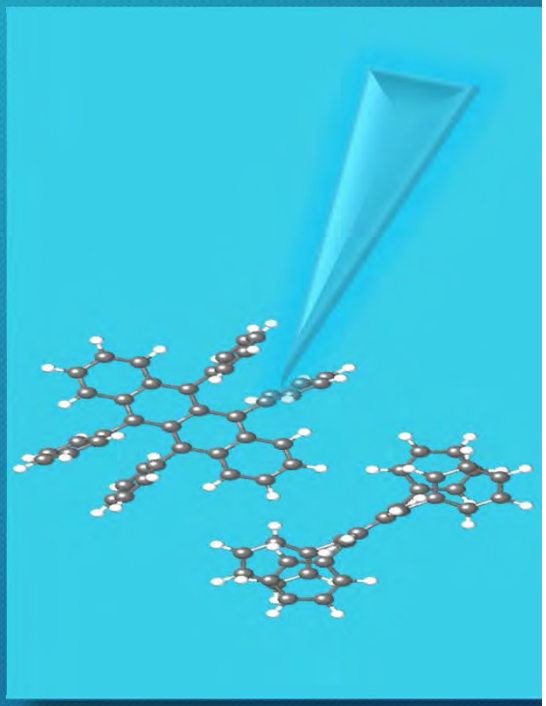
21/SEP 2017 @Tomsk, Russia
Nano and Giga Challenges in Electronics, Photonics and Renewable Energy 2017

# Tracking Charge Transport of Organic Semiconductor Material by Electronic Structure Measurement



大学共同利用機関法人 自然科学研究機構
分子科学研究所
National University
The Graduate University for Advanced Studies [SOKENDAI]
CHIBA UNIVERSITY

Satoshi Kera
Institute for Molecular Science

解良　聡

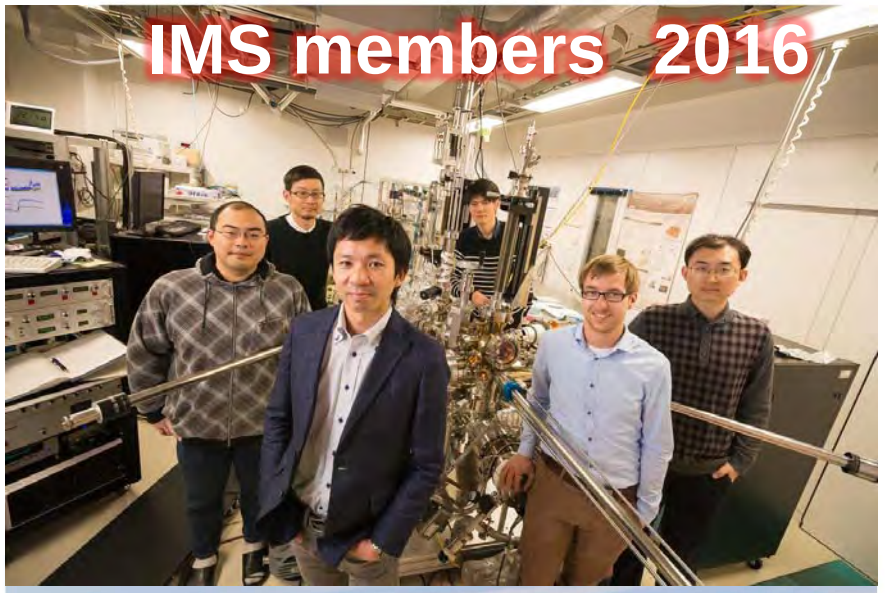
# Collaborators

**Chiba Univ**
Prof. N. Ueno

Institute of Materials Research and Engineering
A*STAR

- **Dr. F. Bussolotti** (-> IMRE), low-E ARUPS
Dr. J. Yang (-> China) , low-E ARUPS
Mr. T. Yamaguchi (-> IMS), low-E ARUPS, gasUPS
Dr. K. Yonezawa (-> IMS), gas UPS
Prof. S. Duhm（-> China） ARUPS, high-reso UPS
Dr. Q. Xin (-> China), ARUPS, high-reso UPS
Mr. S. Hosoumi, Gas UPS, high-reso UPS, calculation
Mr. K. Sato, high-reso UPS, calculation
Prof. H. Ishii, crystal
Dr. Y. Nakayama (-> Tokyo Univ Sci), crystal, ARUPS
Dr. S. Nagamatsu (Univ Elec-Comm), theory

**IMS (BL7U)**
Prof. K. Kimura (-> Osaka Univ) , beamline
Prof. K. Tanaka, beamline
Dr. M. Matsunami (-> Toyota Inst Univ) , beamline





**FUND**
JSPS, MEXT KAKENHI

THANKS

# OUTLINE

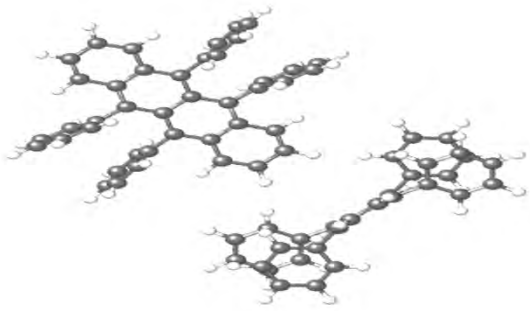
Motivation

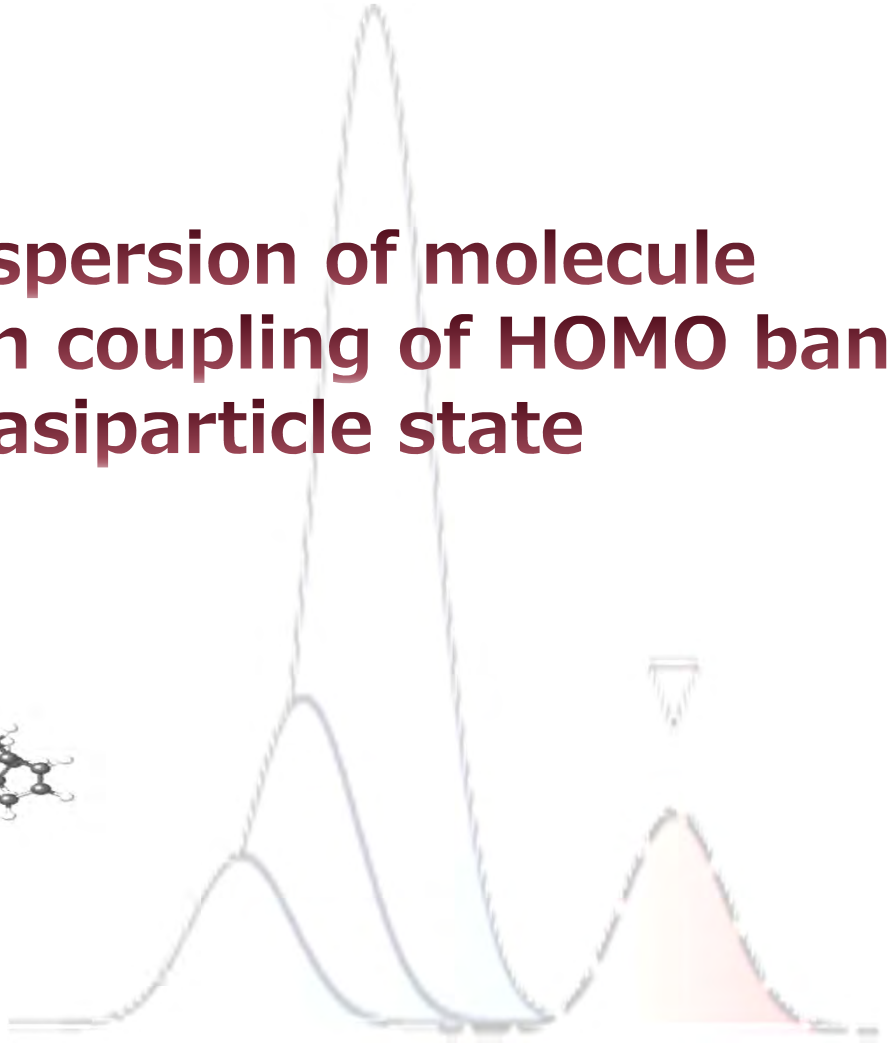
1. Key character of molecular solid

UPS band shape

2. Energy-band dispersion of molecule
3. Electron-phonon coupling of HOMO band
4. Character of quasiparticle state

Summary

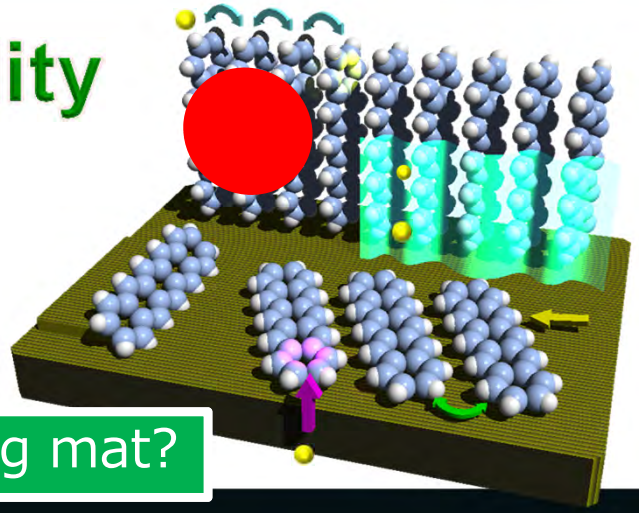




# Carbon based industrial

## Rich Functionality

Semiconductor (LED, FET, PVC,..)
Org.Condcut, Magnet, SuperCond.
Mol.Recognition (Mol. Machine)
Self-assemble, Self-healing
Bio-mimic, etc



**Characteristics of molecule**

Rich degree of freedom
(Structure, crystal, orbital)
Intermolecular interaction (vdW)
Charge localization (wavefunciton)
Molecular spin (Coordination)

## Electronic structure

Different concept to inorg mat?

*motivation*

What is key differences bw organic semicon. and inorganic counterpart ?

# Organic Semicon. Physics

Mechanism of energy-level alignment, charge transport

*Surface & Interface*

New concept in the device fabrication
Freedom in combination
Easy to handle

**Molecular synthesize**

**Quantum cage design**

Message to device application
Guideline of design to property

**Assemble Design**

**Rich utilization**

# Carbon based industrial

ERA

**How much does the wave-function spread change in the assembly?**

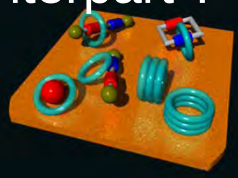
## = Molecular film functions are controlled by a weak interaction

*motivation*

What is key differences bw organic semicon. and inorganic counterpart ?

## Organic Semicon. Physics

Mechanism of energy-level alignment, charge transport



*Surface & Interface*

New concept in the device fabrication
Freedom in combination
Easy to handle

Molecular synthesize

**Quantum cage design**

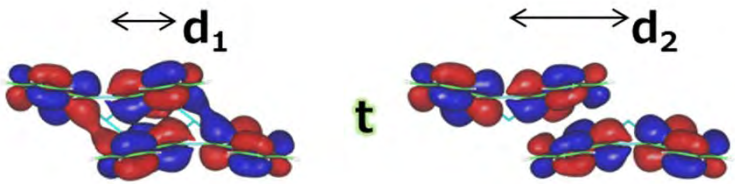
Message to device application
Guideline of design to property

Assemble Design

**Rich utilization**

# "Molecules are vibrating"

**Molecular solid by vdW force: ~~Physics based on isolated states, nor condensed matter~~**

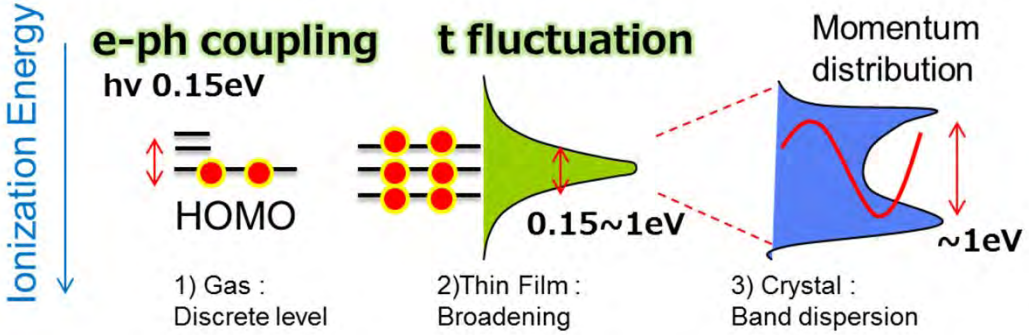



*Orbital phase matching (DOS, Band)*

Wavefunction is not smoothly overlapping in the solid

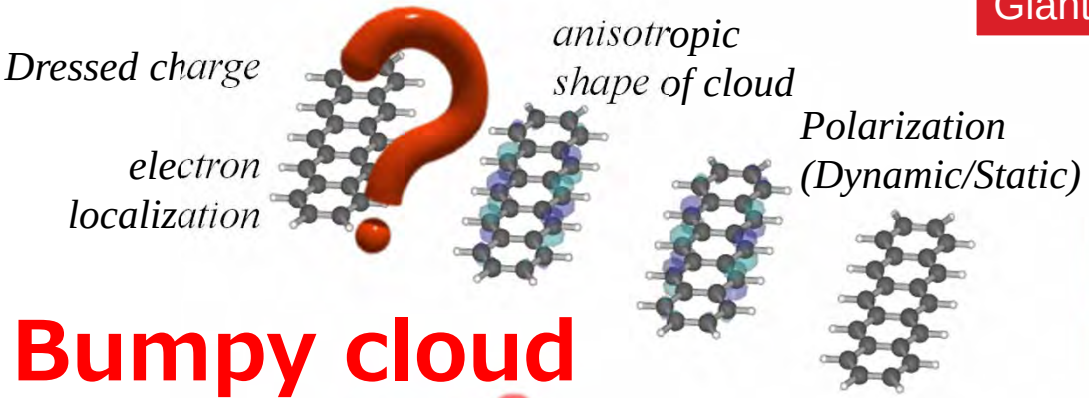
Amorphous (disorder) ~ hopping transport

Crystal (order) ~ band transport




Giant Seebeck effects in organics

C60, 150mV/K(300K), Kojima et al, APEX (2015)




**Bumpy cloud**

$\Psi^2$

*Soft/frexible structure*

**Itinerancy**

**Light element, but heavy cage unit**

**Assemble ≠ Isolated**

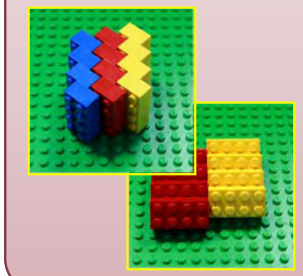
## Electron is…

localized in a molecule (LCAO)

delocalized MO

Slightly

& extended and/or distorted



by **weak e-e coupling**

with neighbors

with substrate

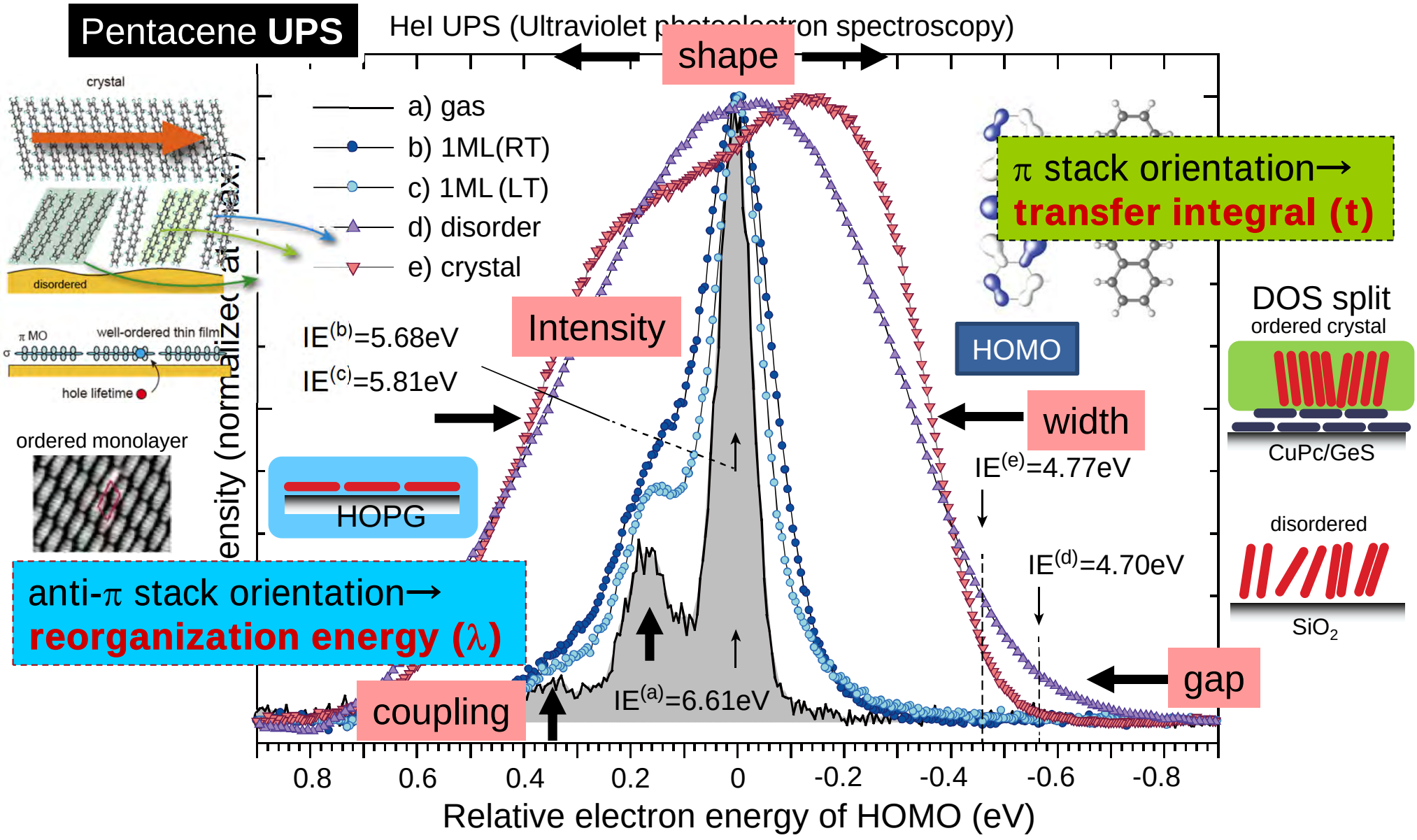
by **strong e-ph coupling**

with lattice phonon

with molecular vibration

# Origin of UPS band shape?

Electronic structure depends largely on molecular orientation even in **vdW solids**.
Universal picture is requested for a conventional/trivial material to understand,…



KEY natures

(1) Weak intermolecular interaction → 2-face character: isolated vs aggregate

(2) Low dimensional → “bumpy” state by molecular orbital

(3) Very large & heavy complex with light elements → polaron phenomena

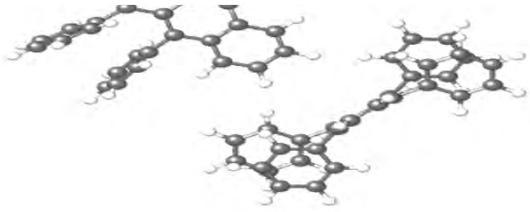
**Intrinsic behavior of organic materials, but not of inorganic**

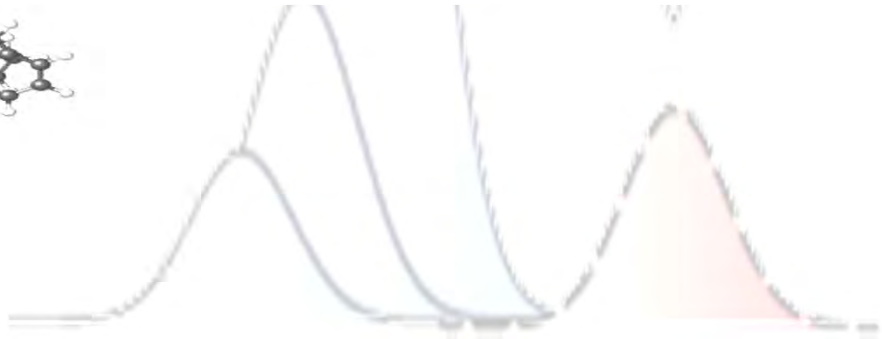
Tnag, Bussolotti, SK, Ueno, **J. Phys. D: Appl. Physics (2017)**

## UPS band shape

2. Energy-band dispersion of molecule
3. Electron-phonon coupling of HOMO band
4. Character of quasiparticle state

# See an electron in molecular solid !





# Tracking Charge Transport

λ & t are measurable parameter by UPS

挑戦


**How does an electron look like?**

**Transport charge in molecular film**

**λ** Easier to access for gas, well-ordered monolayers (anti-π stacking: small t )

**t** From ordered crystalline films and bulk single crystals (well-π stacking)

λ: reorganization energy

t: transfer integral

# Theory: two boundaries

UPS fine features will be appeared upon charge-boson coupling

N.Ueno, S.Kera, Prog. Surf. Sci. **83**, 490 (2008).

A. Troisi, Chem. Soc. Rev. 40, 2347(2011)

F. Ortmann *et al*, Adv. Funct. Mater. 1 (2014)

S. Kera *et al*., Prog. Surf. Sci. **84**, 135 (2009).

$\lambda < t$

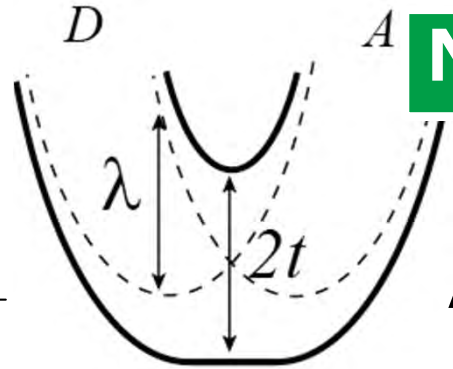
$\lambda \sim t$

$\lambda > t$

**BAND transport**

**HOPPING transport**

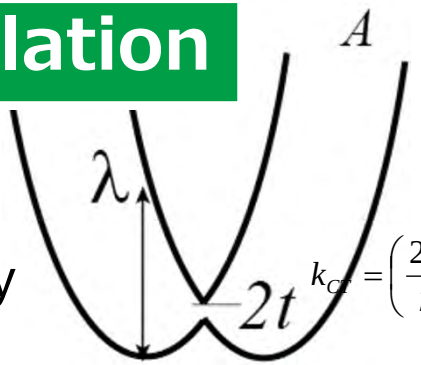
## Numerical simulation




$$\mu = \frac{e\tau}{m^*}$$

t: transfer integral

λ: reorganization energy




$$\mu = \frac{ea^2}{k_B T} k_{CT}$$

$$k_{CT} = \left(\frac{2\pi}{\hbar}\right) t^2 \frac{1}{\sqrt{4\pi\lambda_{reorg} k_B T}} \exp\left(\frac{-\lambda_{reorg}}{4k_B T}\right)$$

Delocalized into adjacent molecules

Charge is localized in a molecule

# Theory: two boundaries

UPS fine features will be appeared upon charge-boson coupling

N.Ueno, S.Kera, Prog. Surf. Sci. **83**, 490 (2008).

S. Kera *et al*., Prog. Surf. Sci. **84**, 135 (2009).

A. Troisi, Chem. Soc. Rev. 40, 2347(2011)

F. Ortmann *et al*, Adv. Funct. Mater. 1 (2014)

$\lambda < t$

$\lambda \sim t$

$\lambda > t$

+

**BAND transport**

**HOPPING transport**


**Numerical simulation**

$t$: transfer integral

$$\mu = \frac{ea^2}{k_B T} k_{CT}$$

**“Not hopping nor band transport”**

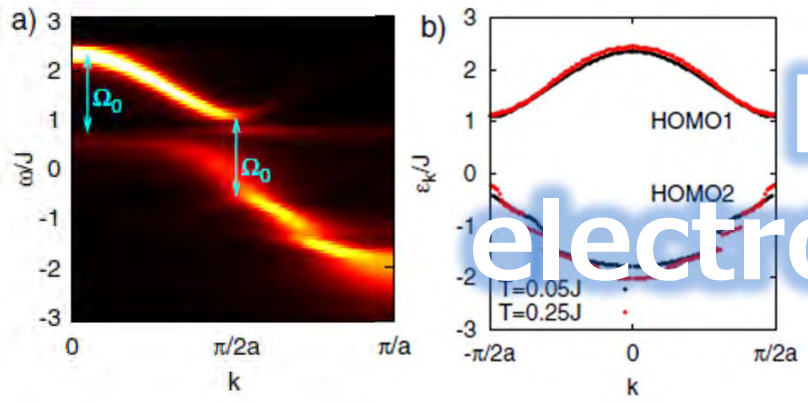
# Extend : electron-phonon coupling

Motion of charges is not simple: a dressed quasiparticles

## Electron couples to phonons affects to localizability

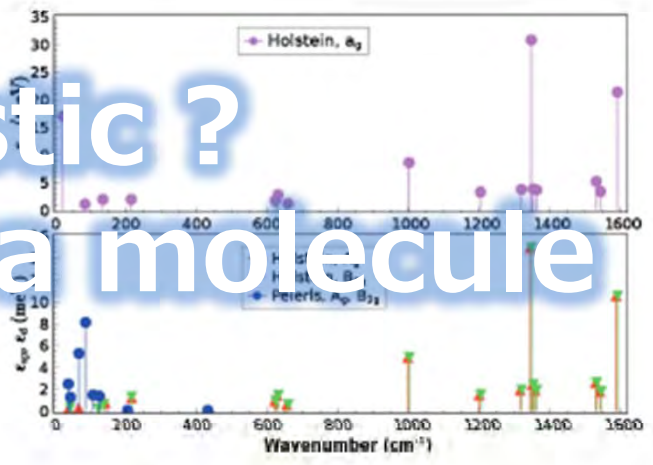
**Transient Localiztion Scenario**
Fratini et al, Adv. Funct. Mater. 26, 2292(2016)

Band dispersion : spectral function ???




Ciuchi et al, PRL106,166403(2011) "pentacene Theory"

Complicate vibronic coupling



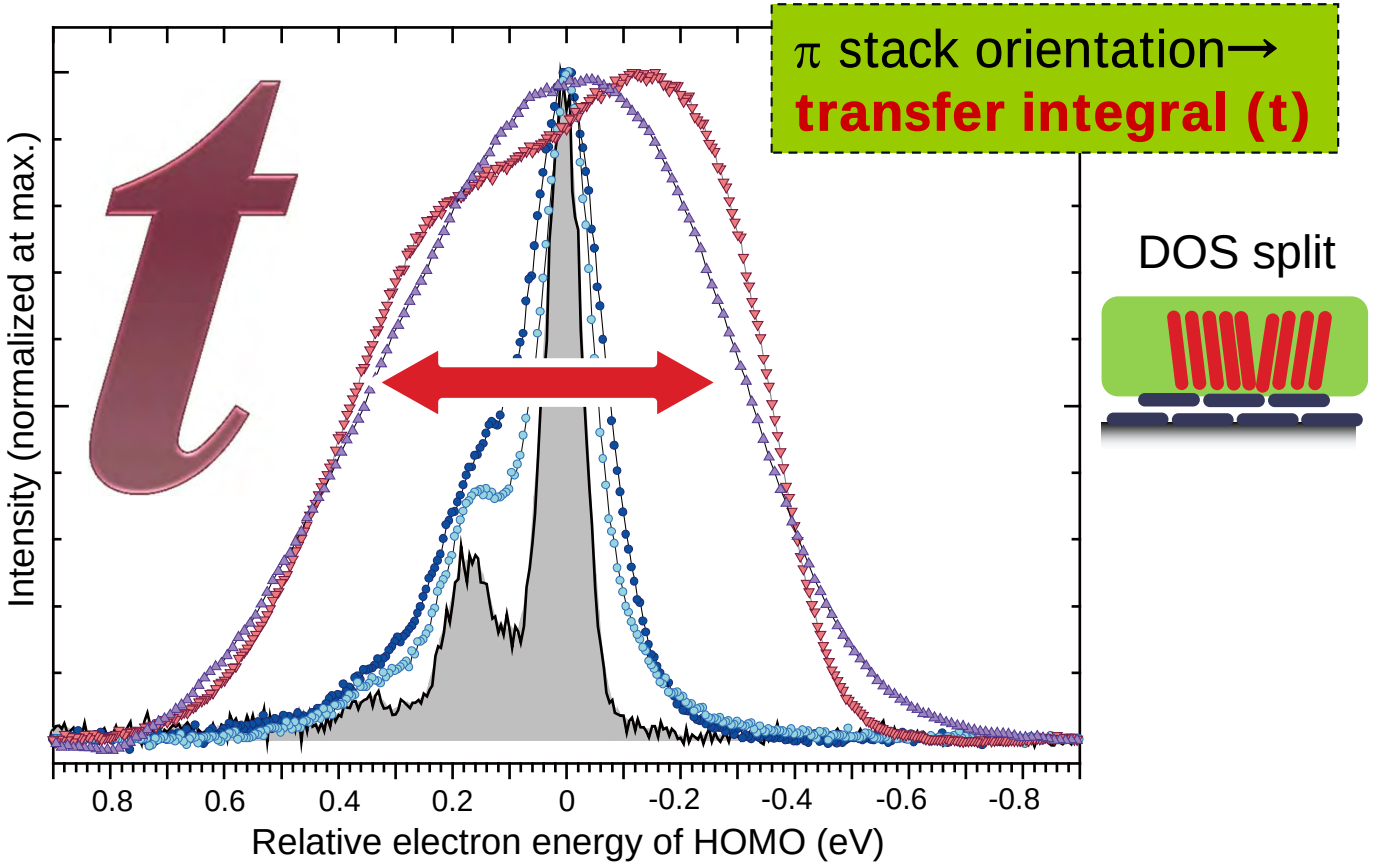

Girlando et al, PRB 82, 35208 (2010) "rubrene Theory"

**Realistic ? electron in a molecule**

# Innovation

## Angle-resolved PES: band dispersion

### UPS band width



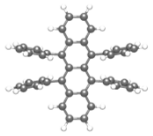

*Can we measure dispersion? How to prepare ?*

# HOMO-band dispersion of Rubrene Crystal

## Band Mapping: E(k)

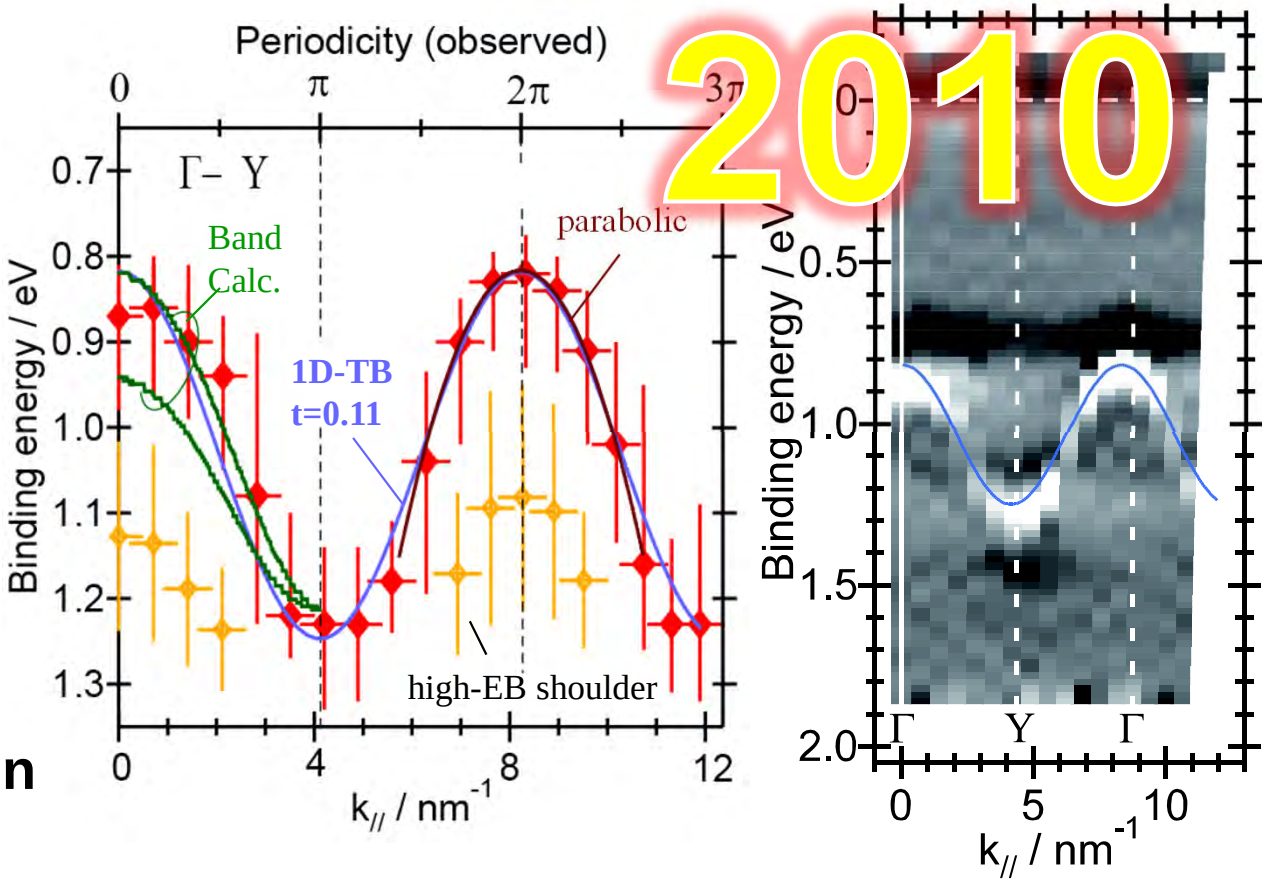
t = 0.11eV **mfp > 2.1nm**

$m^*_h$=0.65 $m_0$



$\mu_h$> ~31cm²/Vs @ 295K

$$\mu_{band} = \frac{e\tau}{m^*} > \frac{e\hbar}{m^* W} \sim 20\frac{m_0}{m^*}\frac{300}{T}$$




### 1D tight-binding approximation

$E_B = E_c - 2t\cos(bk_\parallel)$ $\quad b = 0.76$ nm

transfer integral $t$ = 0.11 eV

$$m_h^* = \frac{\hbar^2}{d^2E_B/dk_\parallel^2} = \frac{\hbar^2}{2tb^2} = 0.65 \pm 0.05\, m_0$$

**Evidence of band transport**
**Highest mobility**

PEN/Bi/Si (4t=0.2~0.3 , m*=1.3$m_0$)
BTQBT/HOPG (4t=0.4 , m*=3.1$m_0$)
PTCDA/$MoS_2$ (4t=0.2, m*=5.2$m_0$)

Ueno, Kera, Prog.Surf.Sci.83 (2008) 490

***t* is rather estimated as usual small BZ (large lattice) gives smallest m* among organic solids**

# Institute for Molecular Science

大学共同利用機関法人 自然科学研究機構
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Since 1983
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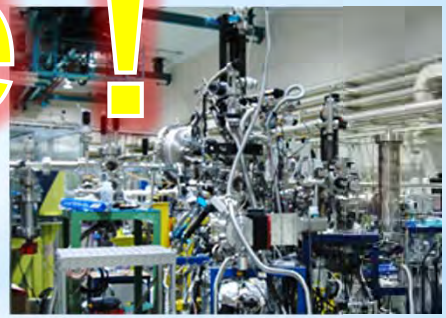
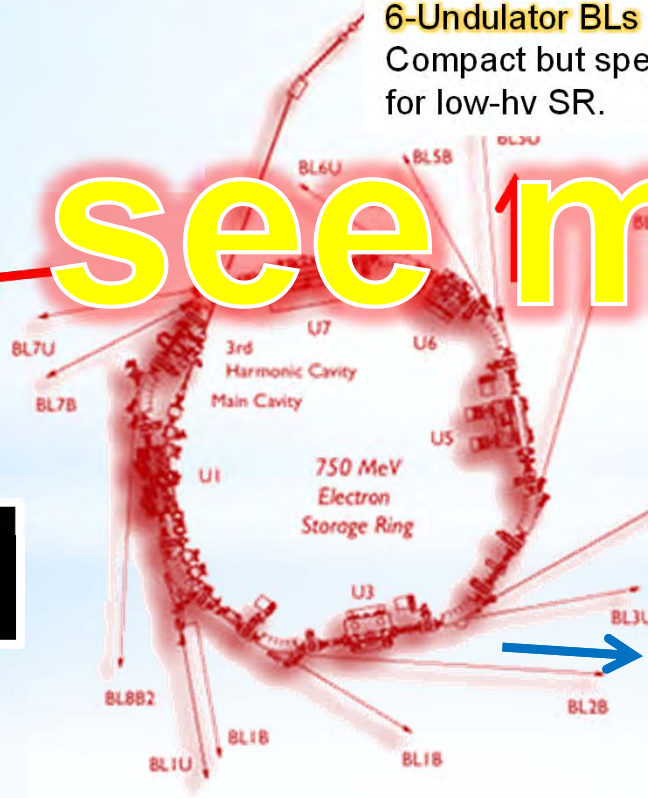
for low-hv SR.

**BL6U**
ARUPS, NEXAFS, XPS

**BL5U** (commissioning)
Spin/Deflector ARUPS

To see more !






**BL7U**
High-reso ARUPS

hv=6~40eV (undulator)
MBS-A1, 6-axis, 14-400K
▶ ARUPS, LEED

**BL2B**
ARUPS for organic solids

hv=24~205eV
VG-SCIENTA-R3000, 5-axis, 12-400K
▶ARUPS, XPS, MAES(He*), LEED

# Experiments: UVSOR (BL7U)

**Low kinetic energy is requested to see the events**

**APPLE II undulator**

Variable polarization, hv=6-40eV

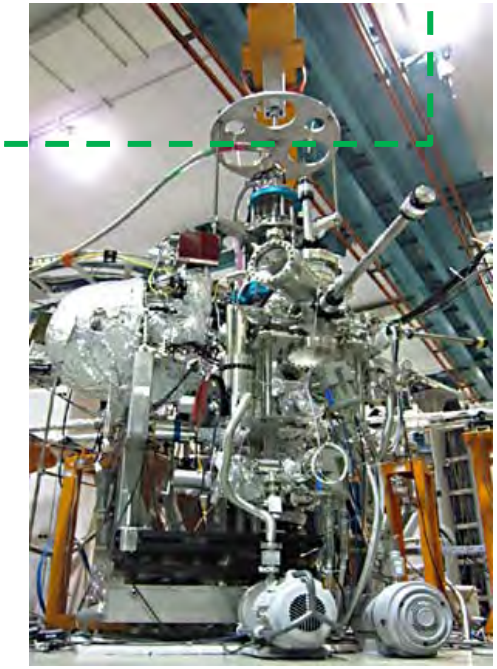
Modified Wadsworth monochlomater

E/ΔE > 10,000, spots ~50 x200 μm

**Analyzer: MBS-A1**

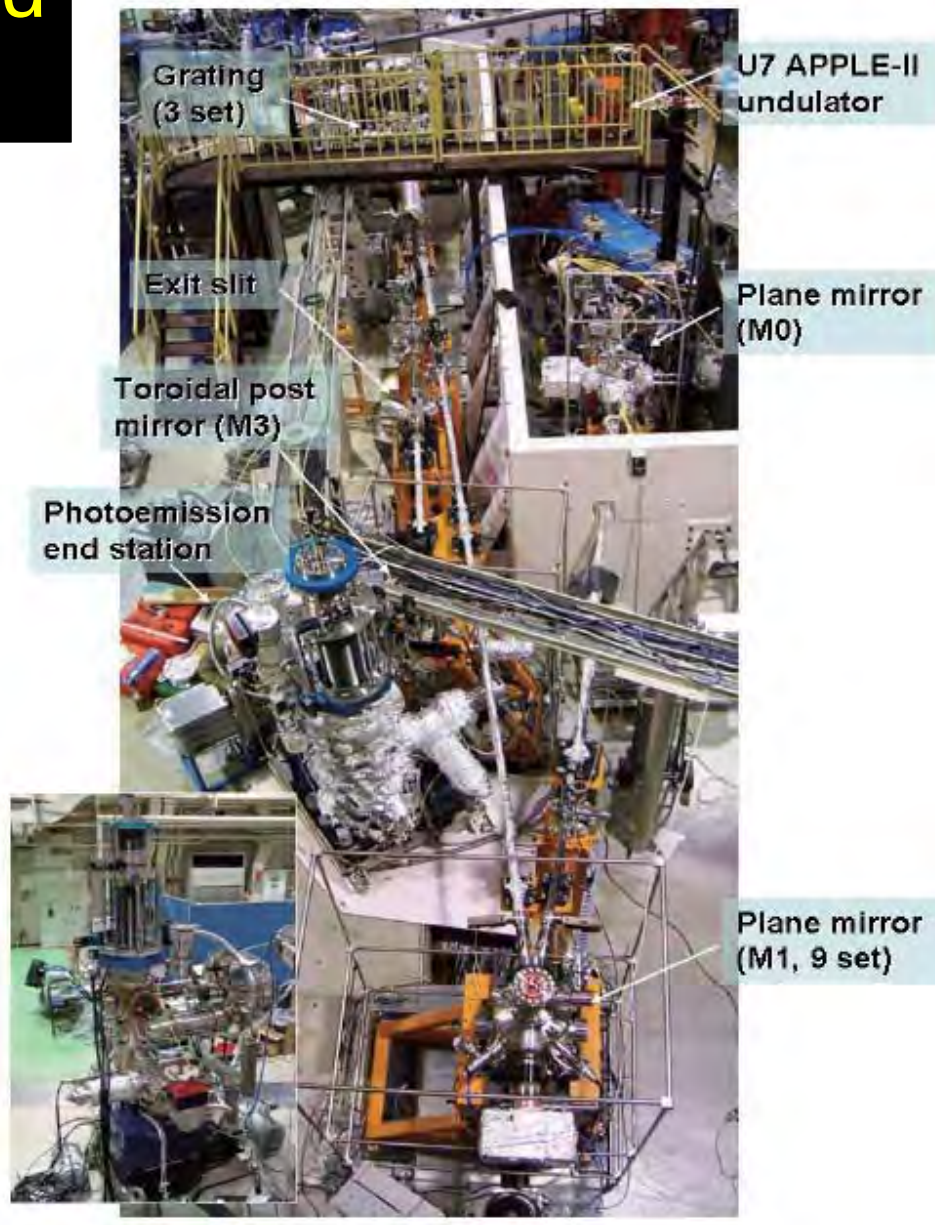
ΔR < 1meV, 6-axis

14K ~ 400K



Prof. S. Kimura

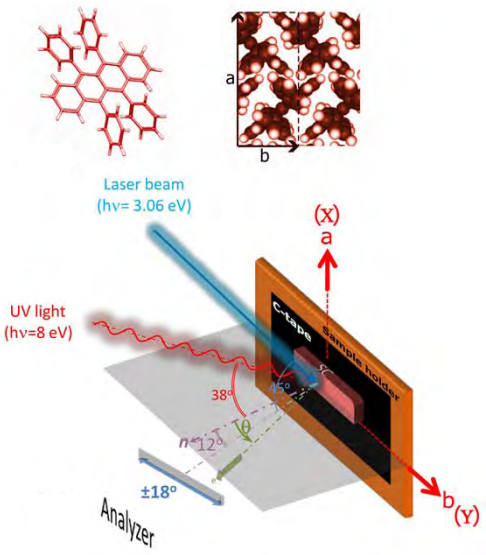
**"SAMRAI" system**



# Experiments: UVSOR (BL7U)

1) High-energy resolution
2) Small irradiation spot

**+ Low-energy excitation UPS**




advantages

1) Bulk sensitive measurement
2) Higher photoelectron intensity
3) Low irradiation damage
4) High momentum resolution

**HOMO fine feature**

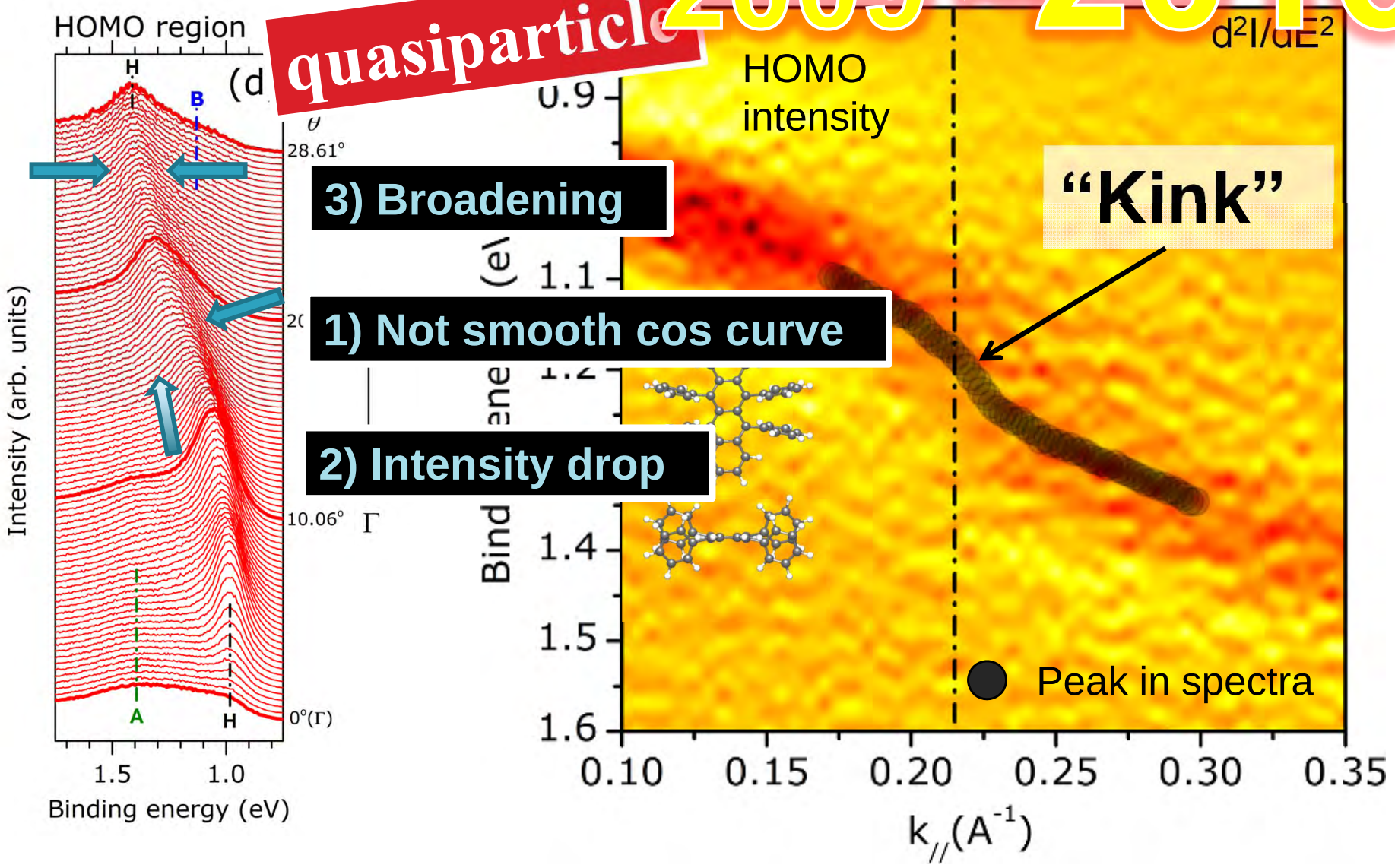
# Low-energy excitation UPS

Rubrene SC, ARUPS (UVSOR/ BL7U, **hν=8 eV**, **297K**)

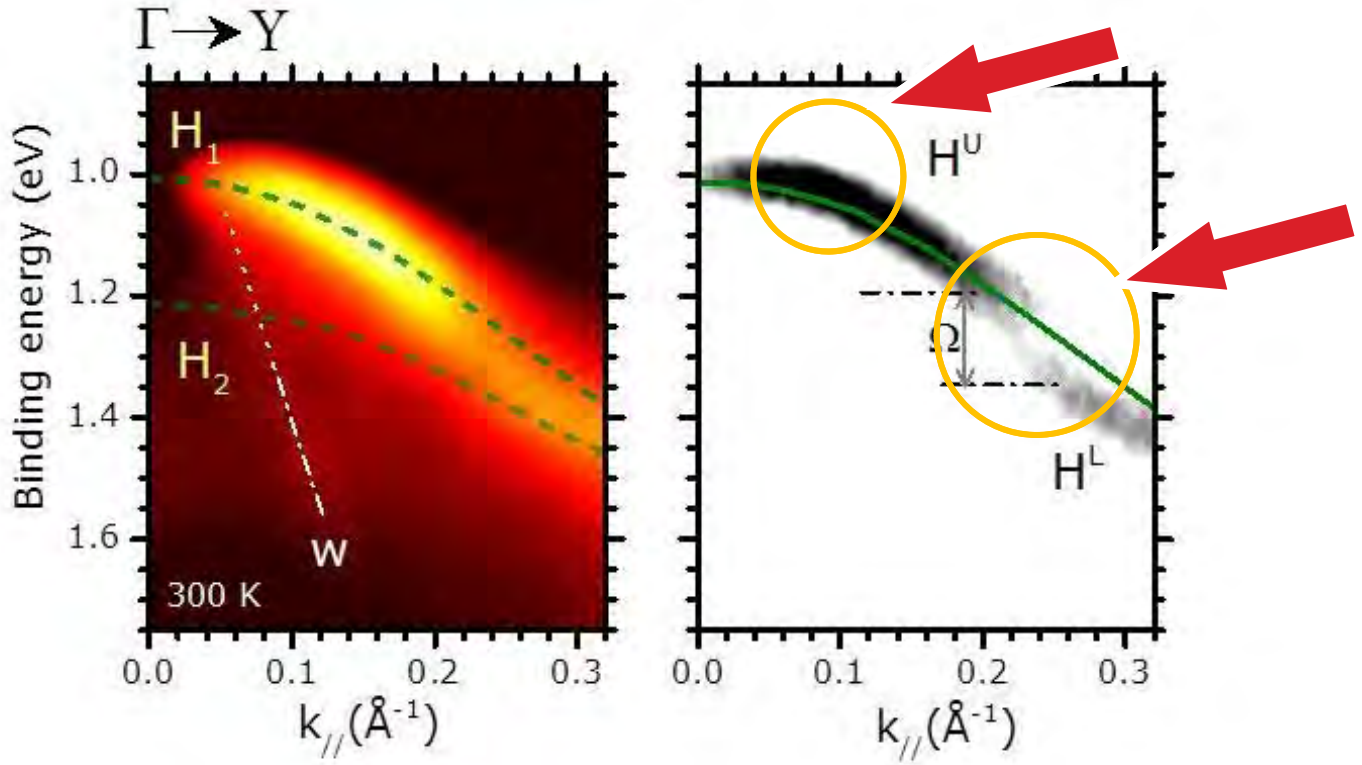
**Bulk sensitive, High intensity, Small spot**

**2009~2016**

**quasiparticle**



# What is a nature of KINK features of spectral band for organic crystal?



# Phonon coupling: multimode

**Collective nonlocal phonons**
**crystal lattice vibration**

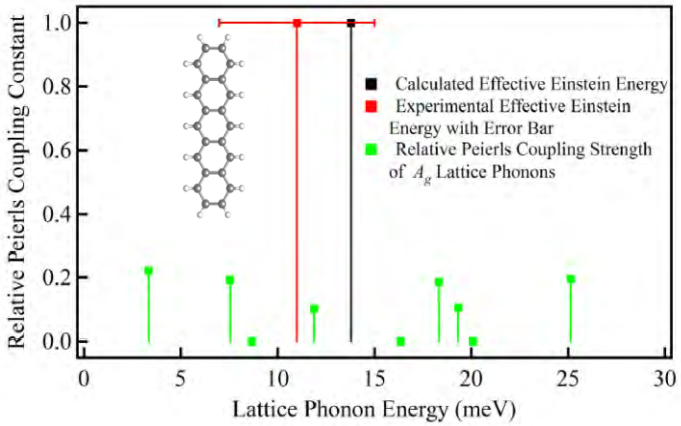
+

**Localized phonons**
**intramolecular vibrations**

Small energy (low THz) phonons

Large energy (high IR) phonons

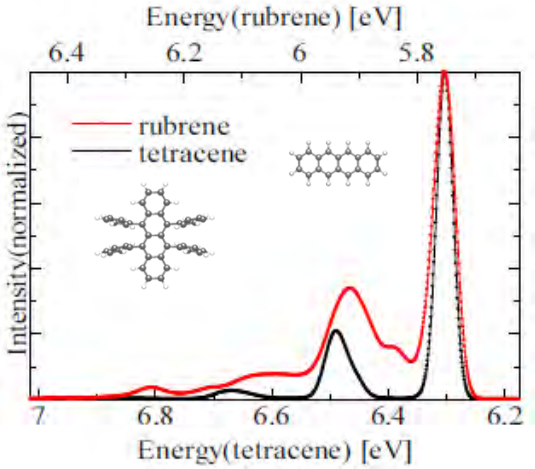
Effective Einstein energy 11meV for pentacene




Girlando et al, Mater. Sci-Poland 22, 307 (2004)
Hatch et al PRL104 (2010) in SI.

$\theta_D$= 254.5K (rubrene)
PhysRevB.83.113305

crystal's highest normal mode of vibration = 22meV

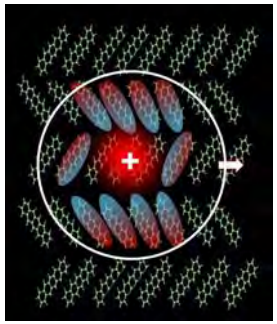



| No. | meV | H.-R. |
|---|---|---|
| 156 | 183 | 0.38759 |
| 76 | 107 | 0.21258 |
| 136 | 164 | 0.10529 |
| 2 | 4 | 0.10159 |
| 143 | 169 | 0.09978 |
| 168 | 201 | 0.06146 |
| 146 | 170 | 0.04694 |
| 116 | 138 | 0.03794 |
| 8 | 8 | 0.03183 |
| 21 | 28 | 0.01892 |
| 14 | 14 | 0.01759 |
| 102 | 126 | 0.01146 |
| 132 | 155 | 0.00929 |
| 70 | 98 | 0.00702 |
| 160 | 189 | 0.00582 |

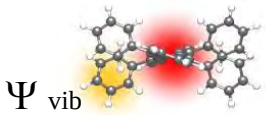
**Wide variety of polaron**

| *Frohlich* | *Holstein* | *Molecular polaron* |
|---|---|---|
| *(r >lattice)* | *(r ~lattice)* | *(r < molecule)* |

- **Inelastic scattering events**
- **Sensitive to transfer integral**
- **Thermal impacts**



- **Rich of vibration modes**
- **Major impact on charge hopping dynamics**




**Dynamic polarization of $h^+(e^-)$ = impact of polaron depends on t / λ ratio**

# Phonon coupling: multimode

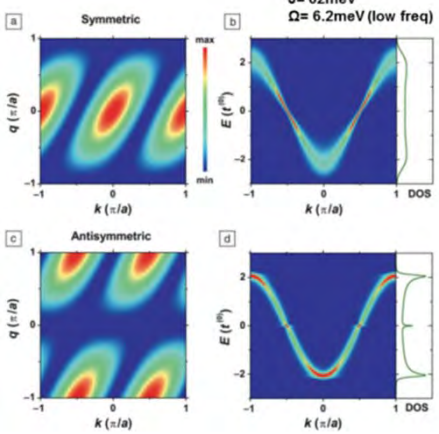
**Collective nonlocal phonons**
**crystal lattice vibration**

+

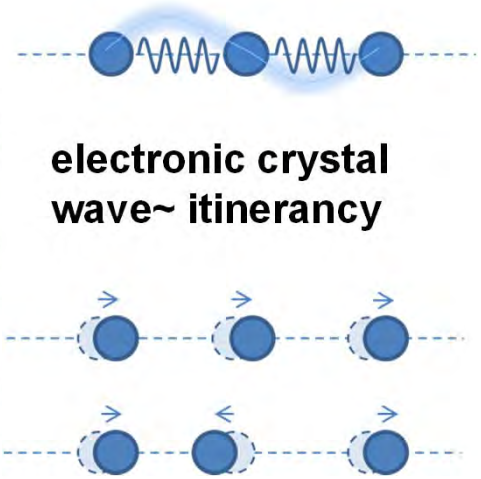
**Localized phonons**
**intramolecular vibrations**

Small energy (low THz) phonons

hω=6 meV
t=62 meV




MRS bull 38, 57 (2013)



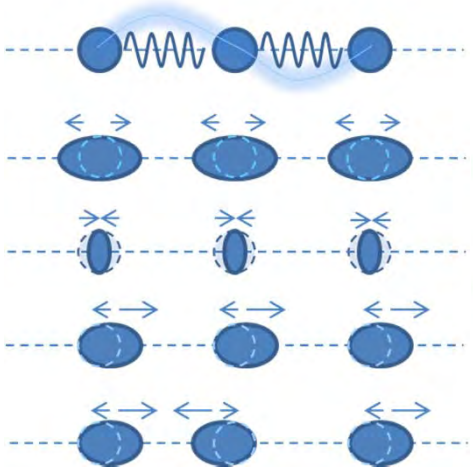
**electronic crystal wave~ itinerancy**

**symm**

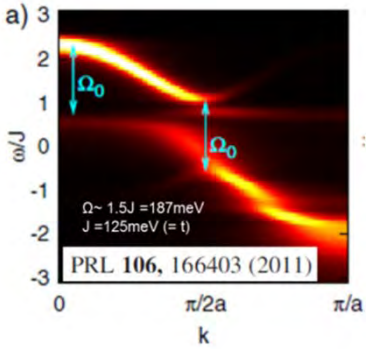
**or**

**antisymm**

Large energy (high IR) phonons



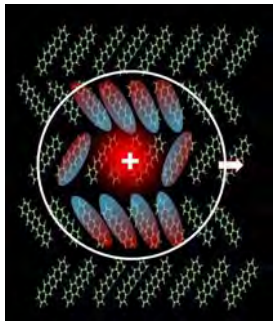
hω=187 meV
t=125 meV



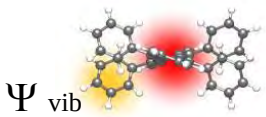

**Wide variety of polaron**

| *Frohlich* | *Holstein* | *Molecular polaron* |
|---|---|---|
| *(r >lattice)* | *(r ~lattice)* | *(r < molecule)* |

- **Inelastic scattering events**
- **Sensitive to transfer integral**
- **Holstein polaron**



- **Rich of vibration modes**
- **Major impact on charge hopping dynamics**




**Dynamic polarization of $h^+(e^-)$ = impact of polaron depends on t / λ ratio**

# Phonon coupling: multimode

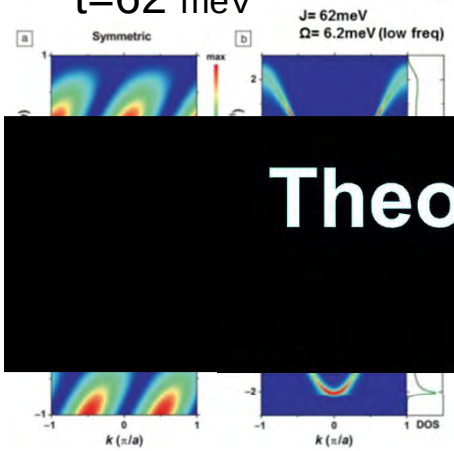
**Collective nonlocal phonons**
**crystal lattice vibration**

+

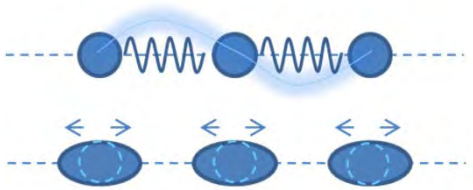
**Localized phonons**
**intramolecular vibrations**

Small energy (low THz) phonons

hω=6 meV
t=62 meV




electronic crystal



Large energy (high IR) phonons

hω=187 meV
t=125 meV


**Theory: too much simplified**
**both impacts should be considered**

MRS bull 38, 57 (2013)

**Wide variety of polaron**

| *Frohlich* | *Holstein* | *Molecular polaron* |
|---|---|---|
| *(r >lattice)* | *(r ~lattice)* | *(r < molecule)* |

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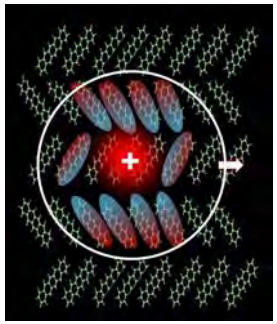
- **Sensitive to transfer integral**
- **Holstein polaron**



- **Rich of vibration modes**
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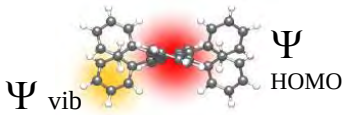


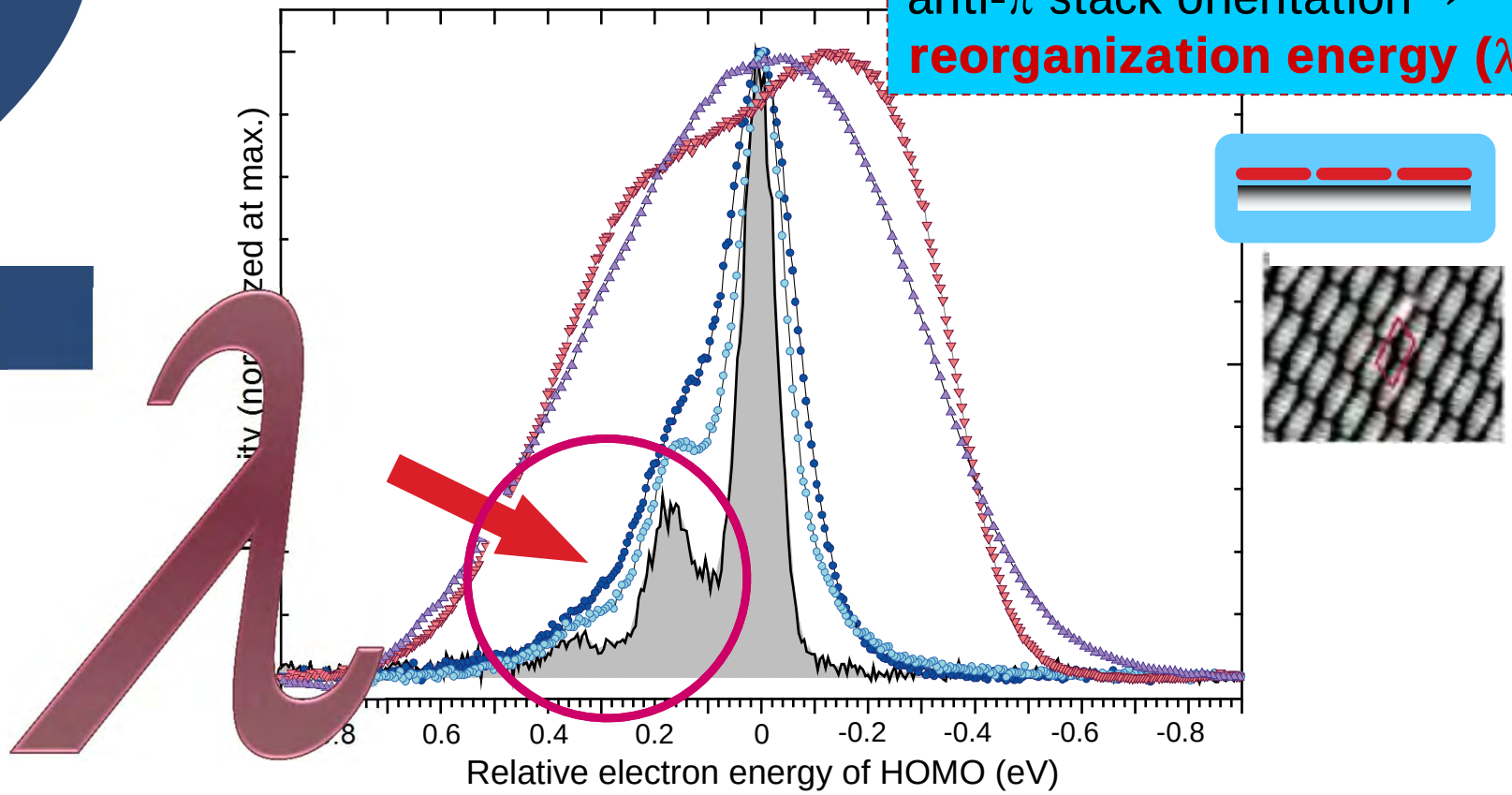

**Dynamic polarization of $h^+(e^-)$ = impact of polaron depends on t / λ ratio**

# Innovation

## High-resolution PES : e-ph coupling

### UPS line shape

anti-π stack orientation→
**reorganization energy ($\lambda_{reo}$)**

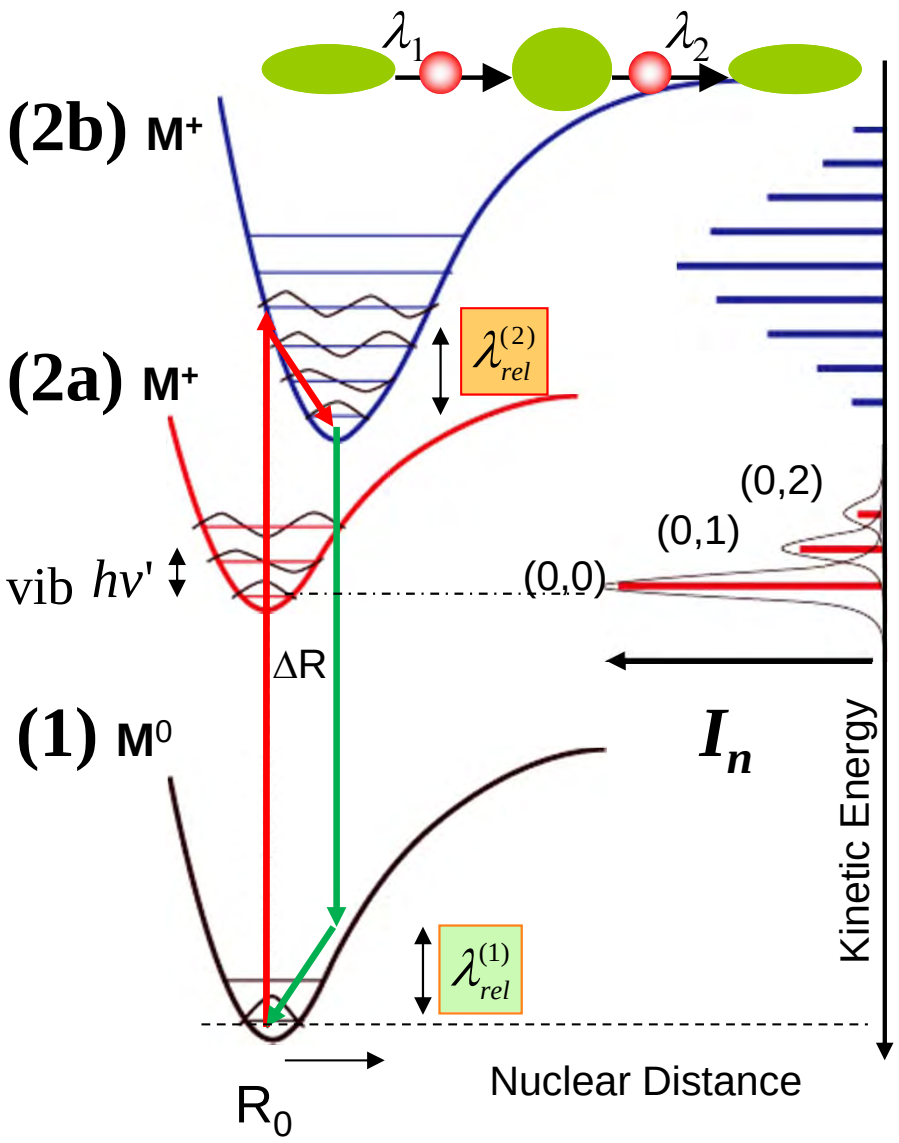





# Vibronic fine feature in the film

# Direct evaluation of $\lambda_{reorg}$

Displacement of potential surface of M and M⁺ state determines the shape




Vibrational distribution

## Intensity of UPS fine features

$$D(\omega) = 2\pi \sum_{fi} g_i \left| \langle f | T | i \rangle \right|^2 \delta(E_f - E_i - \omega),$$

$$\approx 2\pi \sum_{n} \left| \langle \Psi_n | T(\mathbf{r}) | \Psi_0 \rangle \right|^2 \sum_{ij} g_i \left| \left\langle \Phi_j^{(n)} \middle| \Phi_i^{(0)} \right\rangle \right|^2 \delta(E + \omega)$$

electron phonon

Under Franck-Condon approx

$$I_{m-n} = \left| \langle m^* | n \rangle \right|^2 = \frac{n!}{m!} e^{-S} S^{m-n} [L_m^{m-n}(S)]^2$$

~~hot band (50K) kT=4.3meV~~ m=0

$$I_{0-n} = \frac{S^n}{n!} e^{(-S)}$$

Poisson distribution

Huang-Rhys factor : S is obtained from $I_n$

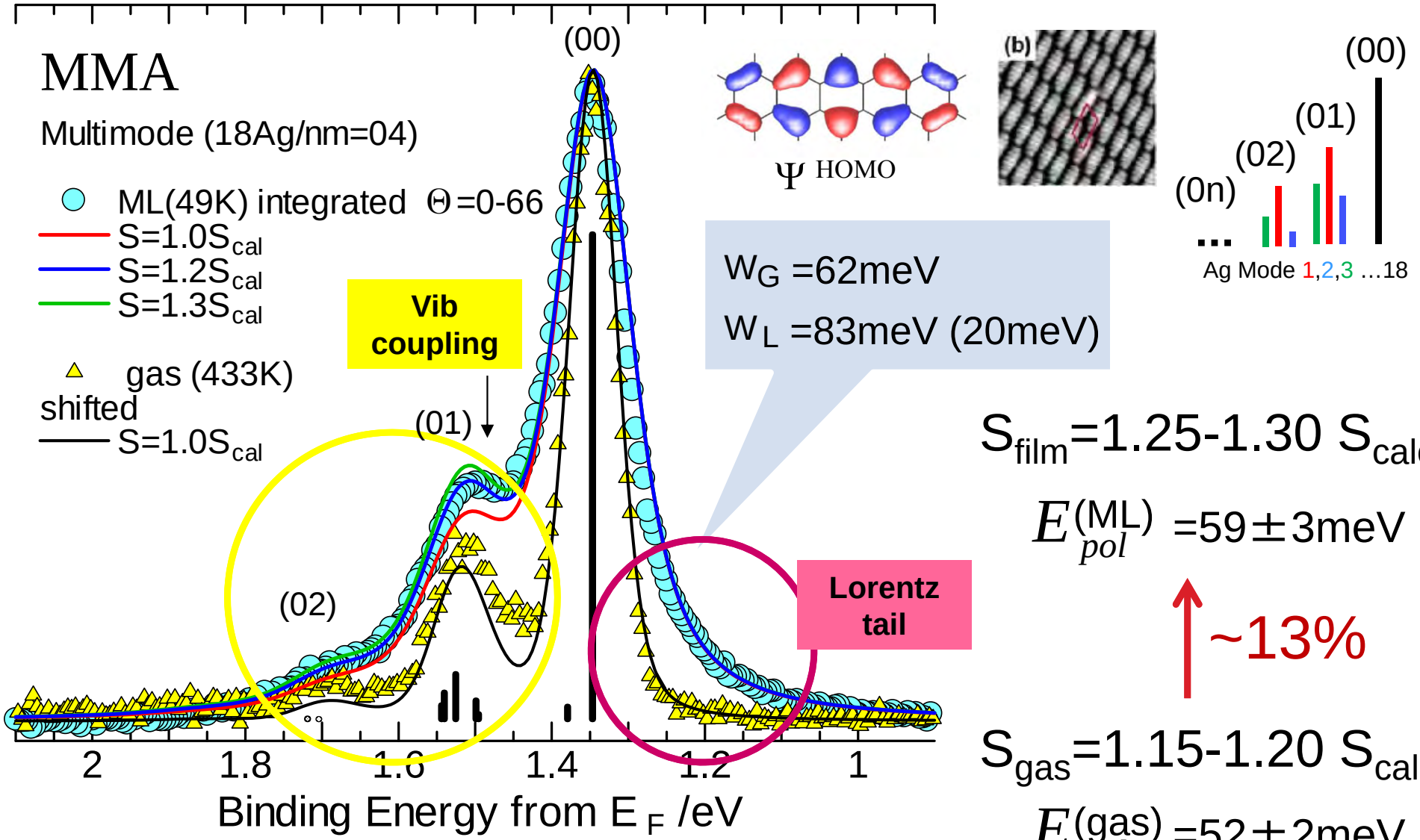
Geometric relaxation Energy $\lambda_{rel} = \sum S_j h\nu_j$

reorganization E $\lambda_{reorg} = \lambda_{rel}^{(1)} + \lambda_{rel}^{(2)} \cong 2\lambda_{rel}$

Coropceanu et al., Chem. Rev. 107, 926 (2007).

# Solid vs Gas: Pentacene λ

**Hel UPS** Obvious difference between the ML film and gas can be found




$S_{film}$=1.25-1.30 $S_{calc}$

$E_{pol}^{(ML)}$ =59±3meV

↑ ~13%

$S_{gas}$=1.15-1.20 $S_{calc}$

$E_{pol}^{(gas)}$ =52±2meV

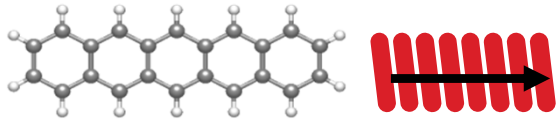

H. Yamane, SK *et al*., PRB.**72**, 153412 (05) 1st analysis repo
SK *et al*., Prog. Surf. Sci.**84**, 135 (09) highlight
SK *et al*, JPCC. **117**, 22428 (13) multimode analysis
SK and Ueno, JESRP. **204**, 2 (15) review

# Impacts of vib coupling: stacking

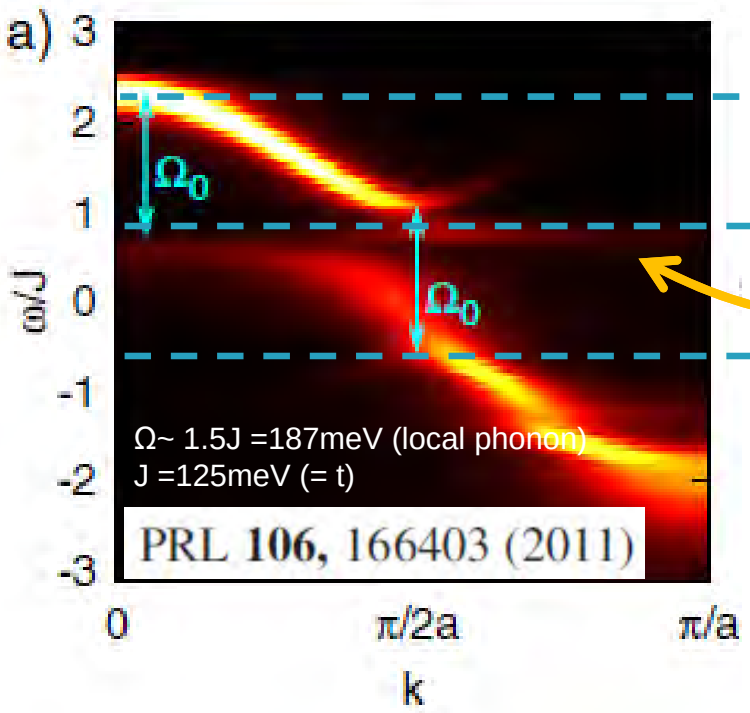
## Local e-ph coupling effect

W= bandwidth

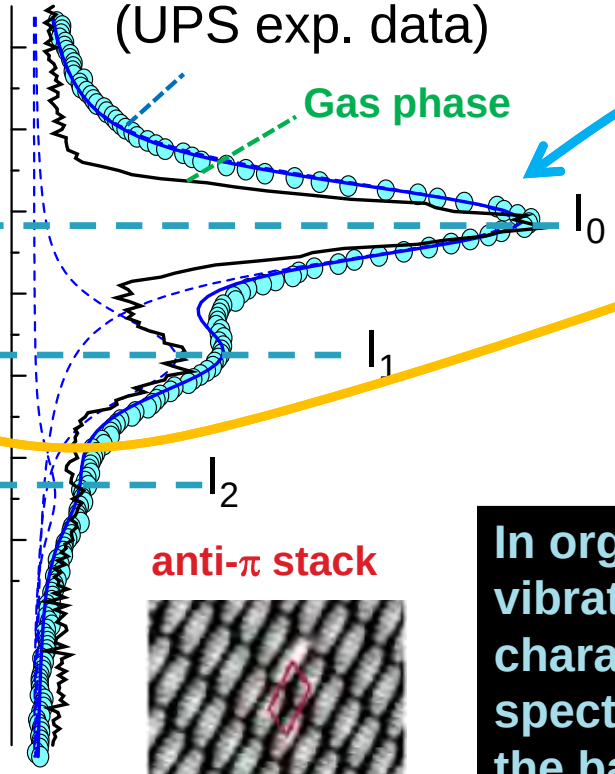
$\Omega_0$= vibrational energy



Pentacene 1D chain + 1-vibration loss:
Spectral function (theory) π stack




**Pen (ML)/HOPG**
(UPS exp. data)




anti-π stack



$\lambda > t$

**anti-π stack (ML)**
**t ~ 4meV (calc)**
**λ = 118meV**

$\lambda \sim t$

**π stack (crystal)**
**t = ~0.1eV**
**λ ~ 0.1eV (calc)**

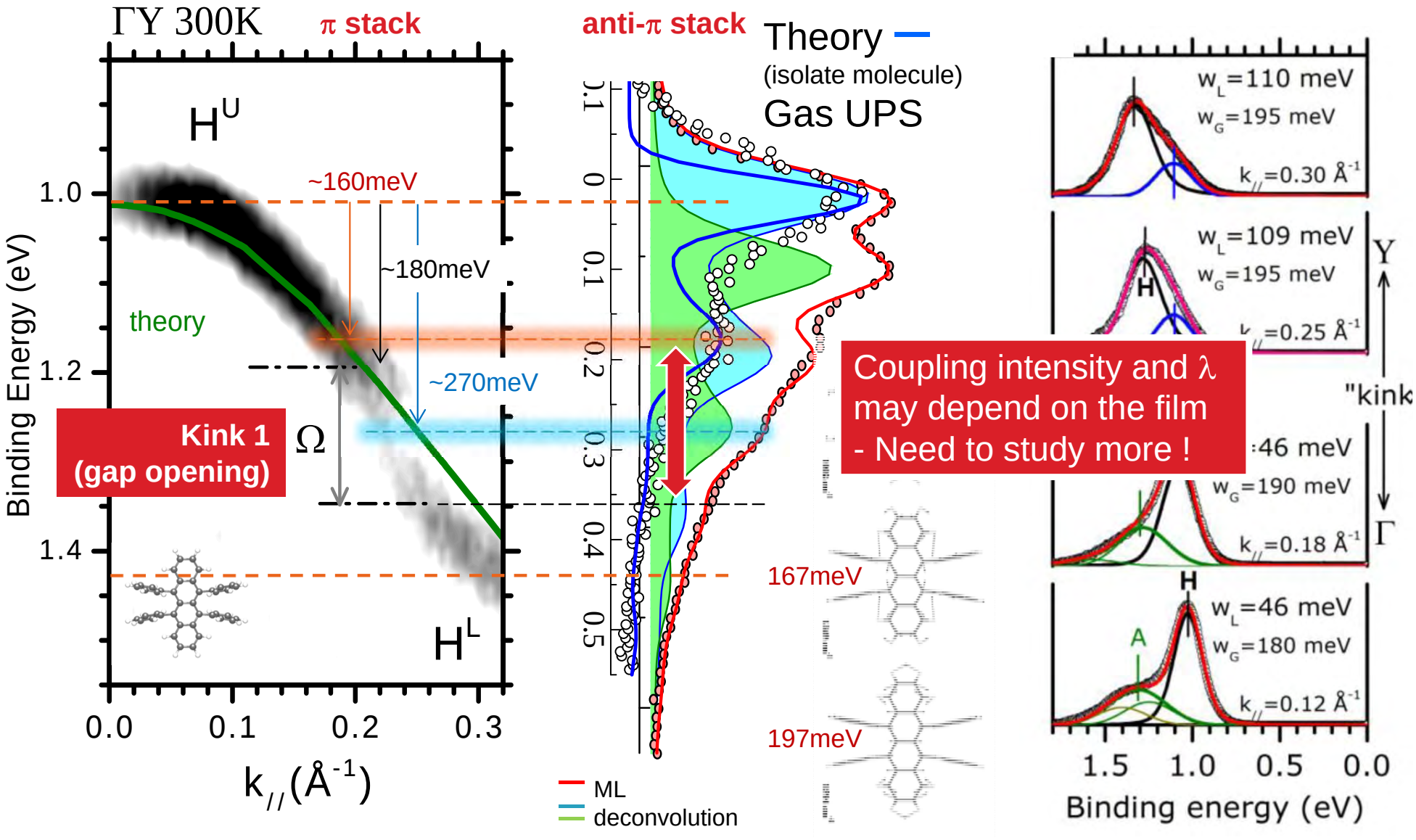
Bredas, PRB**78**, 041403R (08)
Kakuta, PRL98, 247601 (07)
Nakayama, Jpn.J.Appl.Phys.**53**,01AD03(14)

**In organic SCs, if W >$\Omega_0$ (t > λ), vibrational fine structure characteristic of the molecular spectra are replaced by "cuts" in the band structure**

**Kinks (CUT) in the band structure are related to high-freq phonon ~ intramolecular vibrations**

# Origin of kink structure: rubrene

**"KINK" in the band dispersion at major energies of vibration coupling**

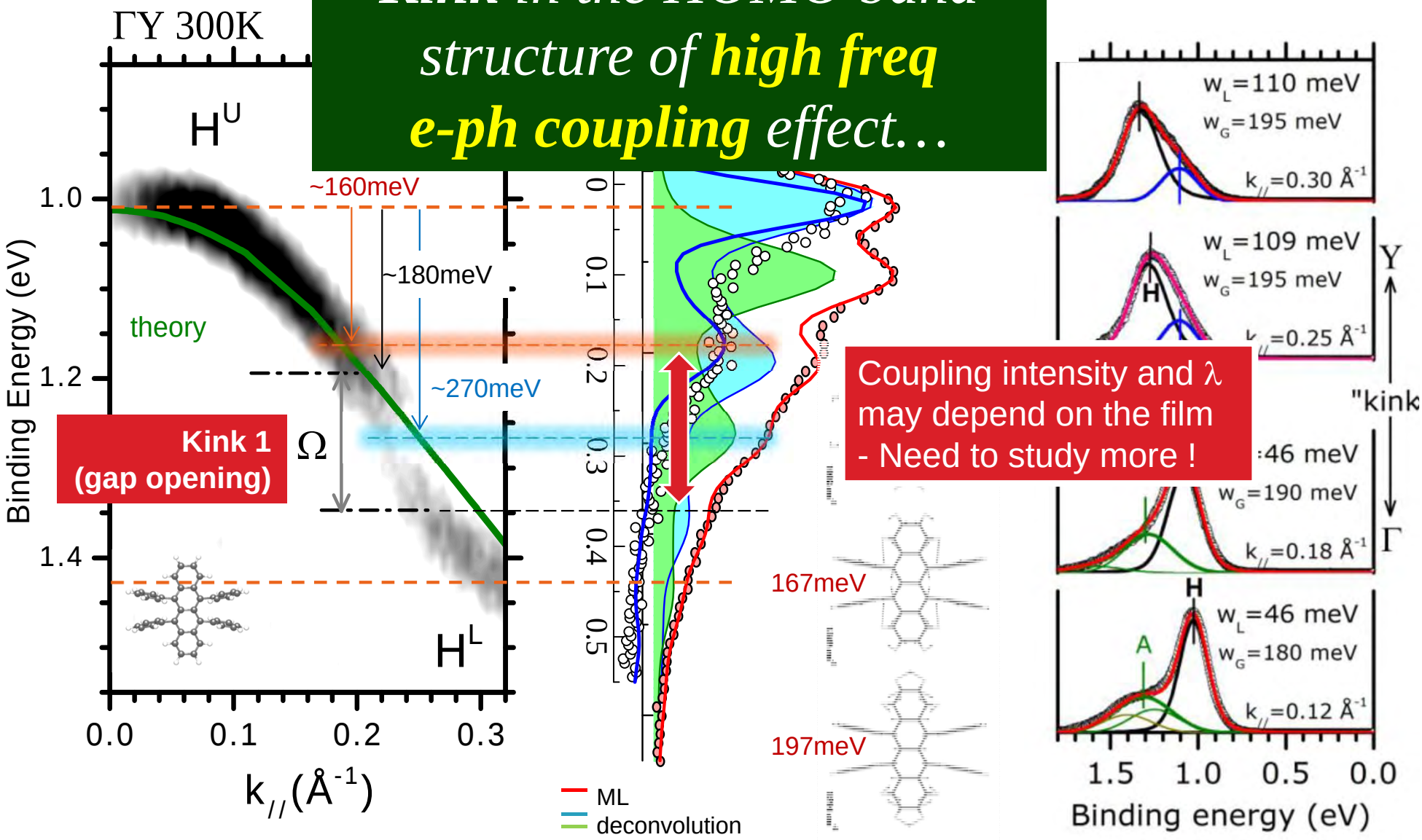



Duhm, SK, Adv.Mat.24,901(2012) (*ML is complicated)

# Origin of kink structure: rubrene

"KINK" in the ... ration coupling

***Kink** in the HOMO band structure of **high freq e-ph coupling** effect…*



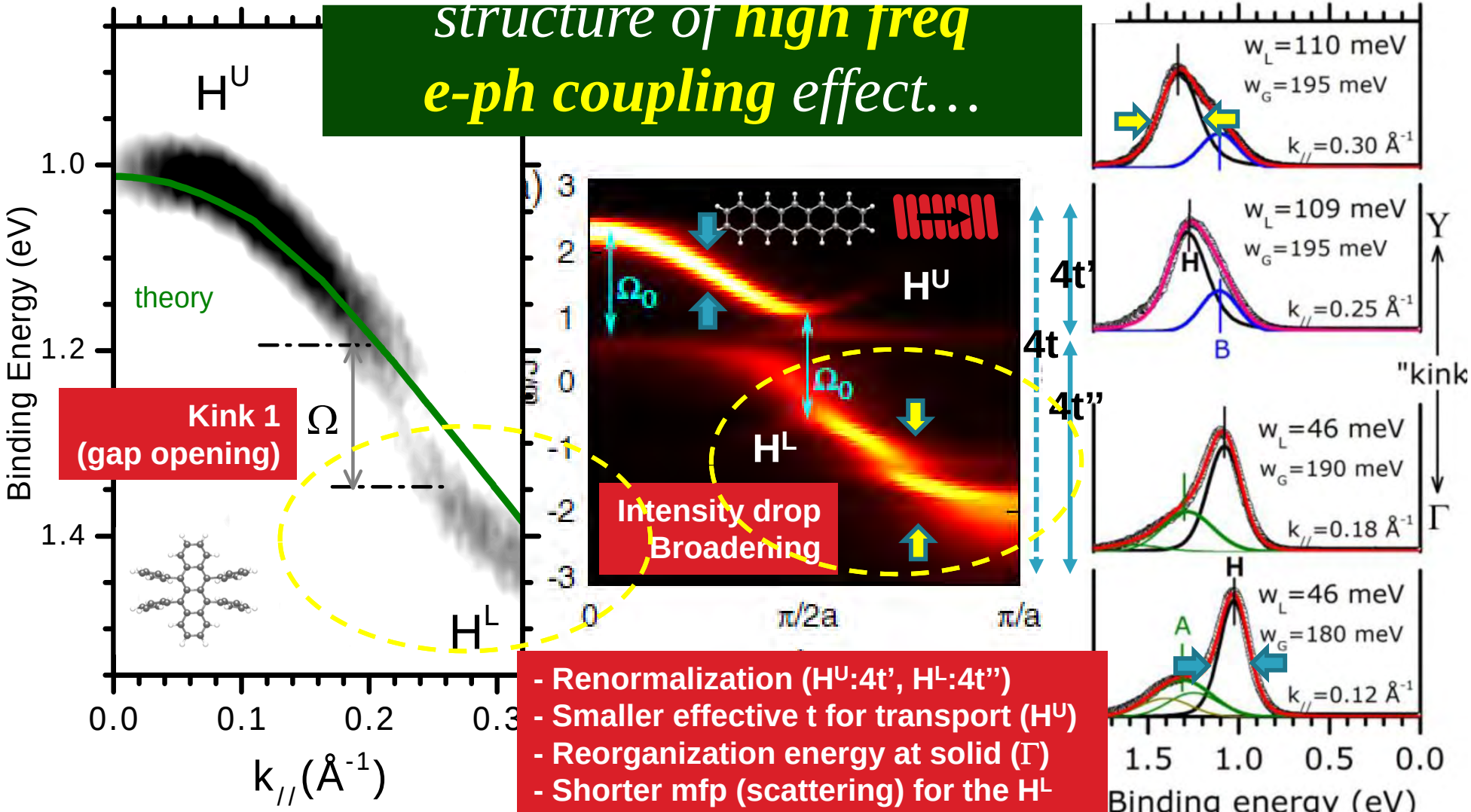

Duhm, SK, Adv.Mat.24,901(2012) (*ML is complicated)

# brene

tion coupling

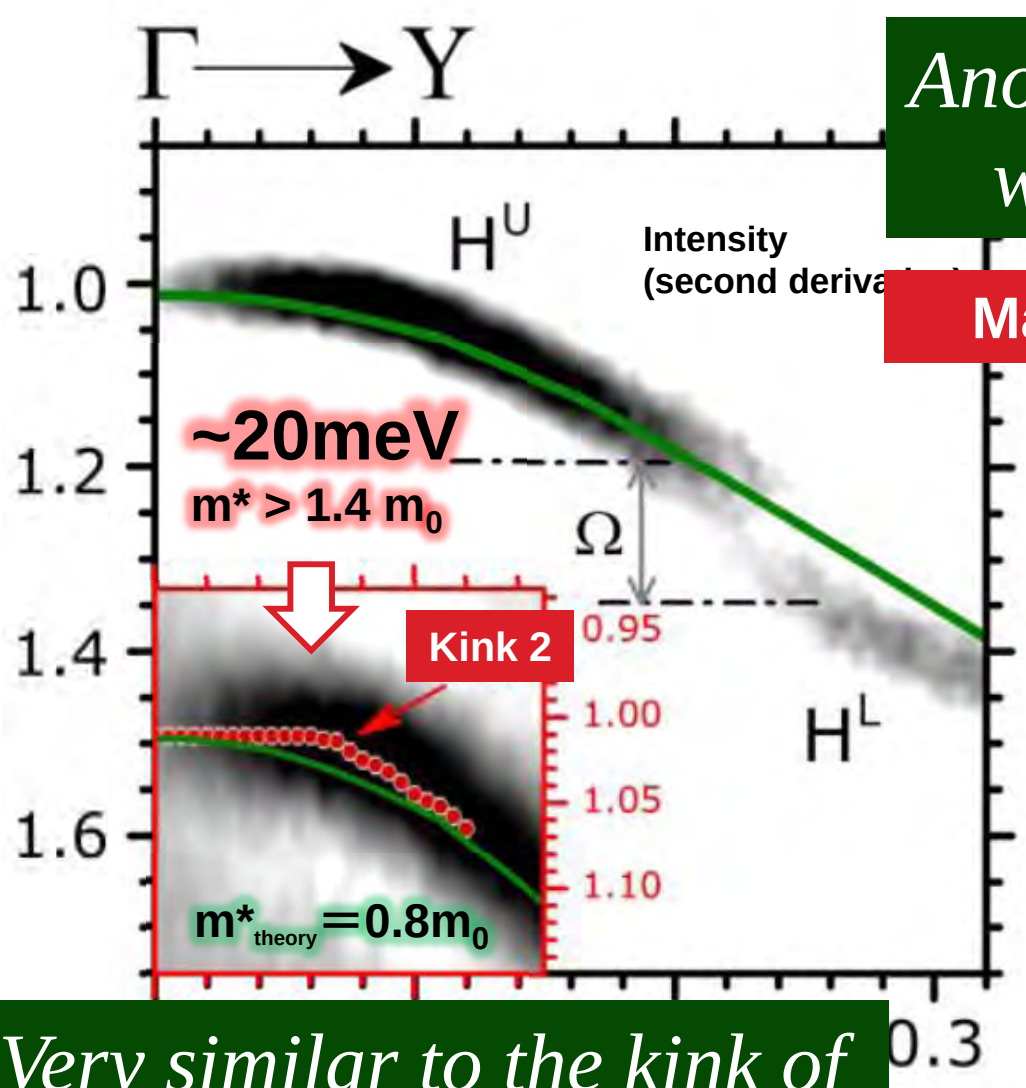
**"Charge localization phenomena upon the coupling"**
**$H^L$ is affected much more**
**= Transport $h^+$ is defined by the $H^U$ band shape**
**Changes in the reorganization energy & effective m*…**

*structure of* ***high freq e-ph coupling*** *effect…*



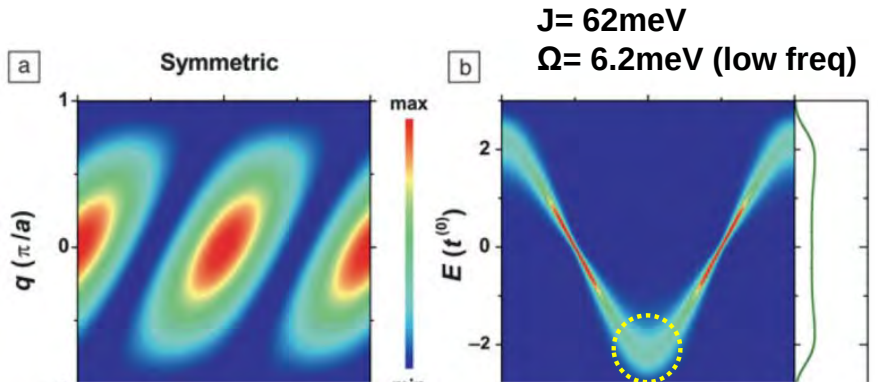

- Renormalization ($H^U$:4t', $H^L$:4t'')
- Smaller effective t for transport ($H^U$)
- Reorganization energy at solid (Γ)
- Shorter mfp (scattering) for the $H^L$ ,comparing to theory

# HOMO mass renormalization

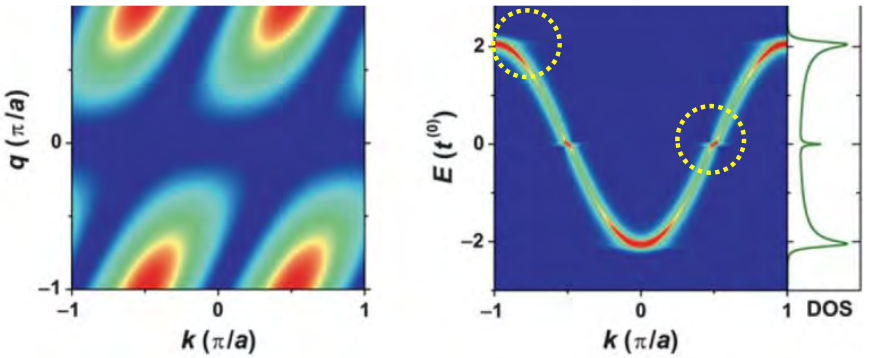



*Another **kink** in the HOMO band with **low freq e-ph coupling***

**Mass enlargement x1.5 theory**




**Collective e-ph coupling appears differently depending on the symm**




Coropceanu et al, MRS bull 38, 57 (2013): 1D model band + 2D phonons

*Very similar to the kink of **collective non-local e-ph coupling "bend"***

# Does KINK feature give any important aspects?

# Impact of phonons on UPS shape

**Band dispersion is arranged by various Boson couplings**

**Collective phonon: Symmetric / Antisymm modes contribution, phonon dispersion?**

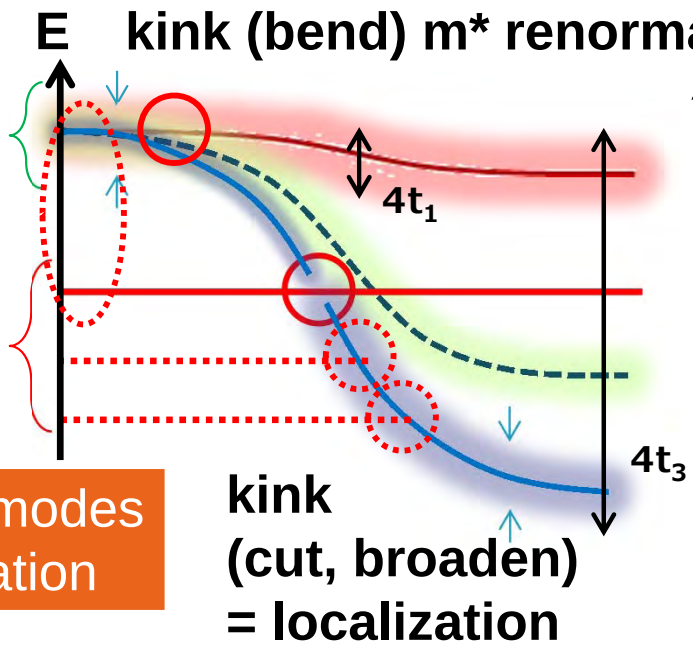
**Local phonon: Symmetric / Antisymm molecular vibrations, coherency?**

collective phonon (optical/acoustic)

ω 10~ 20meV

ω 124~ 197meV
v(CC) etc
2v,3v

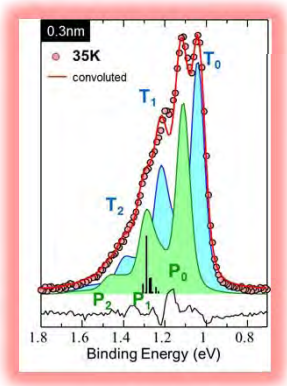
Normal modes Combination



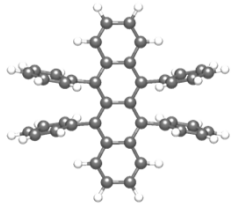

π-MO localization
$4t_1$ ~ 40meV

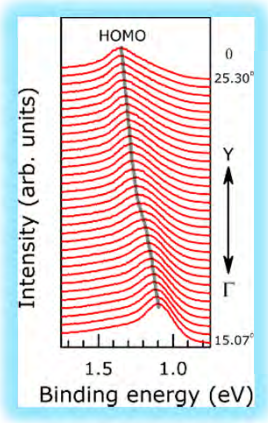
$4t_2$~ 200meV

$4t_3$~ 400meV




$\lambda > t$





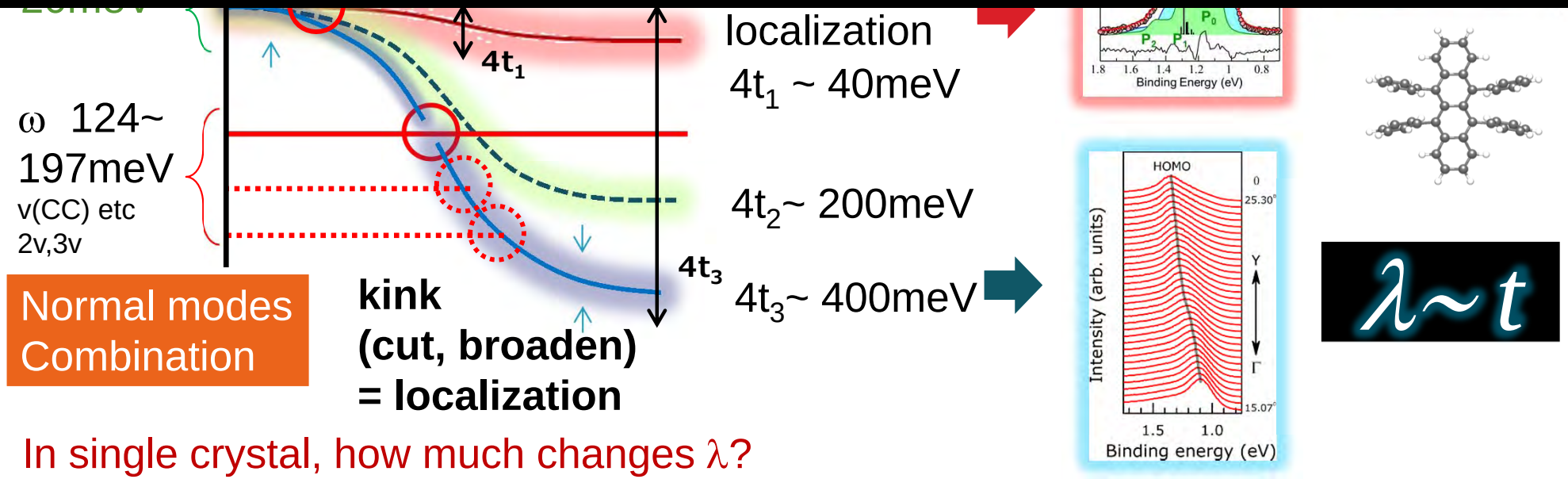

$\lambda \sim t$

In single crystal, how much changes λ?

**UPS band shape shows an electron in molecular solids**

# Impact of phonons on UPS shape

**Dressed states are differently appeared in the main band ( λ & t )**
**Molecular vibration affects in any case**




In single crystal, how much changes λ?

**UPS band shape shows an electron in molecular solids**

# Design the crystal: BZ vs scattering

JPCL, 3, 3325 (2012)

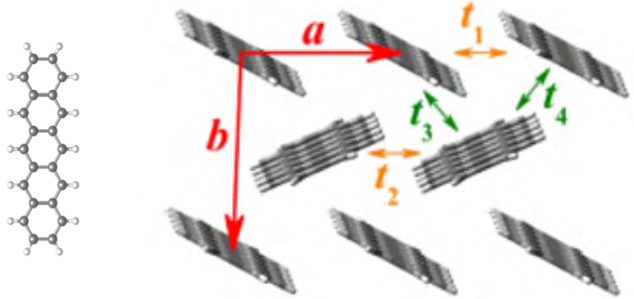
**Thermal Narrowing of the Electronic Bandwidths in Organic Molecular Semiconductors: Impact of the Crystal Thermal Expansion**

Yuan Li, Veaceslav Coropceanu,* and Jean-Luc Brédas*,†

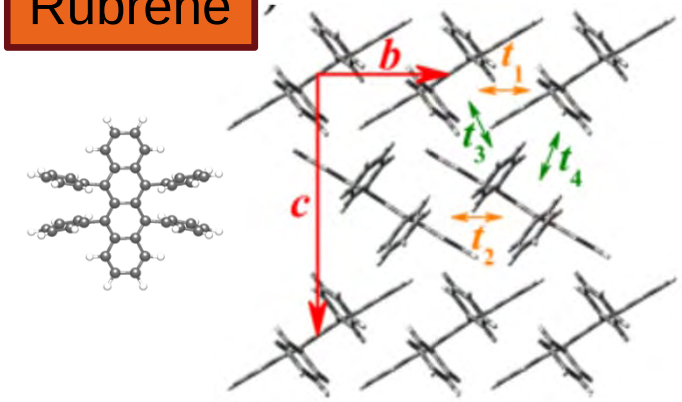
**t**: comparable for $C_{2p}$

**m***, **mfp** = tune the properties, μ

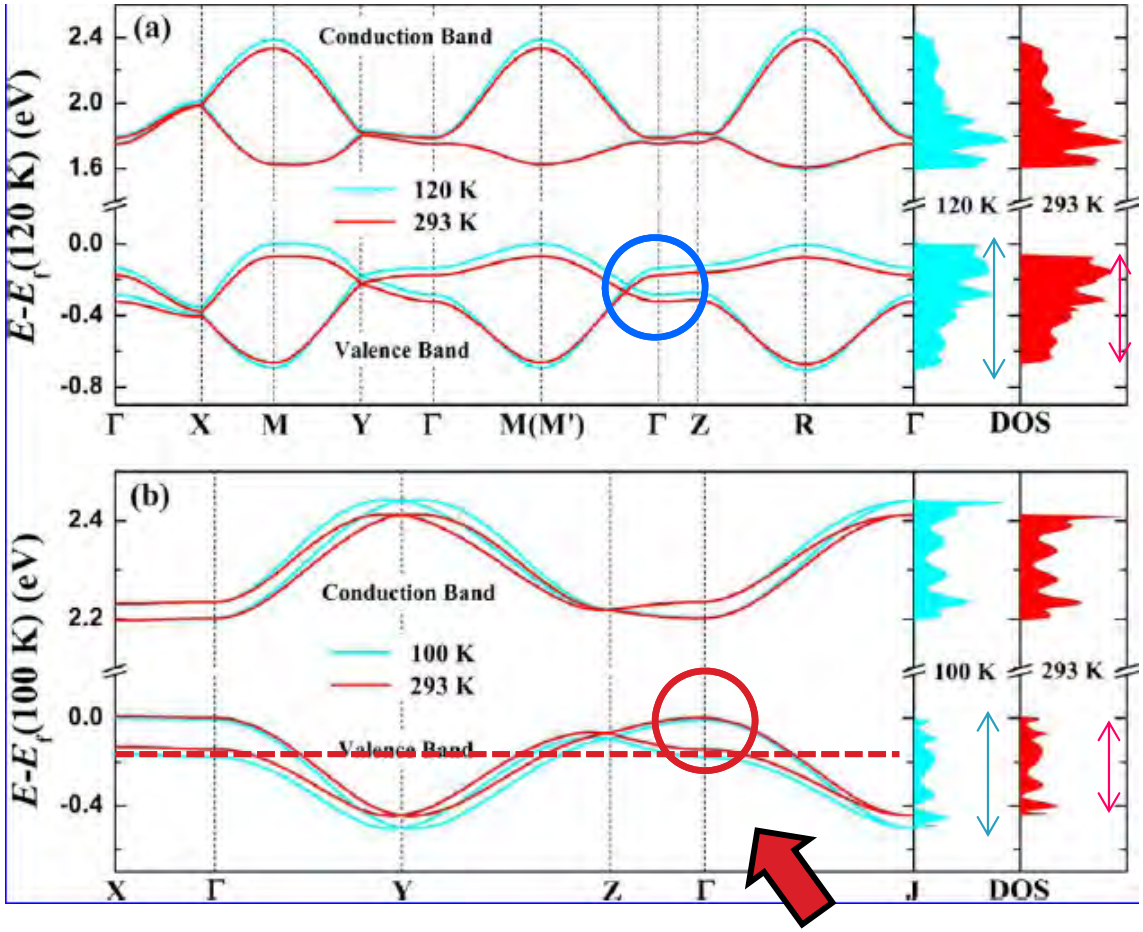
Pentacene




Rubrene




Lattice thermal expansion (fluctuating t )




**Γ point gives lowest level ($h^+$ transport) = less effects on scattering**

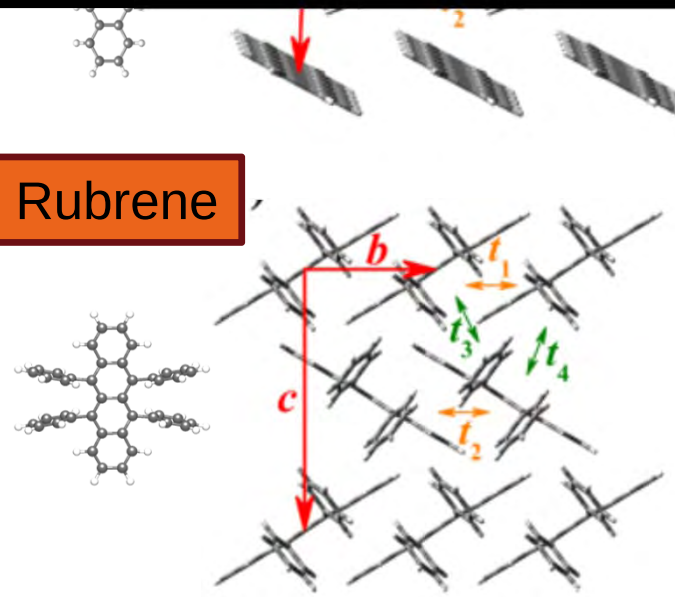
✕ Polaronic band narrowing upon heating (renormalization t)
Holstein (1959) NOTE: **for t<λ**

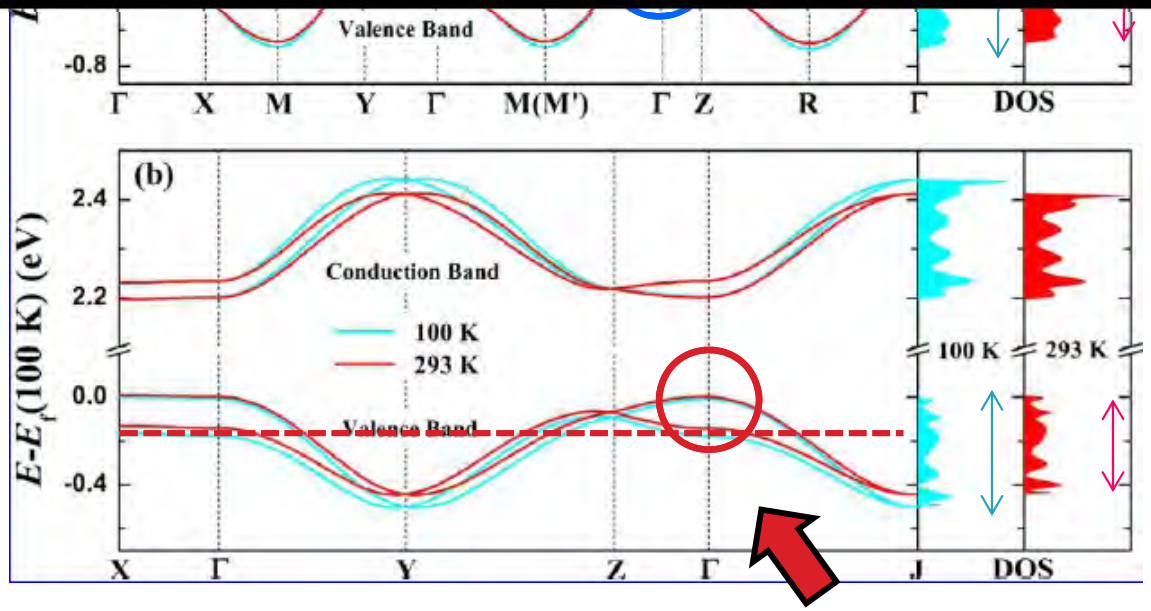
# Design the crystal: BZ vs scattering

**Experiment:**
**Any other measurement to demonstrate**

**Theory:**
**Adequate description of a charge in molecule**

Rubrene




Lattice thermal expansion (fluctuating t )

✕ Polaronic band narrowing upon heating (renormalization t)
Holstein (1959) NOTE: **for t<λ**

**Γ point gives lowest level ($h^+$ transport)**
**= less effects on scattering**

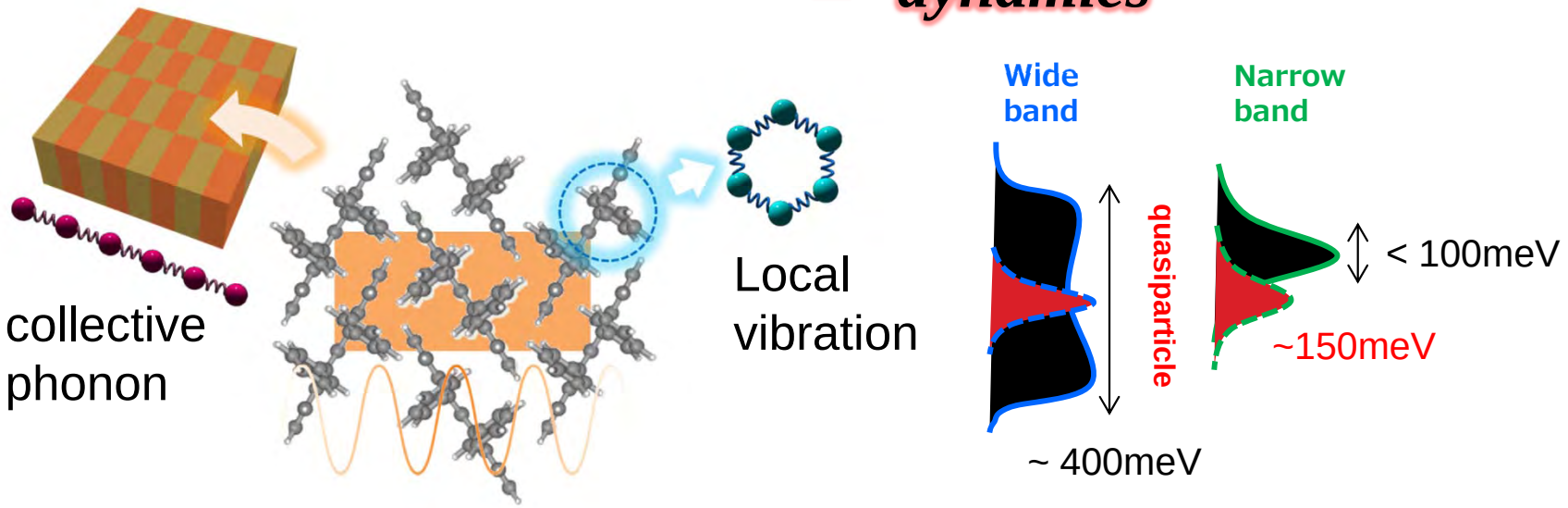
# Summary : rubrene SC

- ✔ HOMO band “renormalization” caused by strong local e-ph (molecular vibration) and weak nonlocal e-ph (collective) coupling effects

**“Kink” = UPS fine features “cut” & “bend” 110K ~320 K**

- ✔ Phonon(vibration) coupling is crucial to charge transport (mfp and m*)
- ? Does the spectrum represent a specific coupling instead of multiplicity ?

***= “dynamics”***




**Design of chem structure** (reorganization energy: molecular vibration and MO) **and BZ structure** (MO connection: t & phonon momentum, symmetry) **is a key parameter to control the charge transport property**

***“Architecture”***