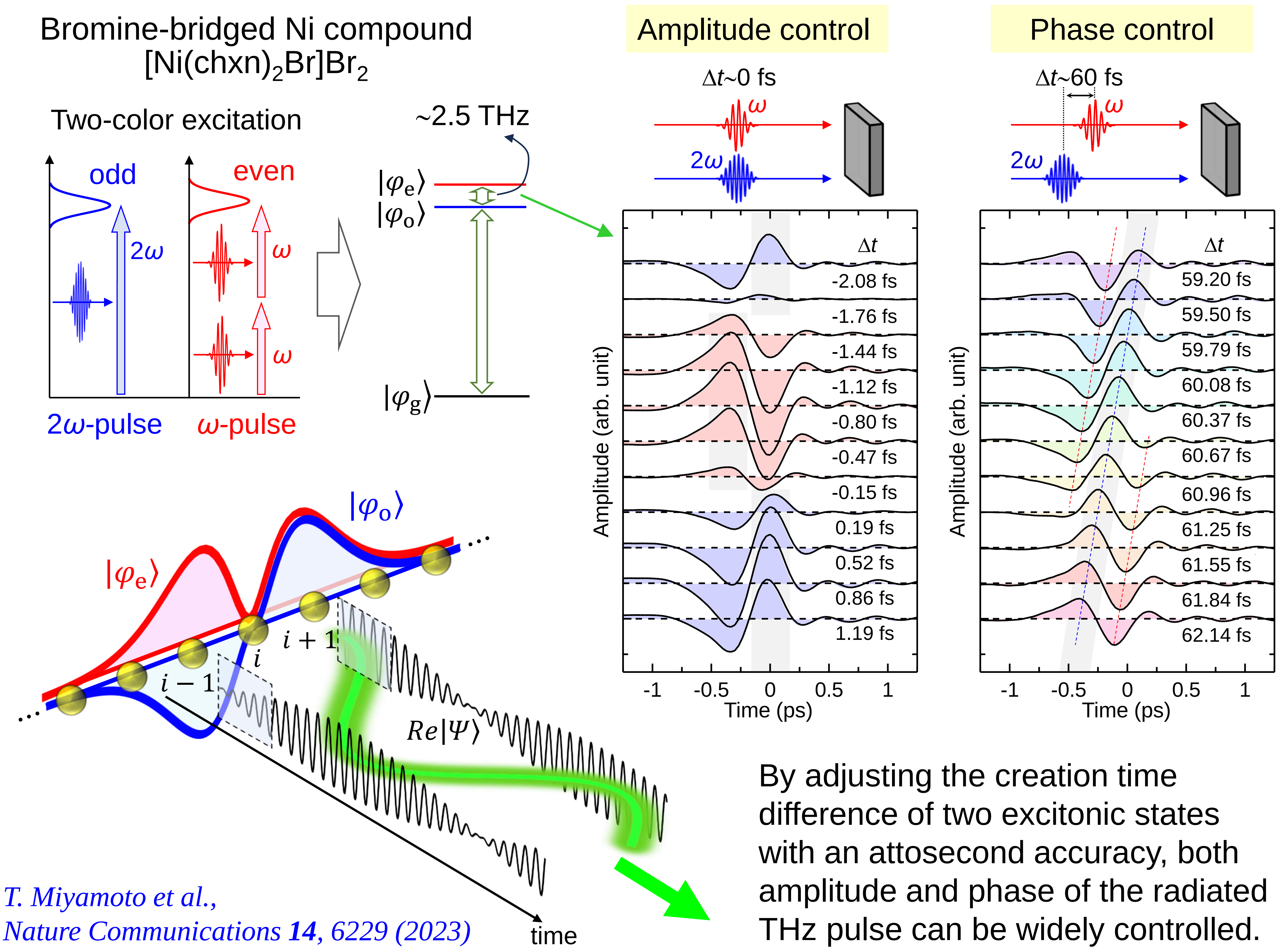
Strong THz radiation
because of large $\langle\varphi_o|x|\varphi_e\rangle$

electromagnetic wave

$$E_\mathrm{THz}(t) \propto \frac{\partial^2 P_\mathrm{LF}}{\partial t^2}$$

T. Miyamoto et al.,
Nature Communications ***14****, 6229 (2023)*

Bromine-bridged Ni compound $[Ni(chxn)_2Br]Br_2$



T. Miyamoto et al.,
Nature Communications ***14****, 6229 (2023)*

By adjusting the creation time difference of two excitonic states with an attosecond accuracy, both amplitude and phase of the radiated THz pulse can be widely controlled.

Subcycle spectroscopy on 1D Mott insulators to investigate Floquet states formed by a mid-IR pulse

○ Photon-dressed Floquet state in 1D Mott insulators

T. Yamakawa et al., New J. Phys. ***25****, 093044 (2023)*

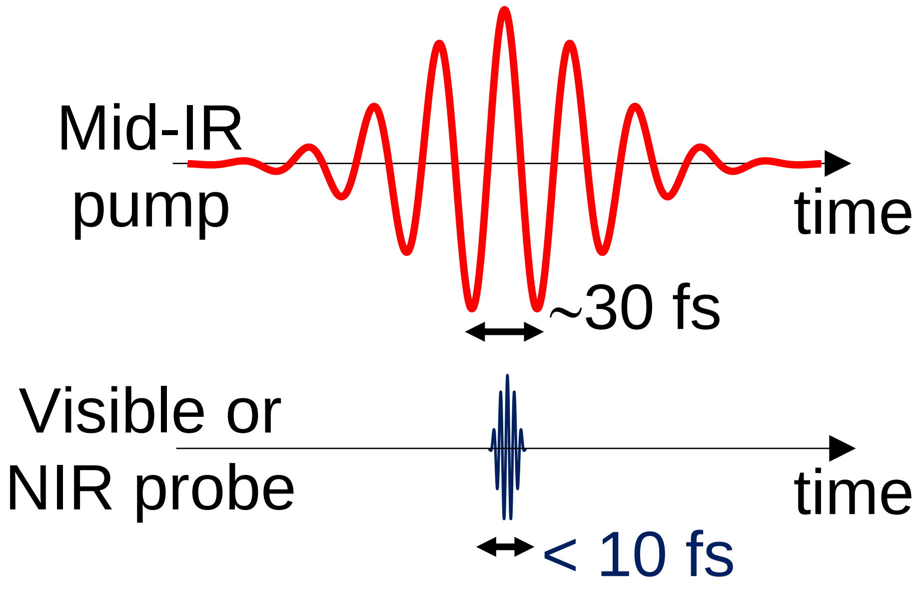
○ Phonon-dressed Floquet state in 1D dimerized Mott insulators

N. Sono et al., Commun. Phys. ***5****, 72 (2022)*

○ Destabilization of a spin-Peierls phase via phonon-dressed Floquet states : Floquet engineering

D. Sakai et al., Commun. Phys. ***7****, 40 (2024)*

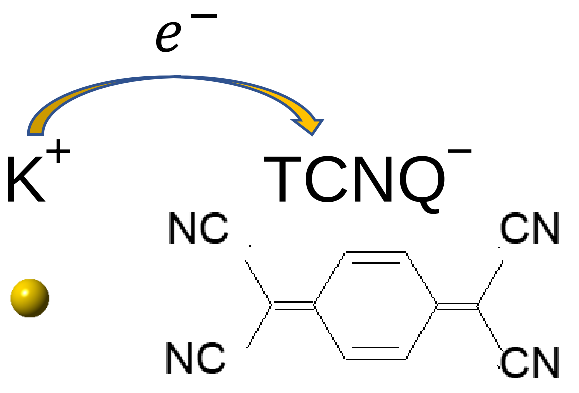
Mid-infrared pump visible sub-cycle probe spectroscopy

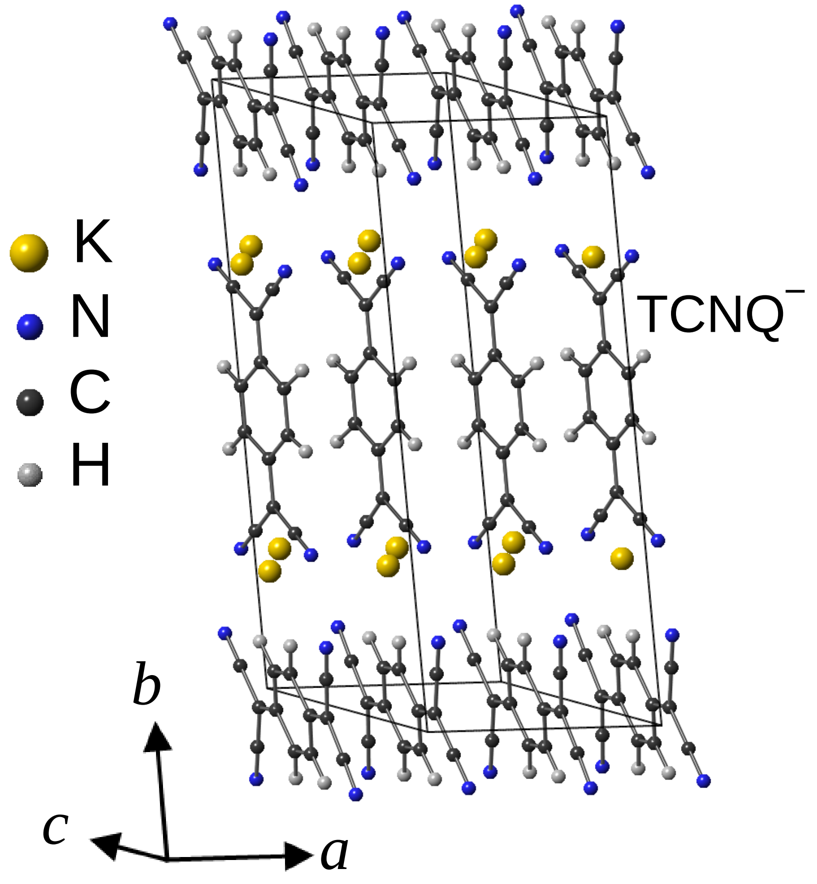


Floquet states can also be formed by a modulation of electronic potentials by a phonon excitation.

A spin-Peierls system of an organic molecular compound : K-TCNQ

K-TCNQ



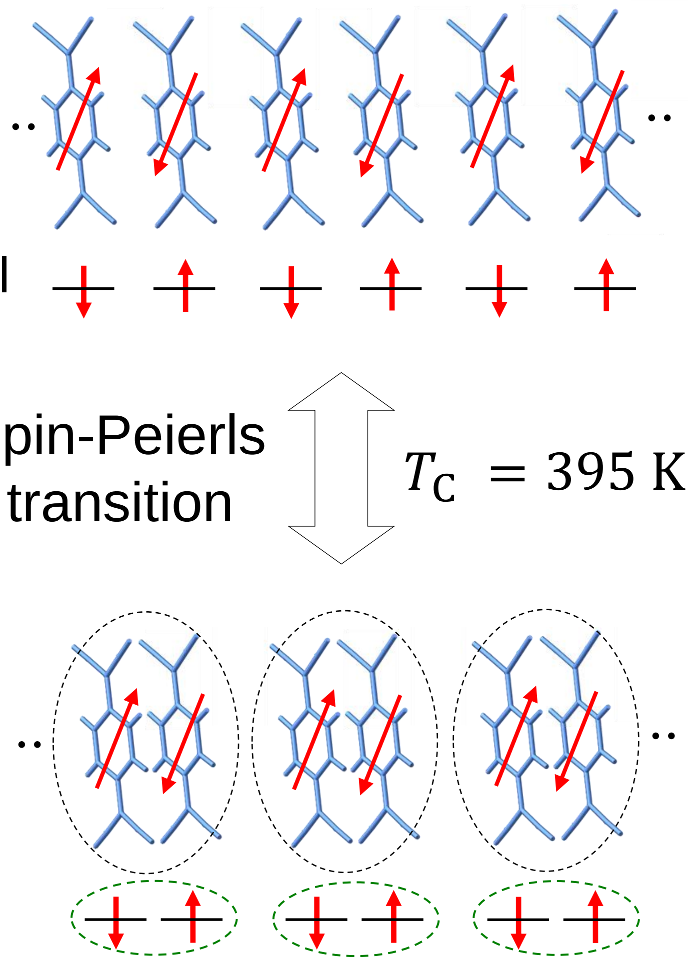


Half-filled 1D Mott-insulator

antiferromagnetic spin ½ chain

on-site Coulomb repulsion
U (~1.5 eV)
>>
t (~ 0.2 eV)
transfer integral

singly occupied molecular orbital (SOMO)



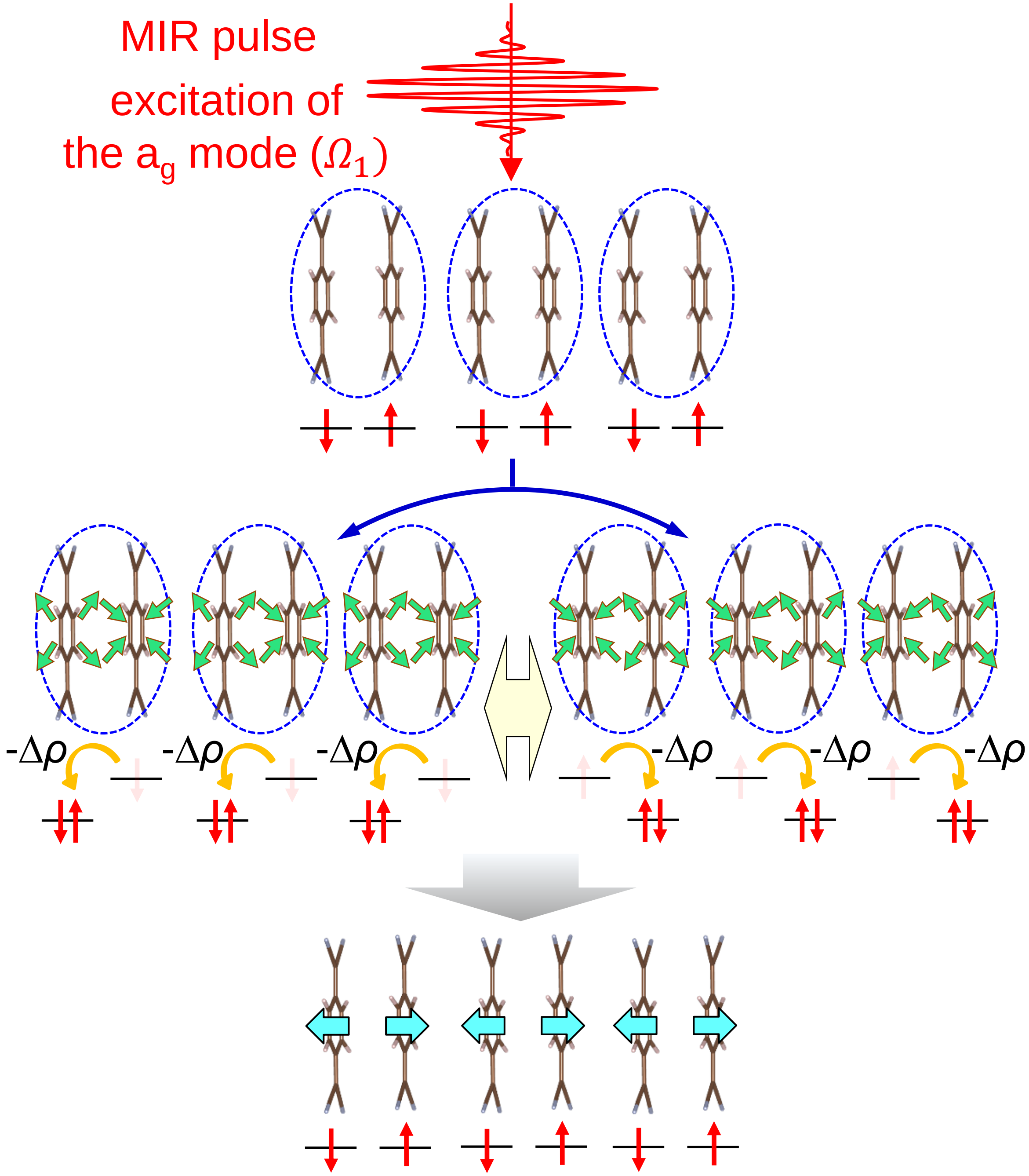
spin-Peierls transition

$T_C = 395$ K

Dimerized 1D Mott insulator

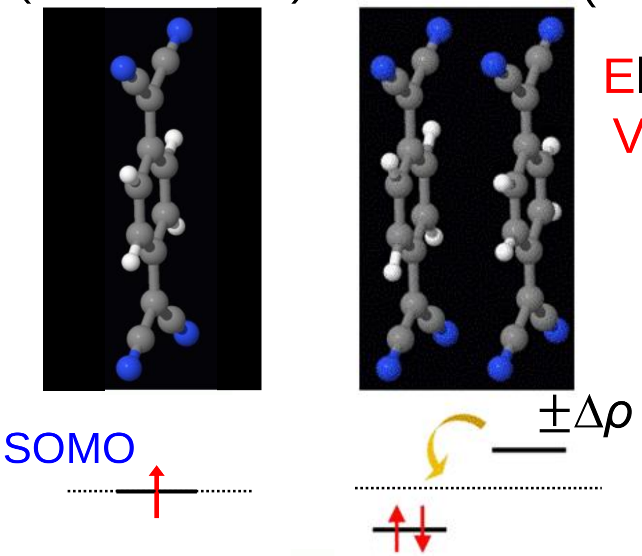
spin-singlet formation in each dimer

Destabilization of spin-Peierls phase by charge- and spin-modulated Floquet state



a_g-mode
(not IR active)

out-of phase
vibration of a_g-mode
in a dimer (IR-active)



Electron-Molecular Vibration coupling (EMV coupling)

Intermolecular charge transfer synchronized with the vibration

Rice *et al.*, *PRL* **39**, 1359 (1977).
Painelli *et al.*, *J. Chem. Phys.* **84**, 5655 (1986).

The out-of phase a_g mode modulates charge- and spin-density in each dimer.

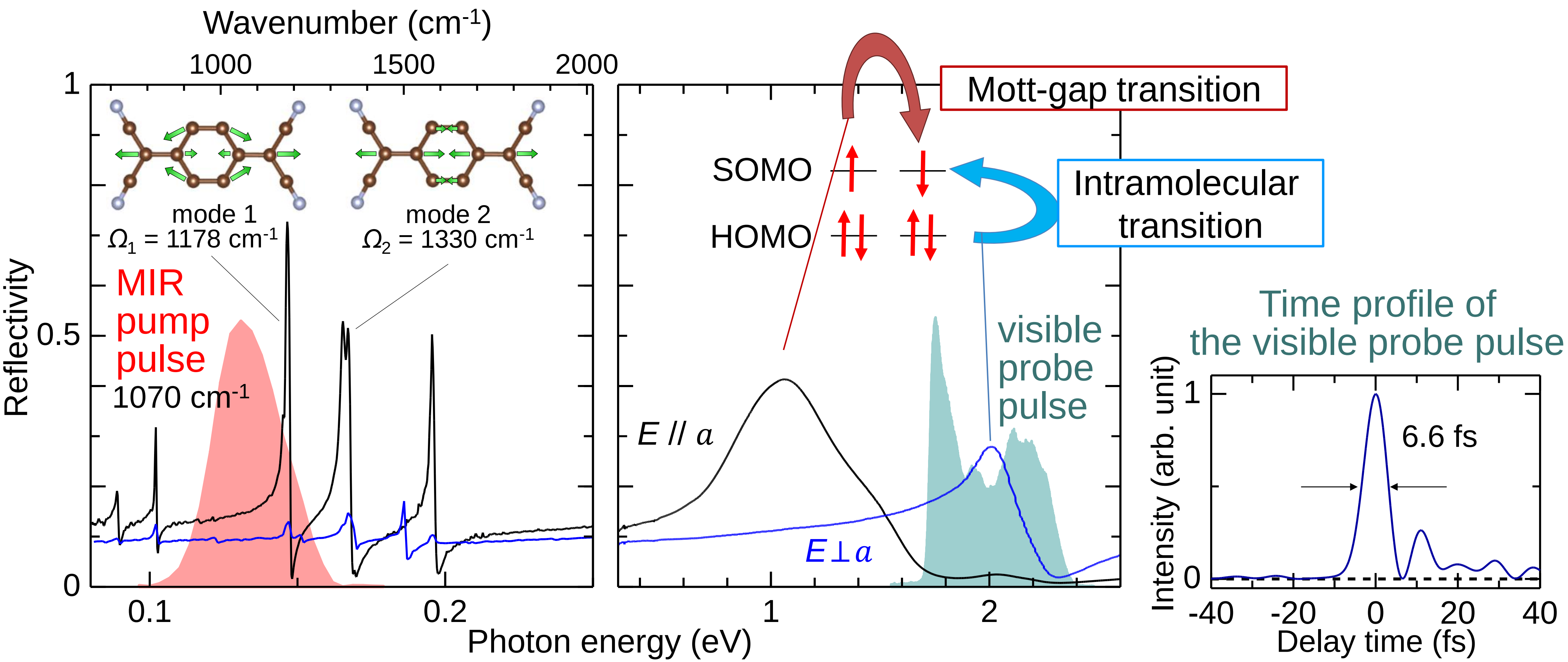
→ phonon-dressed Floquet state

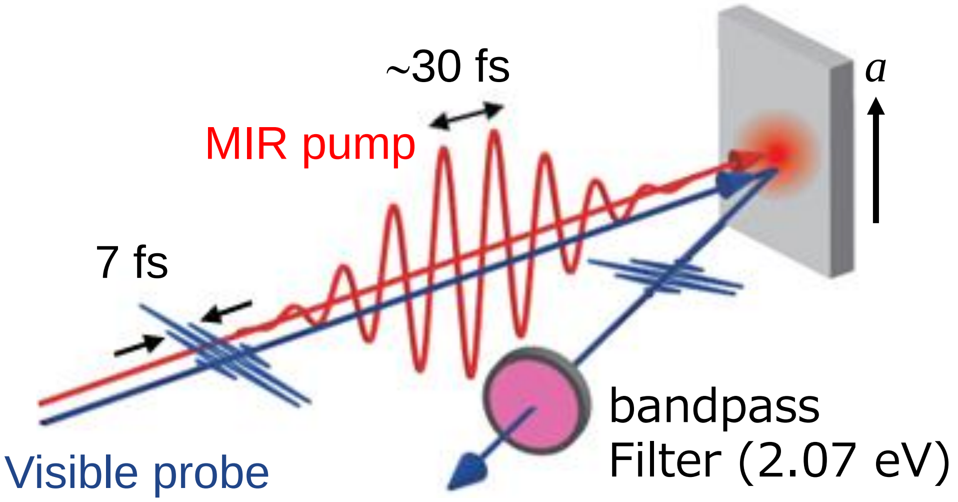
→ Hybridization of
the AFM ground state $|\downarrow\ \uparrow\rangle$ with
non-magnetic states $|\downarrow\uparrow\ —\rangle$, $|—\ \downarrow\uparrow\rangle$

→ Destabilization of the spin-Peierls phase

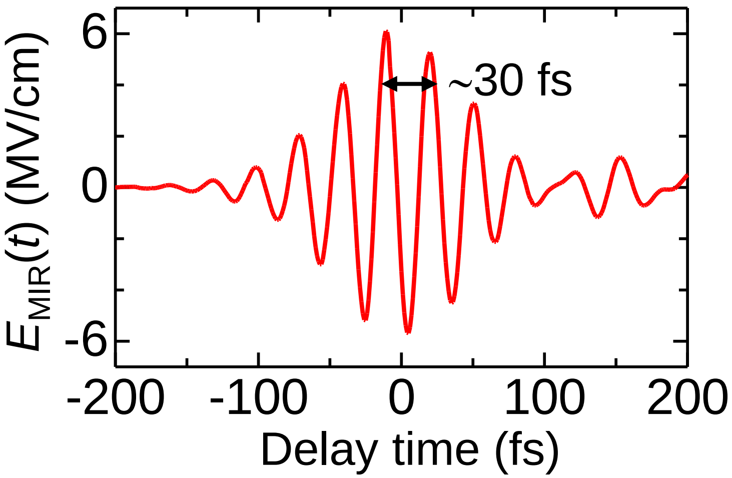
Detect ultrafast dynamics of the decrease
in the spin-Peierls dimerization by this vibrational excitation with a MIR pulse

MIR pump-subcycle reflection probe spectroscopy



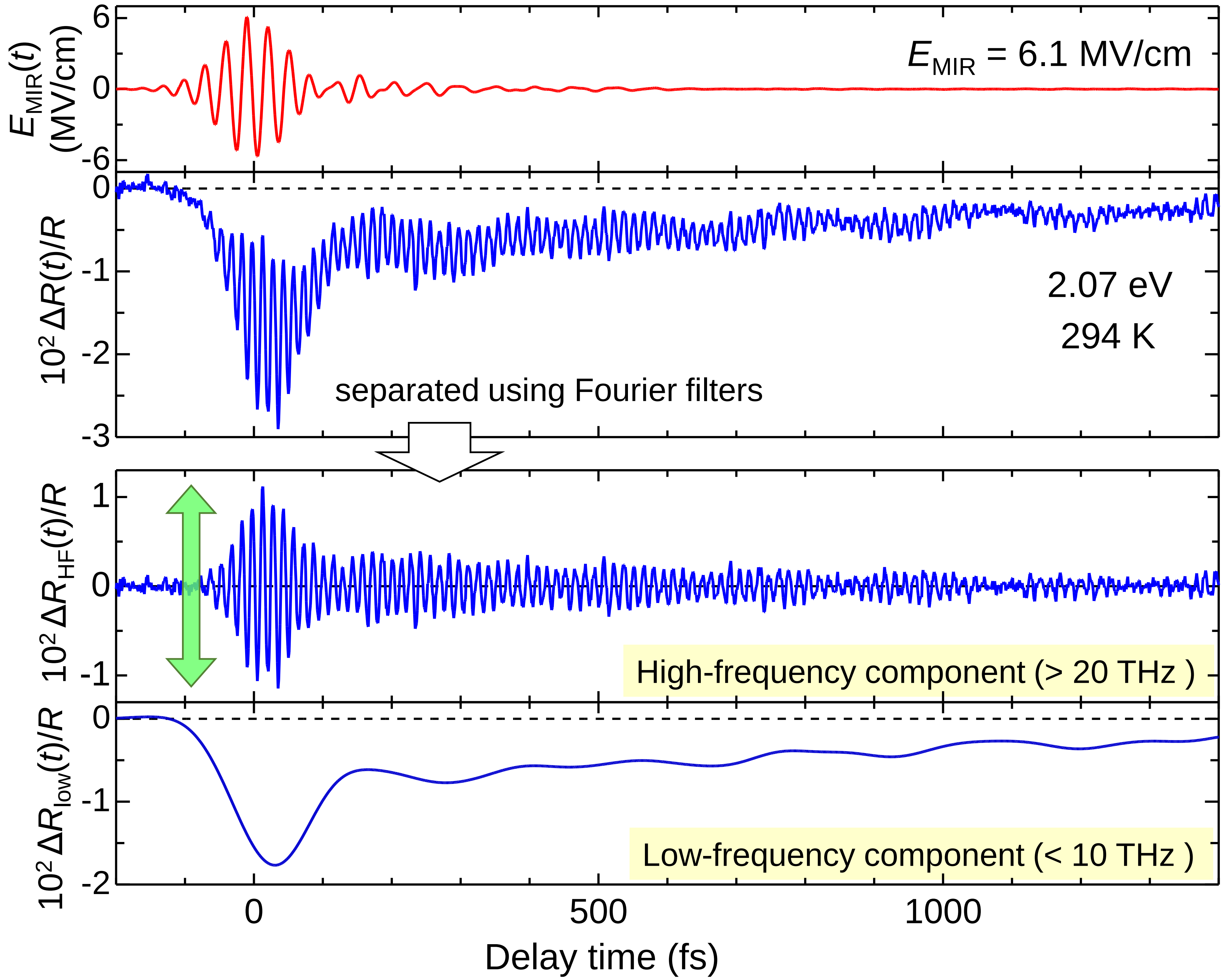


Electric-field waveform of the MIR pulse

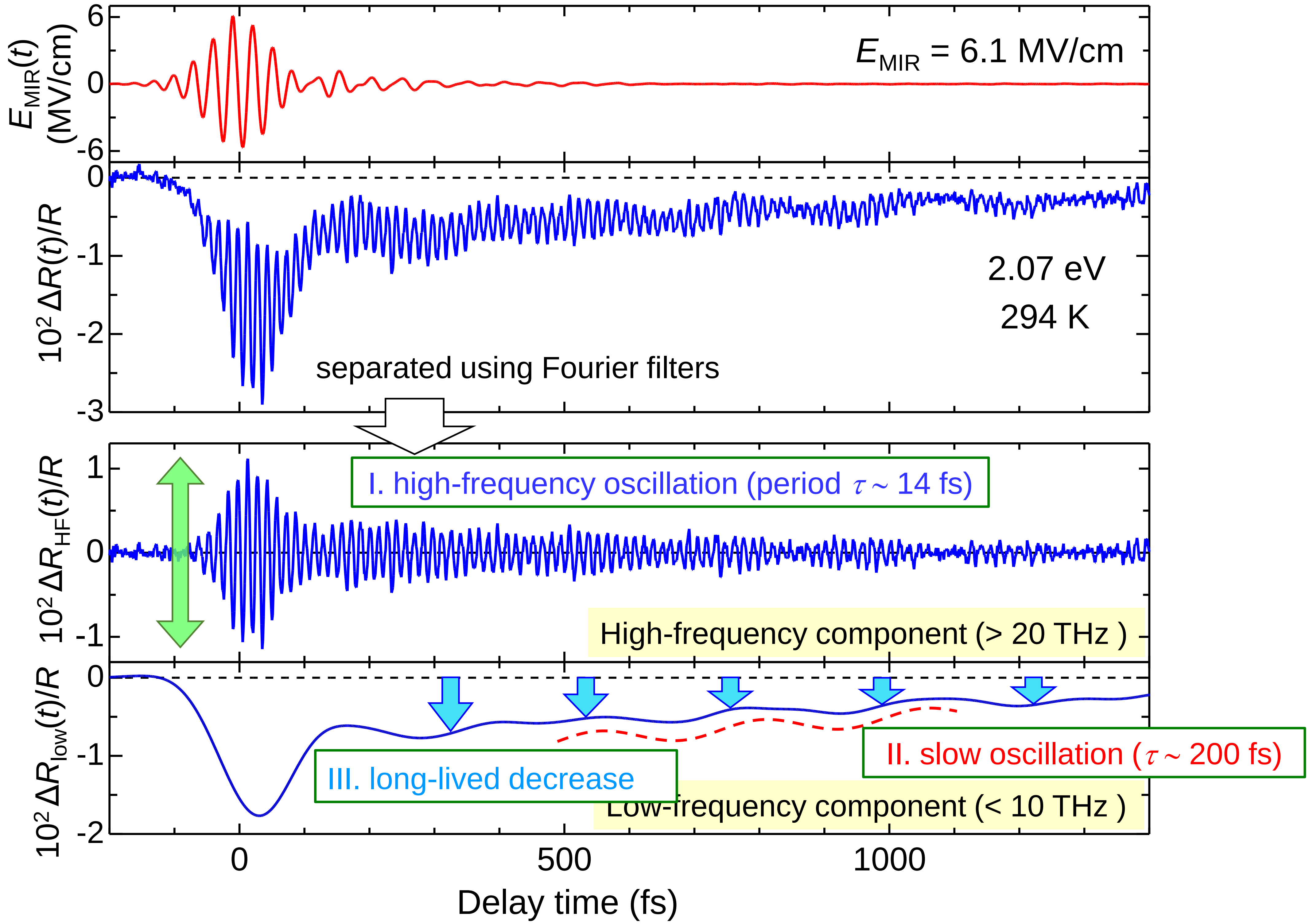


*T. Yamakawa, H.O. et al., AIP Advances **10**, 025311 (2020).*

Reflectivity change by the MIR excitation: subcycle spectroscopy



Reflectivity change by the MIR excitation: subcycle spectroscopy



separated using Fourier filters

I. high-frequency oscillation (period $\tau \sim$ 14 fs)

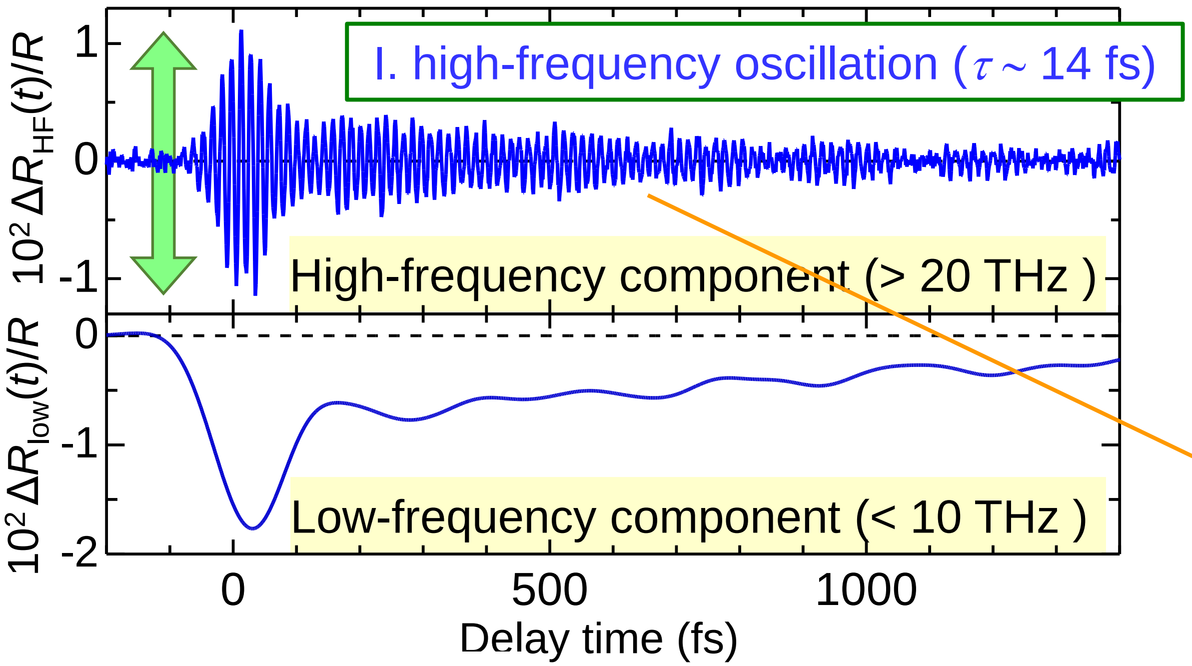
High-frequency component (> 20 THz)

II. slow oscillation ($\tau \sim$ 200 fs)

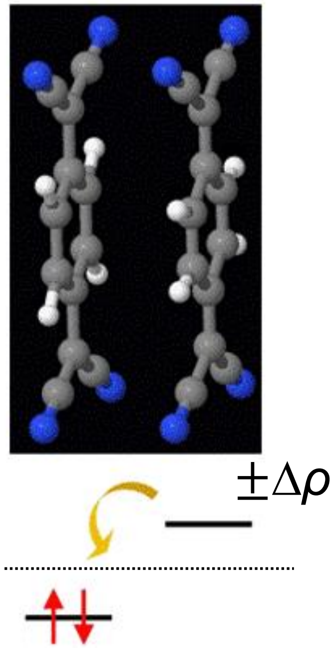
III. long-lived decrease

Low-frequency component (< 10 THz)

Fourier power spectrum of high-frequency (HF) oscillation

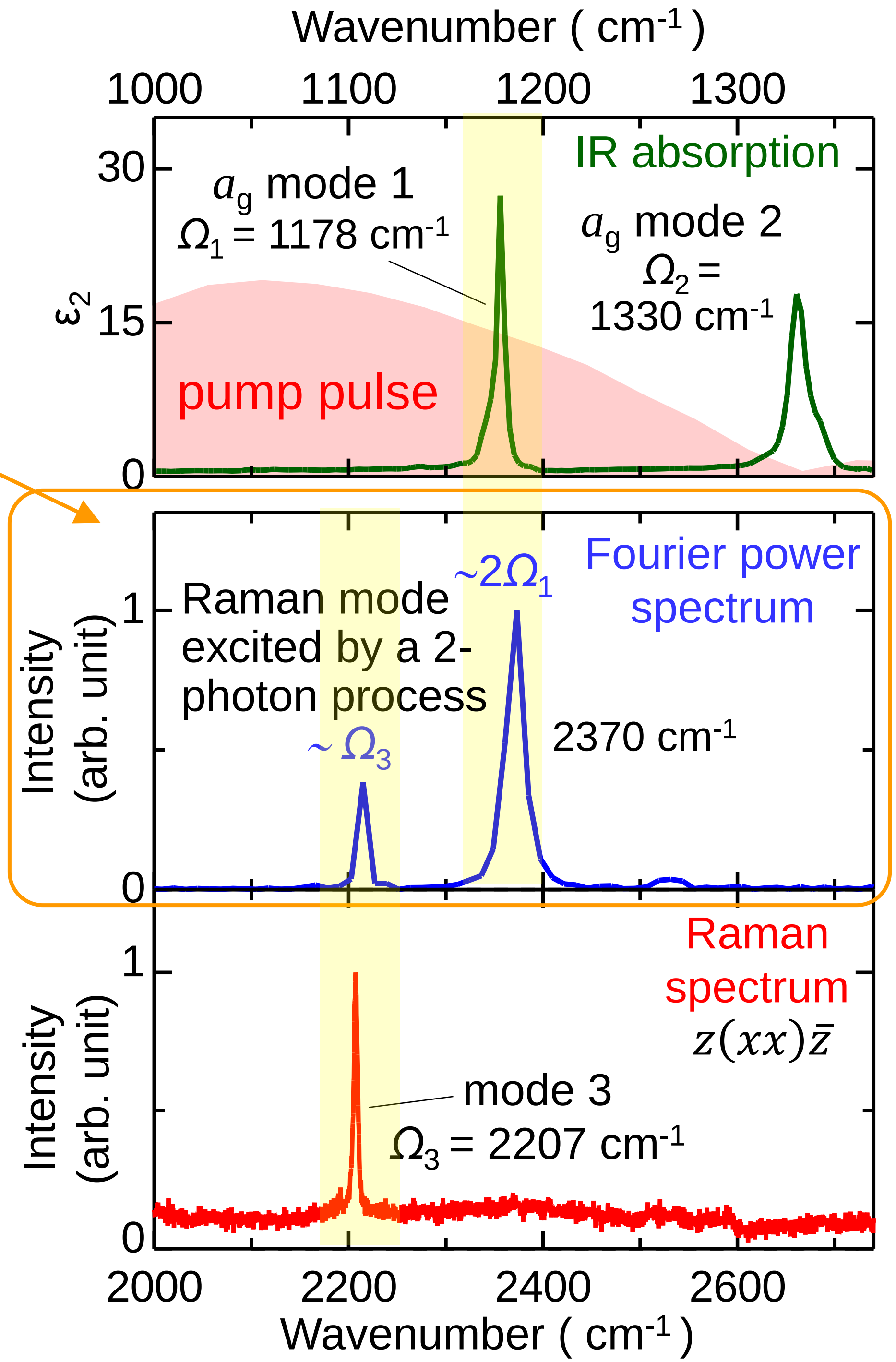


Out-of phase a_g-mode 1 vibration ($2\Omega_1$)



The states of electron transfer to the right and to the left are equivalent.

An oscillation of twice the frequency of a_g mode 1 ($2\Omega_1$) appears.

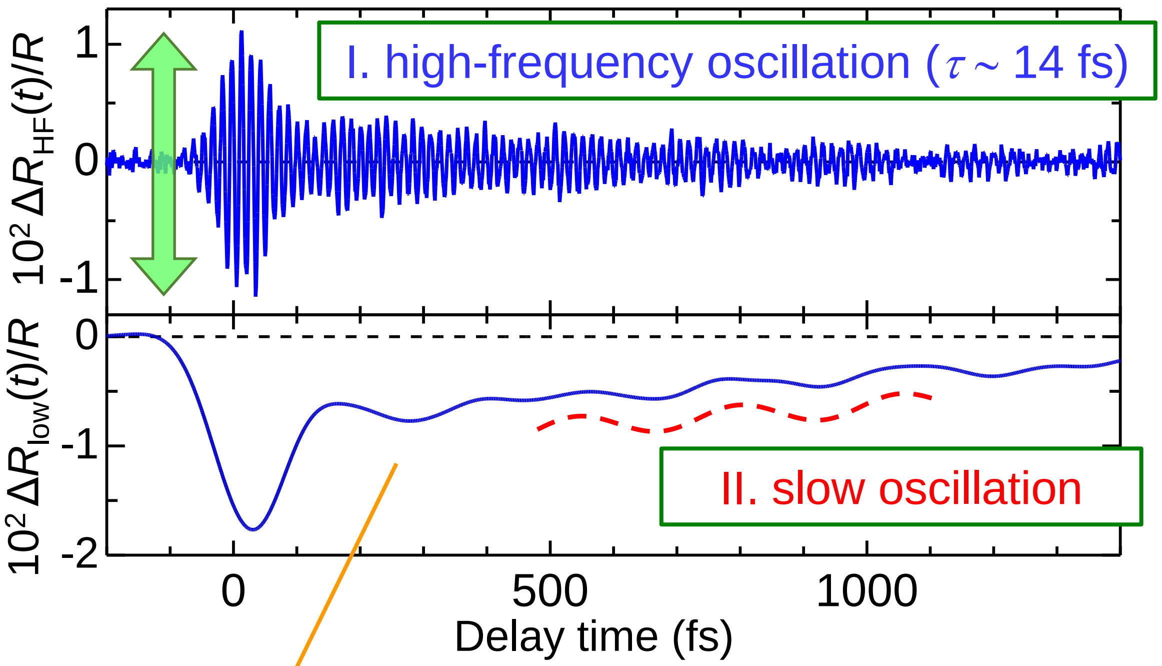


The $2\Omega_1$ oscillation can be considered to originate from phonon-dressed Floquet states.

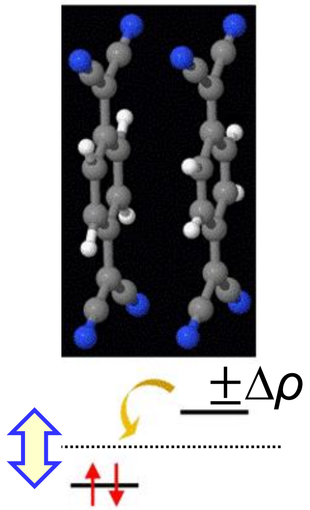
Low-frequency component reflecting the destabilization of the SP phase

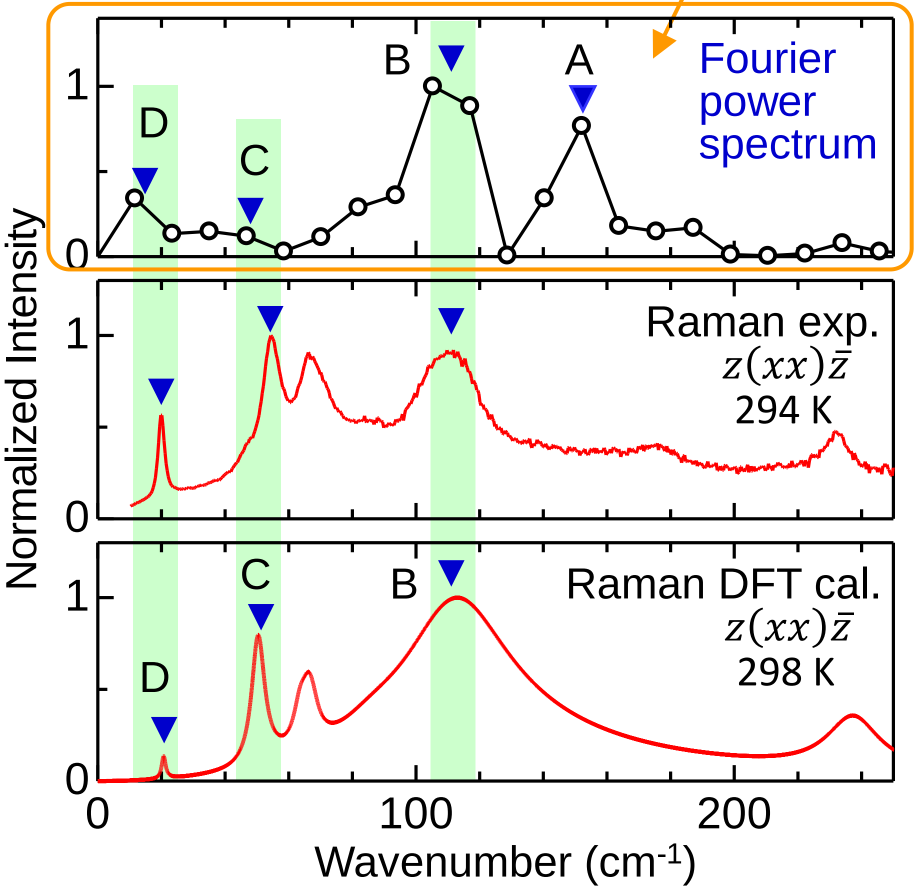
High-frequency component (> 20 THz)

Low-frequency component (< 10 THz)

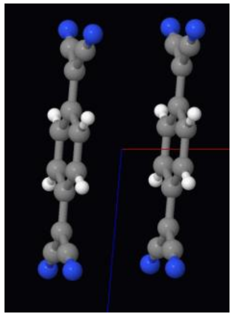


out-of phase a_g vibration charge and spin modulated Floquet state

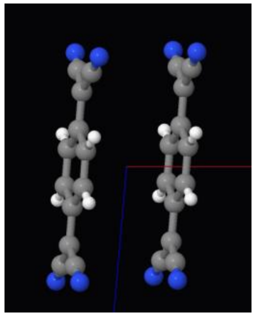




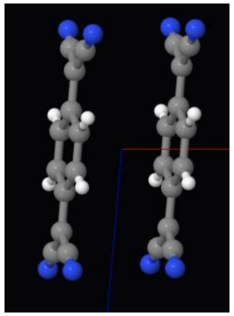
mode B: 113.5 cm^{-1}



mode C: 50.4 cm^{-1}



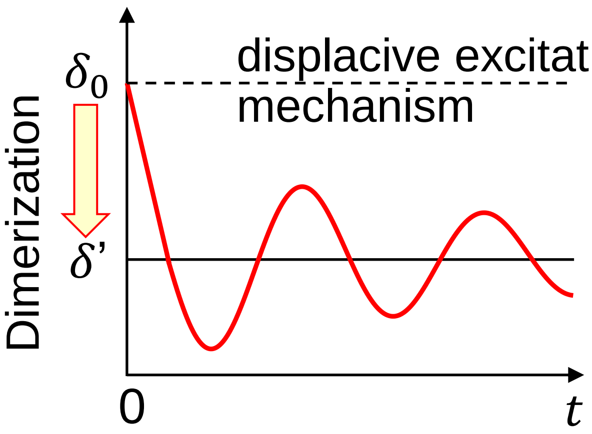
mode D: 20.7 cm^{-1}



DFT calculatin by Otaki

Destabilization of the spin-Peierls phase

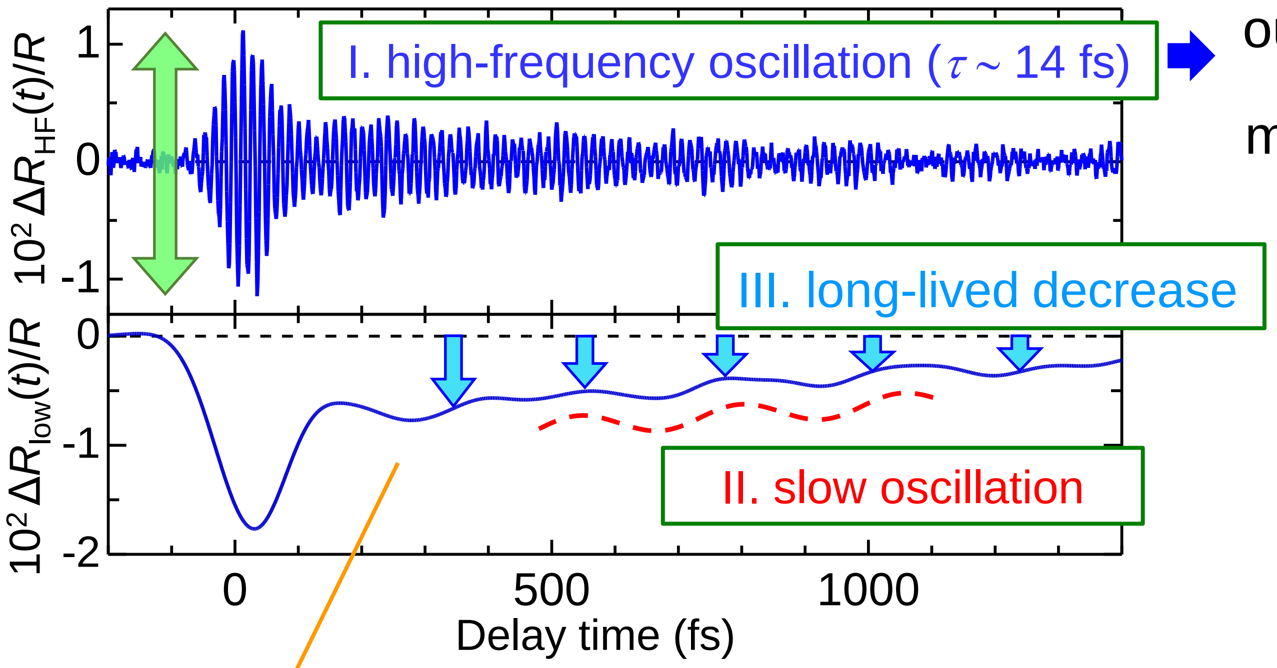
→ Oscillations B-D corresponding to the release of dimerization are generated via the displacive excitation mechanism.



Low-frequency component reflecting the destabilization of the SP phase

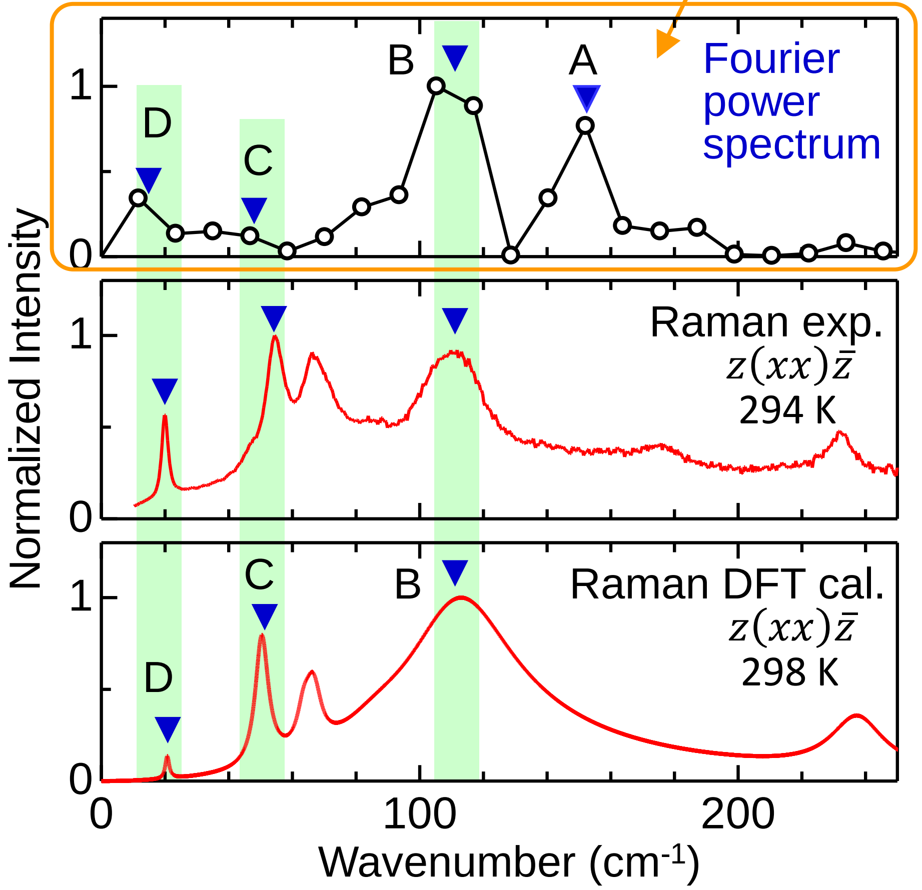
High-frequency component
(> 20 THz)

Low-frequency component
(< 10 THz)

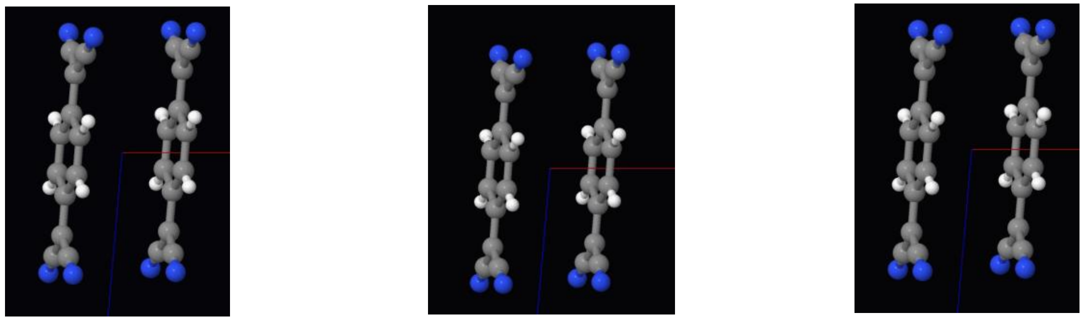


→ out-of phase a_g vibration
charge and spin
modulated Floquet state

→ Reduction in the averaged dimeric molecular displacements.

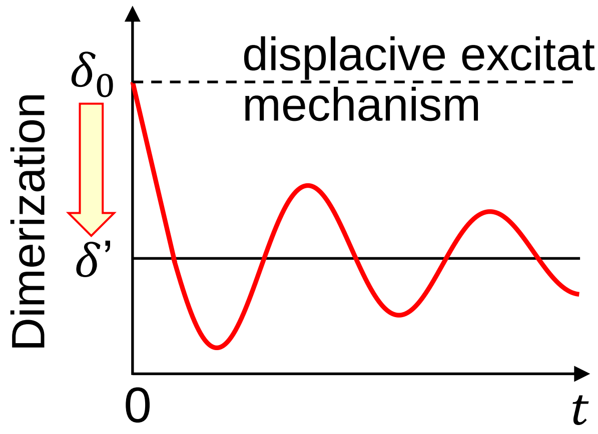


mode B: 113.5 cm^{-1} mode C: 50.4 cm^{-1} mode D: 20.7 cm^{-1}



DFT calculatin by Otaki

Destabilization of the spin-Peierls phase
→ Oscillations B-D corresponding to the release of dimerization are generated via the displacive excitation mechanism.



Summary 3 : Observations of Floquet states and Floquet engineering

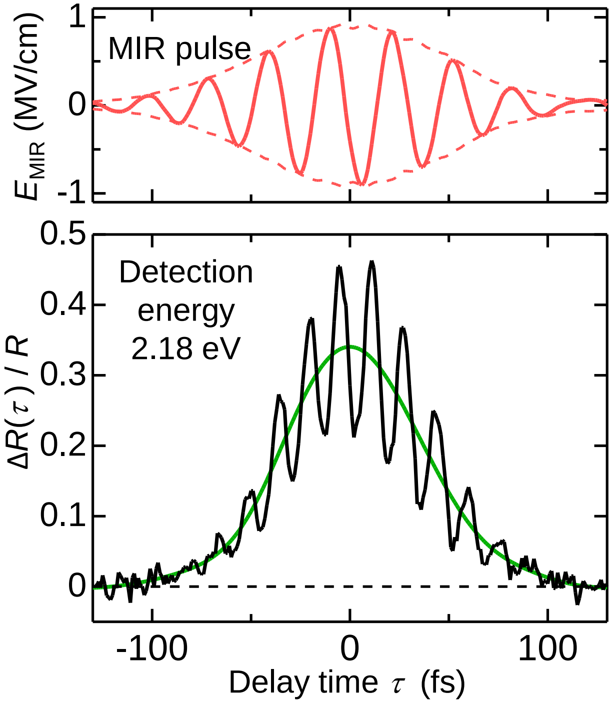
○ Photon-dressed Floquet state

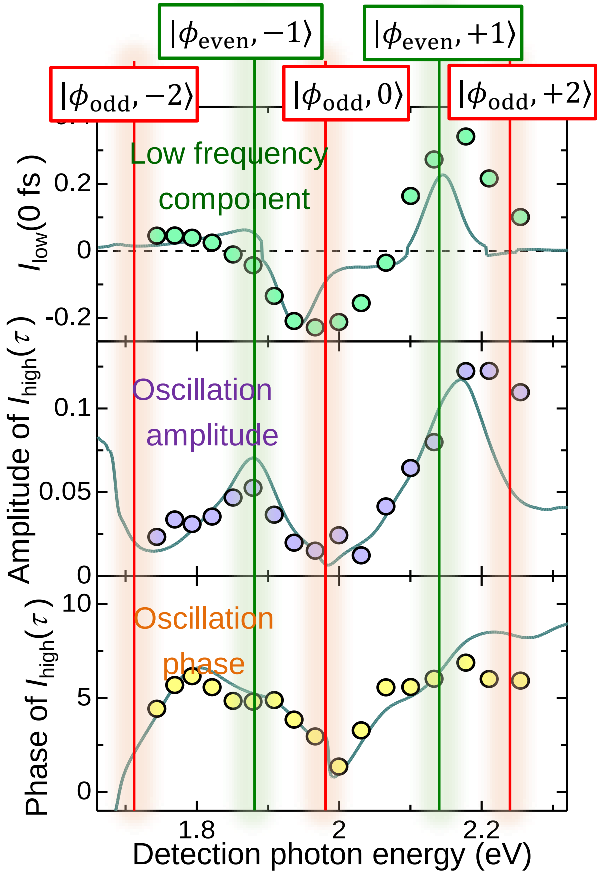
Application of an MIR electric-field with a frequency Ω on a Ni-Cl chain compound

→ Large reflectivity changes accompanied with a high-frequency oscillation with 2Ω

Analyses based upon third-order optical nonlinearity

→ Photon-dressed Floquet states





T. Yamakawa et al., New J. Phys. ***25****, 093044 (2023)*

○ Phonon-dressed Floquet state

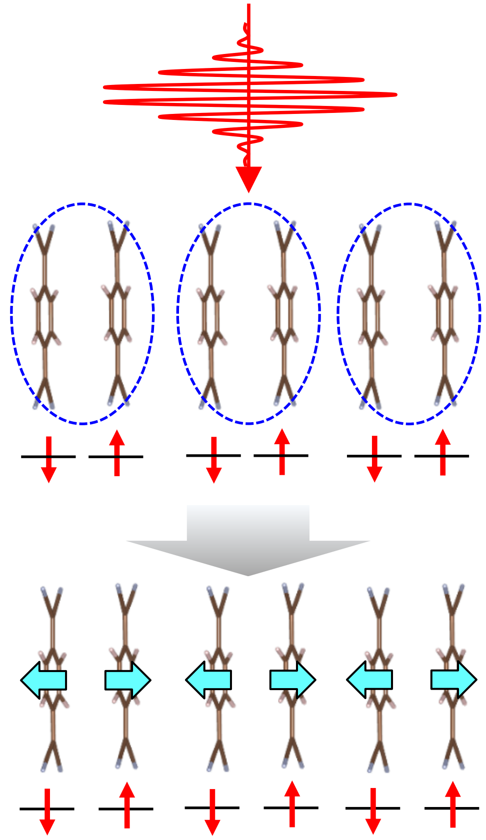
Charge and spin density modulations by an out-of phase a_g mode in the SP phase of K-TCNQ

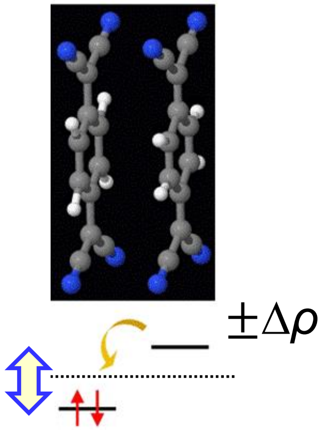
→ Hybridization of AFM ground state and non-magnetic states

→ Phonon-dressed Floquet states

→ Destabilization of spin-Peierls phase

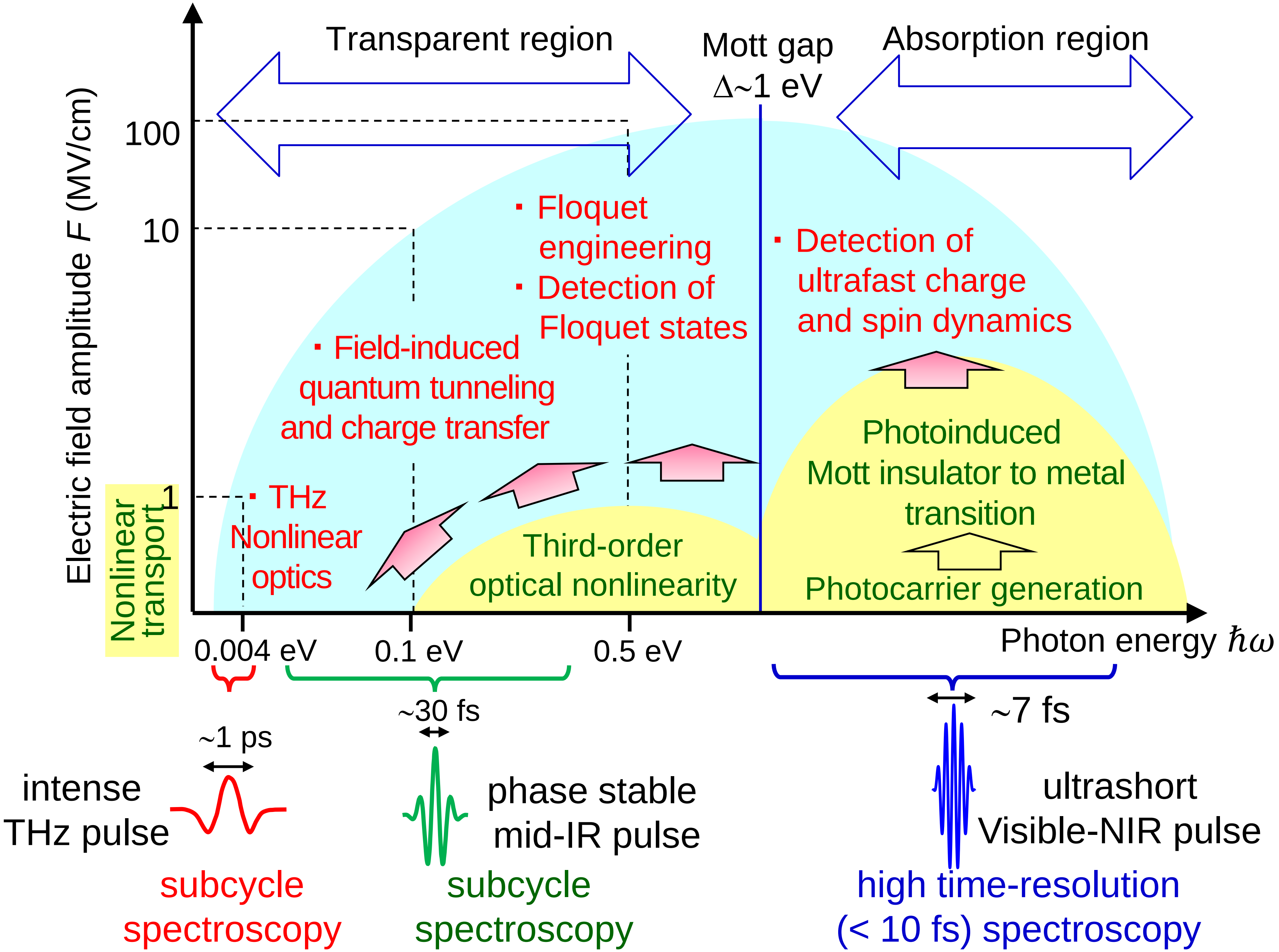
Floquet engineering





D. Sakai et al., Commun. Phys. ***7****, 40 (2024)*

Responses of half-filled Mott insulators to lights and electric fields



The experimental techniques and approaches presented here may be applied to various types of correlated electron materials to derive novel optical responses.

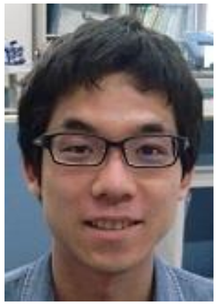
Collaborators

- Femtosecond transient spectroscopy and analyses


T. Miyamoto


H. Yamakawa


N. Sono


N. Takamura


T. Yamakawa


D. Sakai


M. Yamamoto


R. Ikeda

T. Otaki, T. Morimoto, S. Liang, and N. Kida (UT)

- Sample preparations

H.M. Yamamoto, T. Nakamura (IMS) and M. Suda (Kyoto univ.)
K. Miyagawa, K. Kanoda, T. Hasegawa, and H. Mori (UT)
S. Horiuchi, A. Sawa, T. Ito, and Y. Tomioka (AIST)
M. Sasagawa (Tokyo Tech.), K. Yamamoto (Okayama Unic. Sci.)

- Theoretical studies

S. Ishihara (Tohoku Univ.)
K. Iwano (KEK), A. Takahashi, and S. Ohmura (Nagoya Inst. Tech.)
T. Tohyama and K. Shinjo (Tokyo Univ. Sci)