Electronic properties of organic semiconductors: bands or no bands?

Simone Fratini
Institut Néel - CNRS, Grenoble

Collaborations

Theory

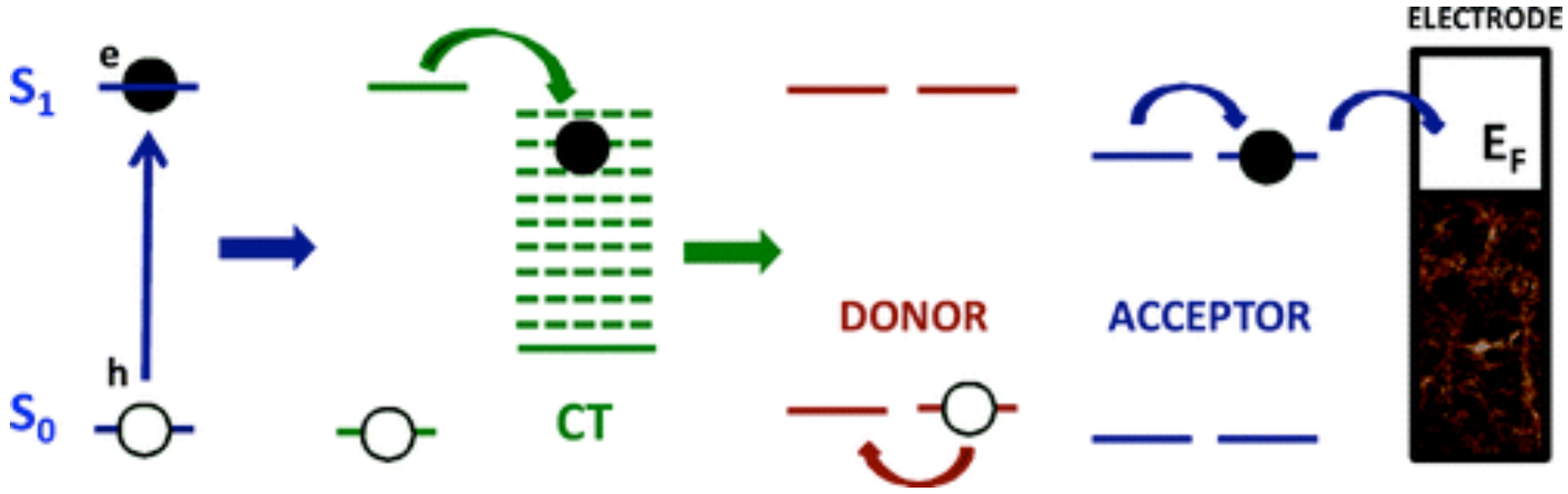
S. Ciuchi

Experiment

R. C. Hatch, H. Höchst
ARPES measurements

D. Mayou, X. Blase,
C. Faber

Energy & thermoelectricity? organic solar cells

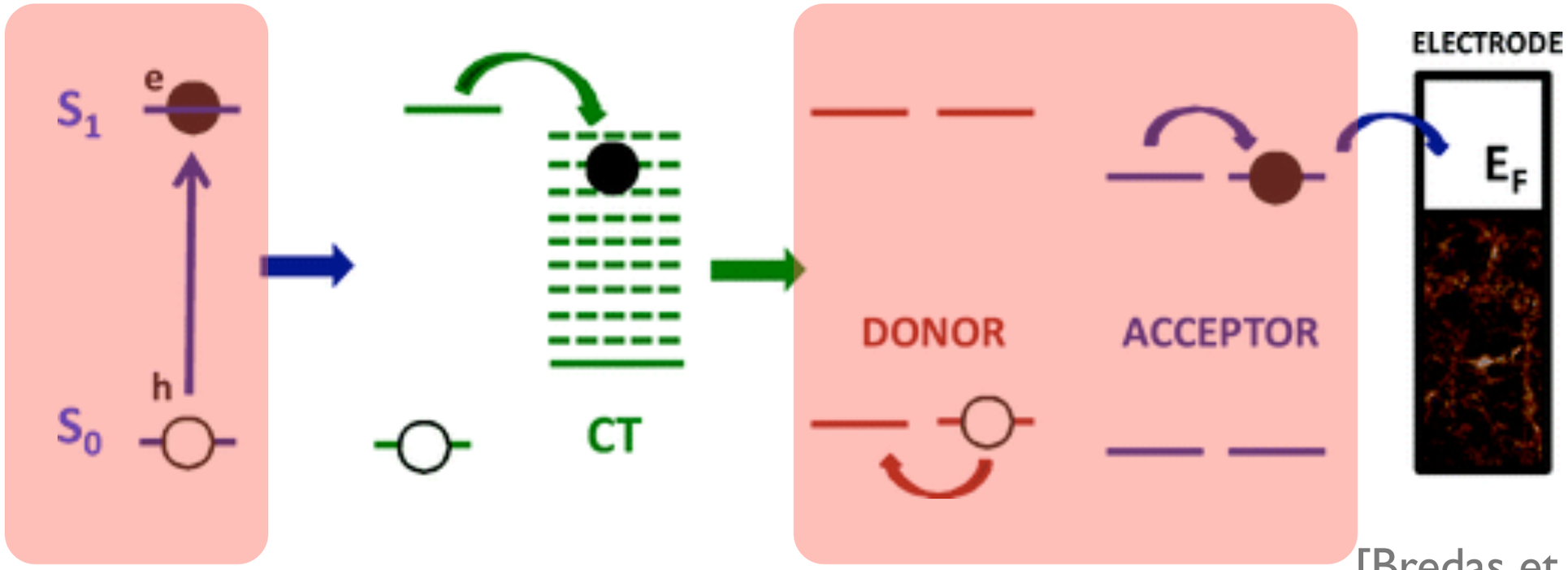


[Bredas et al, ACR 2009]

5 steps in the generation of current

- absorption of light -> exciton formation (e-h pair)
- exciton diffusion to the donor-acceptor interface
- exciton dissociation at the interface into separate electron and hole carriers
- electron and hole diffusion towards the electrodes
- charge collection at electrodes

Energy & thermoelectricity? organic solar cells



[Bredas et al, ACR 2009]

5 steps in the generation of current

- absorption of light -> exciton formation (e-h pair)
- exciton diffusion to the donor-acceptor interface
- exciton dissociation at the interface into separate electron and hole carriers
- electron and hole diffusion towards the electrodes
- charge collection at electrodes

Outline

- Introduction: something's wrong with the "common wisdom"

- **ARPES**:

the role of intramolecular vibrations and disorder

- **Transport properties:**

the role of intermolecular vibrations and the concept of transient localization

- **Kubo formula revisited**: carrier diffusivity from optical experiments

- Concluding remarks

Outline

- Introduction: something's wrong with the "common wisdom"

- **ARPES**:

the role of intramolecular vibrations and disorder

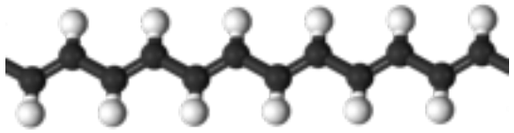
- **Transport properties:**

the role of intermolecular vibrations and the concept of transient localization

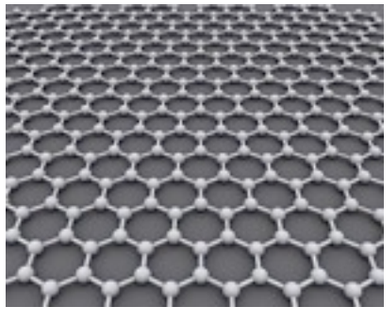
- **Kubo formula revisited**: carrier diffusivity from optical experiments

- Concluding remarks

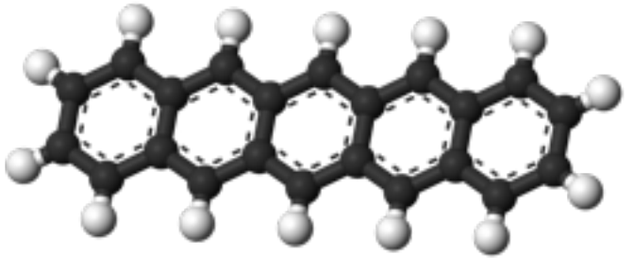
Organics



Polyacetylene

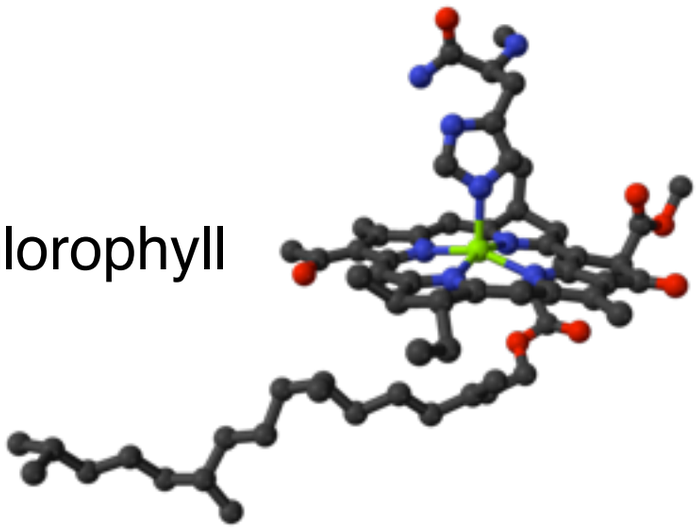


Graphene

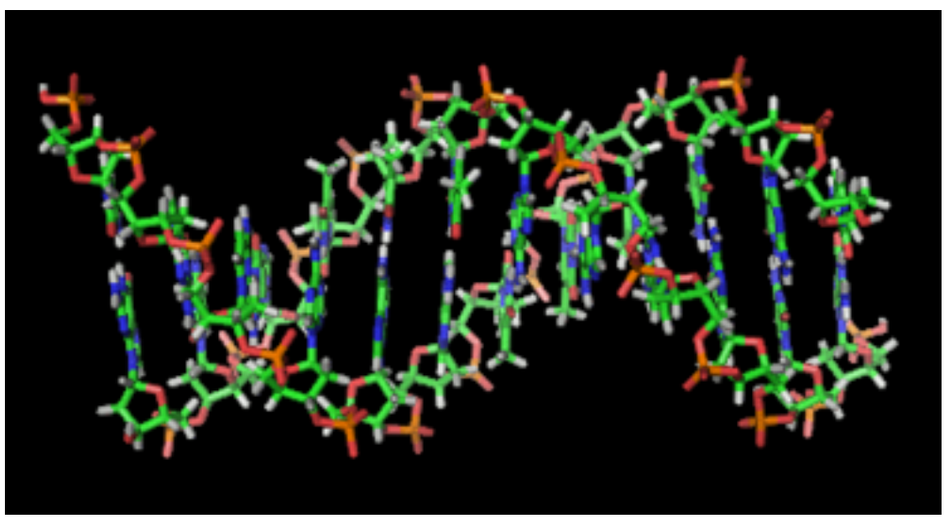


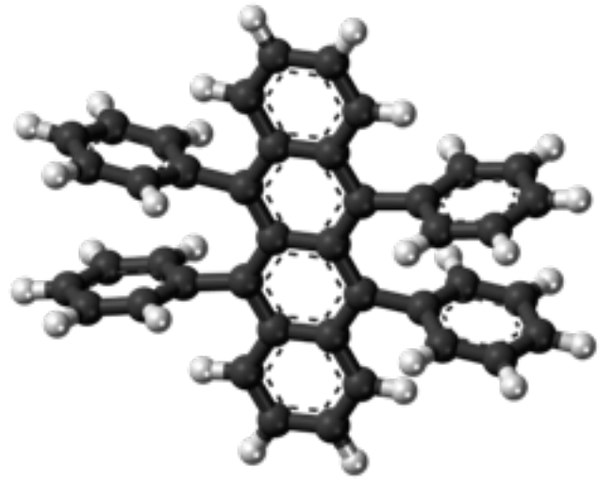
Pentacene

Chlorophyll



DNA

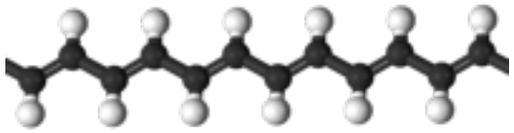




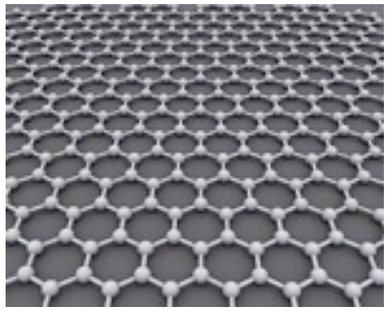
rubrene

Fullerene

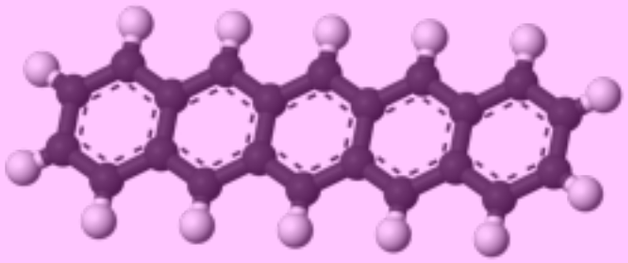
Organics



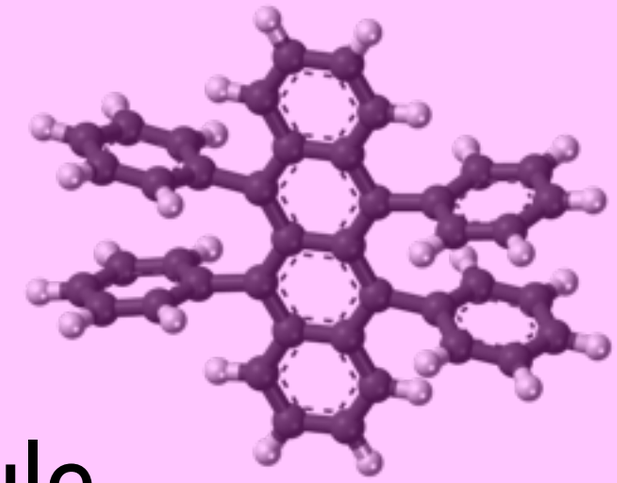
Polyacetylene



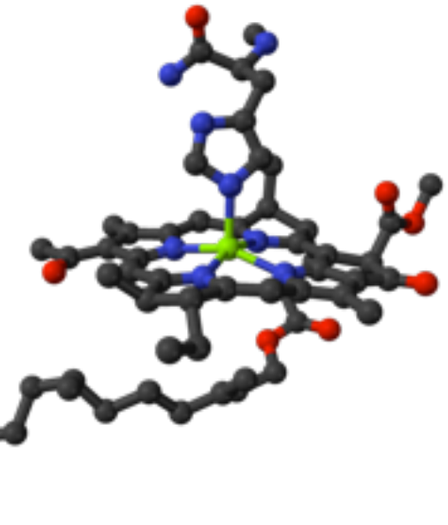
Graphene



Pentacene



rubrene

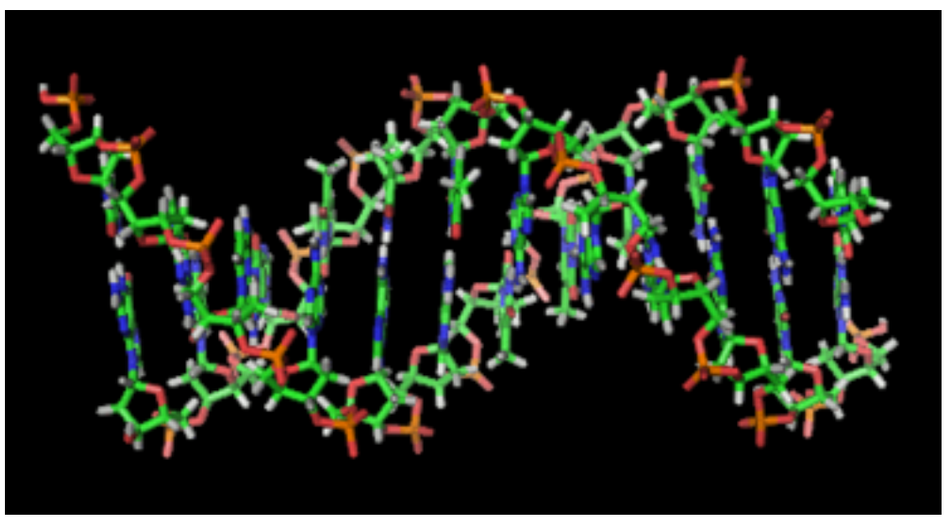


Chlorophyll

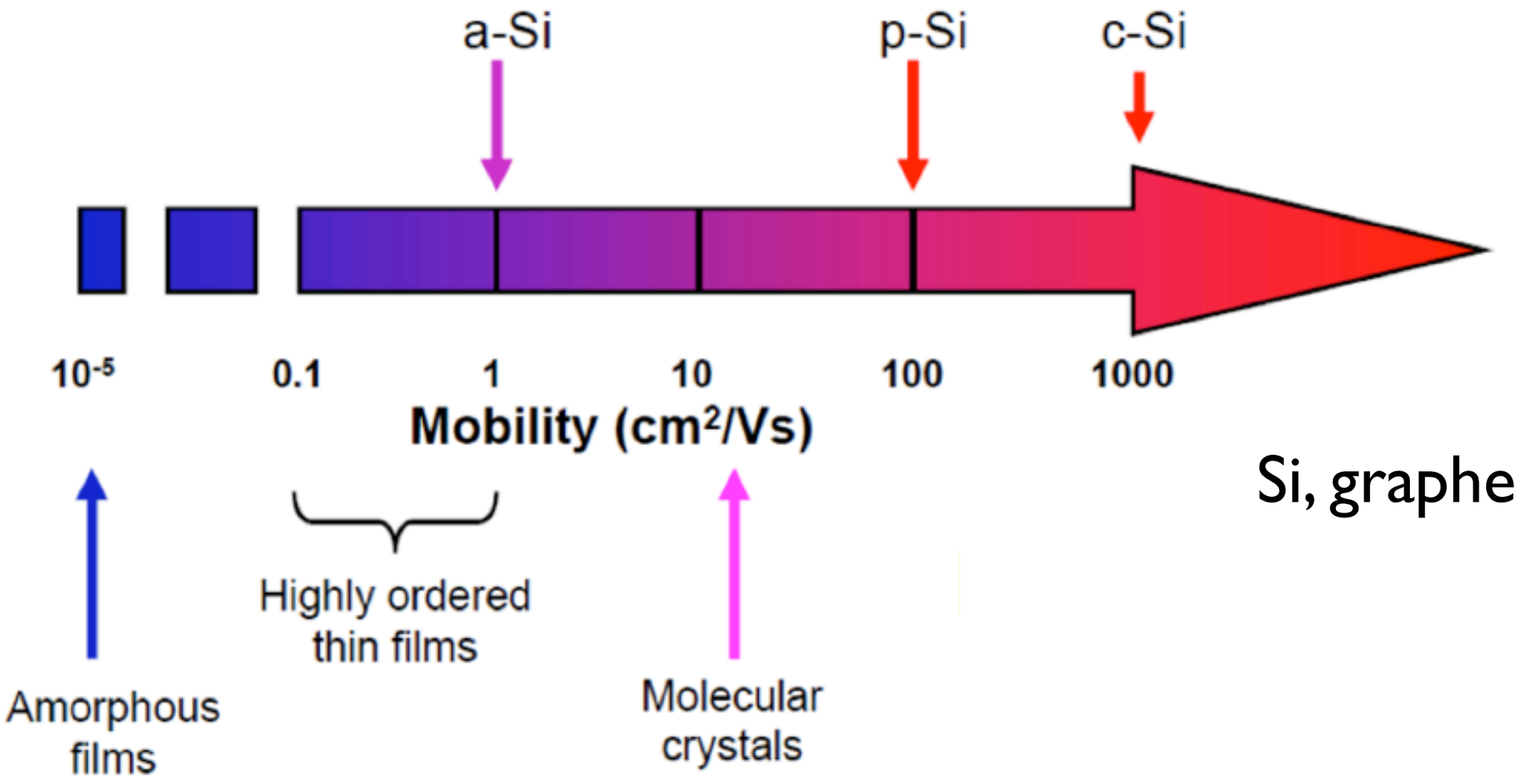
Fullerene

Small molecule organic solids

DNA



Organic semiconductors: somewhere “in-between”



Si, graphene

hopping dynamics

(incoherent)

?

Bloch-Boltzmann transport

(wave-like)

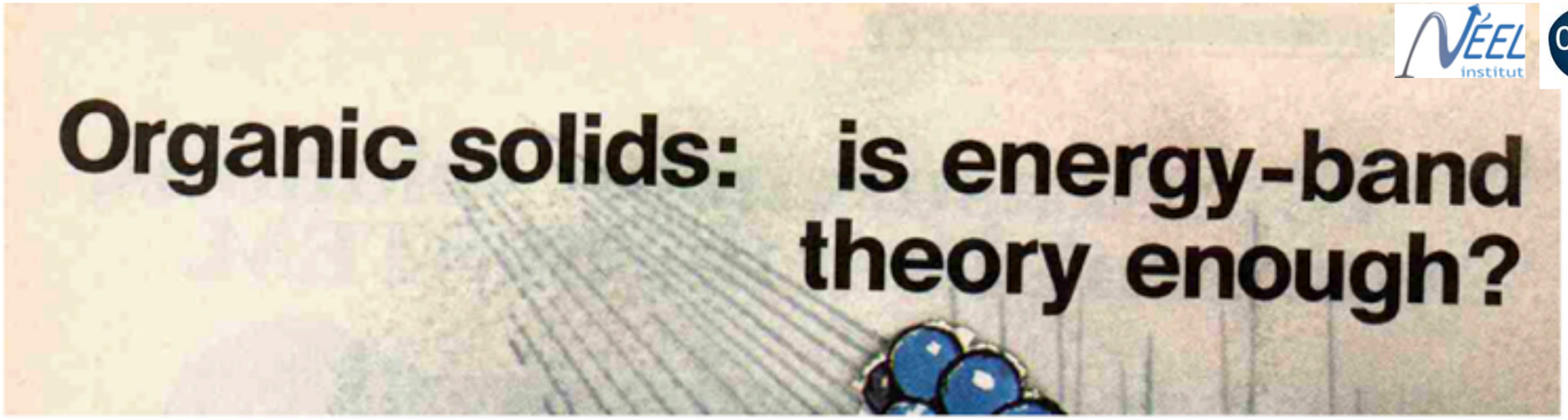
[readapted from Brütting, talk 2007]

Organic semiconductors: somewhere “in-between”

Do electrons behave as predicted by band theory?

- narrow electronic bands
- large electron-phonon coupling (molecular vibrations)
- intrinsically large disorder (plastic is soft)

Everything seems to favor electron localization



Chemist's view... real space
Electrons hop from molecule to molecule

The molecular property

As we mentioned earlier, a pre-eminent feature of the organic solid state is the persistence of molecular identity.

Physicist's view... momentum space
Electrons form weakly scattered Bloch states

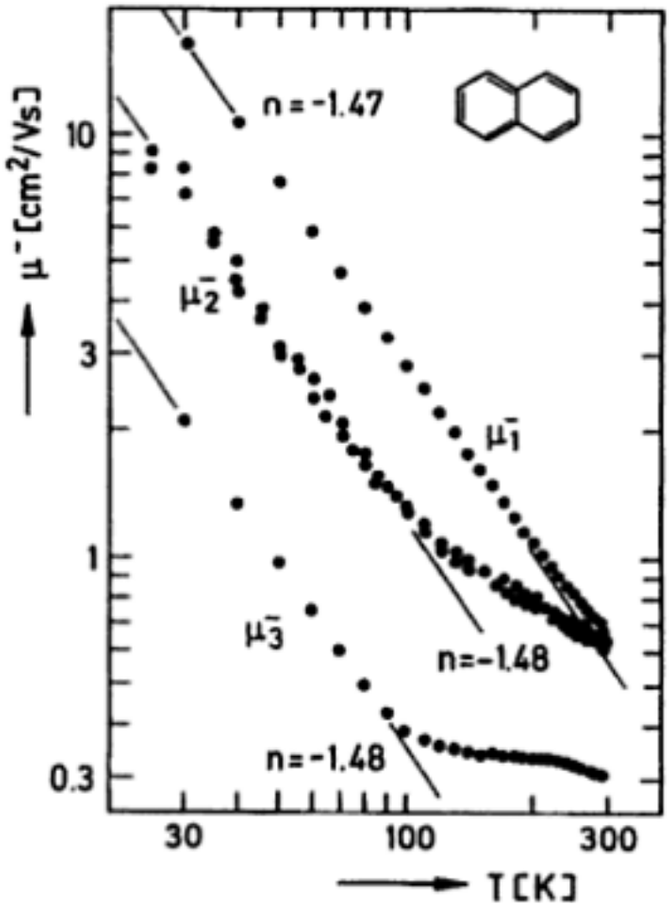
served behavior. Hence, Bloch-type states *do* appear to occur in some molecular crystals in certain temperature ranges. Above 100 K in naphthalene, however, another mechanism appears to limit the mobility. The usual alternative to transport via Bloch-type states is the hopping of localized carriers. It would

for solid-state physicists. But perhaps their most interesting aspect, however, is the persistent challenge that organic crystals afford to conventional theories of transport in solids. After over two decades of intensive investigation, the temperature and field dependence of the mobilities of charge carriers in van der Waals crystals remain unexplained by extant models of either band or hopping transport. Thus, organic materials con-

« one of the major outstanding mysteries in solid-state physics »
→ the problem is still open

[Duke & Schein, Physics Today 1980]

Carrier mobility: TOF vs FET

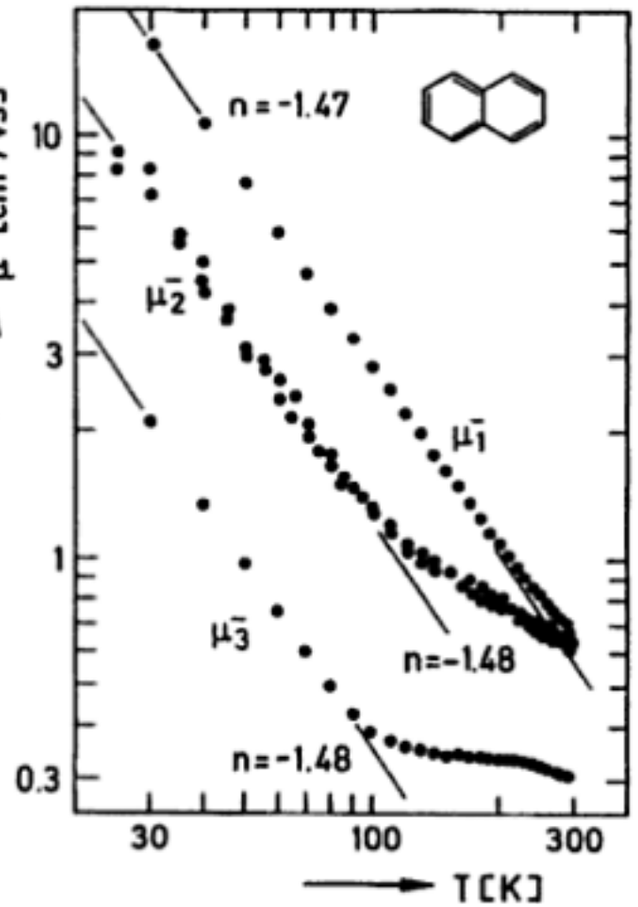


Naphthalene, TOF

[Karl SynthMet 03]

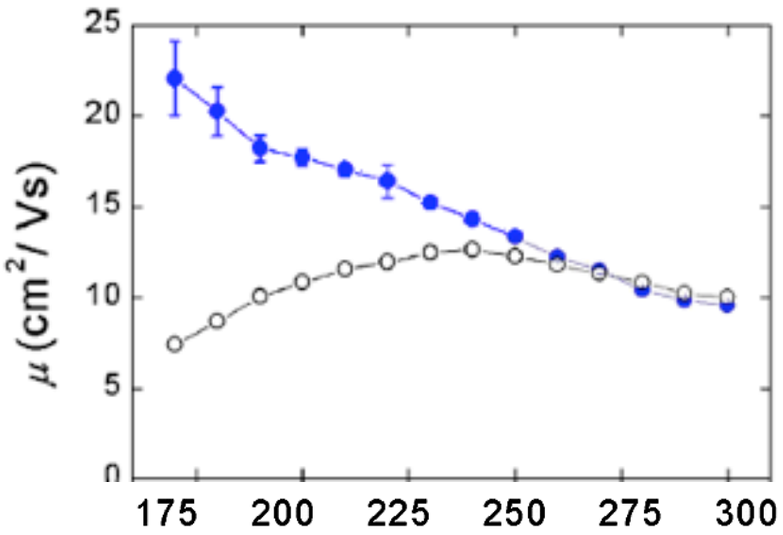
- carrier mobility in Time of Flight experiments shows ubiquitous “band-like” power-law dependence on temperature
- moderate values of mobility, ~ 10 cmˆ2/Vs
- In FETs, clear “band-like” behavior is only seen in 4 compounds (rubrene is one of them)

Carrier mobility: TOF vs FET



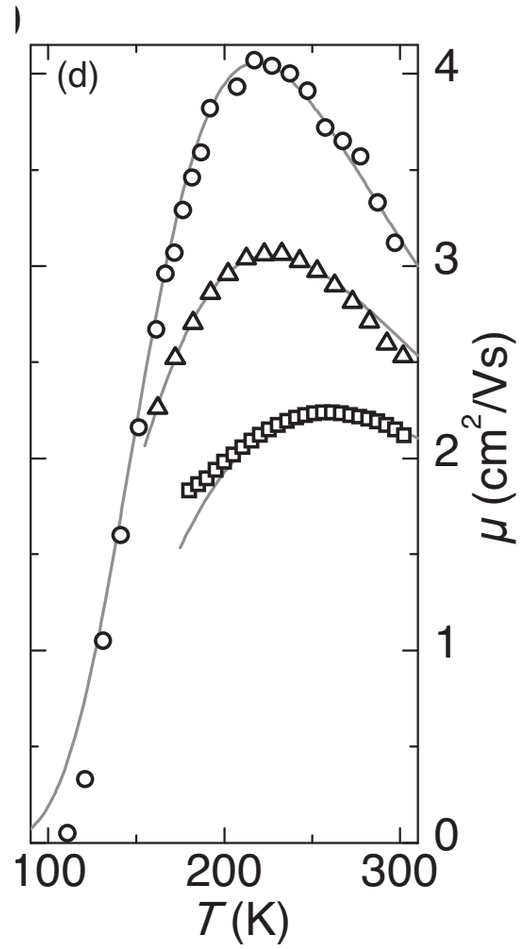
Naphthalene, TOF

[Karl SynthMet 03]



Rubrene FET, Hall mobility

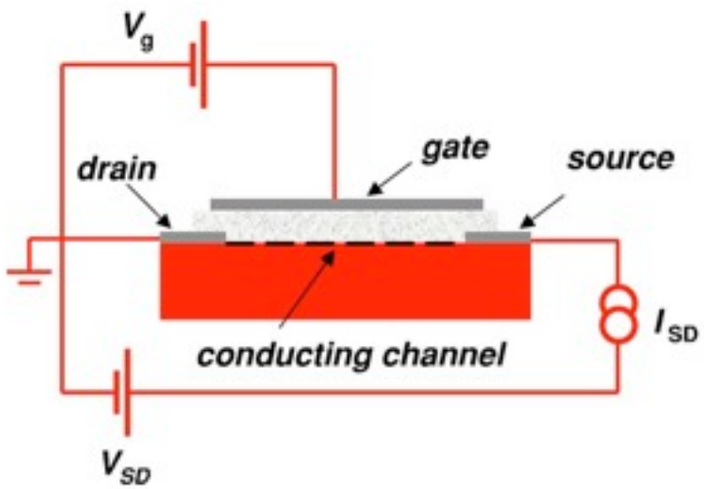
[Podzorov PRL05]



PDIF-CN2 FET

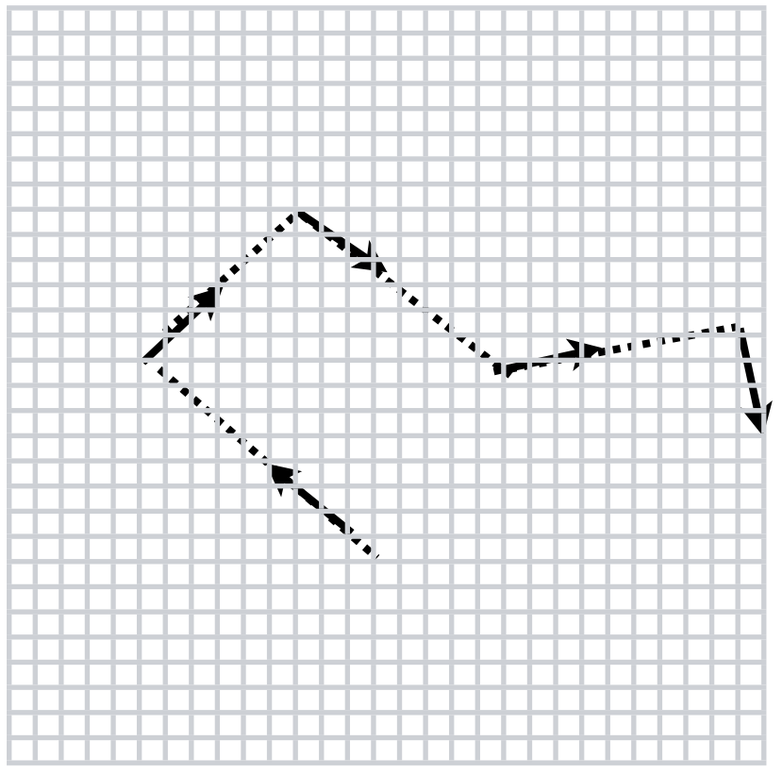
[Minder Adv Mat (2012)]

- carrier mobility in Time of Flight experiments shows ubiquitous “band-like” power-law dependence on temperature
- moderate values of mobility, ~ 10 cmˆ2/Vs
- In FETs, clear “band-like” behavior is only seen in 4 compounds (rubrene is one of them)



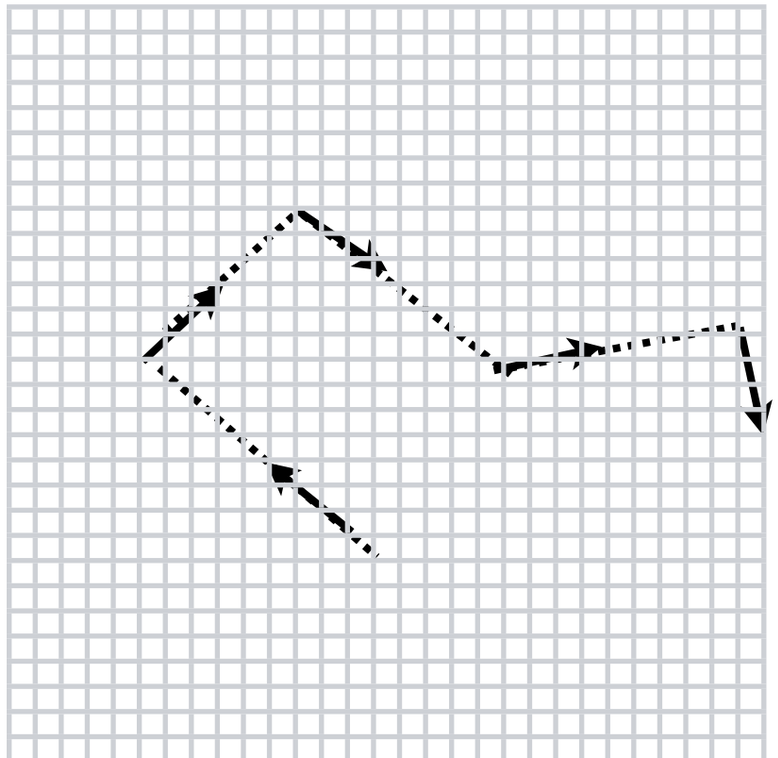
Problem: breakdown of semiclassical assumption

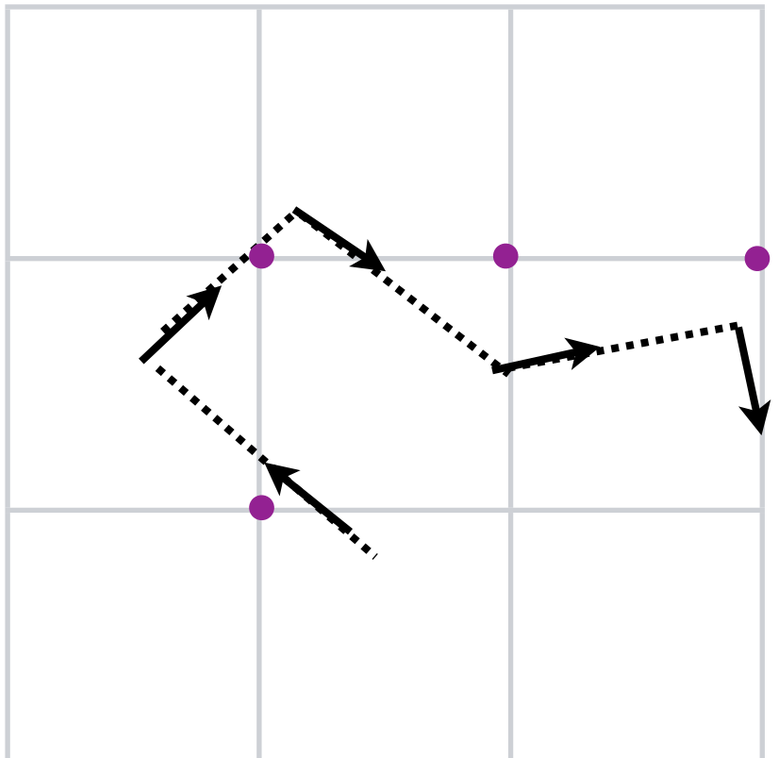
- Boltzmann approach: particles moving freely between (rare) scattering events
- (Quantum) quasiparticle picture must be valid, q.p. well defined
  on a lattice the semiclassical assumption breaks when mean free path ≈ lattice spacing



Problem: breakdown of semiclassical assumption

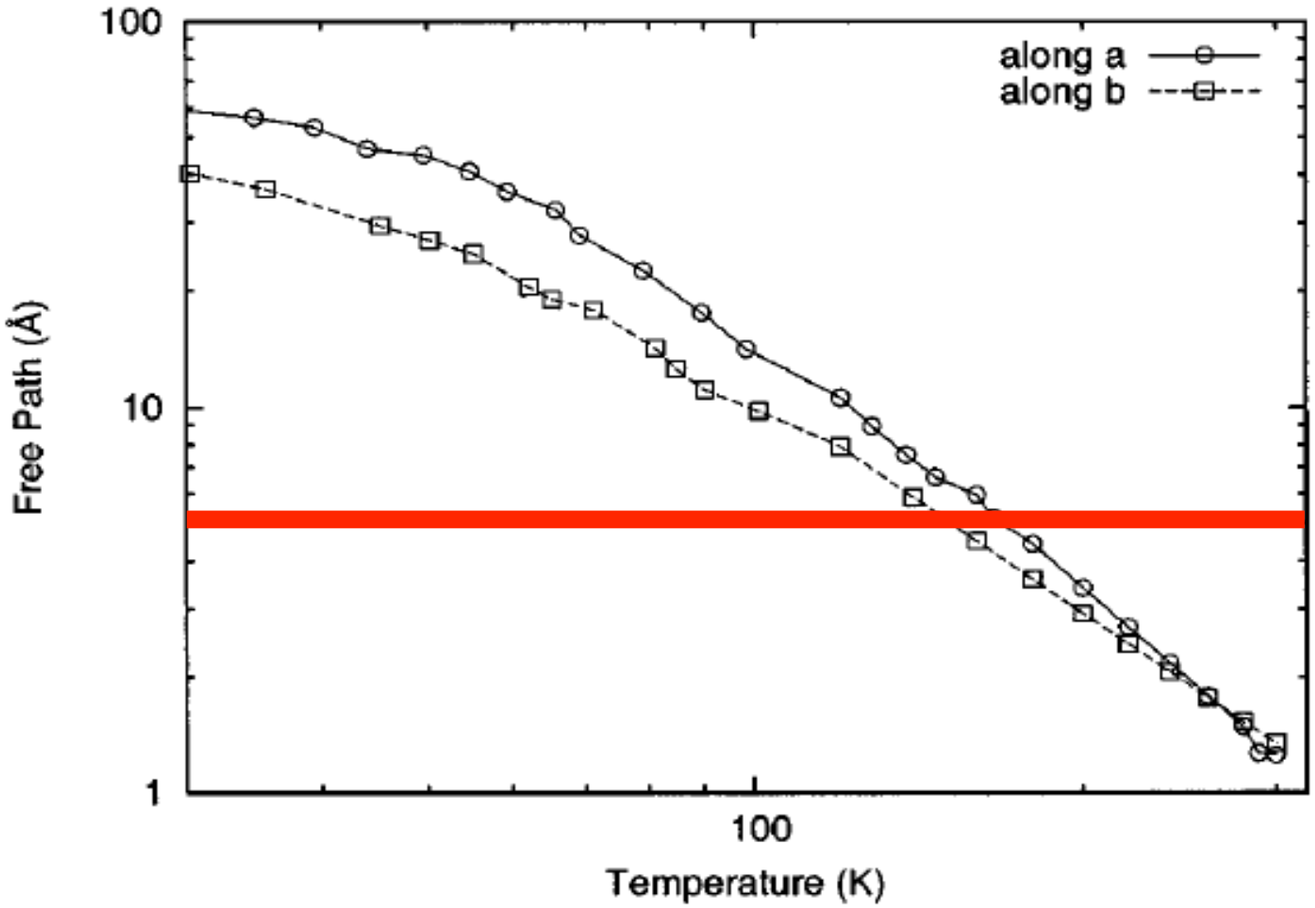
- Boltzmann approach: particles moving freely between (rare) scattering events
- (Quantum) quasiparticle picture must be valid, q.p. well defined
  on a lattice the semiclassical assumption breaks when mean free path ≈ lattice spacing





Problem: breakdown of semiclassical assumption

- Boltzmann approach: particles moving freely between (rare) scattering events
- (Quantum) quasiparticle picture must be valid, q.p. well defined
  on a lattice the semiclassical assumption breaks when mean free path ≈ lattice spacing
- in OSC breakdown of semiclassical assumption occurs around room temperature



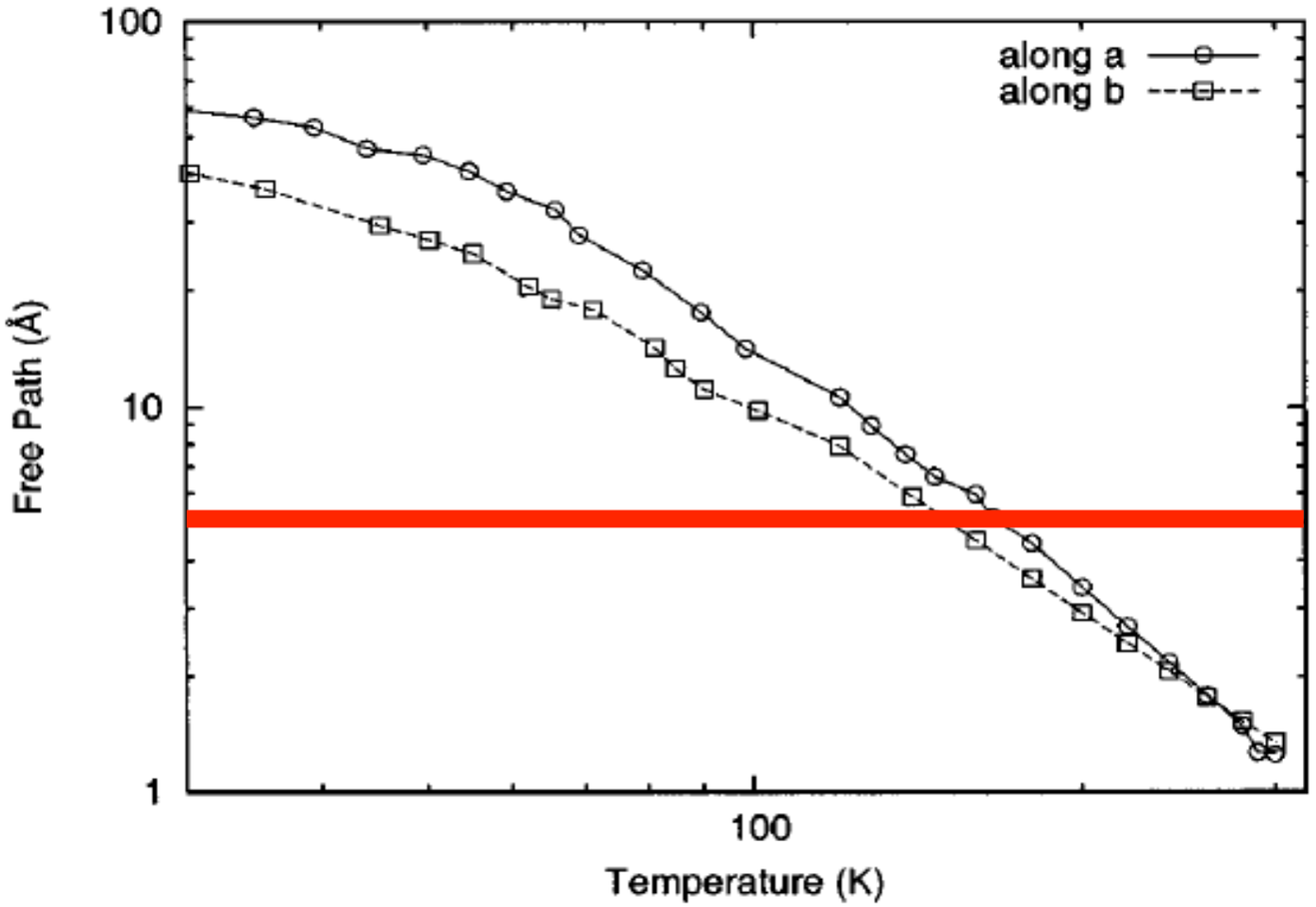
$$\mu_{ij} = (e\lambda/kT)\langle v_i v_j / |\mathbf{v}(\mathbf{k})| \rangle,$$

$l_{\mathrm{mfp}} \sim a$

Extractred from fitting the hole mobility in naphthalene via tight binding band-structure calculations
[Cheng et al. J. Chem. Phys. 118, 3764 (2003)]

Problem: breakdown of semiclassical assumption

- Boltzmann approach: particles moving freely between (rare) scattering events
- (Quantum) quasiparticle picture must be valid, q.p. well defined
  on a lattice the semiclassical assumption breaks when mean free path ≈ lattice spacing
- in OSC breakdown of semiclassical assumption occurs around room temperature



Extractred from fitting the hole mobility in naphthalene via tight binding band-structure calculations
[Cheng et al. J. Chem. Phys. 118, 3764 (2003)]

$$\mu_{ij} = (e\lambda/kT)\langle v_i v_j / |\mathbf{v}(\mathbf{k})| \rangle,$$

$$l_{\mathrm{mfp}} \sim a$$

we need new tools to describe this regime, beyond Boltzmann theory

Optical properties

- Rubrene optical conductivity
- light quasiparticles (m*≈1-2) from sum rules
- BUT: unexplained peak at 500 cm^{-1}=61meV

-> indicative of localization

Light Quasiparticles Dominate Electronic Transport in Molecular Crystal Field-Effect Transistors

Z. Q. Li,[1,*] V. Podzorov,[2] N. Sai,[1,3] M. C. Martin,[4] M. E. Gershenson,[2] M. Di Ventra,[1] and D. N. Basov[1]

PRL 99, 016403 (2007) PHYSICAL REV

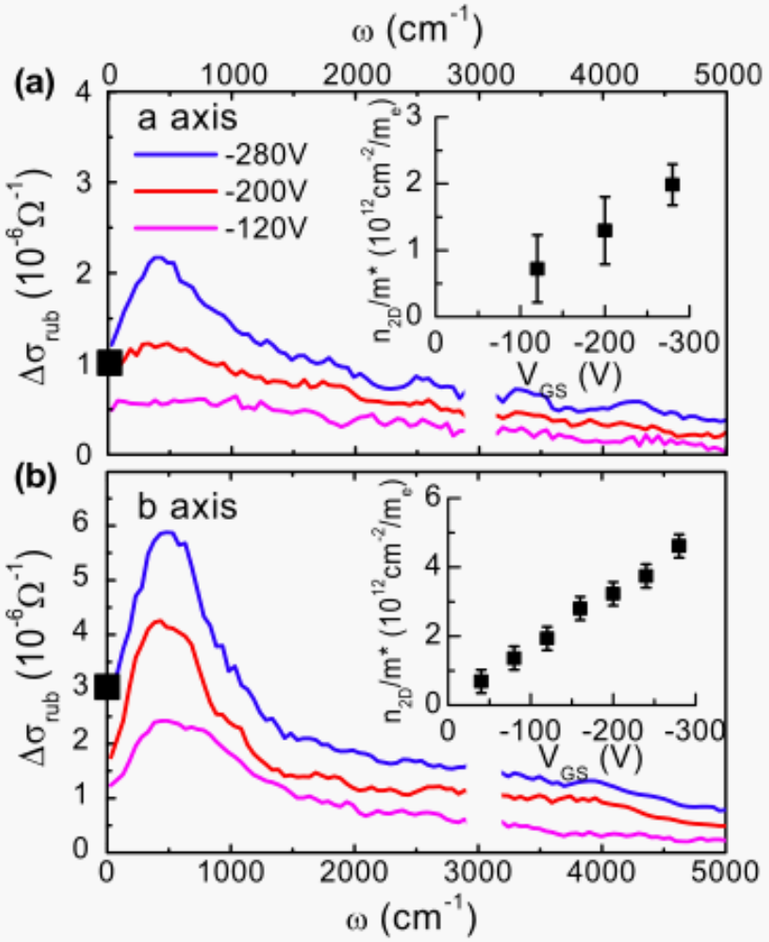
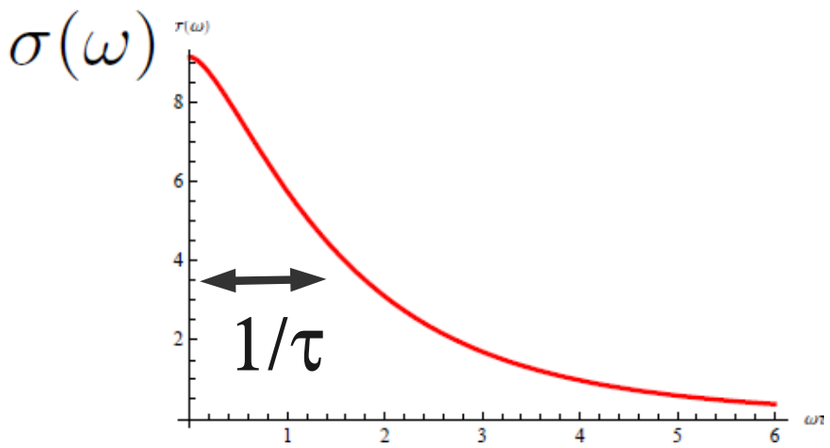


FIG. 3 (color online). The optical conductivity of the two-dimensional system of field-induced charges at the rubrene-parylene interface $\Delta\sigma_{\mathrm{rub}}(\omega)$ at different gate voltages V_{GS} at 300 K. (a) $E \parallel a$-axis data. (b) $E \parallel b$-axis data. Black squares on the left axes: dc conductivity at −280 V. Insets: the evolution of the spectral weight $n_{2\mathrm{D}}/m^{\star}$ with V_{GS}.

Optical properties

- Rubrene optical conductivity
- light quasiparticles (m*≈1-2) from sum rules
- BUT: unexplained peak at 500 cm^{-1}=61meV

-> indicative of localization



Drude model
(free carriers)

Light Quasiparticles Dominate Electronic Transport in Molecular Crystal Field-Effect Transistors

Z. Q. Li,[1,*] V. Podzorov,[2] N. Sai,[1,3] M. C. Martin,[4] M. E. Gershenson,[2] M. Di Ventra,[1] and D. N. Basov[1]

PRL 99, 016403 (2007) PHYSICAL REV

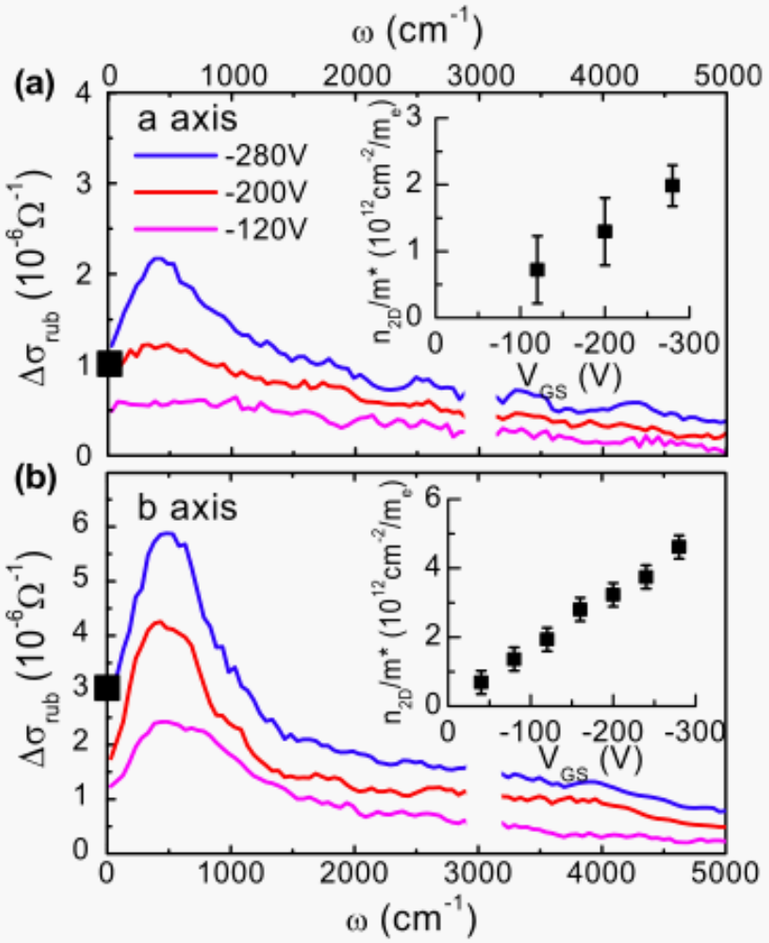


FIG. 3 (color online). The optical conductivity of the two-dimensional system of field-induced charges at the rubrene-parylene interface $\Delta\sigma_{rub}(\omega)$ at different gate voltages V_{GS} at 300 K. (a) $E \parallel a$-axis data. (b) $E \parallel b$-axis data. Black squares on the left axes: dc conductivity at −280 V. Insets: the evolution of the spectral weight n_{2D}/m^* with V_{GS}.

Outline

- Introduction: something's wrong with the "common wisdom"

- **ARPES**:

the role of intramolecular vibrations and disorder

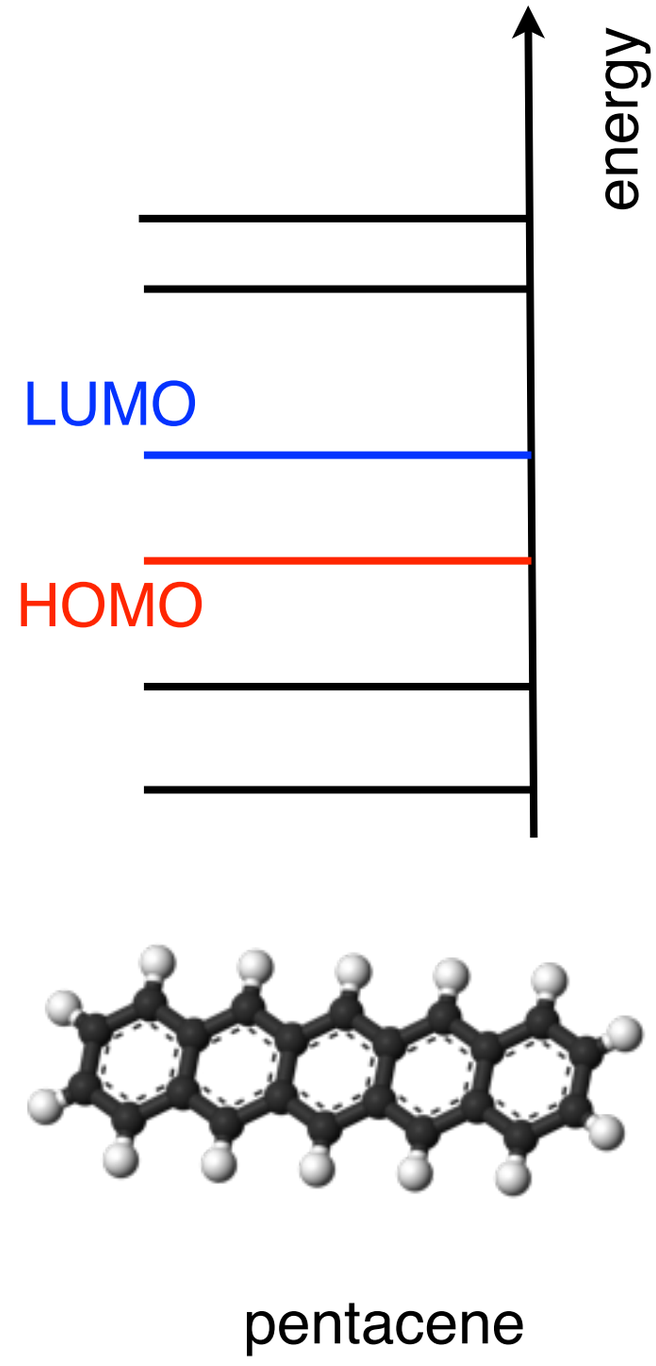
- **Transport properties:**

the role of intermolecular vibrations and the concept of transient localization

- **Kubo formula revisited**: carrier diffusivity from optical experiments

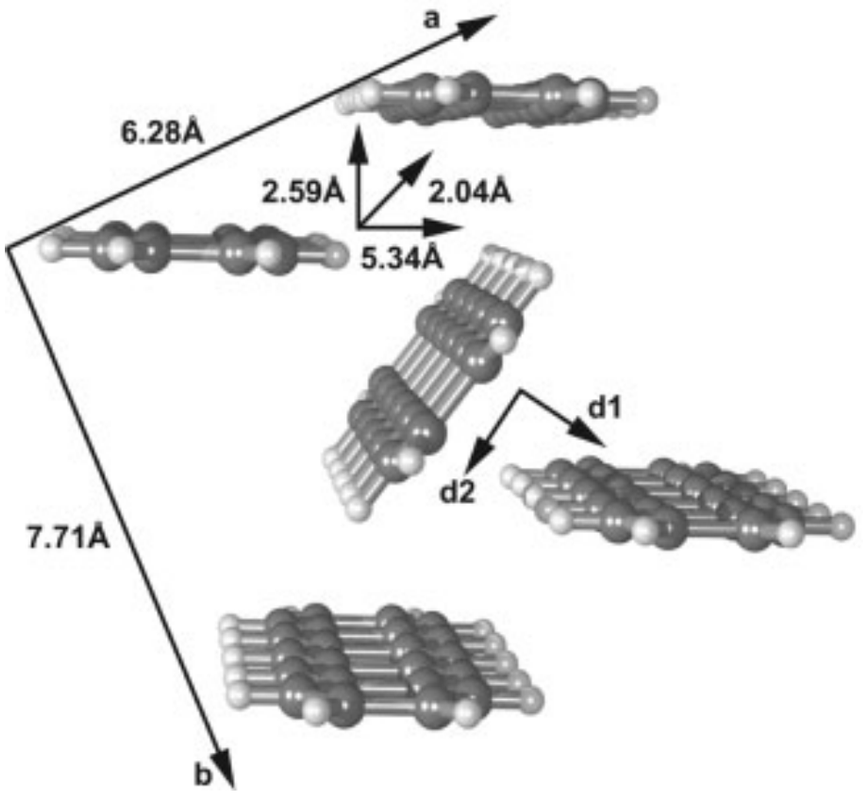
- Concluding remarks

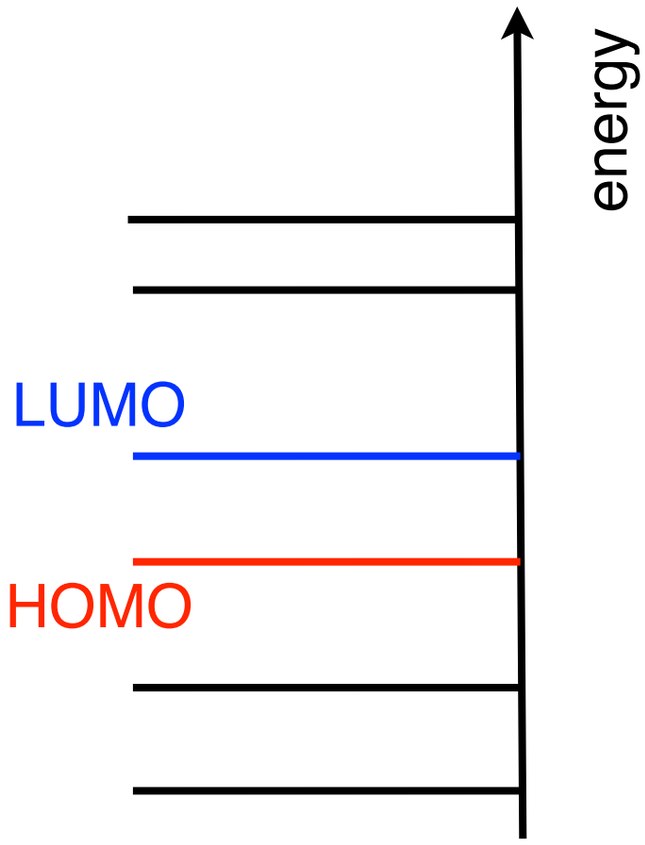
The molecular crystal: band structure

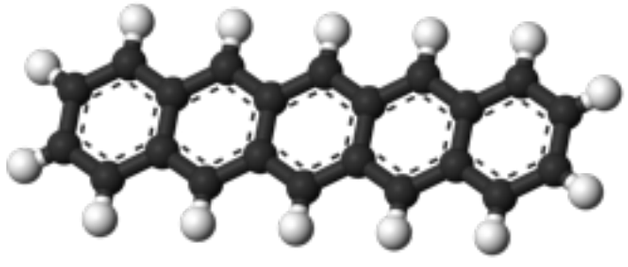


pentacene

The molecular crystal: band structure

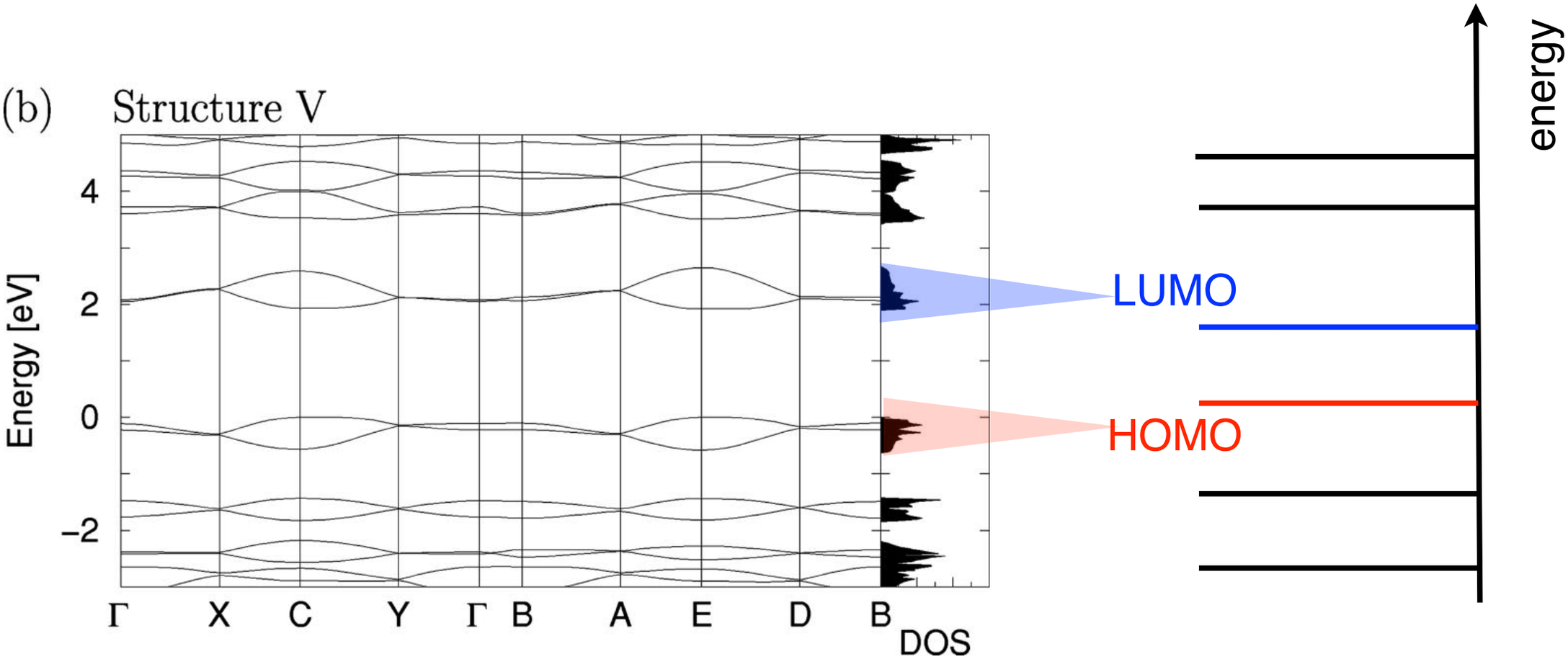






pentacene

The molecular crystal: band structure

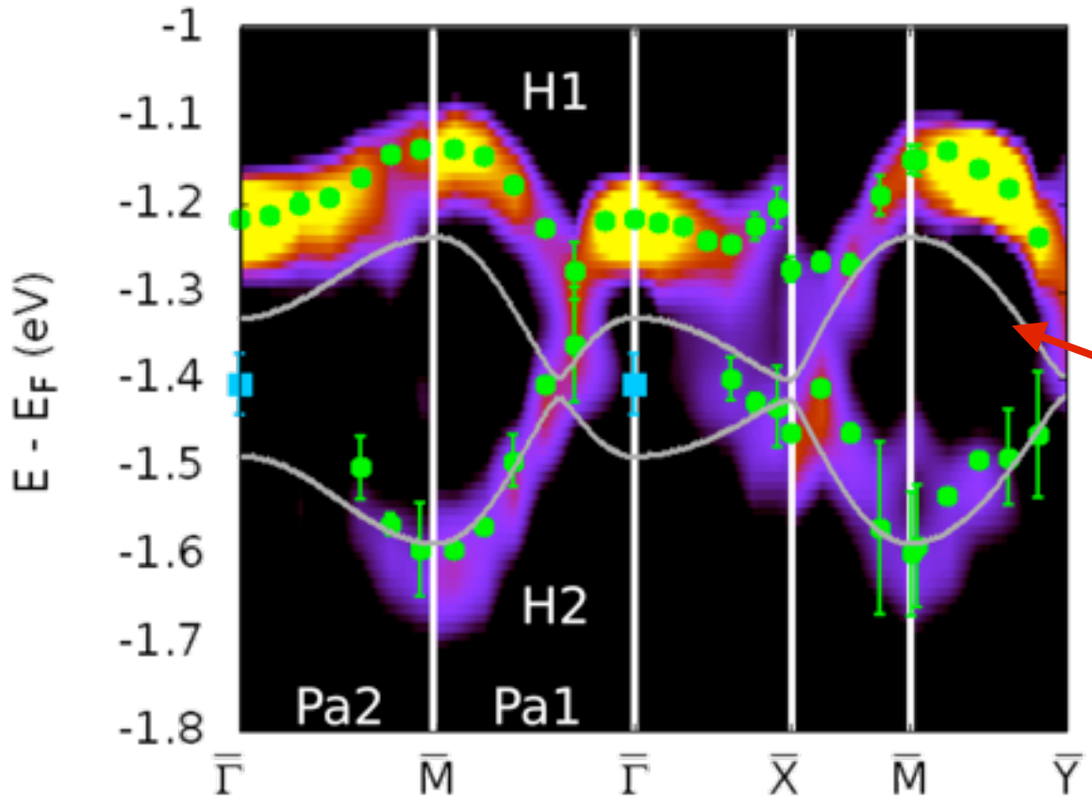


[GW, M. Tiago and S. Louie, PRB (2003)]

- Van der Waals bonding
  → Narrow bands, W~350 meV, “persistence of molecular identity”
- Two inequivalent Pn sites result in two HOMO bands H1,H2

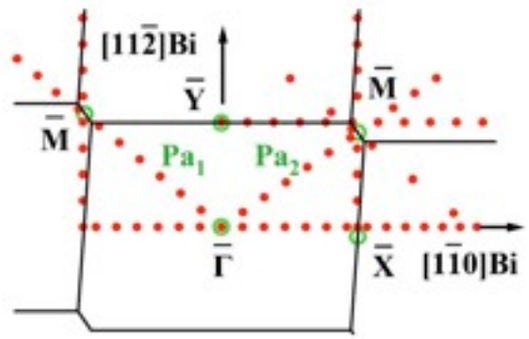
ARPES Pentacene: Expt. vs *ab initio*

[S. Ciuchi, R. C. Hatch, H. Höchst, C. Faber, X. Blase, S. Fratini, PRL (2012) to appear]



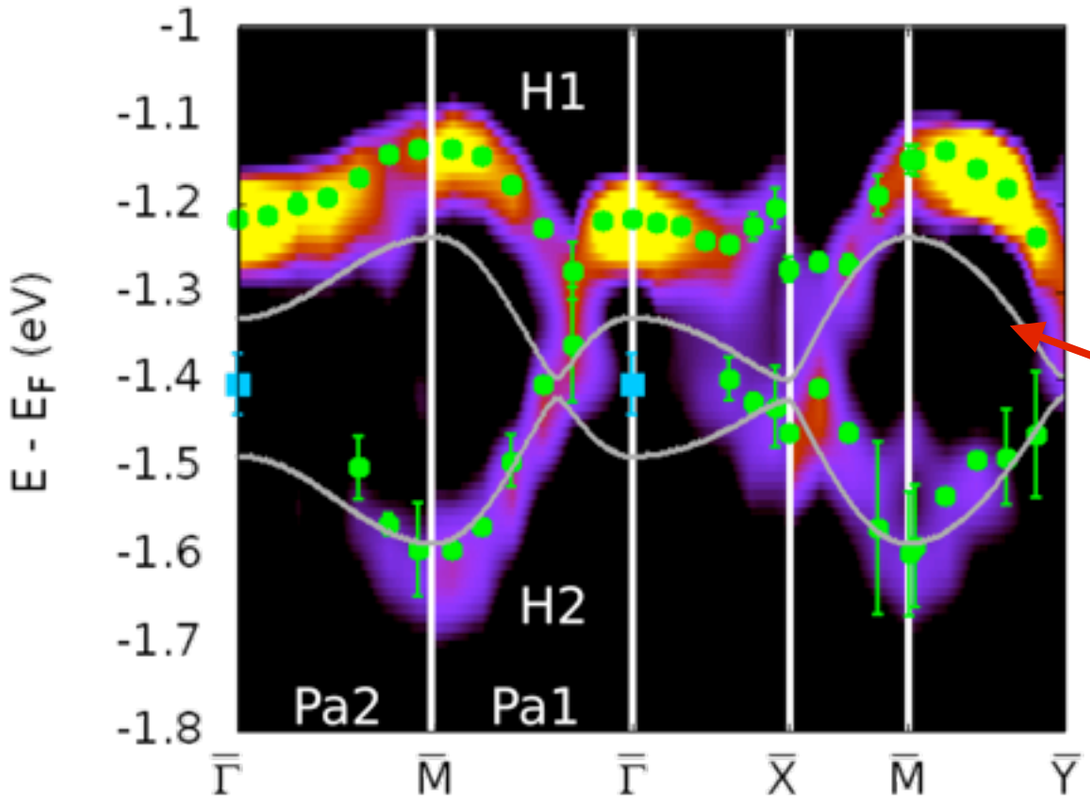
Crystalline film on Bi(001) substrate
HOMO band dispersion at T=75K

ab initio band structure



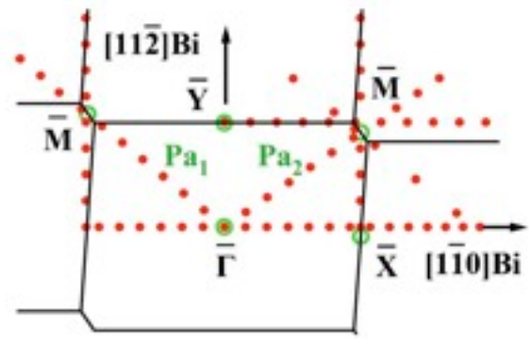
ARPES Pentacene: Expt. vs *ab initio*

[S. Ciuchi, R. C. Hatch, H. Höchst, C. Faber, X. Blase, S. Fratini, PRL (2012) to appear]



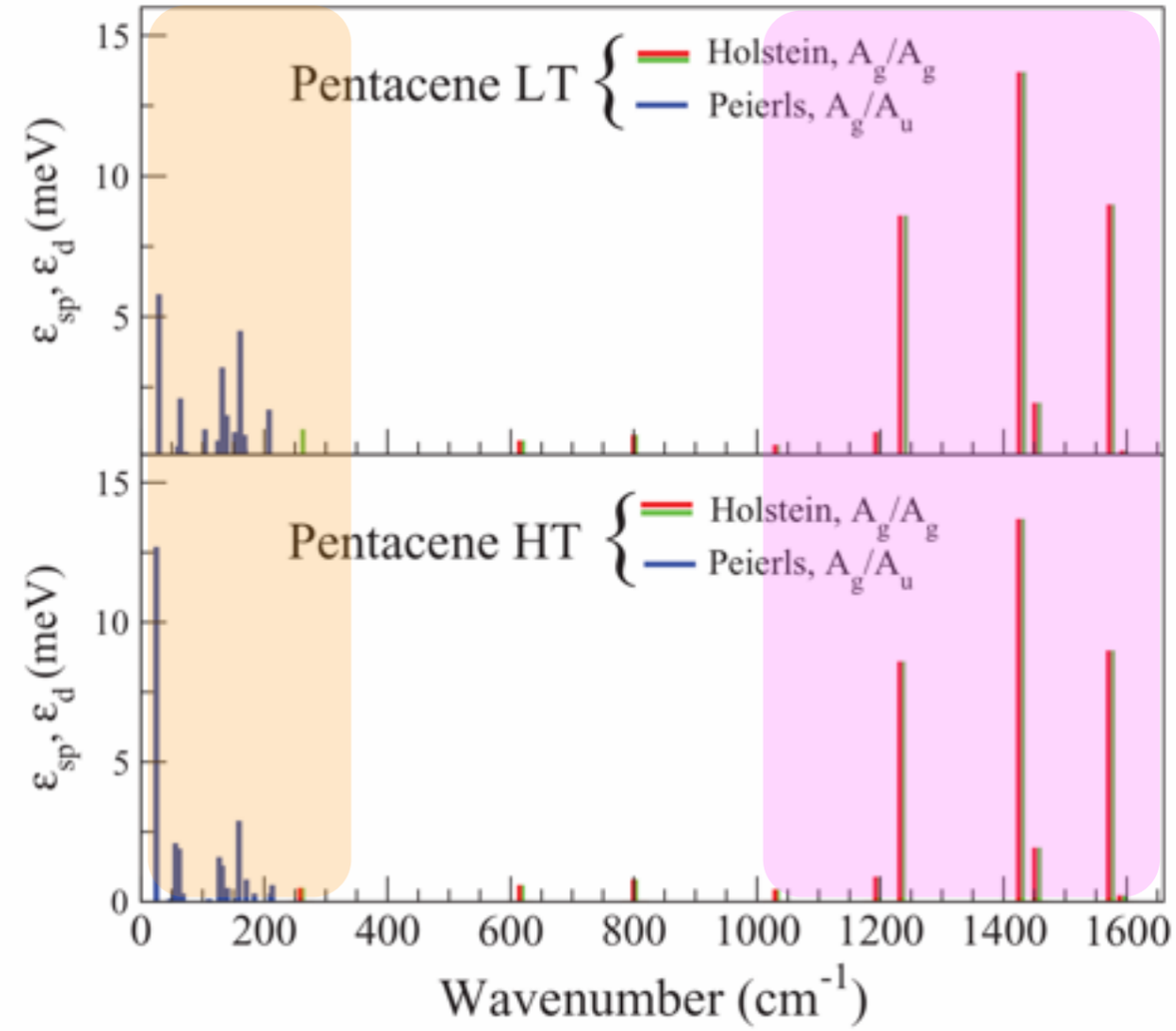
Crystalline film on Bi(001) substrate
HOMO band dispersion at T=75K

ab initio band structure

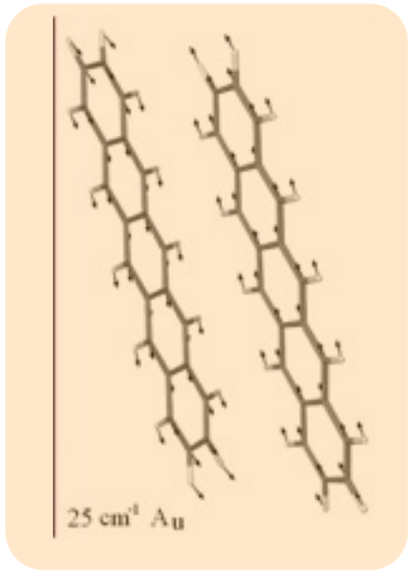


- *ab initio* calculations never fully agree with experiment (even GW)
- Unpredicted large H1/H2 separation systematically observed in all recent ARPES measurements in clean organic semiconductors (Pn and rubrene)
- Experimental bandwidth is **W = 450±15 meV >>** calculated **W= 350±5 meV (DFT,GW)**
- peaks are extremely broad --> interactions!

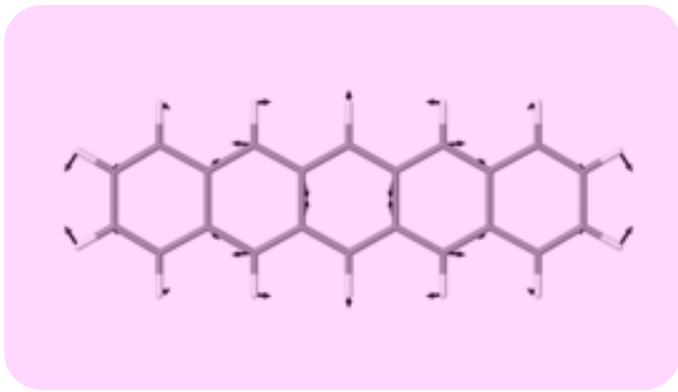
Interactions with molecular vibrations



Peierls



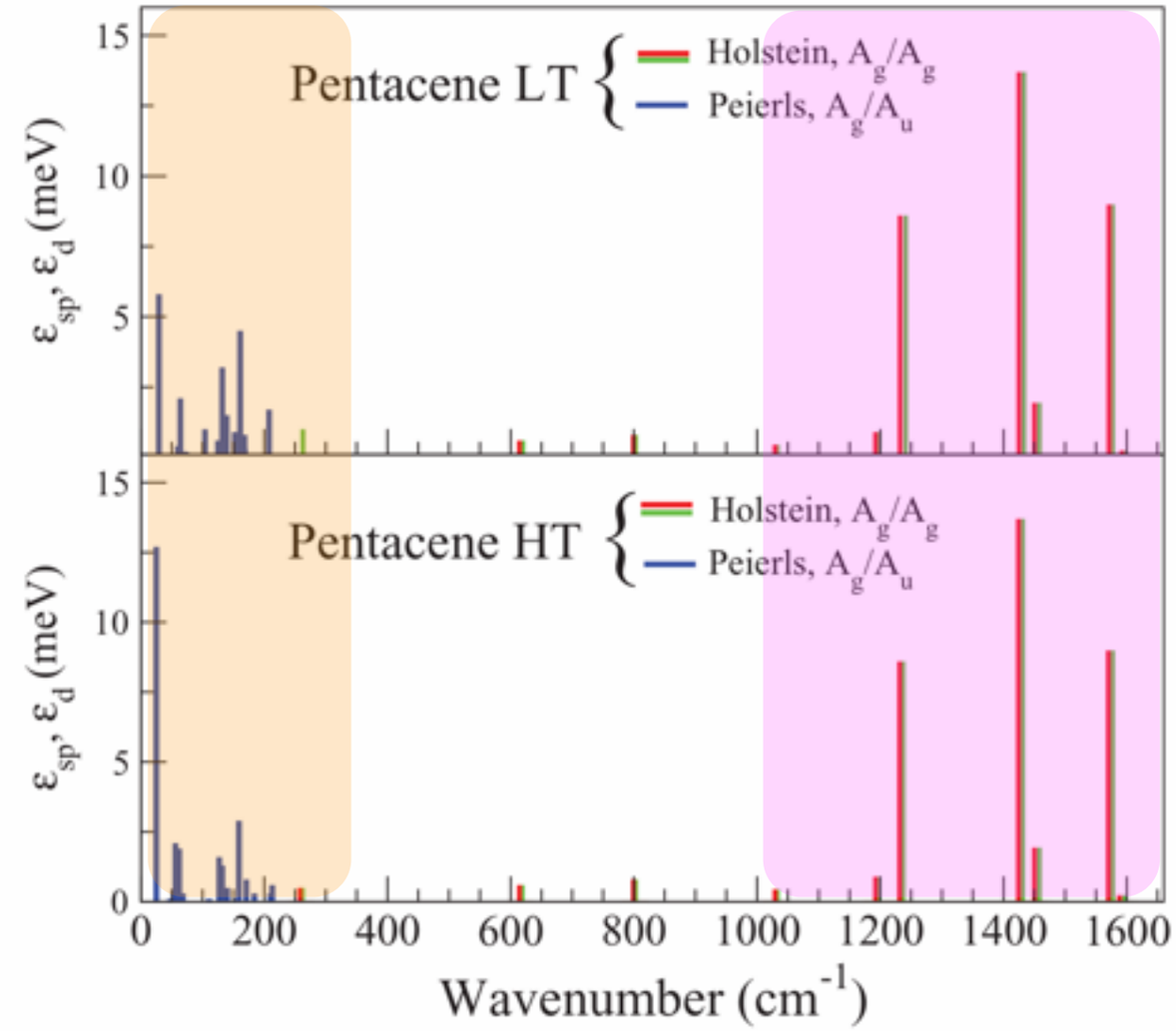
Holstein



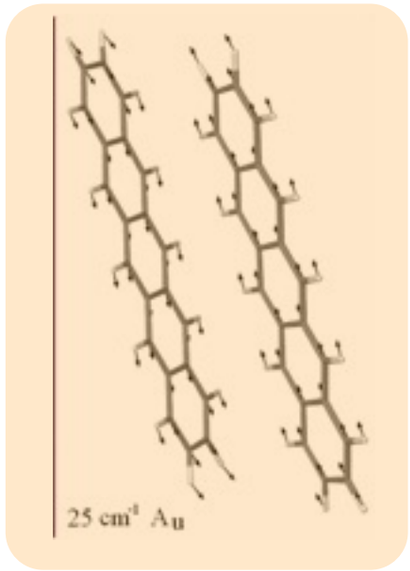
by courtesy of A. Girlando

INDO Calculations by [A. Girlando, et al., J. Chem. Phys. 135, 084701 (2011)]

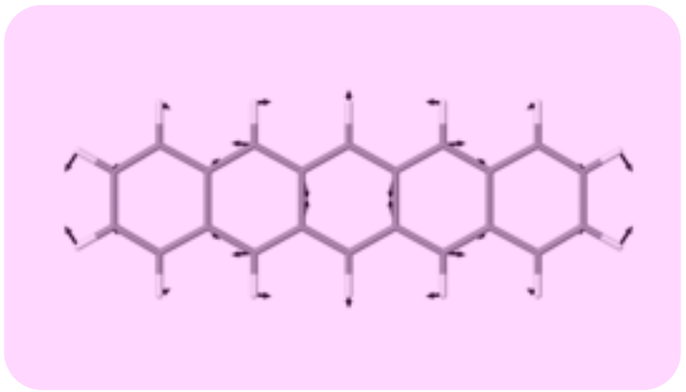
Interactions with molecular vibrations



Peierls



Holstein

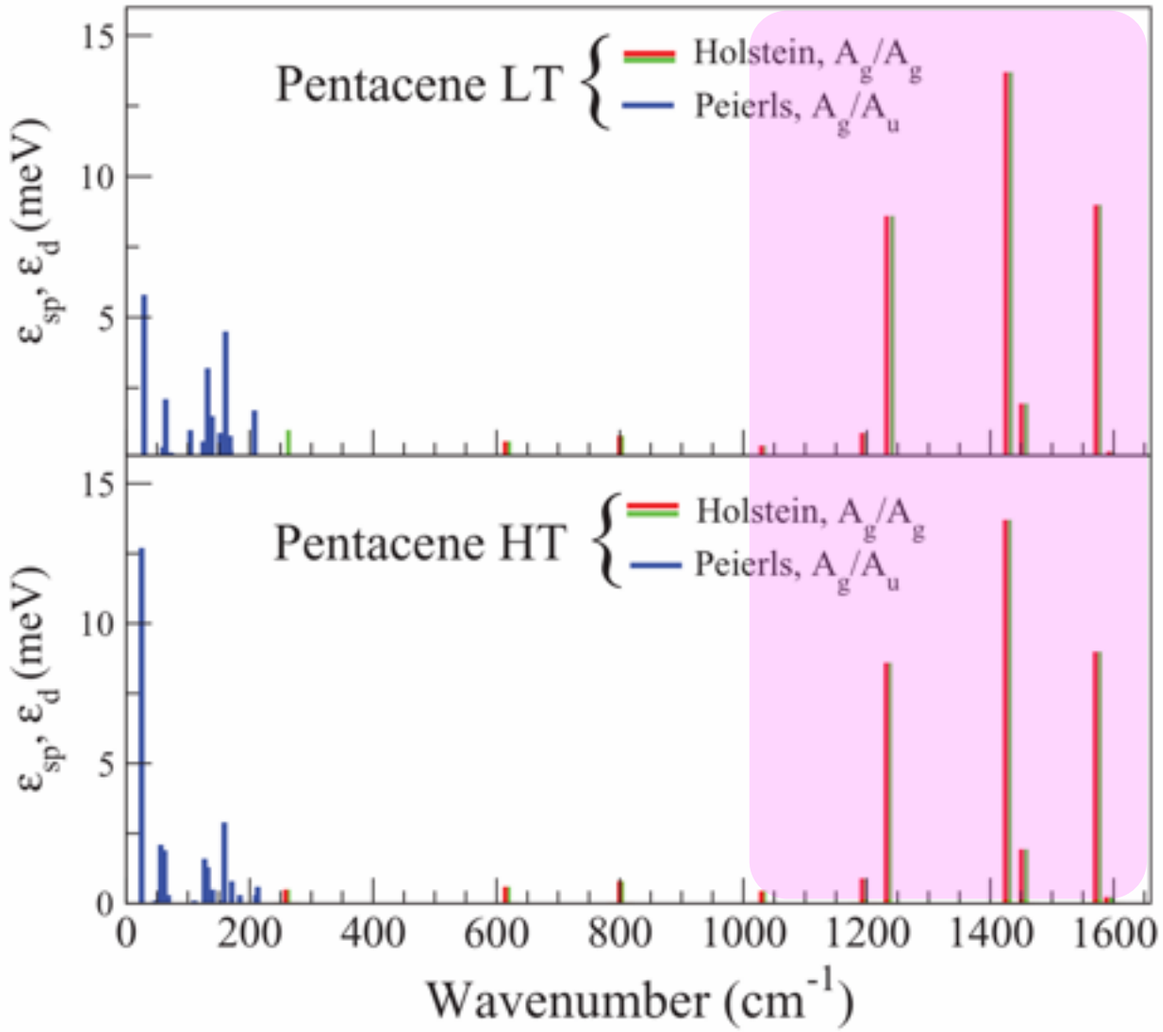


by courtesy of A. Girlando

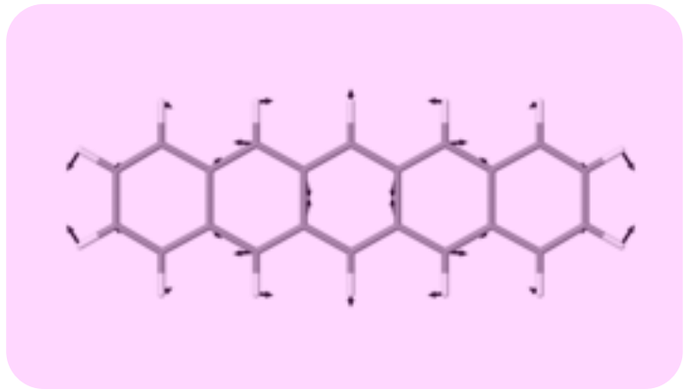
INDO Calculations by [A. Girlando, et al., J. Chem. Phys. 135, 084701 (2011)]

- separation of energy scales between low energy intermolecular modes and high energy intramolecular modes
- Intramolecular (Holstein) FAST: $\omega_0 \approx 120\text{-}200$meV ≈ bandwidth W
- Intermolecular (Periels) SLOW: $\omega_0 \approx 3\text{-}20$meV << bandwidth W

Interactions with molecular vibrations



Holstein



by courtesy of A. Girlando

INDO Calculations by [A. Girlando, et al., J. Chem. Phys. 135, 084701 (2011)]

- separation of energy scales between low energy intermolecular modes and high energy intramolecular modes
- Intramolecular (Holstein) FAST: $\omega_0 \approx 120\text{-}200$meV ≈ bandwidth W
- ~~Intermolecular~~ (Periels) SLOW: $\omega_0 \approx 3\text{-}20$meV << bandwidth W

-> below experimental resolution, neglect

DFT+GW+DMFT

[S. Ciuchi, R. C. Hatch, H. Höchst, C. Faber, X. Blase, S. Fratini PRL to appear (2012)]

Holstein model + disorder (Anderson)

ab initio band structure

$$H = \sum_{<ij>} (t_{ij} c_i^+ c_j + h.c.)$$

DFT+GW+DMFT

[S. Ciuchi, R. C. Hatch, H. Höchst, C. Faber, X. Blase, S. Fratini PRL to appear (2012)]

Holstein model + disorder (Anderson)

ab initio band structure

dispersionless molecular vibrations

$$H = \sum_{<ij>} (t_{ij} c_i^+ c_j + h.c.) + \sum_i \Omega(a_i^+ a_i + 1/2)$$

$$+ \sum_i (\ldots)\sqrt{\lambda} c_i^+ c_i (a_i^+ + a_i) + \sum_i \epsilon_i c_i^+ c_i$$

local electron-vibration coupling

gaussian disorder in molecular energy

DFT+GW+DMFT

[S. Ciuchi, R. C. Hatch, H. Höchst, C. Faber, X. Blase, S. Fratini PRL to appear (2012)]

Holstein model + disorder (Anderson)

ab initio band structure — dispersionless molecular vibrations

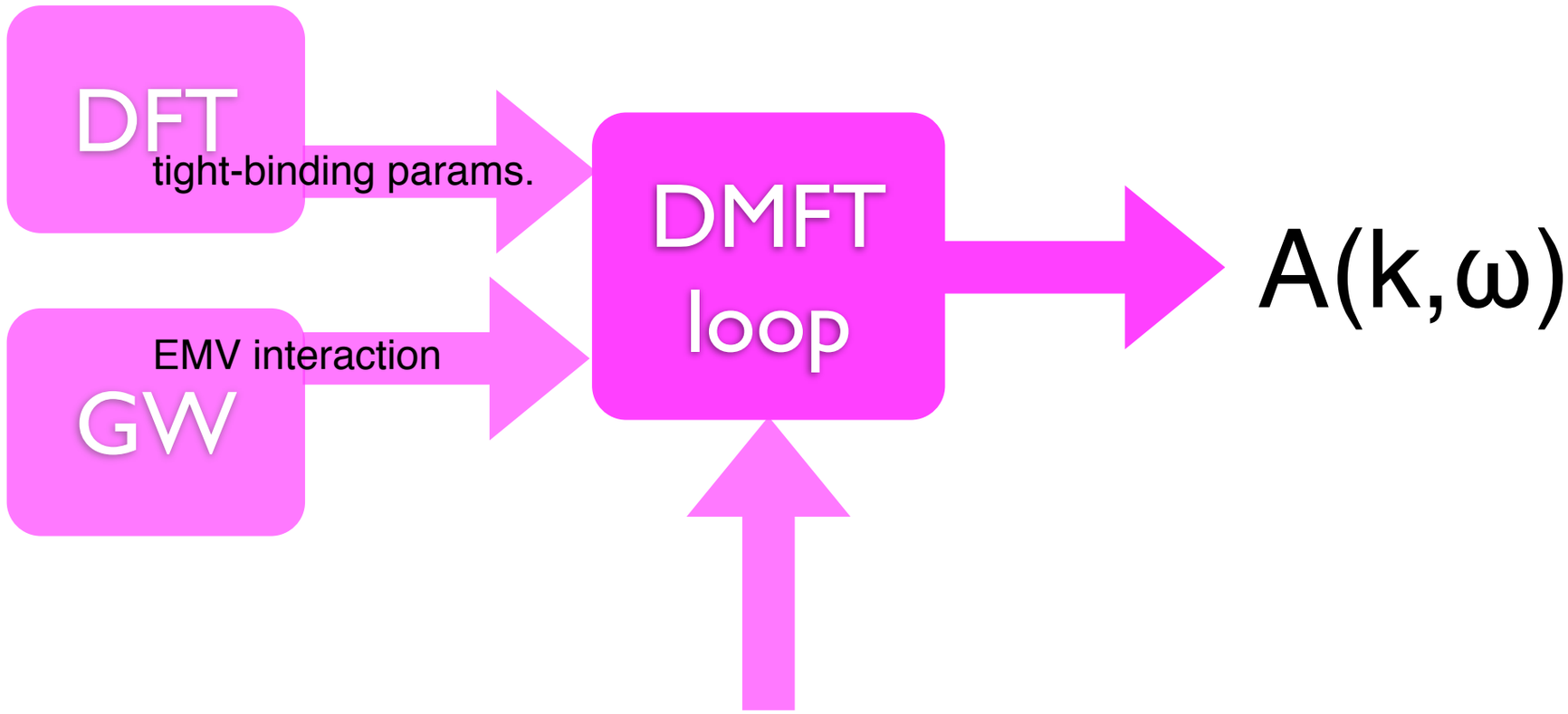
$$H = \sum_{<ij>} (t_{ij} c_i^+ c_j + h.c.) + \sum_i \Omega (a_i^+ a_i + 1/2) + \sum_i (\ldots) \sqrt{\lambda} c_i^+ c_i (a_i^+ + a_i) + \sum_i \epsilon_i c_i^+ c_i$$

local electron-vibration coupling — gaussian disorder in molecular energy

- relevant parameters:
  - noninteracting bandwidth W from DFT/GW
  - Intramolecular Holstein EMV coupling $\lambda = 2 E_P / W = 0.4$ from GW
  - Einstein model phonon frequency $\Omega/W=0.5$
  - Anderson local gaussian disorder variance $\Delta/W=0 \div 0.5$
- Non perturbative approach in both disorder and EMV interaction

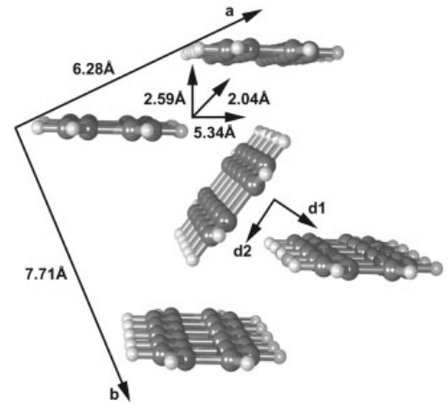
DFT+GW+DMFT

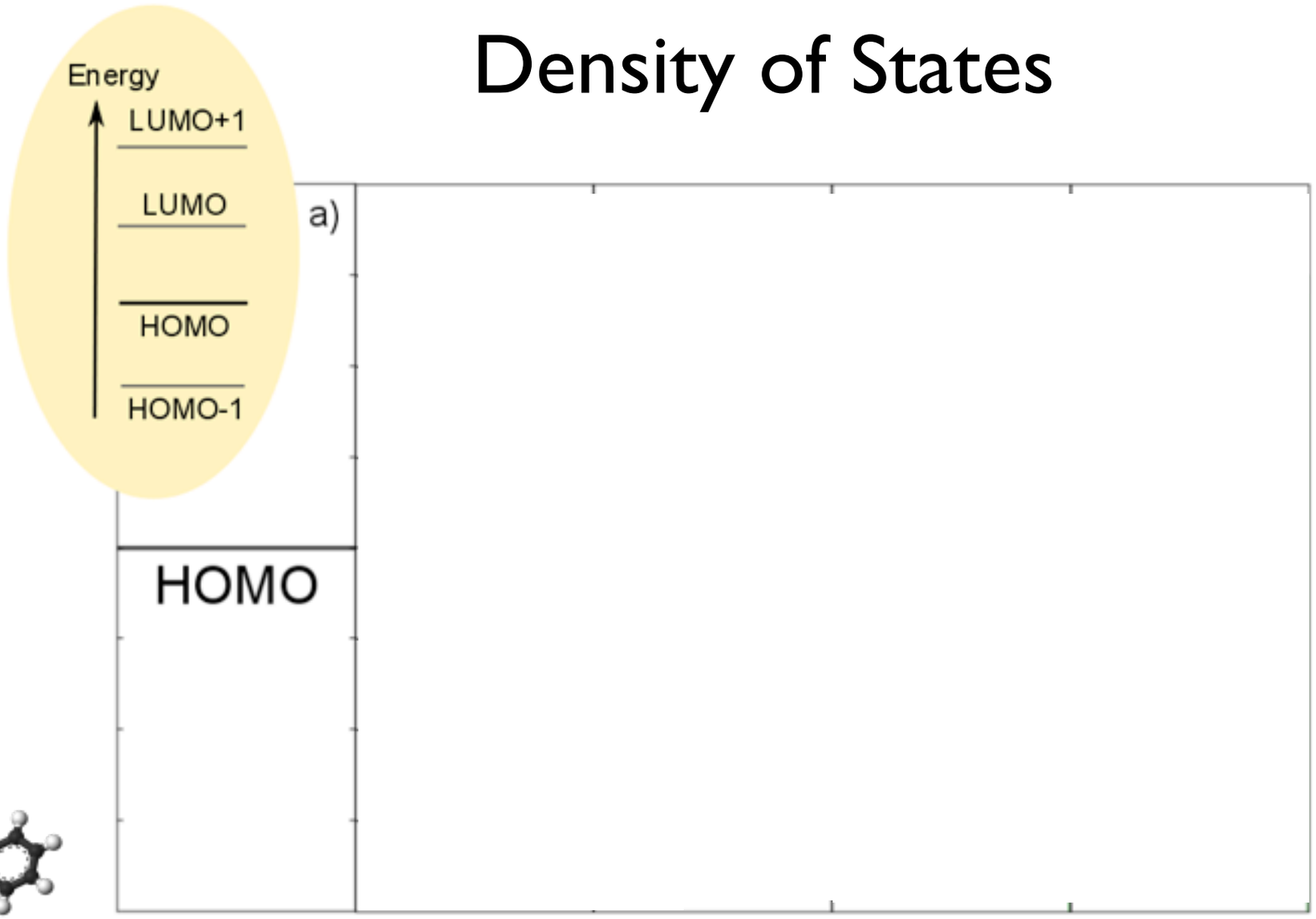
[S. Ciuchi, R. C. Hatch, H. Höchst, C. Faber, X. Blase, S. Fratini PRL to appear (2012)]

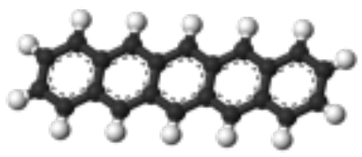


- relevant parameters:
  - noninteracting bandwidth W from DFT/GW
  - Intramolecular Holstein EMV coupling $\lambda = 2 E_P / W = 0.4$ from GW
  - Einstein model phonon frequency $\Omega/W=0.5$
  - Anderson local gaussian disorder variance $\Delta/W=0 \div 0.5$
- Non perturbative approach in both disorder and EMV interaction

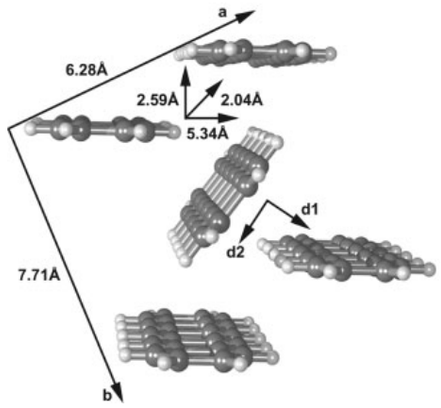
Density of states: between molecules and bands



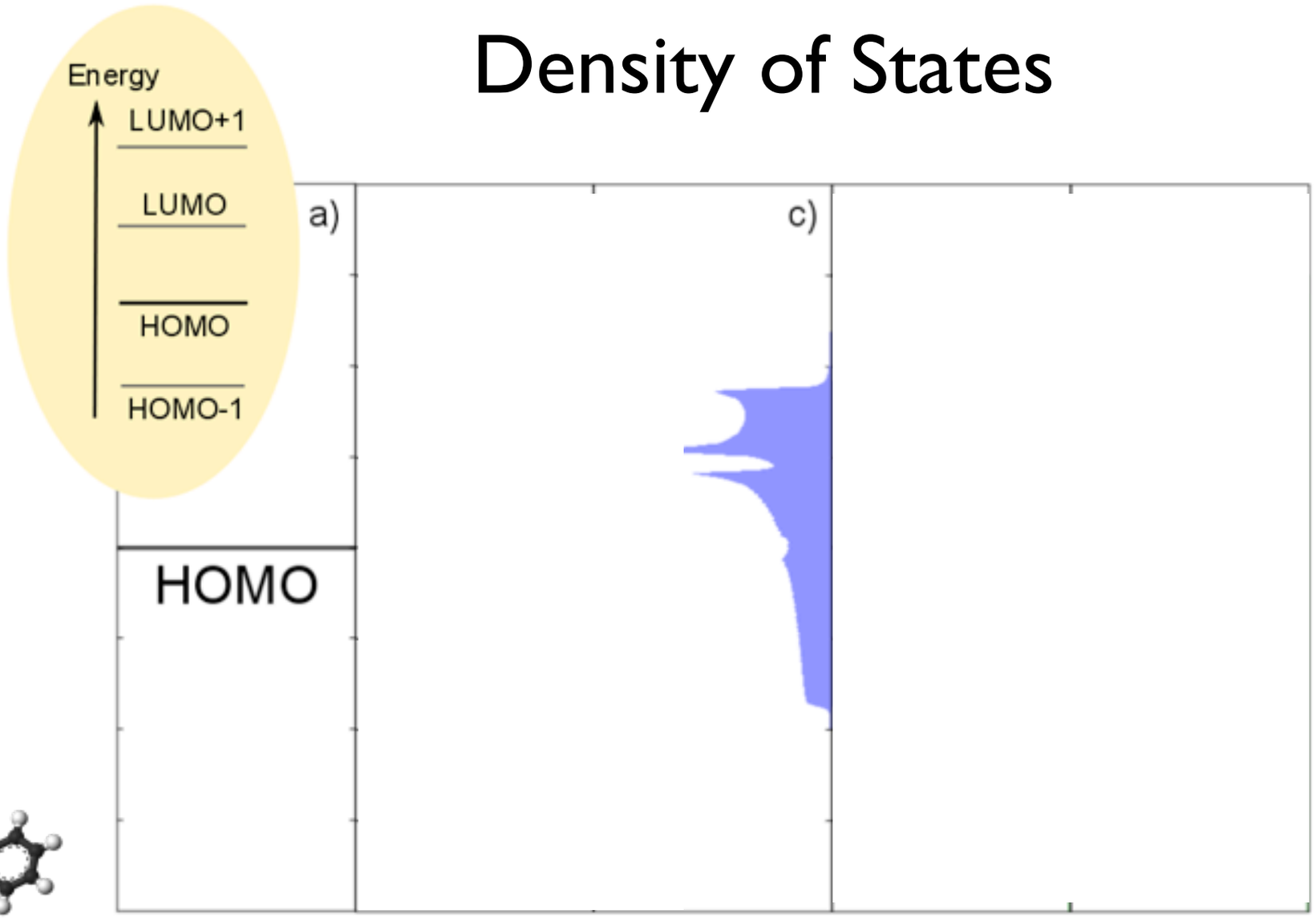


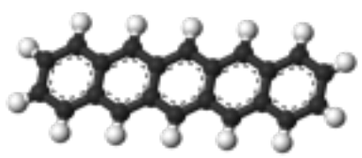


Density of states: between molecules and bands

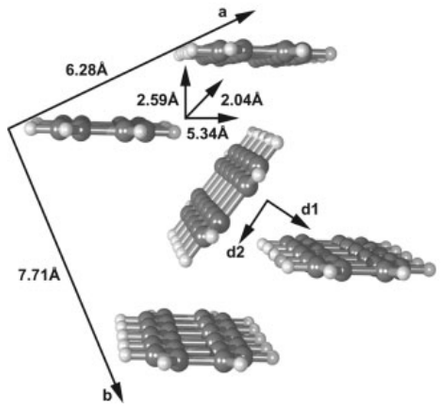


Density of States

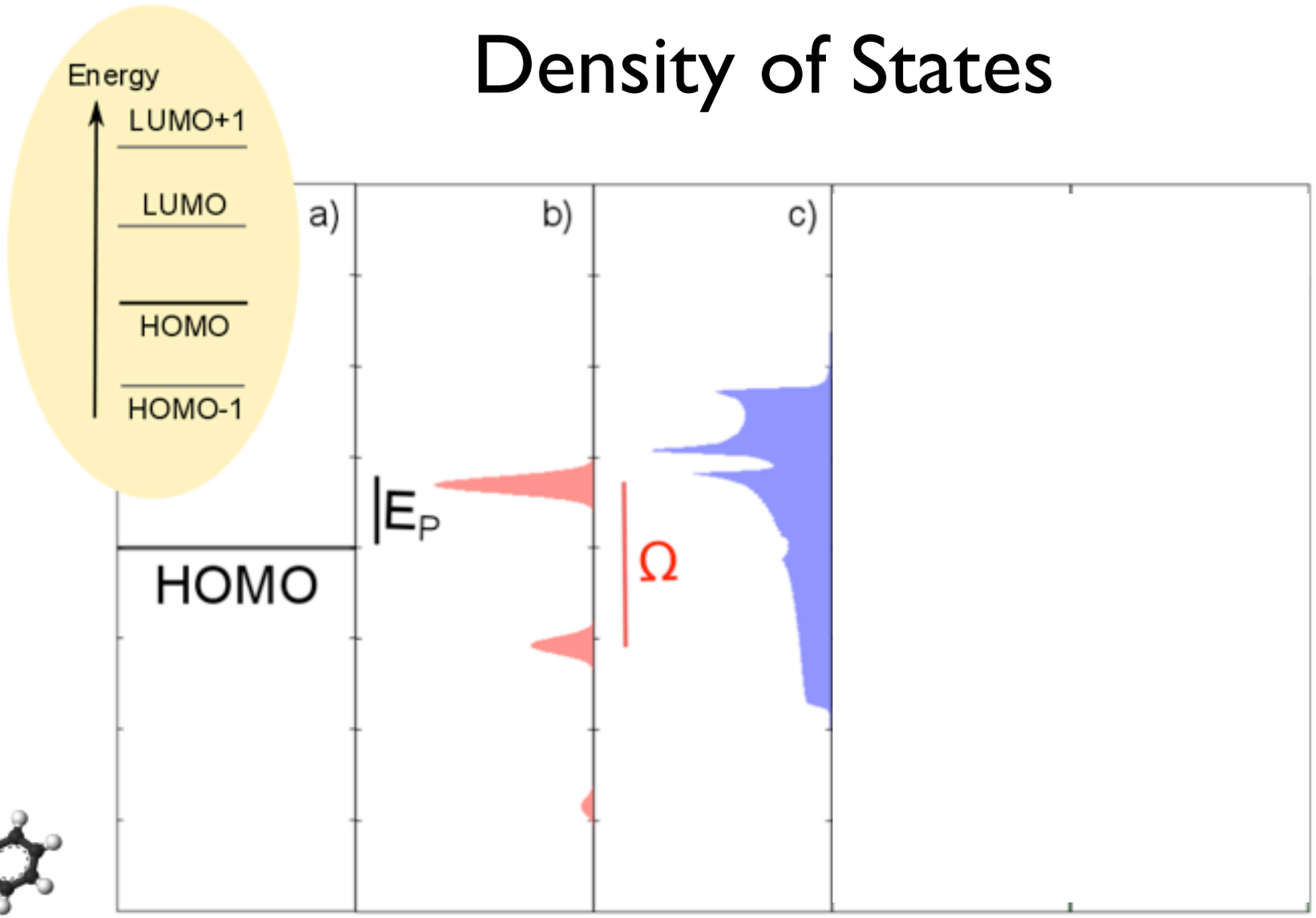


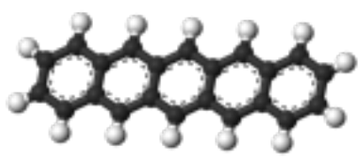


Density of states: between molecules and bands

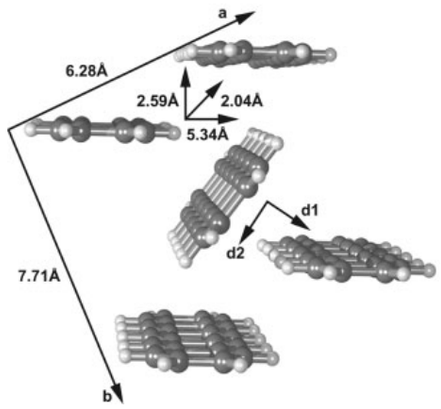


Density of States

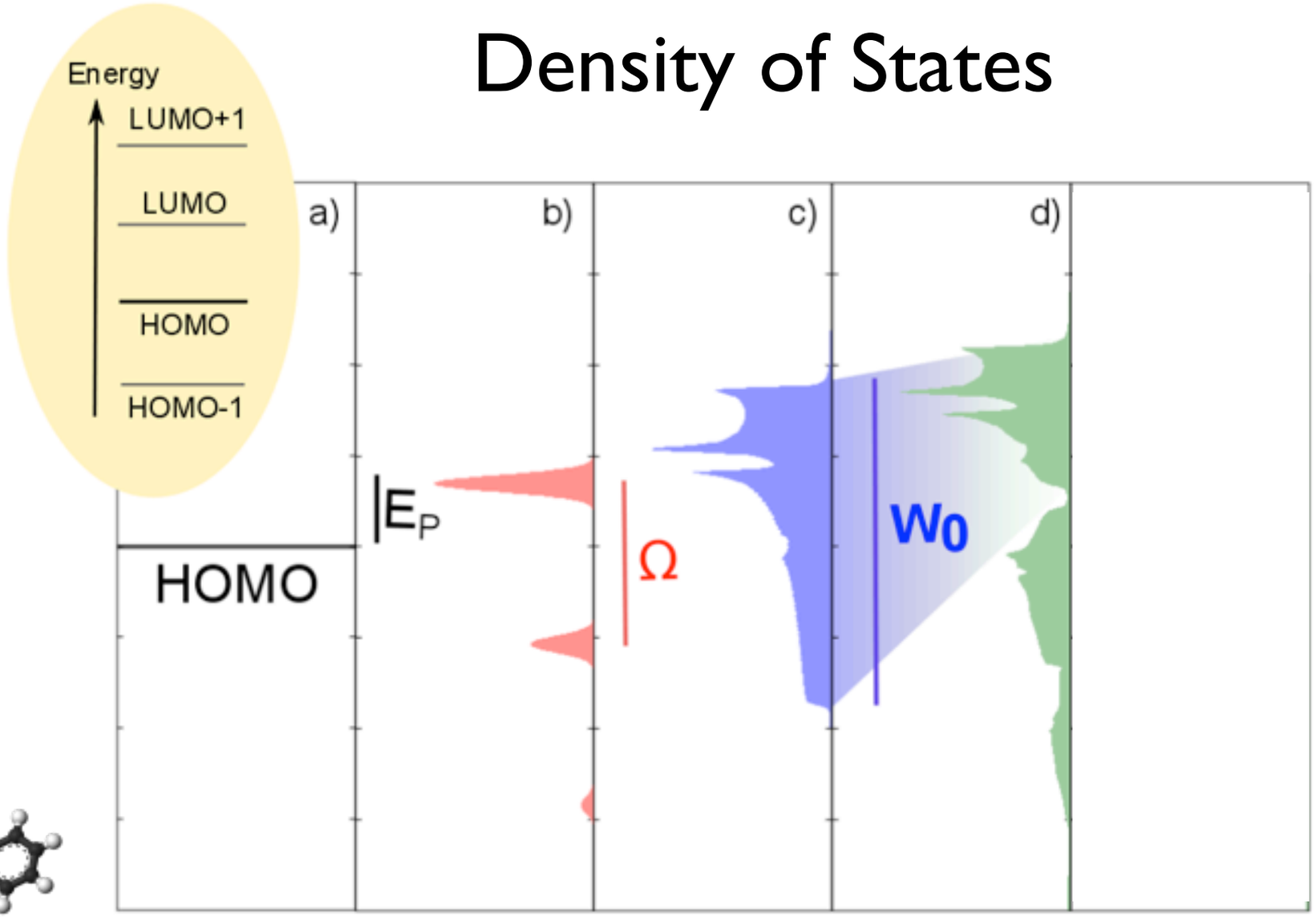


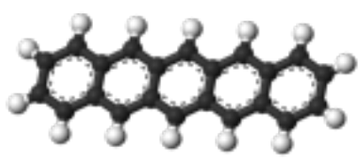


Density of states: between molecules and bands

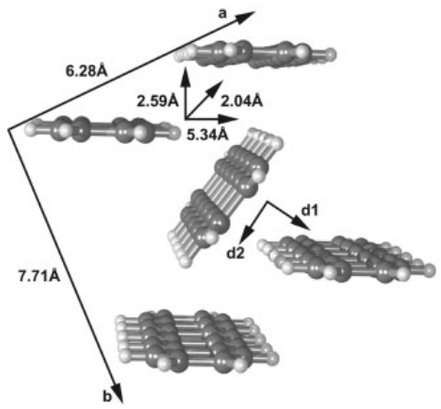


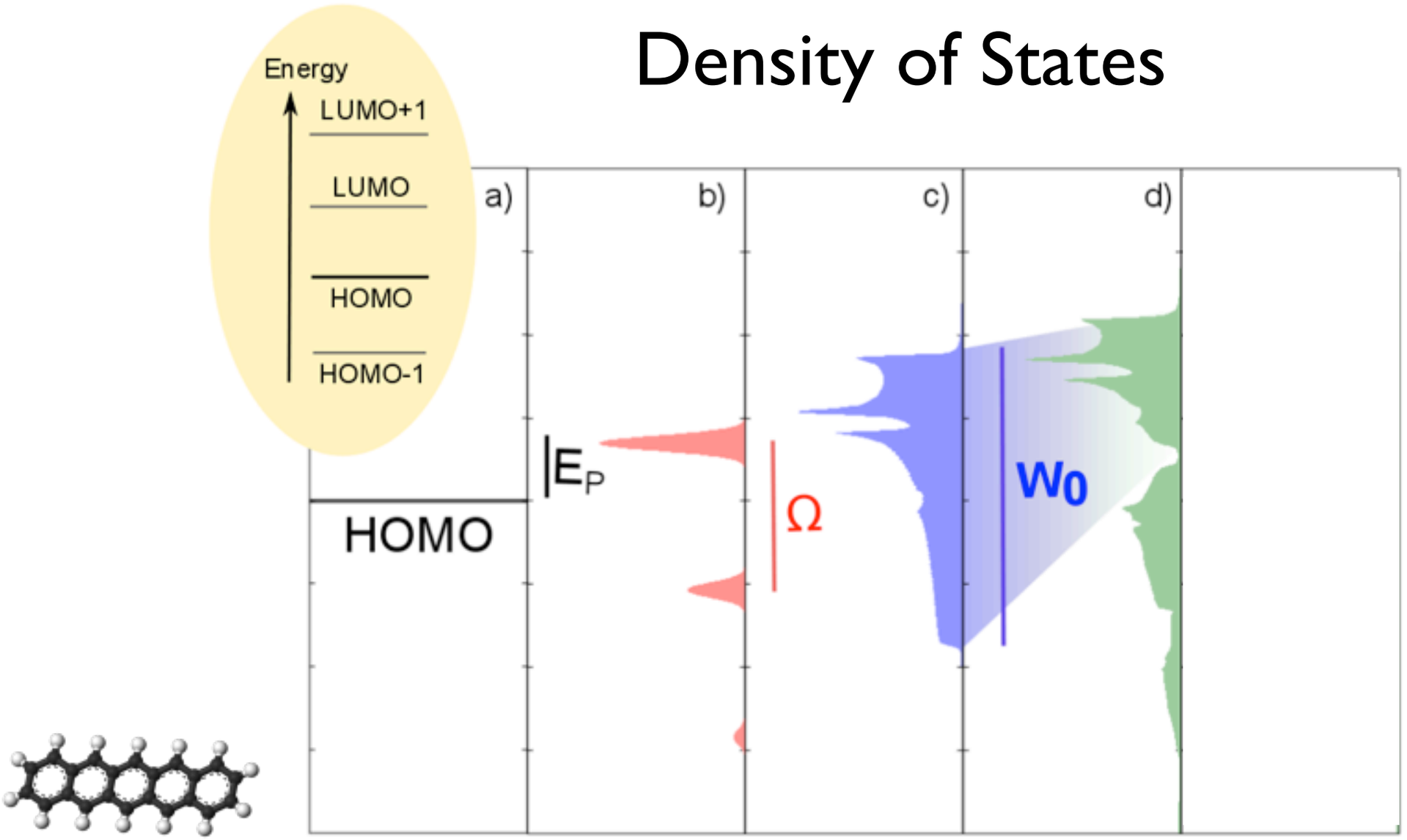
Density of States





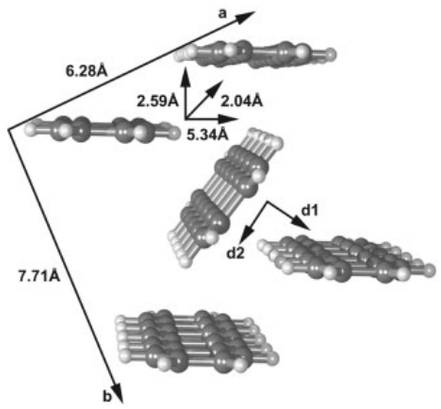
Density of states: between molecules and bands

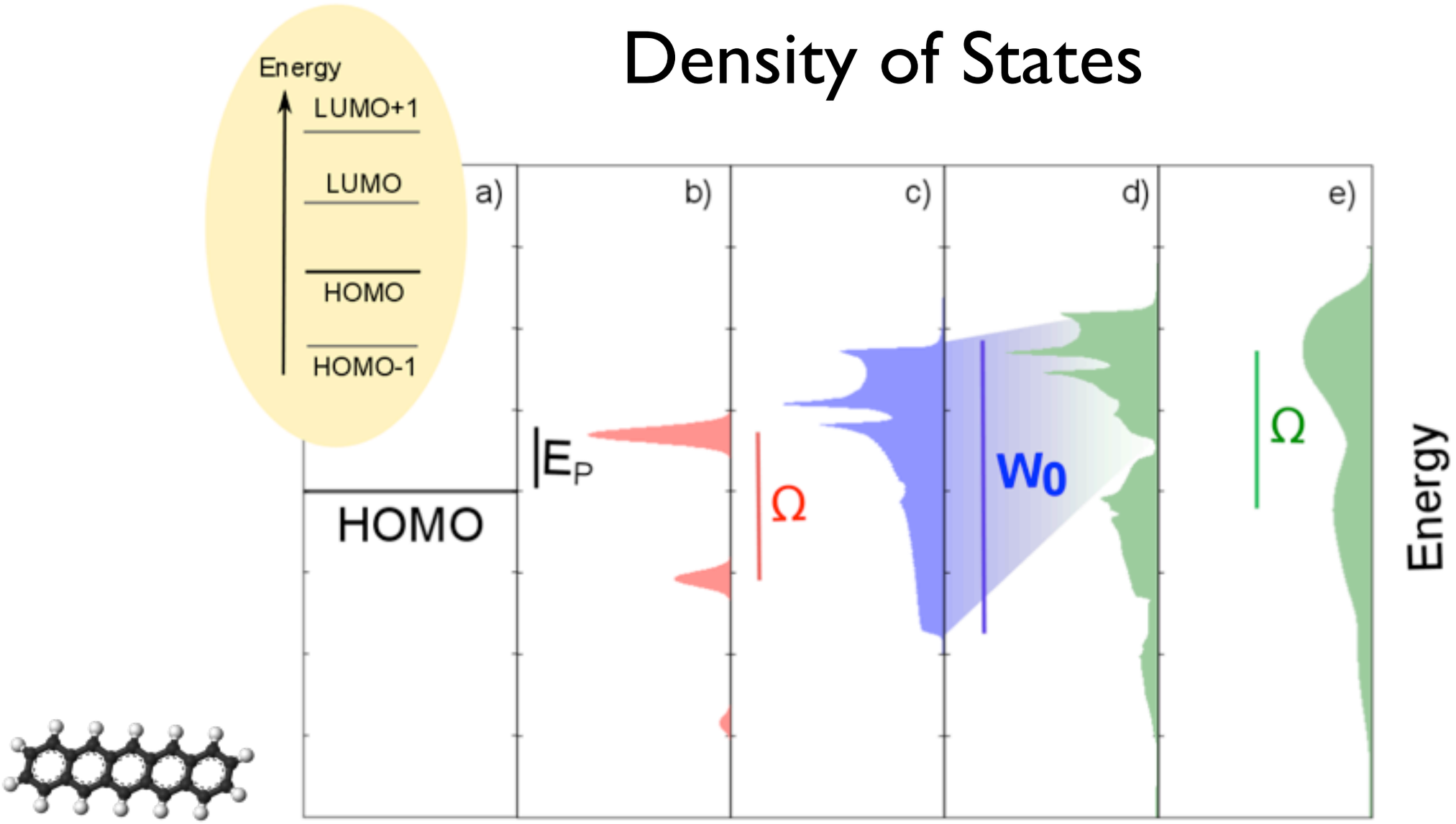




+ structural and thermal disorder (because of VdW bonding, these materials are soft and easily deformable)

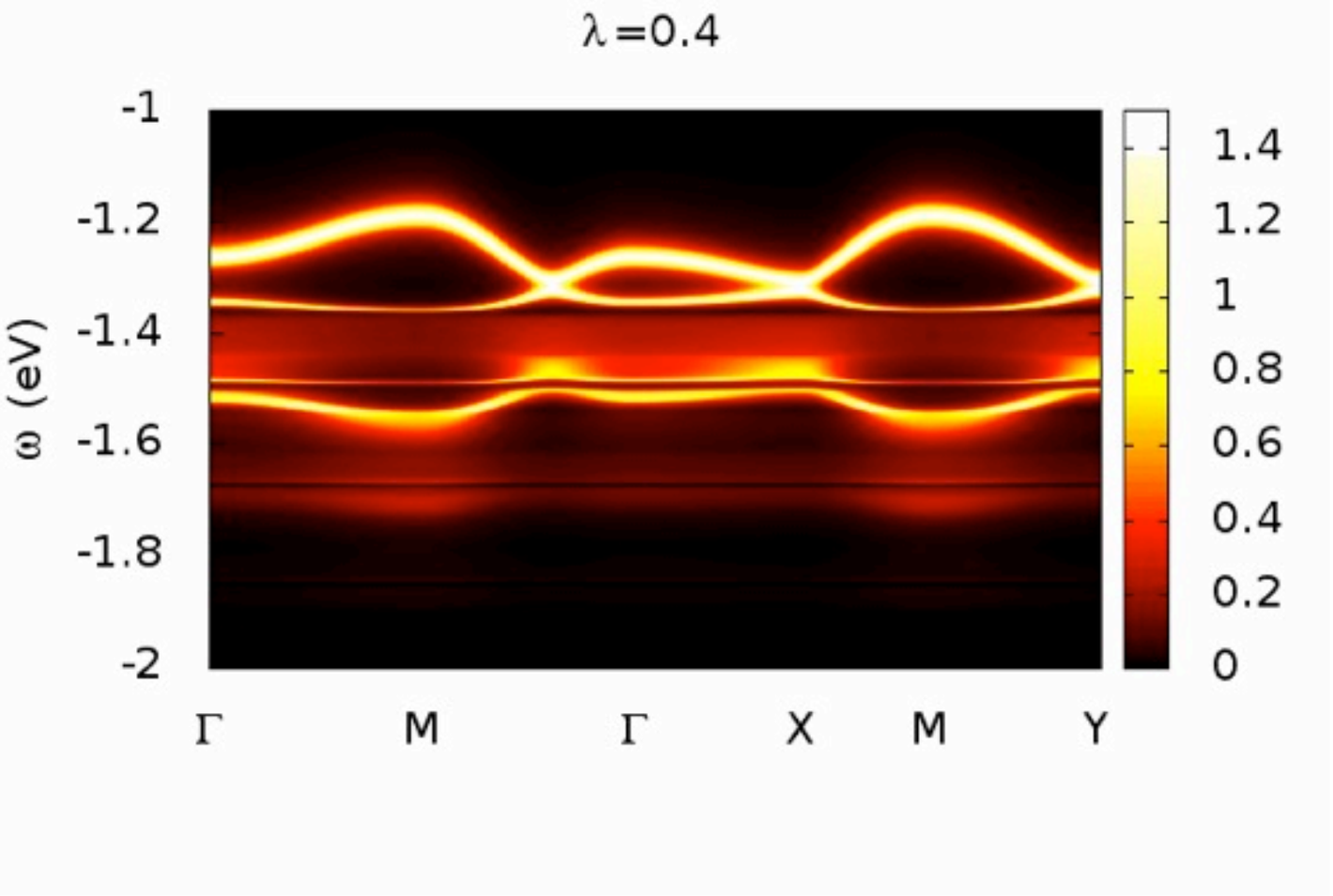
Density of states: between molecules and bands



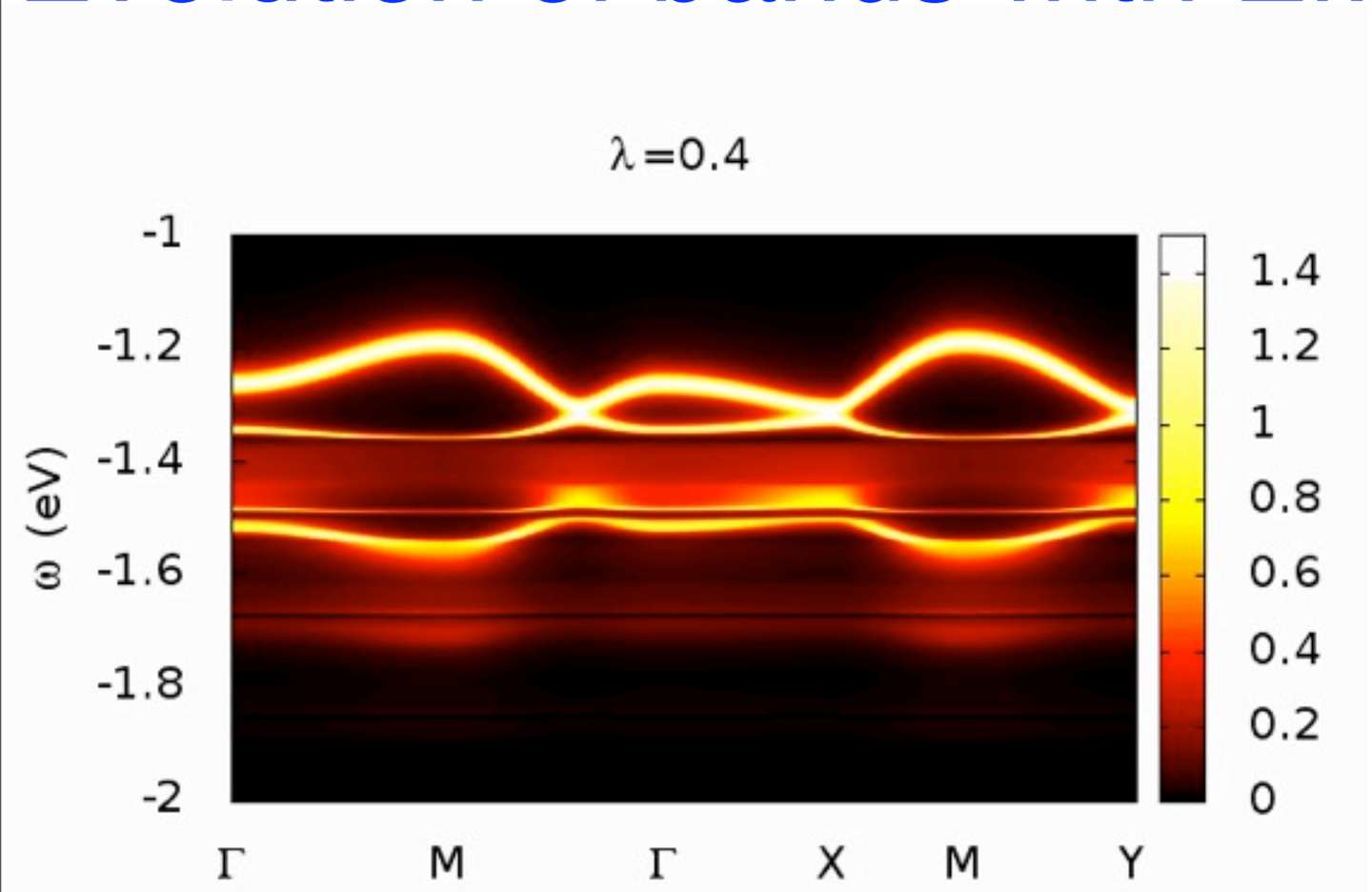


+ structural and thermal disorder (because of VdW bonding, these materials are soft and easily deformable)

Evolution of bands with EMV coupling



Evolution of bands with EMV coupling

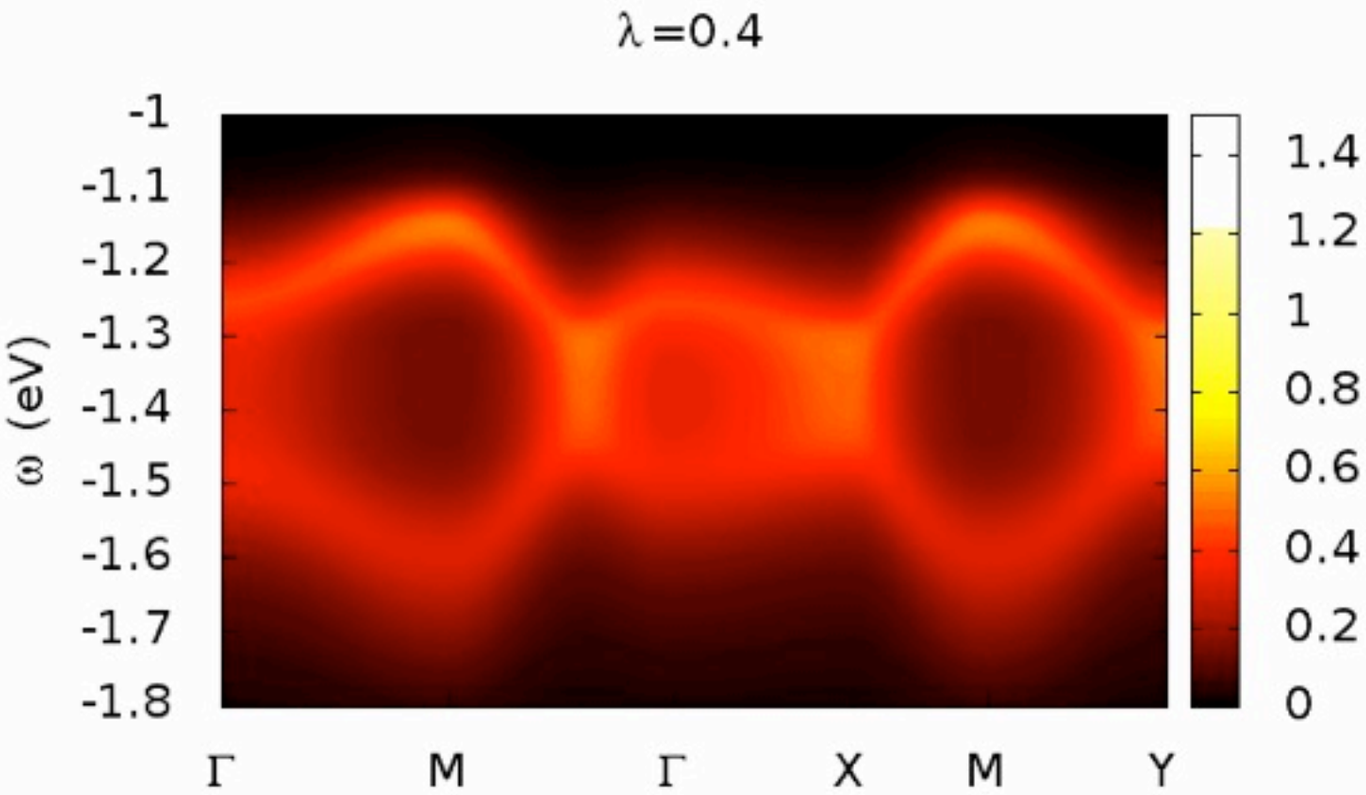


on increasing the coupling strength

--> tends to spectrum of the individual molecule!

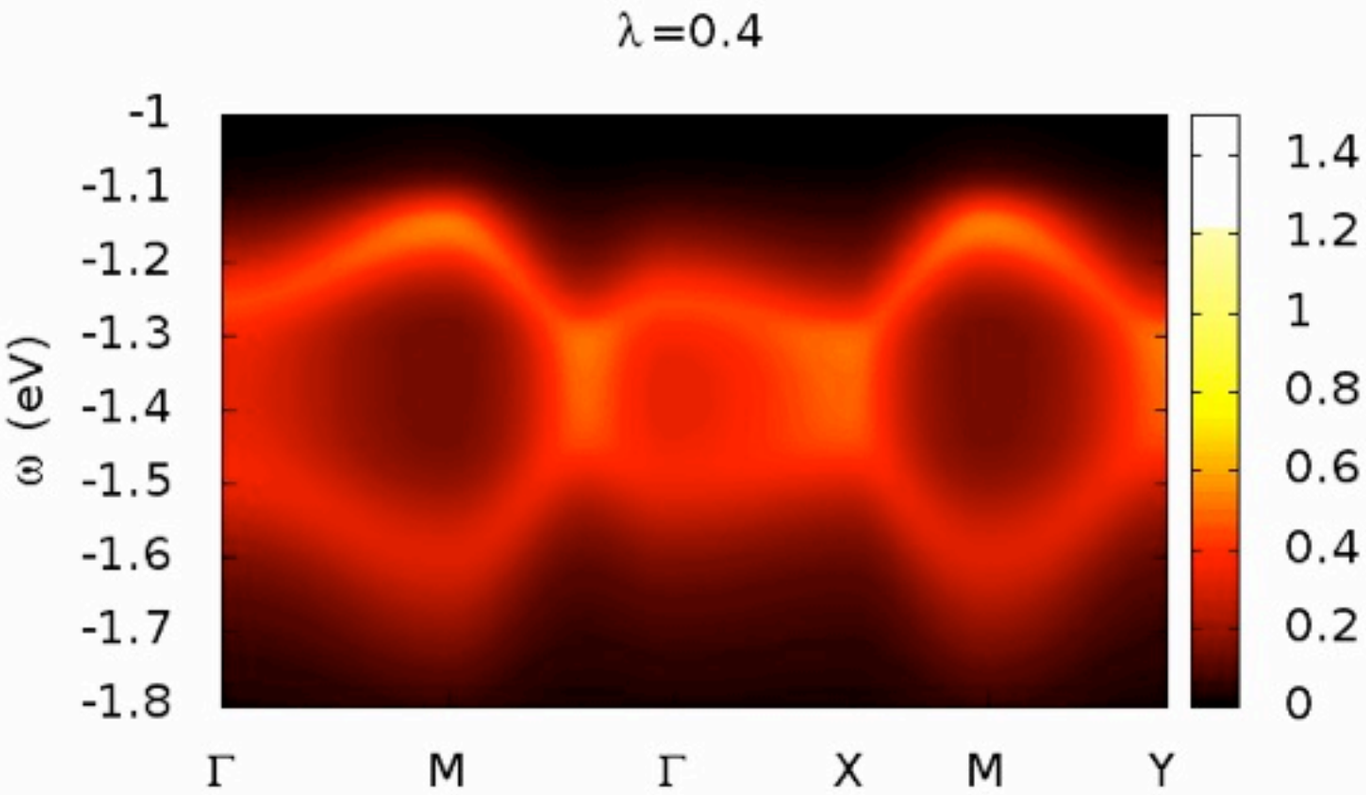
- **redistribution of spectral weight**: EMV interaction shifts the top of band upwards (molecular relaxation energy Ep) and increases the range of electronic excitations

Evolution of bands with EMV coupling



- **band is split into multiphonon resonances** upon increasing the coupling strength --> tends to spectrum of the individual molecule!
- **redistribution of spectral weight**: EMV interaction shifts the top of band upwards (molecular relaxation energy Ep) and increases the range of electronic excitations

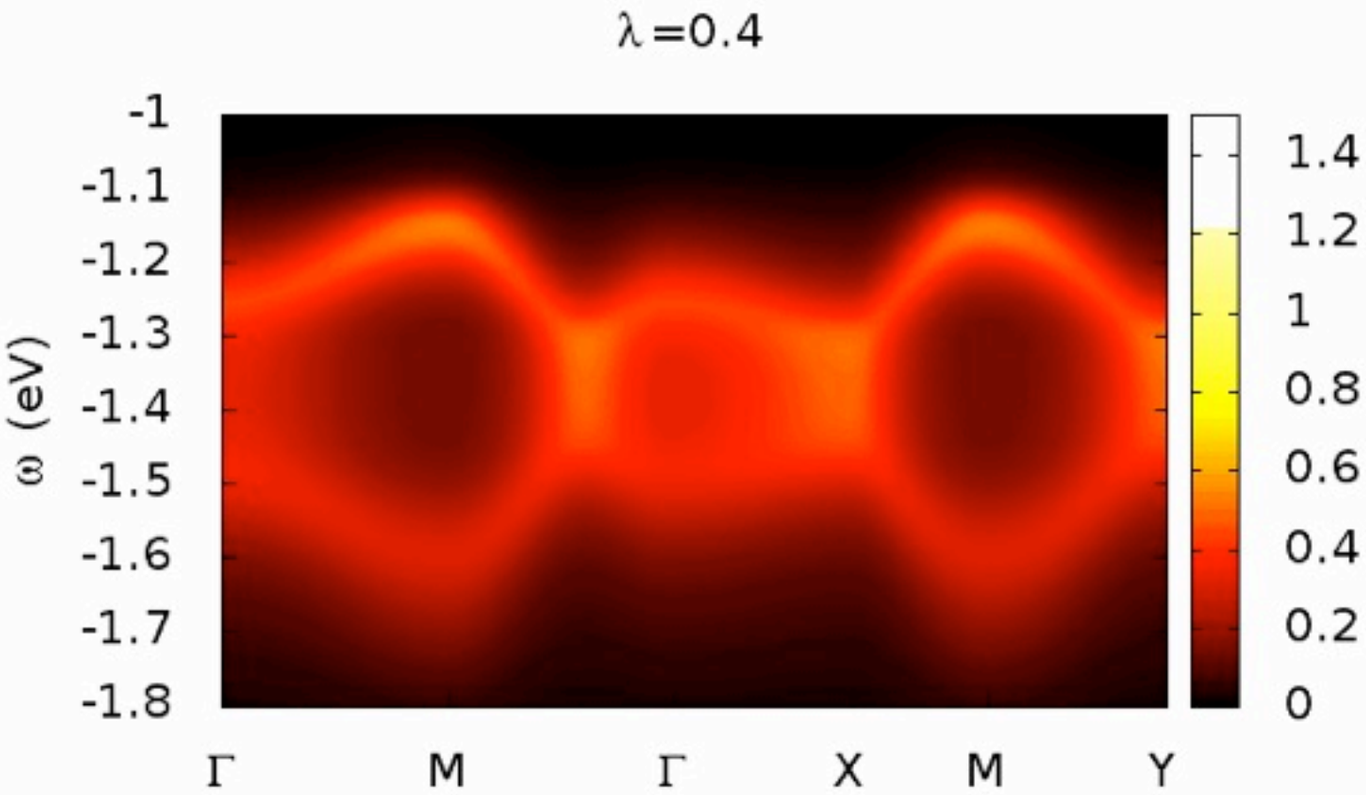
Evolution of bands with EMV coupling



- **band is split into multiphonon resonances** upon increasing the coupling strength --> tends to spectrum of the individual molecule!
- **redistribution of spectral weight**: EMV interaction shifts the top of band upwards (molecular relaxation energy Ep) and increases the range of electronic excitations

- **disorder:** wipes out multiphonon peaks, and further increases the bandwidth
- only two dominant bands are visible, as in the experiment

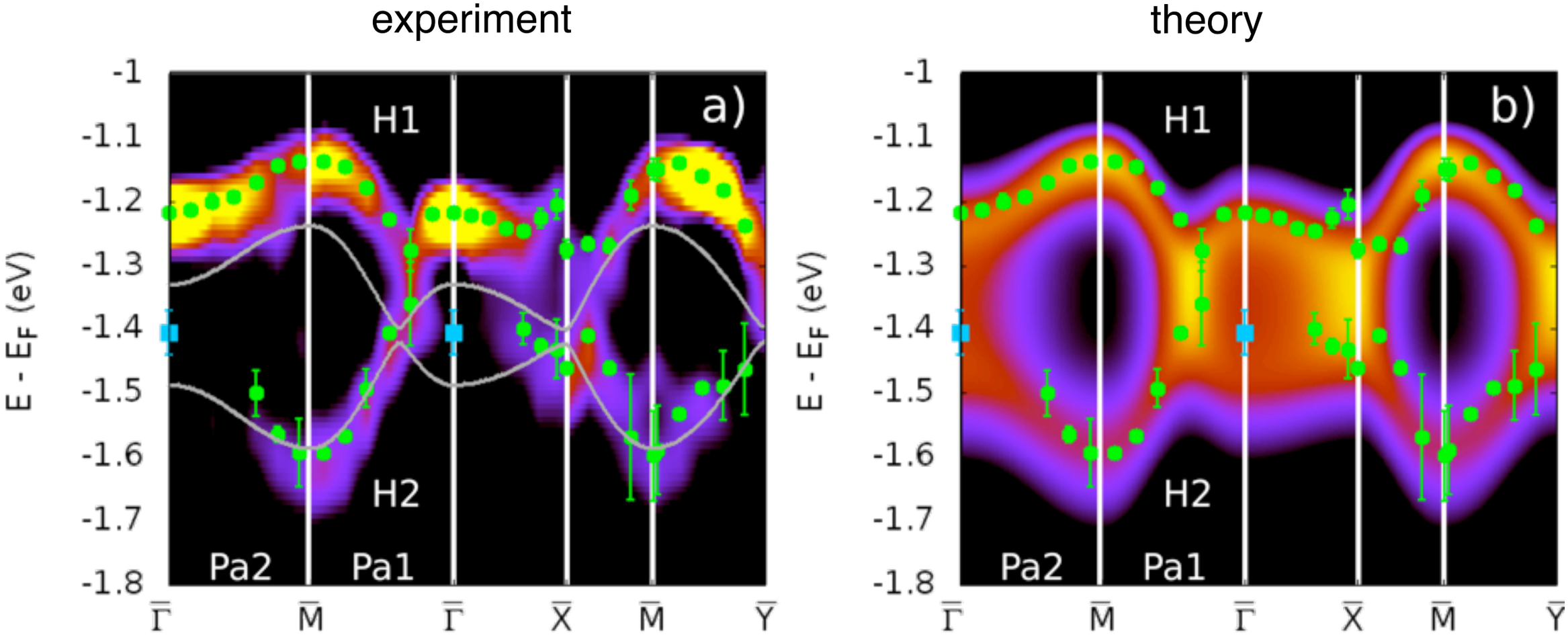
Evolution of bands with EMV coupling



- **band is split into multiphonon resonances** upon increasing the coupling strength --> tends to spectrum of the individual molecule!
- **redistribution of spectral weight**: EMV interaction shifts the top of band upwards (molecular relaxation energy Ep) and increases the range of electronic excitations

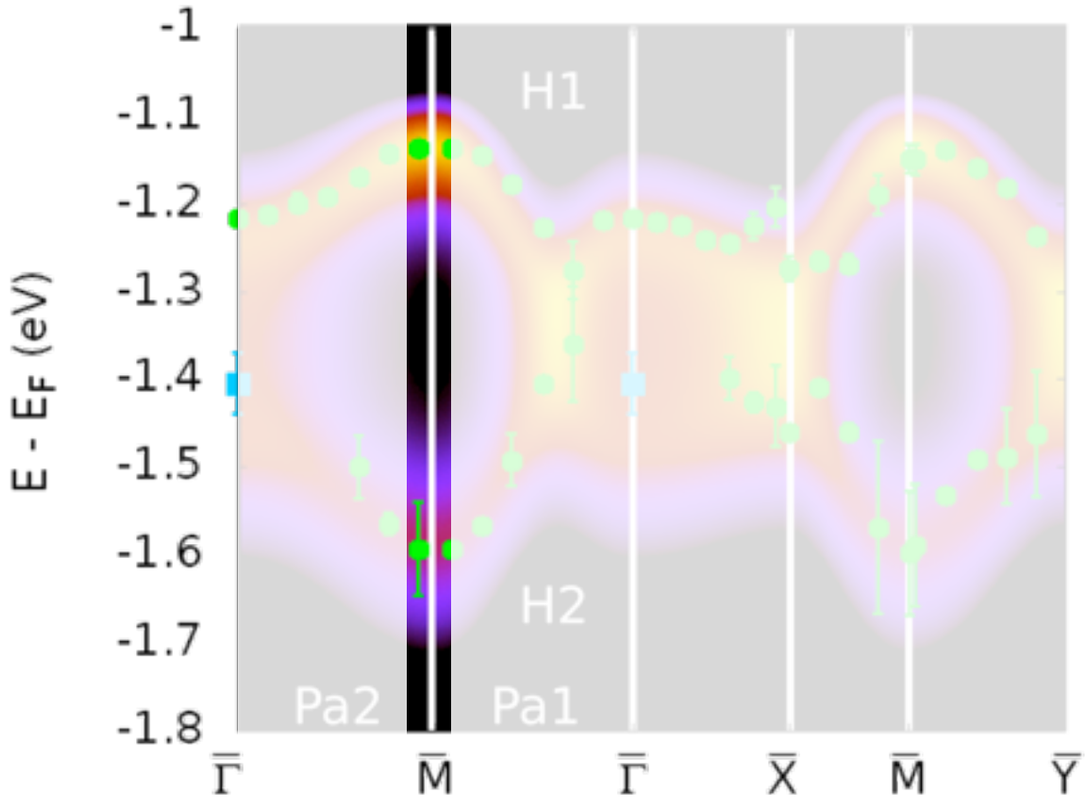
- **disorder:** wipes out multiphonon peaks, and further increases the bandwidth
- only two dominant bands are visible, as in the experiment
- from the GW calculated value λ=0.4, estimate disorder Δ=75±15meV

ARPES: experiment vs theory (EMV interaction and disorder)

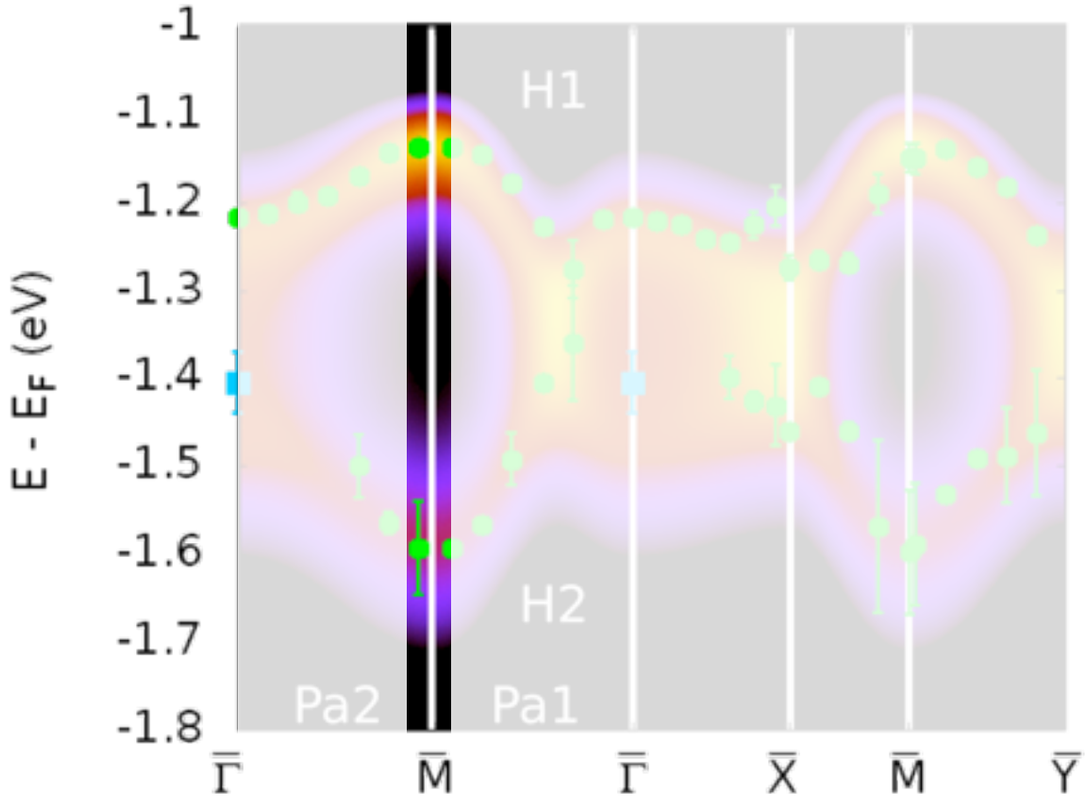


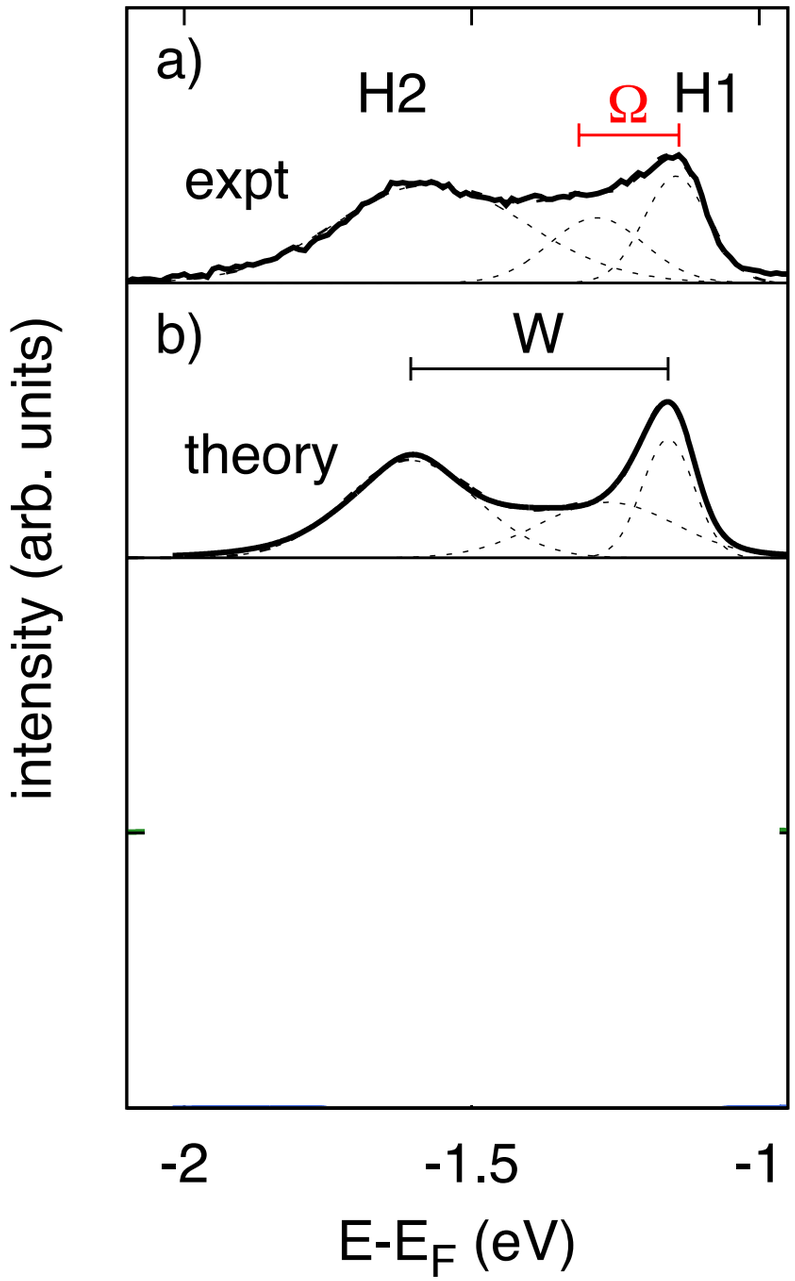
- interplay of EMV interaction and disorder explains the observed band dispersion (H1 band is shifted upwards by the molecular relaxation energy Ep)
- multiphonon fine structure could be seen in future experiments

ARPES Pentacene: hallmarks of EMV

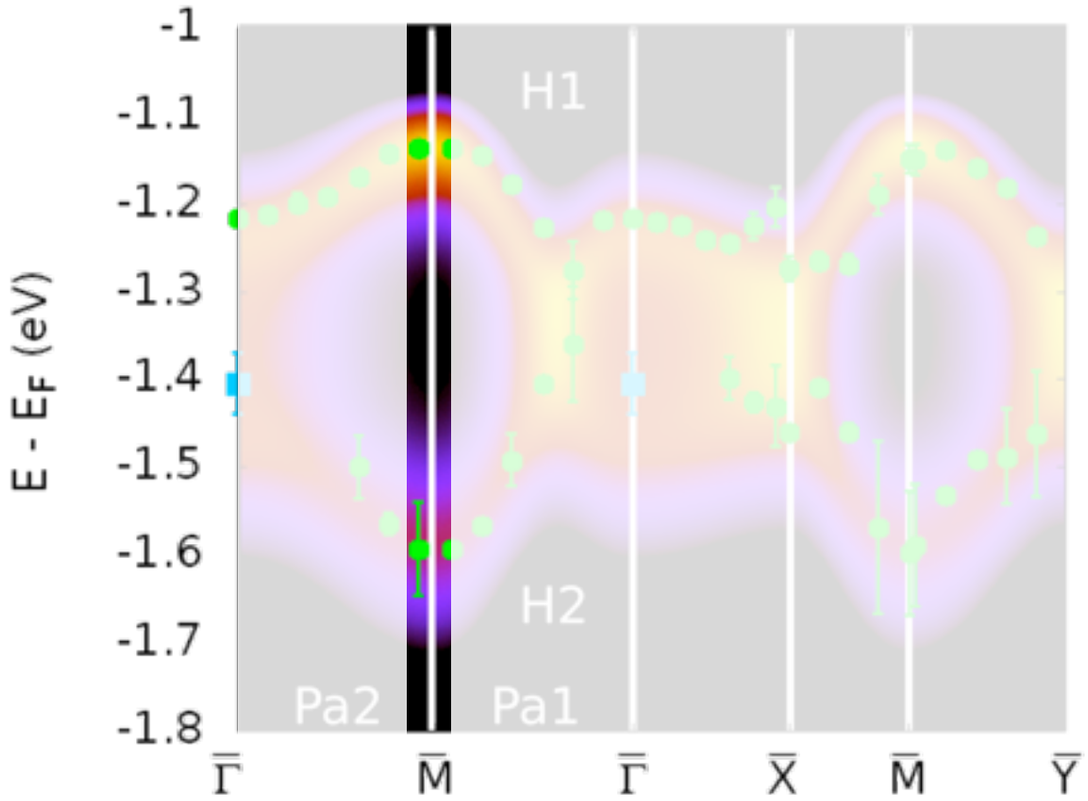


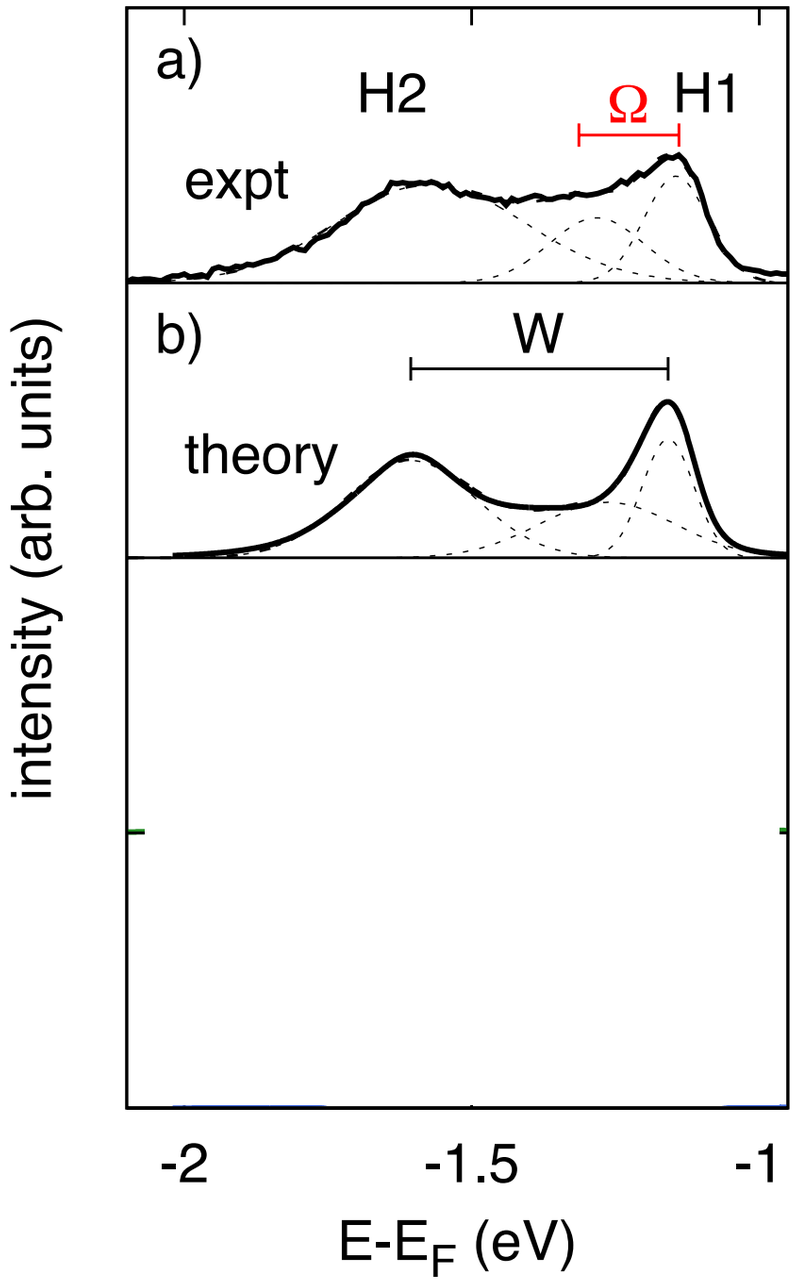
ARPES Pentacene: hallmarks of EMV





ARPES Pentacene: hallmarks of EMV

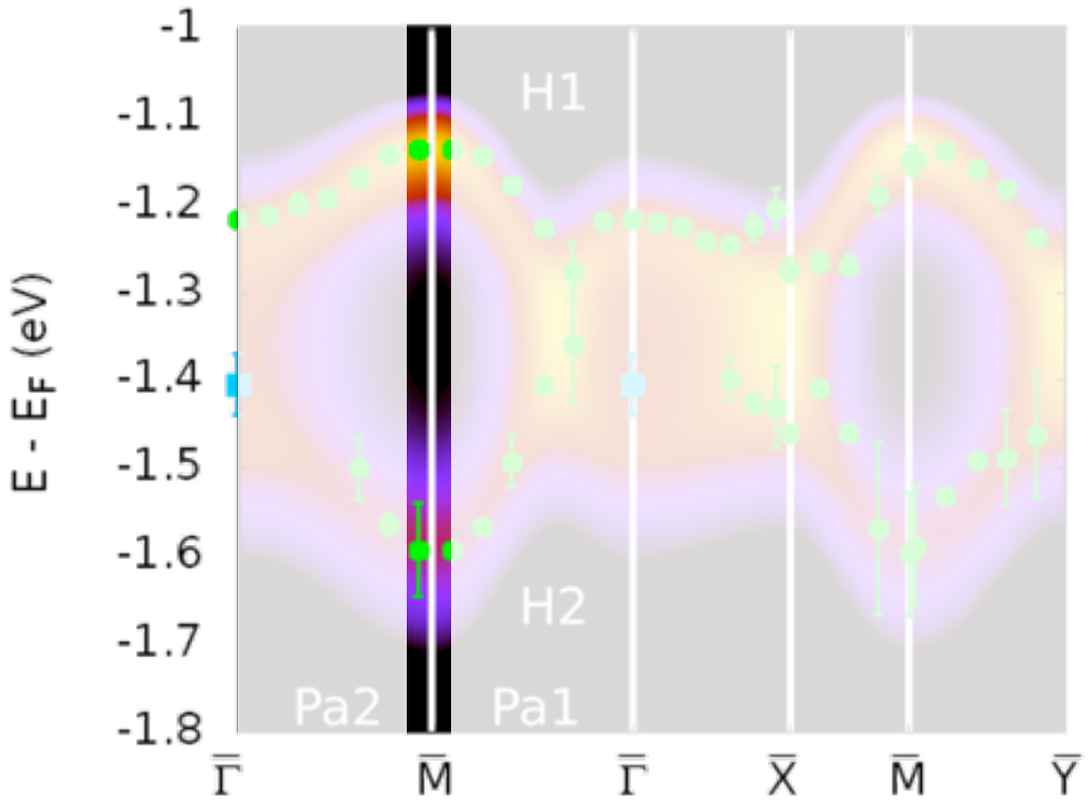


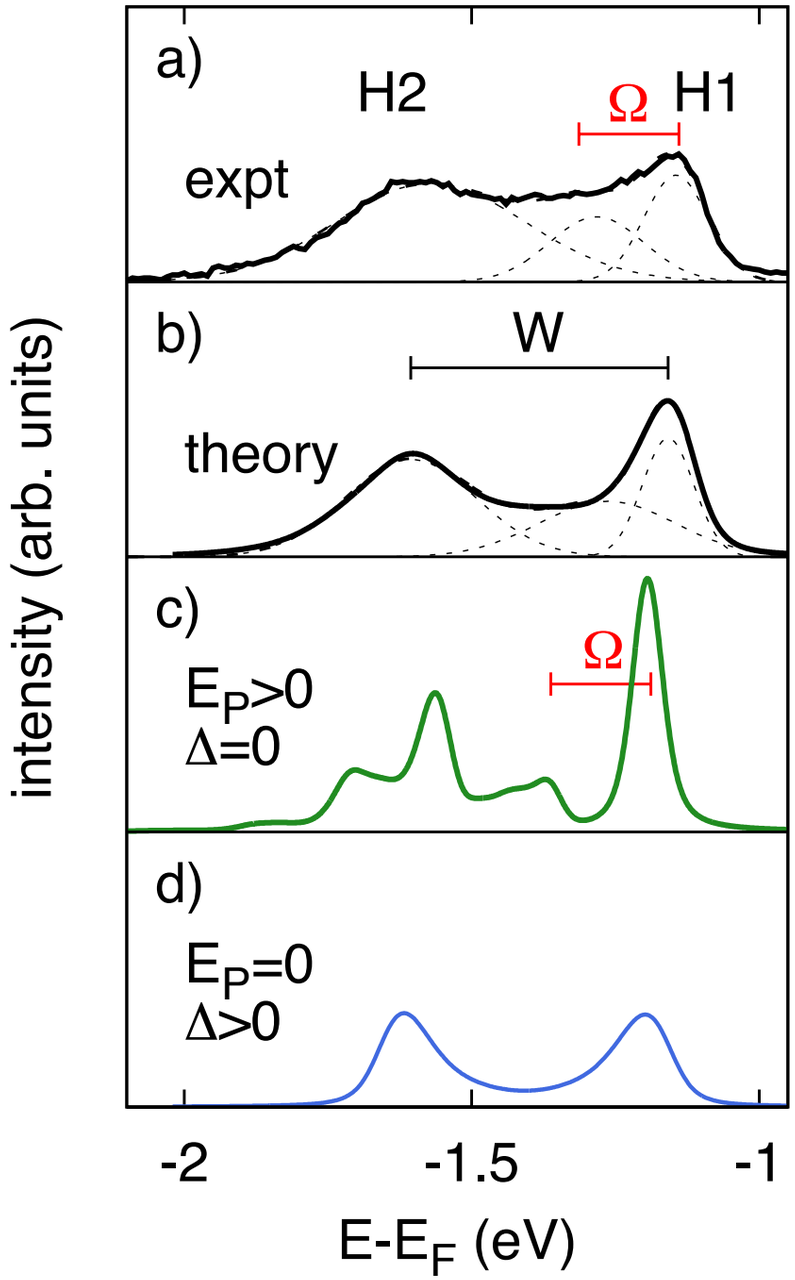


- Large spectral weight inside the H1/H2 gap:
  H1 overtone is there, but broadened by disorder

- "deconvolution": overtone position agrees with calculation without disorder
- large broadening of lines is due to multi-phonon shakeoff processes + disorder

ARPES Pentacene: hallmarks of EMV





- Large spectral weight inside the H1/H2 gap:
  H1 overtone is there, but broadened by disorder

- "deconvolution": overtone position agrees with calculation without disorder
- large broadening of lines is due to multi-phonon shakeoff processes + disorder

Outline

- Introduction: something's wrong with the "common wisdom"

- **ARPES**:

the role of intramolecular vibrations and disorder

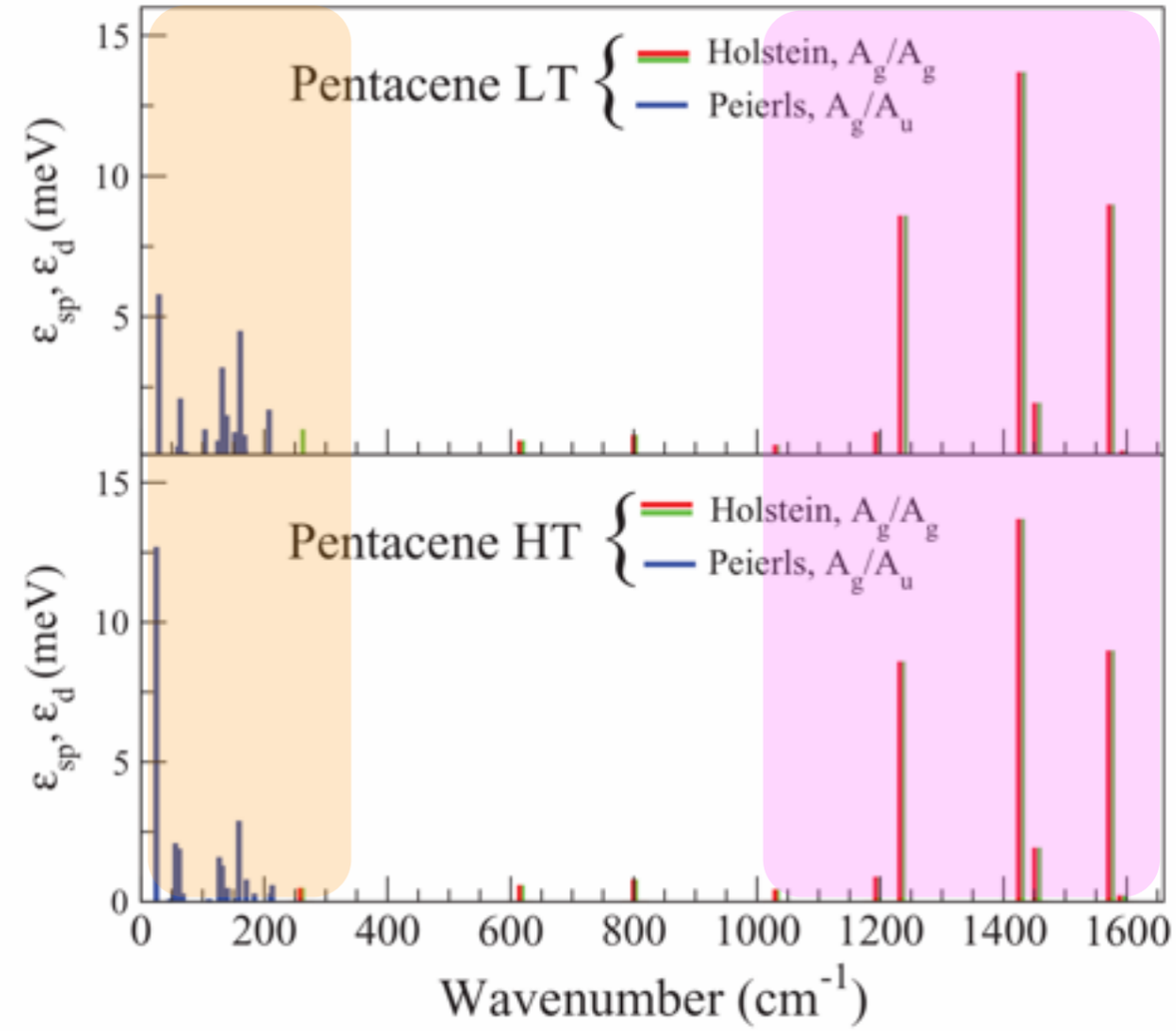
- **Transport properties**:

the role of intermolecular vibrations and the concept of transient localization

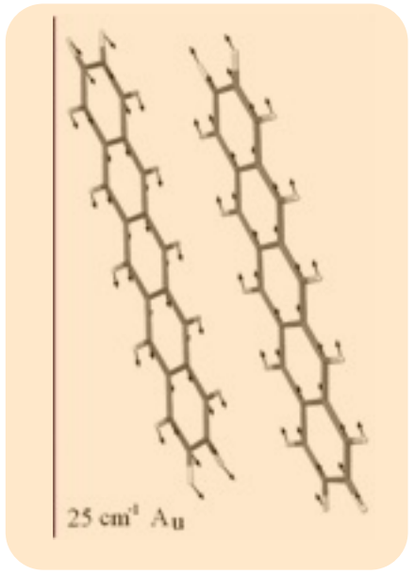
- Kubo formula revisited: carrier diffusivity from optical experiments

- Concluding remarks

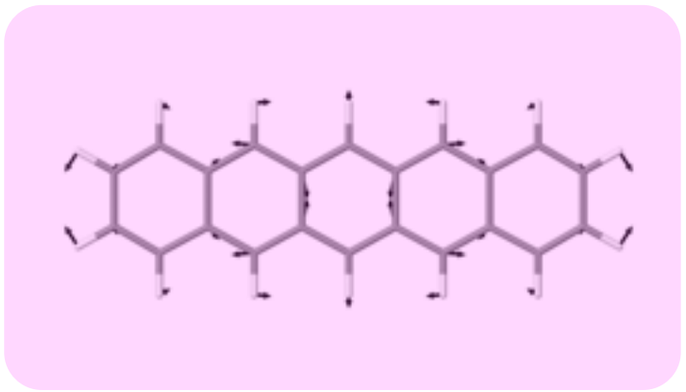
Interactions with molecular vibrations



Peierls



Holstein

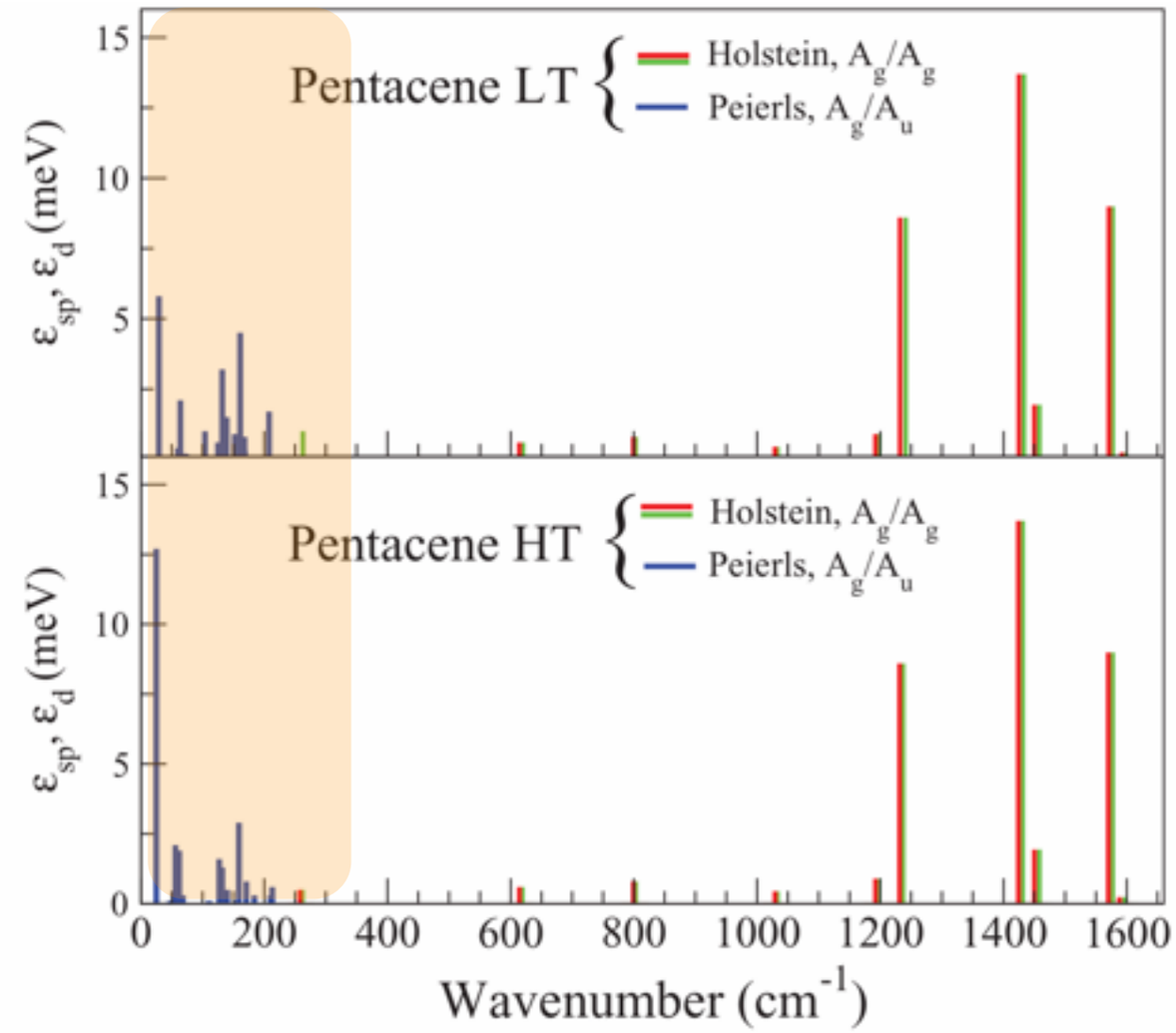


by courtesy of A. Girlando

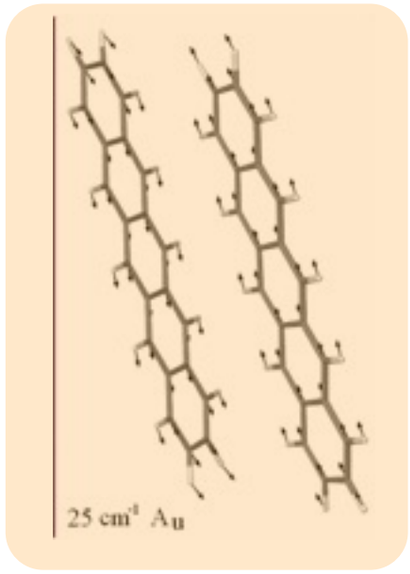
INDO Calculations by [A. Girlando, et al., J. Chem. Phys. 135, 084701 (2011)]

- separation of energy scales between low energy intermolecular modes and high energy intramolecular modes
- Intramolecular (Holstein) FAST: $\omega_0 \approx 120\text{-}200$meV ≈ bandwidth W
- Intermolecular (Periels) SLOW: $\omega_0 \approx 3\text{-}20$meV << bandwidth W

Interactions with molecular vibrations



Peierls



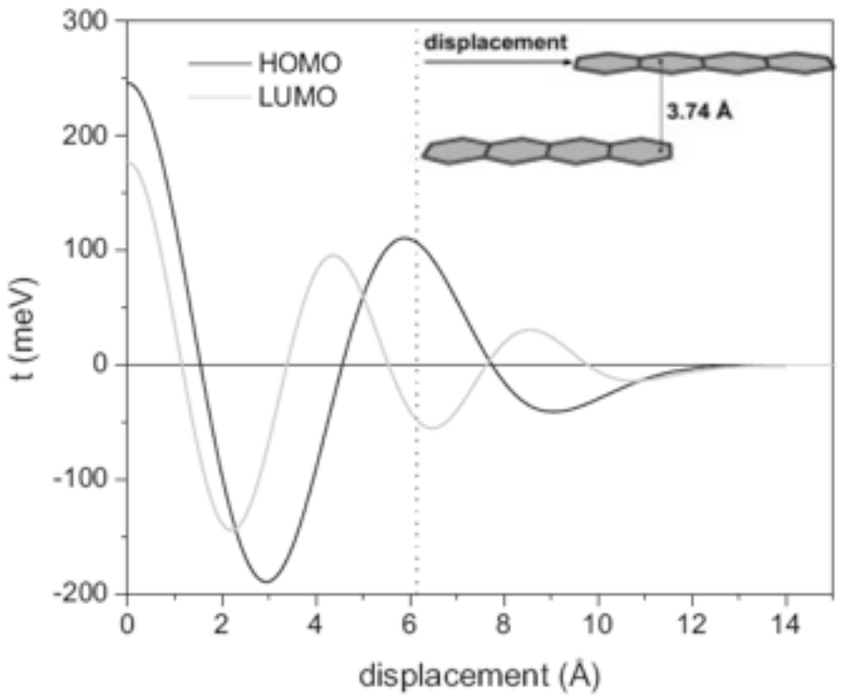
INDO Calculations by [A. Girlando, et al., J. Chem. Phys. 135, 084701 (2011)]

- separation of energy scales between low energy intermolecular modes and high energy intramolecular modes
- Intramolecular (Holstein) FAST: ω0≈120-200meV ≈ bandwidth W
  these modes are too fast to really affect electron transport, and no T dependence
- Intermolecular (Periels) SLOW: ω0≈3-20meV << bandwidth W

The model

- modulation of the transfer integral t due to relative intermolecular vibrations

DFT

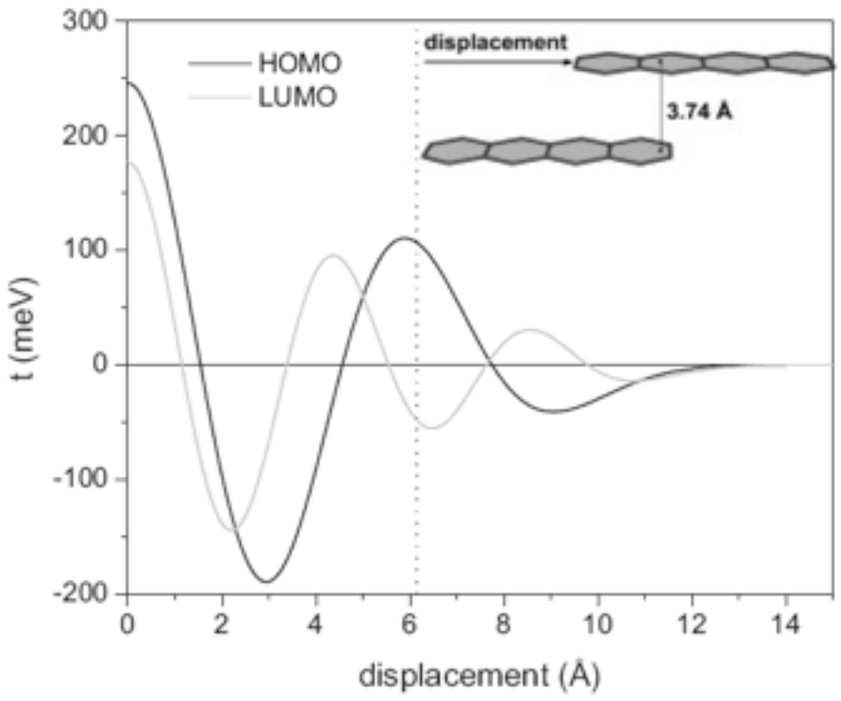


[DaSilva AdvMat05,Cornil AdvMat06]

The model

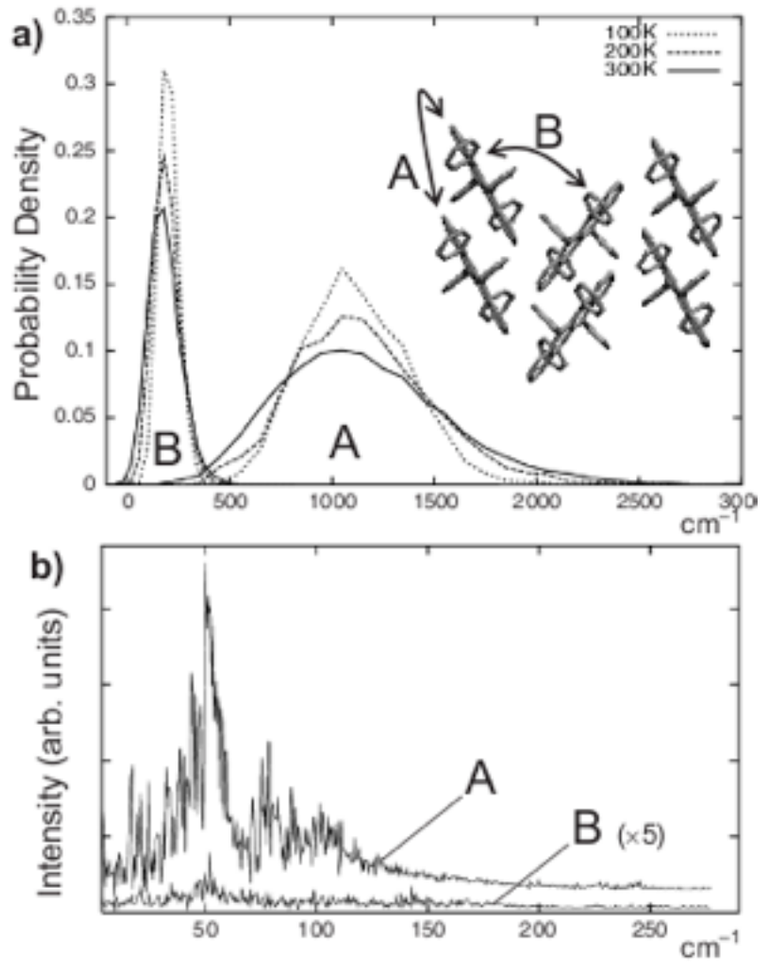
- modulation of the transfer integral t due to relative intermolecular vibrations

DFT



[DaSilva AdvMat05,Cornil AdvMat06]

molecular dynamics

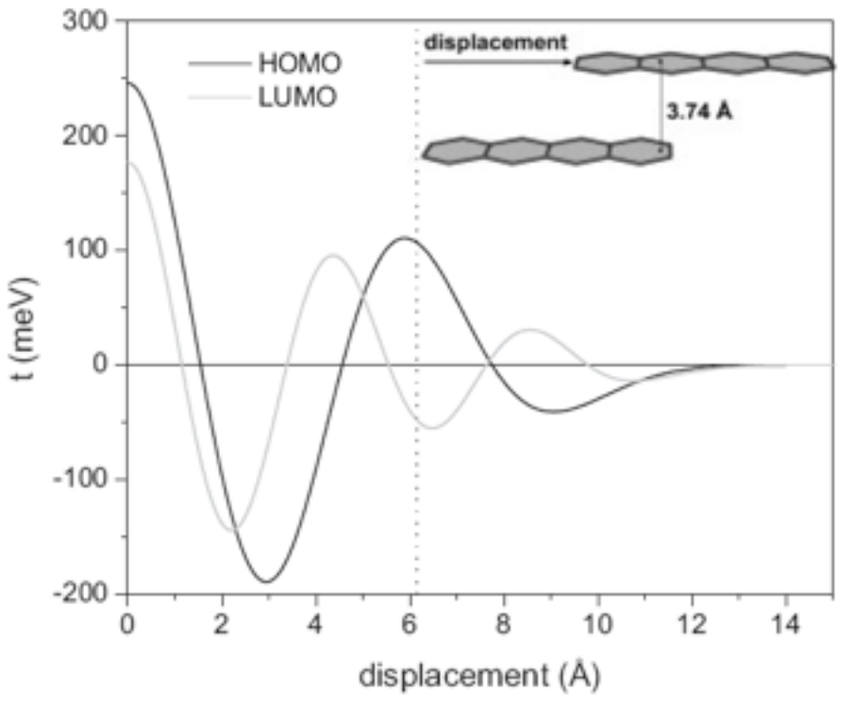


[Troisi AdvMat07]

The model

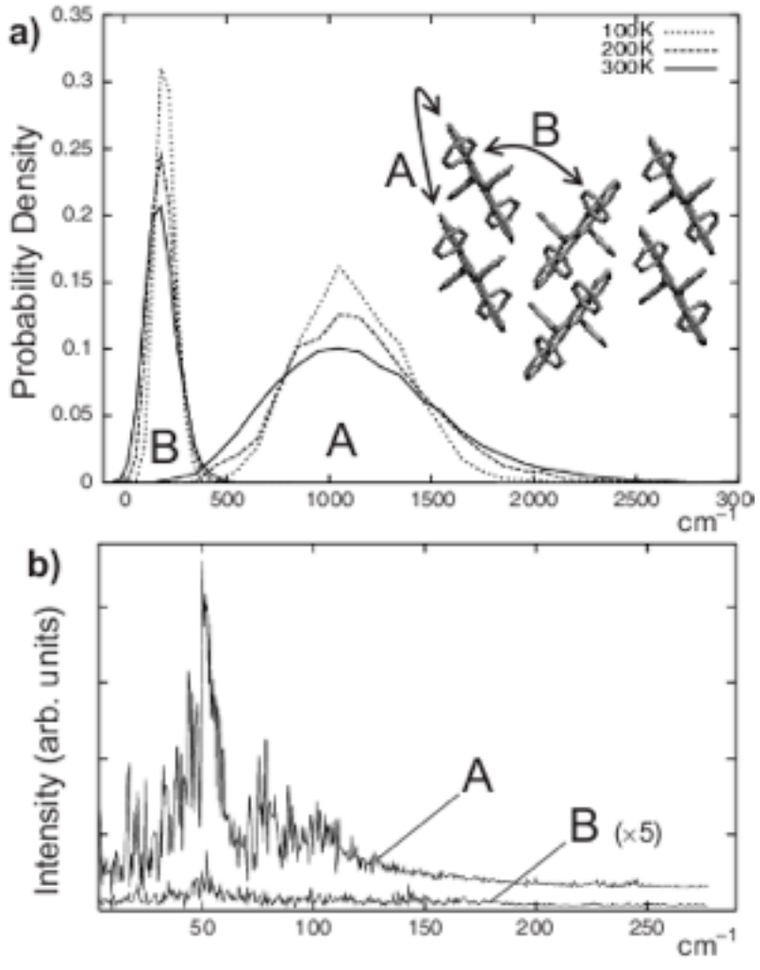
- modulation of the transfer integral t due to relative intermolecular vibrations
- t fluctuates by ~100% , beyond the usual electron-phonon coupling scenario
- better seen as a large dynamical disorder (off-diagonal)

DFT



[DaSilva AdvMat05,Cornil AdvMat06]

molecular dynamics

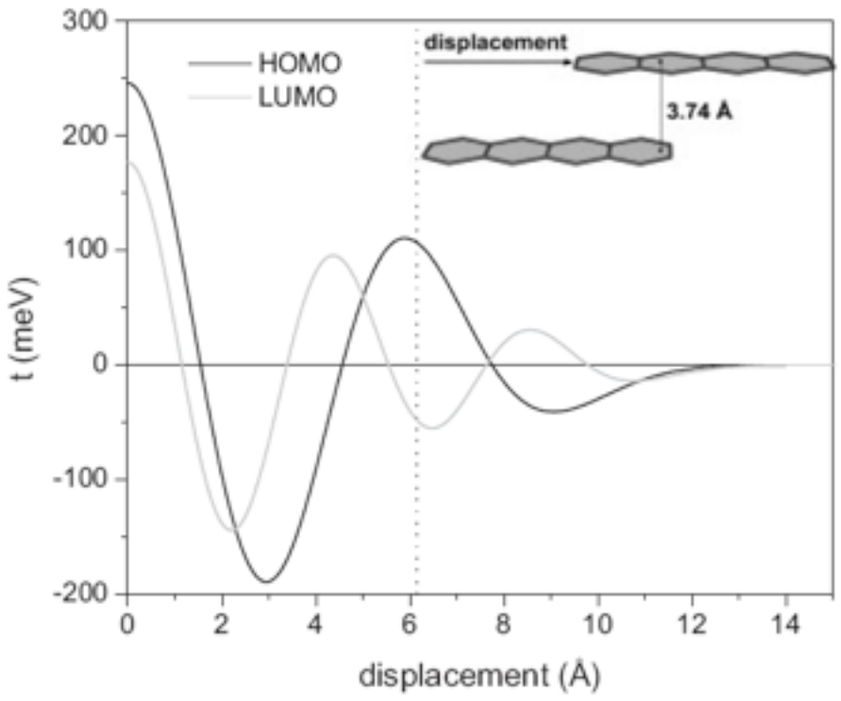


[Troisi AdvMat07]

The model

- modulation of the transfer integral t due to relative intermolecular vibrations
- t fluctuates by ~100% , beyond the usual electron-phonon coupling scenario
- better seen as a large dynamical disorder (off-diagonal)

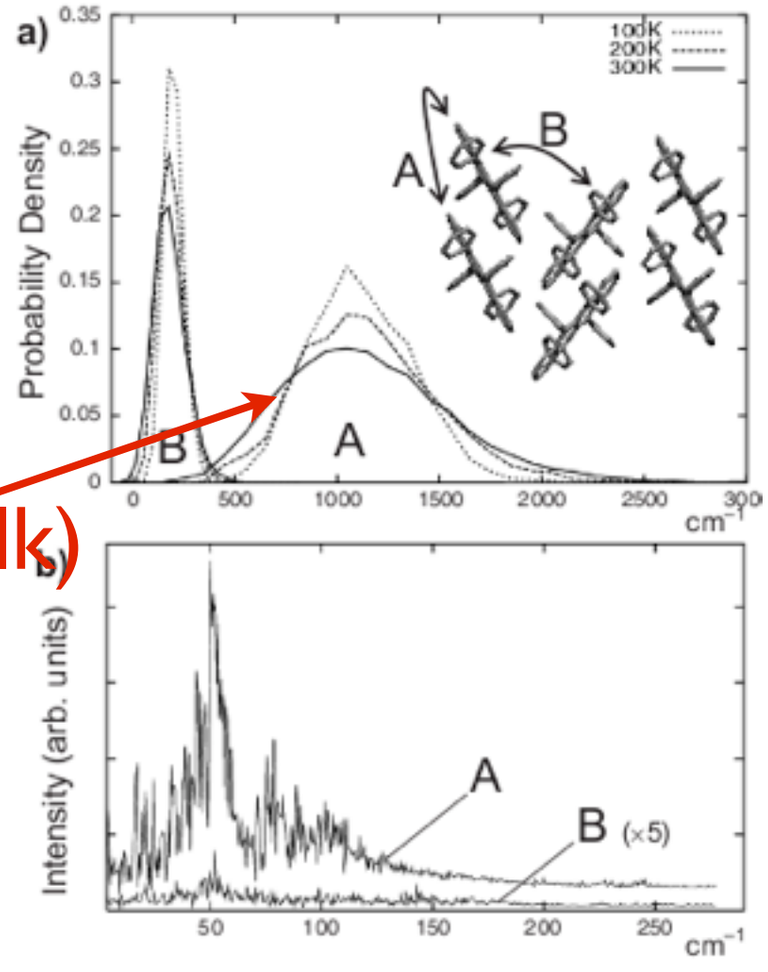
DFT



[DaSilva AdvMat05,Cornil AdvMat06]

the material is soft (cf. A. Chin talk)

molecular dynamics



[Troisi AdvMat07]

The model

- modulation of the transfer integral t due to relative intermolecular vibrations
- t fluctuates by ~100% , beyond the usual electron-phonon coupling scenario
- better seen as a large dynamical disorder (off-diagonal)
- linear coupling --> Su Schrieffer Heeger

a single Einstein mode

$$H = -J \sum_i [1 - \alpha(X_i - X_{i+1})](c_i^+ c_{i+1} + c_{i+1}^+ c_i) + H_{ph}(X)$$

[Friedman PR 1964]
[Gosar & Choi PR 1966]
[Duke & Schein, Physics Today 1980]
[Munn & Silbey JCP 1985]
[M. Capone et. al PRB 1997]
[Hannewald & Bobbert PRB 2004]
[Troisi et. Al PRL 2006,Adv Mat 2007]
[Picon PRB 2007]

The model

- modulation of the transfer integral t due to relative intermolecular vibrations
- t fluctuates by ~100% , beyond the usual electron-phonon coupling scenario
- better seen as a large dynamical disorder (off-diagonal)
- linear coupling --> Su Schrieffer Heeger

a single Einstein mode

$$H = -J \sum_i [1 - \alpha(X_i - X_{i+1})](c_i^+ c_{i+1} + c_{i+1}^+ c_i) + H_{ph}(X)$$

Semiclassical approach, resistivity saturation (bad conductors):
S. F. and S. Ciuchi. Phys. Rev. Lett. 103, 266601 (2009)
Beyond, account for localization phenomena:
S. Ciuchi. S. F. and D. Mayou Phys. Rev. B 83, R081202 (2011)

[Friedman PR 1964]
[Gosar & Choi PR 1966]
[Duke & Schein, Physics Today 1980]
[Munn & Silbey JCP 1985]
[M. Capone et. al PRB 1997]
[Hannewald & Bobbert PRB 2004]
[Troisi et. Al PRL 2006,Adv Mat 2007]
[Picon PRB 2007]

Quantum-Classical dynamics

$$H = H_{el}(X) + \sum_i \frac{P_i^2}{2M} + \frac{M\omega_0^2}{2} X_i^2$$

[A. Troisi, G. Orlandi Phys. Rev. Lett 96, 086601 (2006)]
[L. Wang et al, J. Chem. Phys. 134, 244116 (2011)]
[S. Ciuchi. S. F. and D. Mayou Phys. Rev. B 83, R081202 (2011)]

$$i\partial_t|\psi> = H_{el}(X)|\psi>$$ Quantum degrees of freedom: carriers

$$M\ddot{X}_i = -<\psi|\frac{\partial H}{\partial X_i}|\psi>$$ Classical degrees of freedom: molecular displacements

- Classical approximation for vibrations: ($k_BT/\hbar\omega_0 \geq 1$)
- Ehrenfest dynamics: classical forces evaluated as quantum averages
  4th order RK integration (nord=4), Velocity Verlet, one dimensional chain (N=2048), averaging over 10^4 initial conditions taken from a static equilibrium ensemble

- calculate time dependent electron spread $\Delta x^2(t) = \langle |x(t) - x(0)|^2 \rangle$

- carrier mobility obtained from the long time behavior of the diffusivity

$$D = \lim_{t\to\infty} \frac{1}{2}\frac{\Delta x^2(t)}{dt} \qquad \mu = \frac{eD}{k_BT}$$

Transient localization

electron wavefunction

Frozen molecular displacements

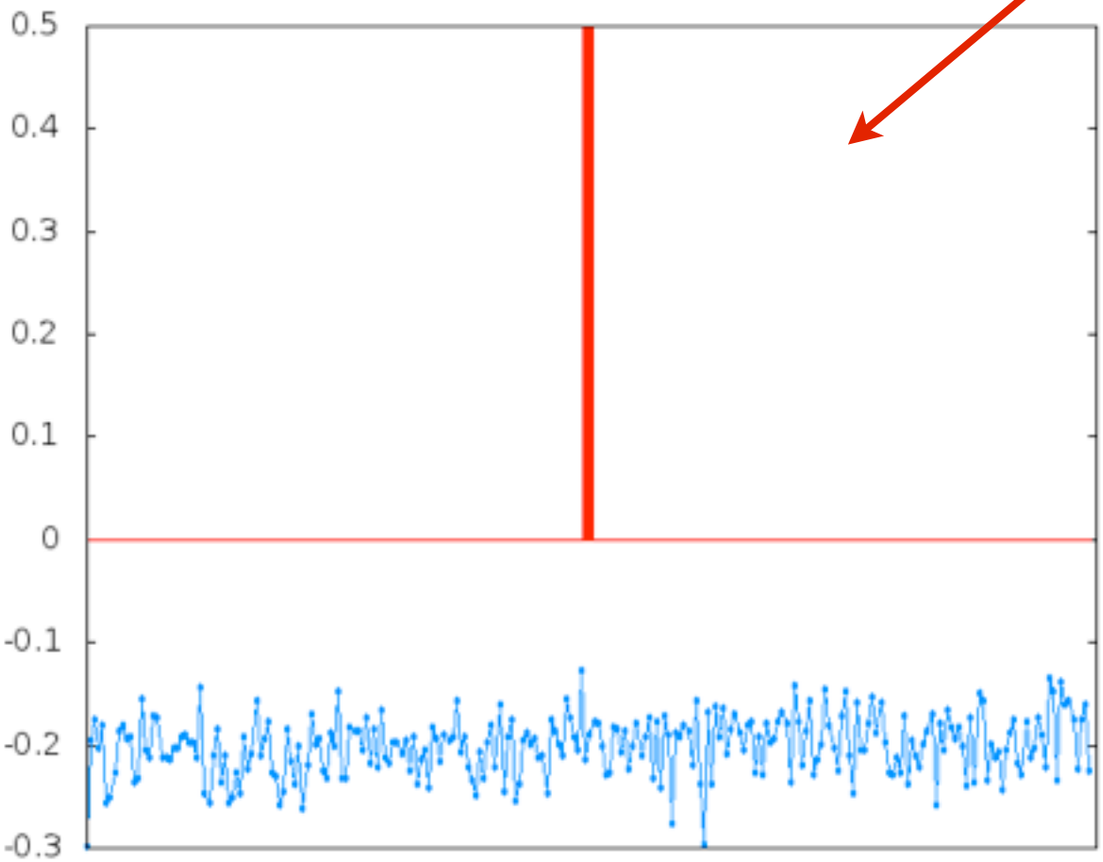
Dynamical molecular displacements

molecular displacements

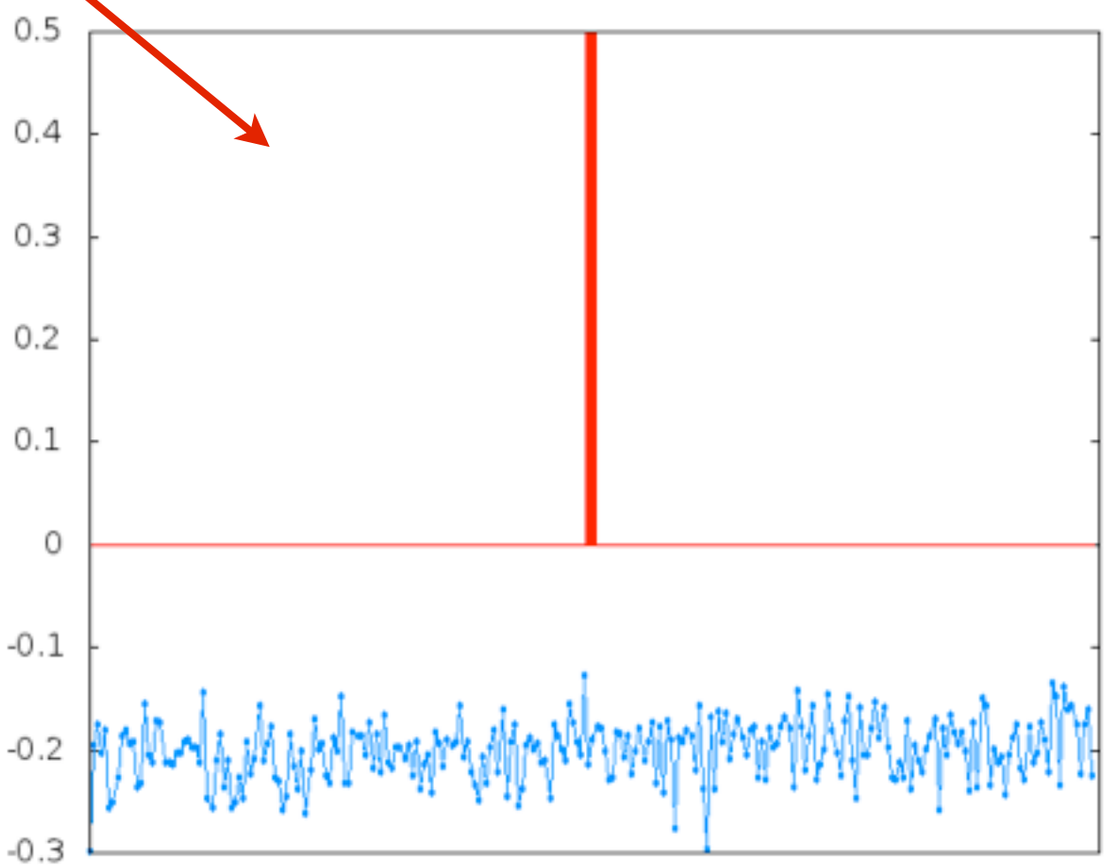
Transient localization

electron wavefunction

Frozen molecular displacements



Dynamical molecular displacements

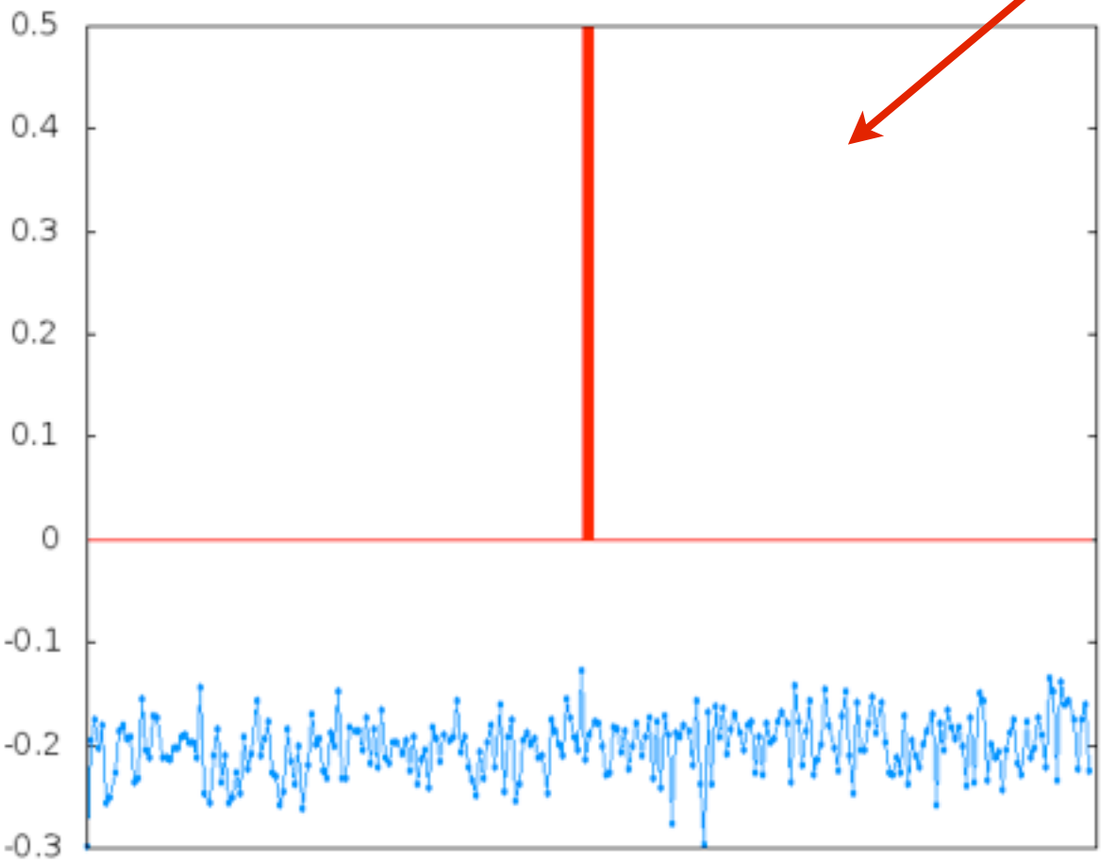


molecular displacements

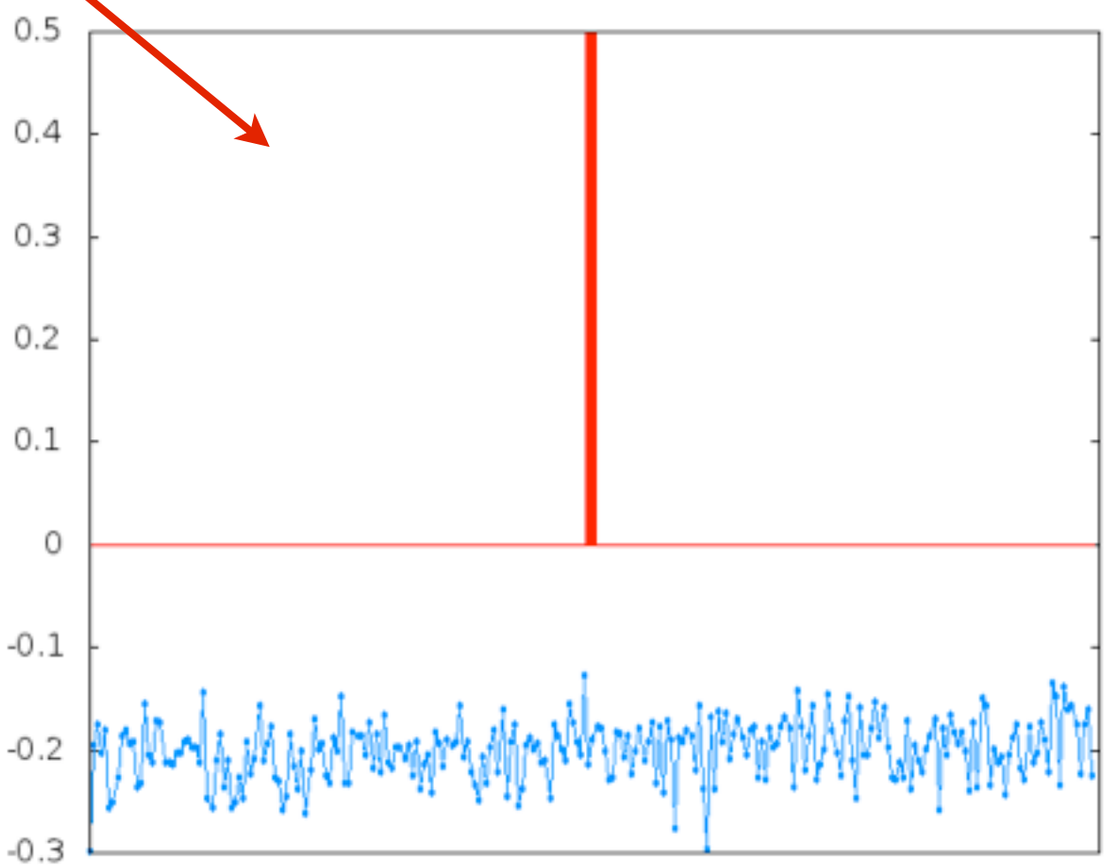
Transient localization

electron wavefunction

Frozen molecular displacements



Dynamical molecular displacements



molecular displacements

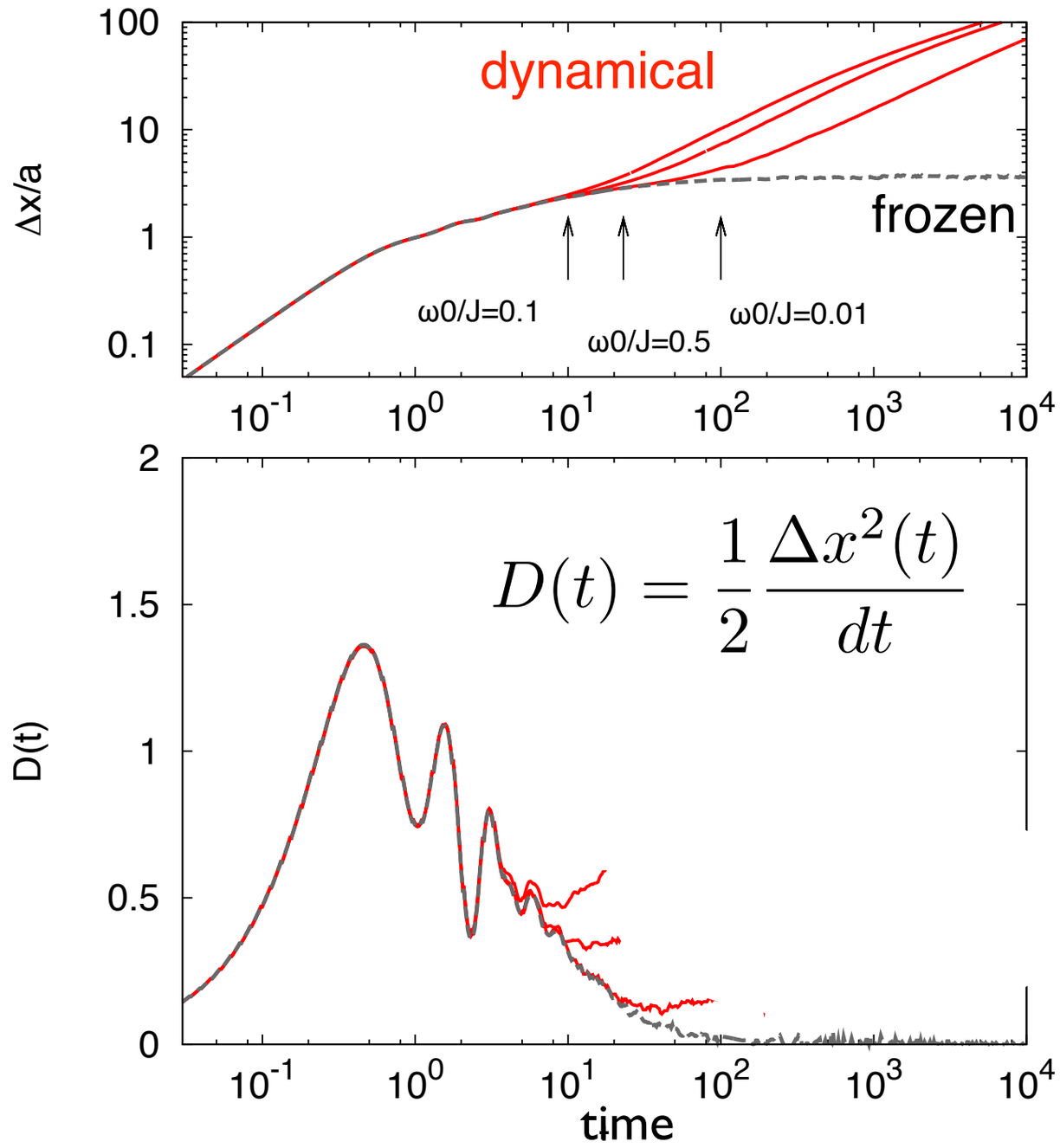
Transient localization

- **Frozen molecular displacements:**

--> **Anderson localization**

finite localization length,
diffusivity vanishes at long times

$$\Delta x^2(t) = \langle |x(t) - x(0)|^2 \rangle$$



Transient localization

- **Frozen molecular displacements:**

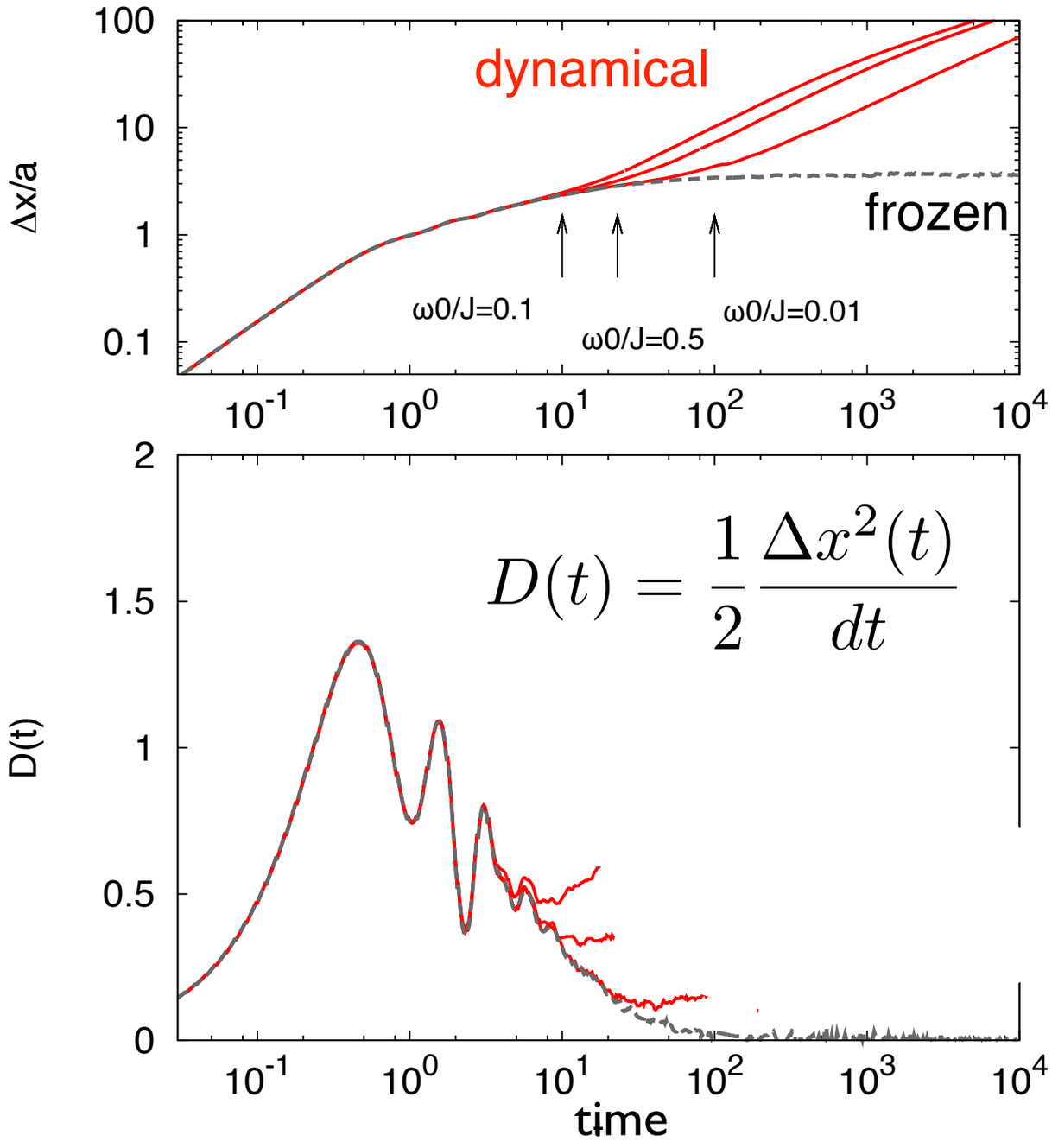
--> **Anderson localization**
finite localization length,
diffusivity vanishes at long times

- **Dynamical molecular displacements:**

--> **transient localization**: initially the diffusivity decreases and the particle localizes as if the disorder were static

- At later times, lattice dynamics destroy the quantum interferences at the origin of localization --> **diffusion sets back in**
- mobility depends on transient localization length and timescale $1/\omega_0$ of lattice dynamics: *the longer it localizes, the lower the mobility*
- The transport mechanism is far from semiclassical

$$\Delta x^2(t) = \langle |x(t) - x(0)|^2 \rangle$$



Transient localization

- **Frozen molecular displacements:**

--> **Anderson localization**
finite localization length,
diffusivity vanishes at long times

- **Dynamical molecular displacements:**

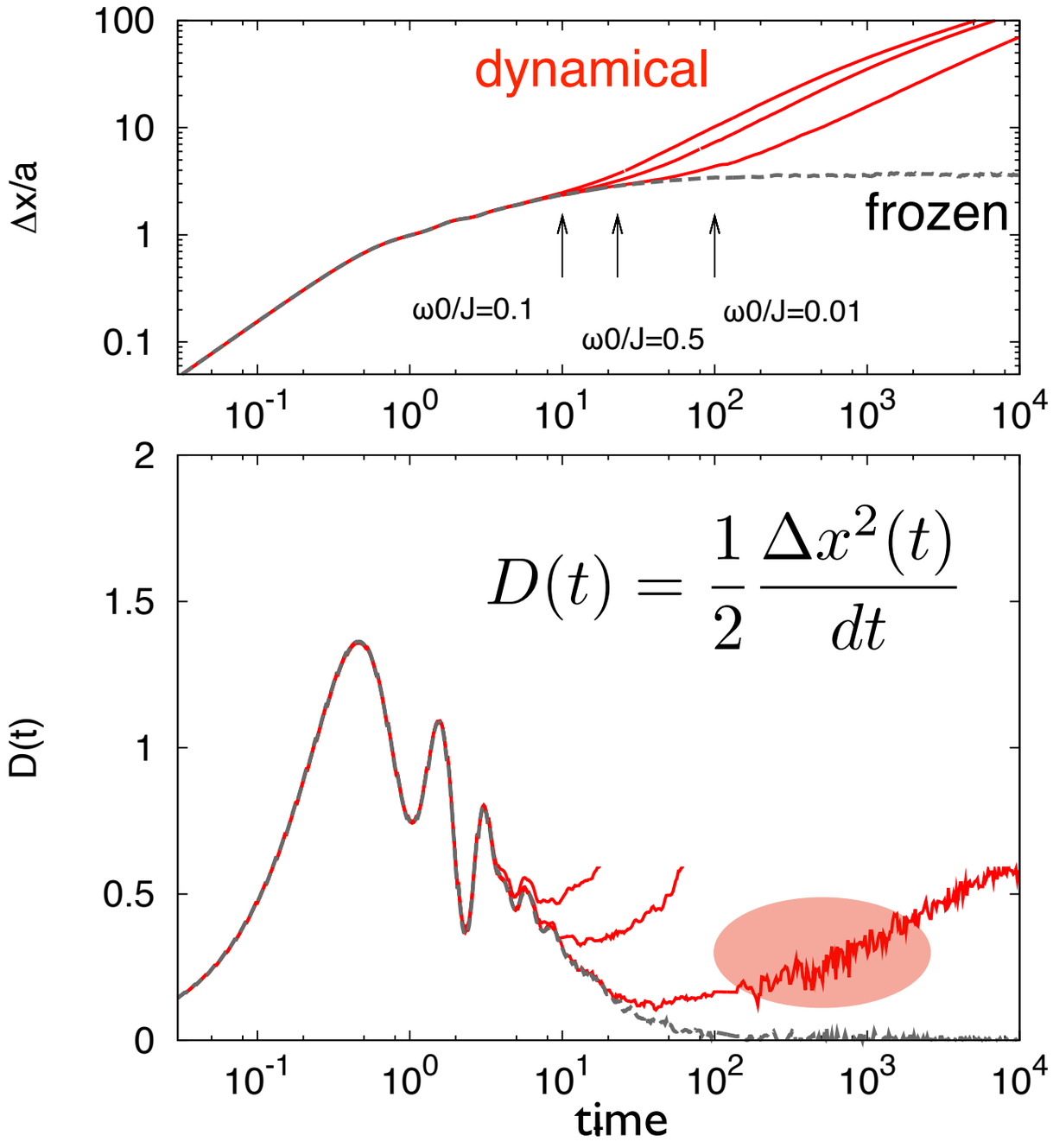
--> **transient localization**: initially the diffusivity decreases and the particle localizes as if the disorder were static

- At later times, lattice dynamics destroy the quantum interferences at the origin of localization --> **diffusion sets back in**

- mobility depends on transient localization length and timescale $1/\omega_0$ of lattice dynamics: *the longer it localizes, the lower the mobility*

- The transport mechanism is far from semiclassical

$$\Delta x^2(t) = \langle |x(t) - x(0)|^2 \rangle$$



Transient localization

- **Frozen molecular displacements:**

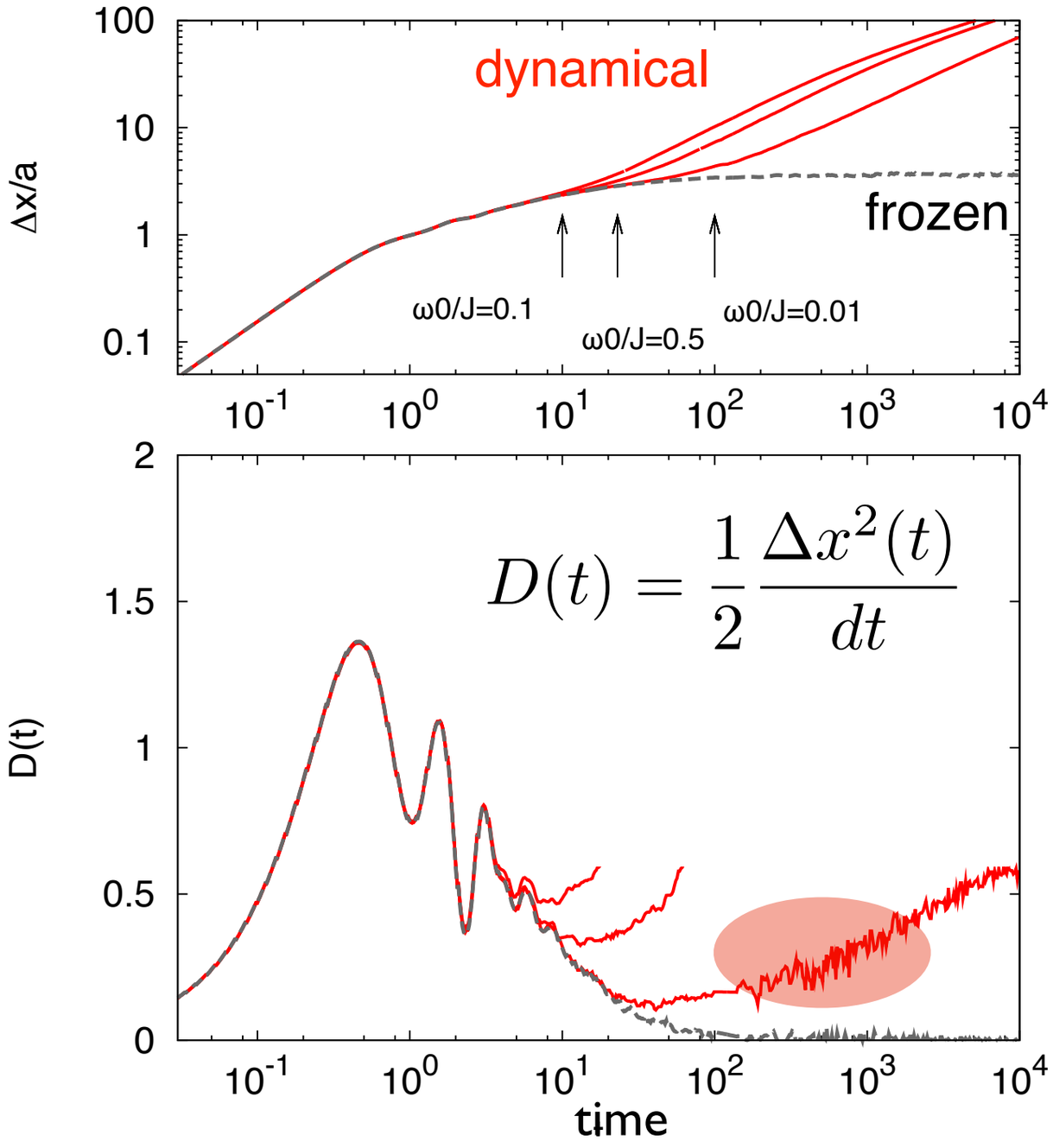
--> **Anderson localization**
finite localization length,
diffusivity vanishes at long times

- **Dynamical molecular displacements:**

--> **transient localization**: initially the diffusivity decreases and the particle localizes as if the disorder were static

- At later times, lattice dynamics destroy the quantum interferences at the origin of localization --> **diffusion sets back in**
- mobility depends on transient localization length and timescale $1/\omega_0$ of lattice dynamics: *the longer it localizes, the lower the mobility*
- The transport mechanism is far from semiclassical

$$\Delta x^2(t) = \langle |x(t) - x(0)|^2 \rangle$$



$$D(t) = \frac{1}{2}\frac{\Delta x^2(t)}{dt}$$

superdiffusive regime ->
drawback of Ehrenfest method, overestimates mobility

phenomenological description: Relaxation time approximation (RTA)

- take the frozen (localized) system as a reference system:

the correlations in the velocity-velocity correlation function that give rise to localization are destroyed after a time $\tau_{in} \sim 1/\omega_0$

$$C_+^{RTA}(t) = C_0(t)e^{-t/\tau_{in}}$$

$C_0(t)$ taken from frozen molecular evolution

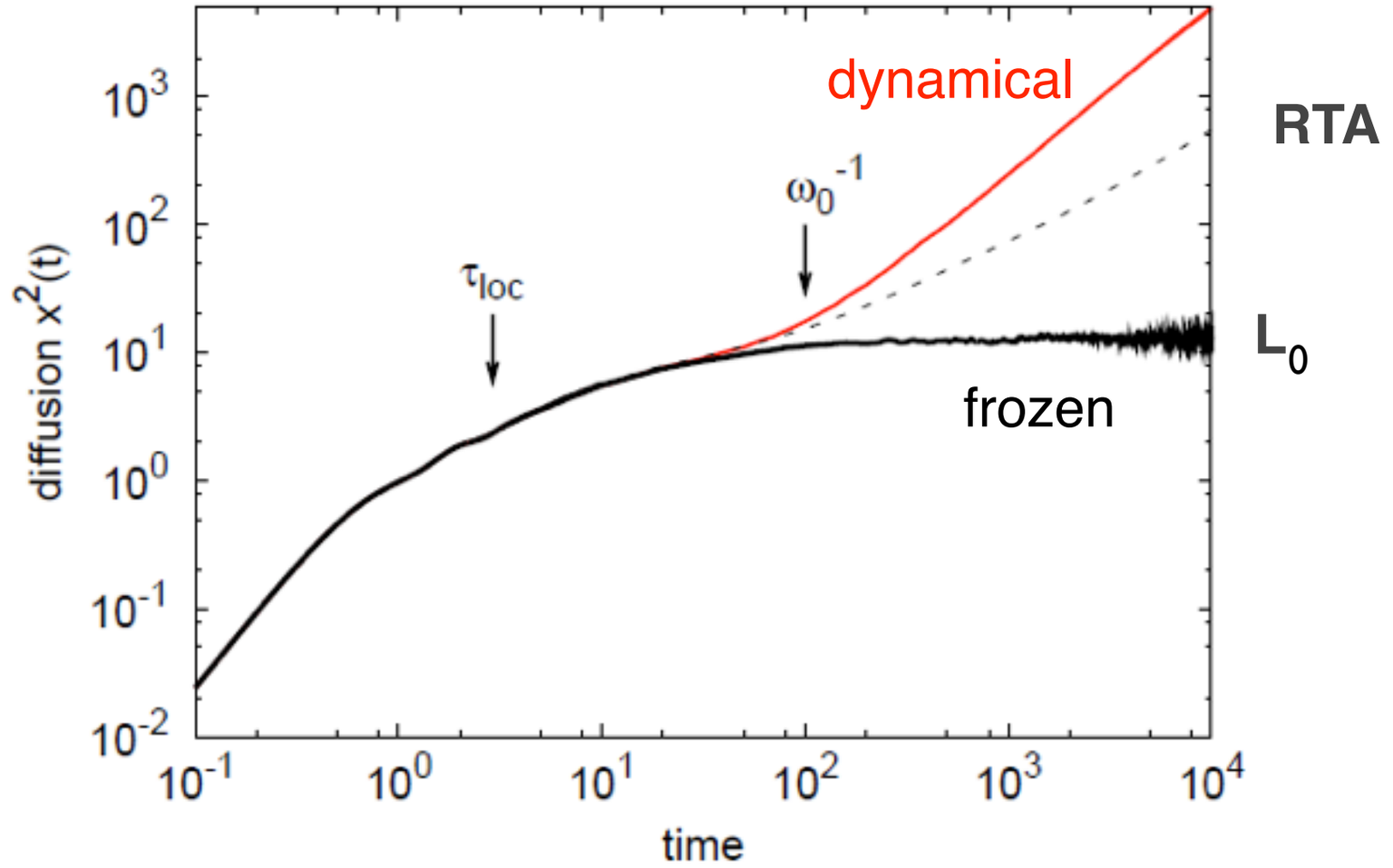
phenomenological description: Relaxation time approximation (RTA)

- take the frozen (localized) system as a reference system:

the correlations in the velocity-velocity correlation function that give rise to localization are destroyed after a time $\tau_{in} \sim 1/\omega_0$

$$C_+^{RTA}(t) = C_0(t) e^{-t/\tau_{in}}$$

$C_0(t)$ taken from frozen molecular evolution



phenomenological description: Relaxation time approximation (RTA)

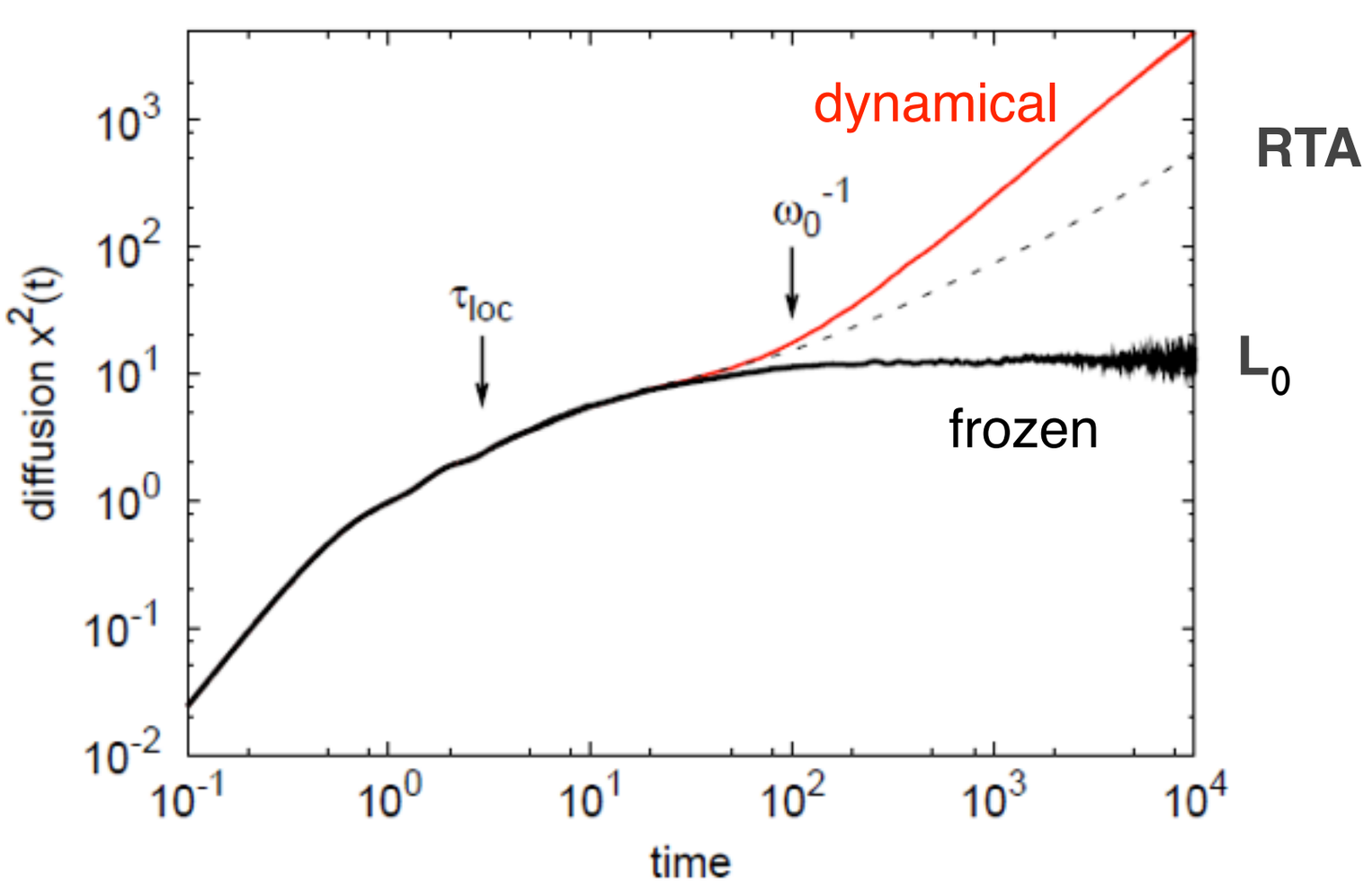
- take the frozen (localized) system as a reference system:
the correlations in the velocity-velocity correlation function that give rise to localization are destroyed after a time $\tau_{in} \sim 1/\omega_0$

$$C_+^{RTA}(t) = C_0(t)e^{-t/\tau_{in}}$$

$C_0(t)$ taken from frozen molecular evolution

- qualitative agreement with Ehrenfest dynamics, numerically much faster (and heals superdiffusive behavior at long t)
- restores a non-zero mobility

$$\mu(T) \simeq \frac{e}{k_B T} \frac{L_0^2(\tau_{\rm in})}{2\tau_{\rm in}}$$



phenomenological description: Relaxation time approximation (RTA)

- take the frozen (localized) system as a reference system: the correlations in the velocity-velocity correlation function that give rise to localization are destroyed after a time $\tau_{in} \sim 1/\omega_0$

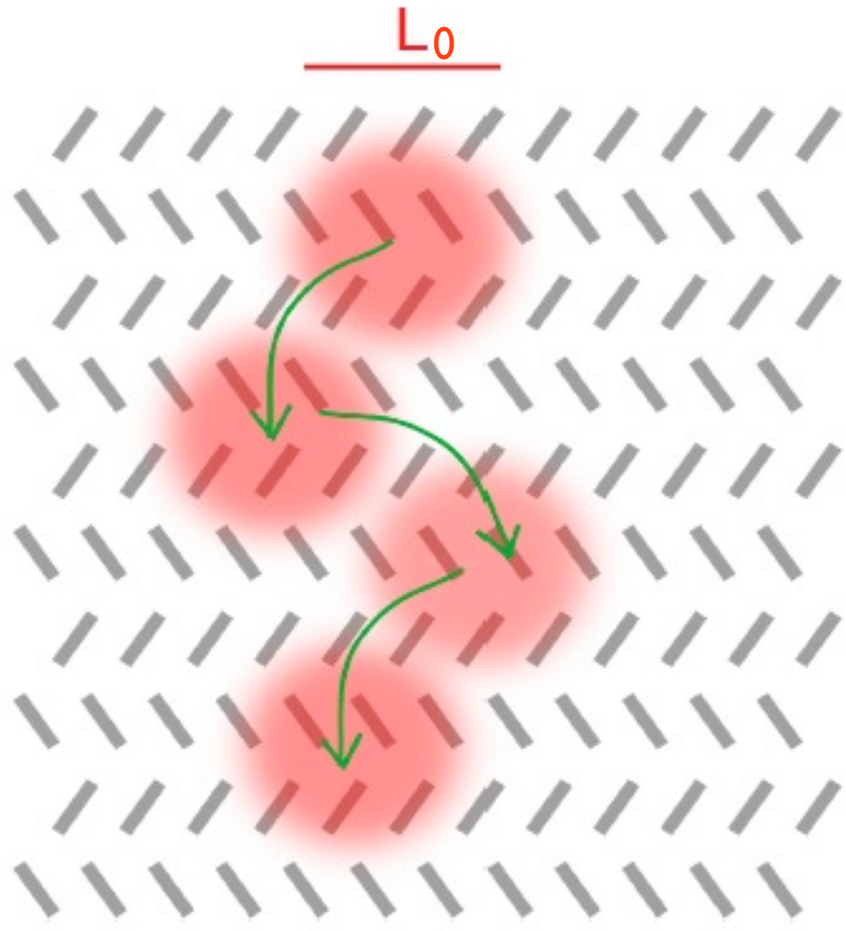
$$C_+^{RTA}(t) = C_0(t)e^{-t/\tau_{in}}$$

$C_0(t)$ taken from frozen molecular evolution

- qualitative agreement with Ehrenfest dynamics, numerically much faster (and heals superdiffusive behavior at long t)
- restores a non-zero mobility

$$\mu(T) \simeq \frac{e}{k_B T} \frac{L_0^2(\tau_{\rm in})}{2\tau_{\rm in}}$$

- equivalent to diffusive jumps of length L_0 with trial rate $1/\tau_{in}$ (Thouless diffusivity)



Outline

- Introduction: something's wrong with the "common wisdom"

- **ARPES**:

the role of intramolecular vibrations and disorder

- **Transport properties**:

the role of intermolecular vibrations and the concept of transient localization

- **Kubo formula revisited**: carrier diffusivity from optical experiments

- Concluding remarks

Quantum diffusion from the Kubo formula

- optical conductivity

$\sigma(\omega) = \frac{1}{\nu\hbar\omega} Re \int_0^\infty dt e^{i\omega t} C_-(t)$ — (-) → $C_-(t) =< [\hat{J}_x(t), \hat{J}_x(0)] >$

- quantum diffusivity

$\Delta X^2(t) = \langle [\hat{X}(t) - \hat{X}(0)]^2 \rangle, \quad \frac{d\Delta X^2(t)}{dt} = \frac{1}{e^2} \int_0^t C_+(t') dt'.$

(+) → $C_+(t) =< \{\hat{J}_x(t), \hat{J}_x(0)\} >$

Quantum diffusion from the Kubo formula

- optical conductivity

$\sigma(\omega) = \frac{1}{\nu\hbar\omega} Re \int_0^\infty dt e^{i\omega t} C_-(t)$ — (-) → $C_-(t) =< [\hat{J}_x(t), \hat{J}_x(0)] >$

- quantum diffusivity

$\Delta X^2(t) = \langle [\hat{X}(t) - \hat{X}(0)]^2 \rangle, \qquad \frac{d\Delta X^2(t)}{dt} = \frac{1}{e^2} \int_0^t C_+(t') dt'.$

(+) → $C_+(t) =< \{\hat{J}_x(t), \hat{J}_x(0)\} >$

- detailed balance $C_-(\omega) = \tanh(\frac{\beta\hbar\omega}{2}) C_+(\omega).$

$$\sigma(\omega) = -\frac{e^2}{\hbar\nu} \omega \tanh(\frac{\beta\hbar\omega}{2}) Re \int_0^\infty dt e^{i(\omega + i\delta)t} \Delta X^2(t)$$

[see also N. H. Lindner and A. Auerbach, PRB 2010]

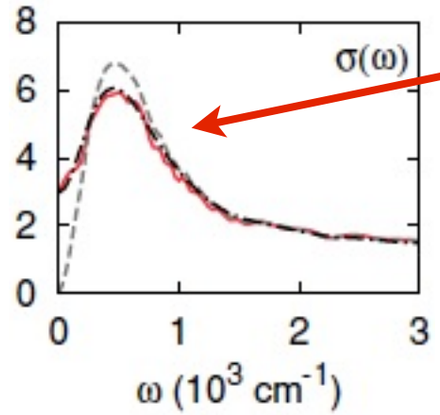
- inversion: quantum diffusion from experiment

$$\Delta x^2(t) = \frac{2\hbar}{\pi e^2} \mathrm{Re} \int_0^\infty (1 - e^{-i\omega t}) \frac{\sigma(\omega)/n}{\omega \tanh(\beta\hbar\omega/2)} d\omega$$

Real time dynamics from experiment

$$\Delta x^2(t) = \frac{2\hbar}{\pi e^2}\mathrm{Re}\int_0^\infty (1-e^{-i\omega t})\frac{\sigma(\omega)/n}{\omega\tanh(\beta\hbar\omega/2)}d\omega$$

Rubrene: measured optical conductivity



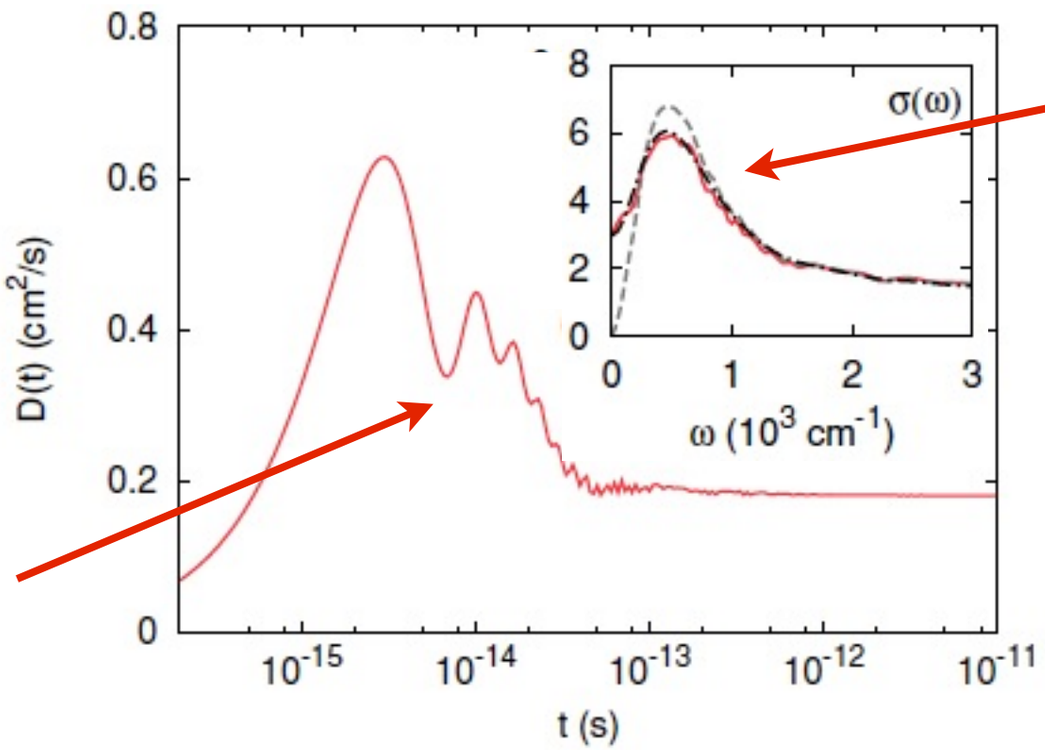
[Z. Q. Li, et al., PRL 99, 016403 (2007)]

Real time dynamics from experiment

$$\Delta x^2(t) = \frac{2\hbar}{\pi e^2}\mathrm{Re}\int_0^\infty (1-e^{-i\omega t})\frac{\sigma(\omega)/n}{\omega\tanh(\beta\hbar\omega/2)}d\omega$$

diffusivity from Fourier transform

diffusivity decreases at intermediate times: experimental proof of transient localization



Rubrene: measured optical conductivity

[Z. Q. Li, et al., PRL 99, 016403 (2007)]

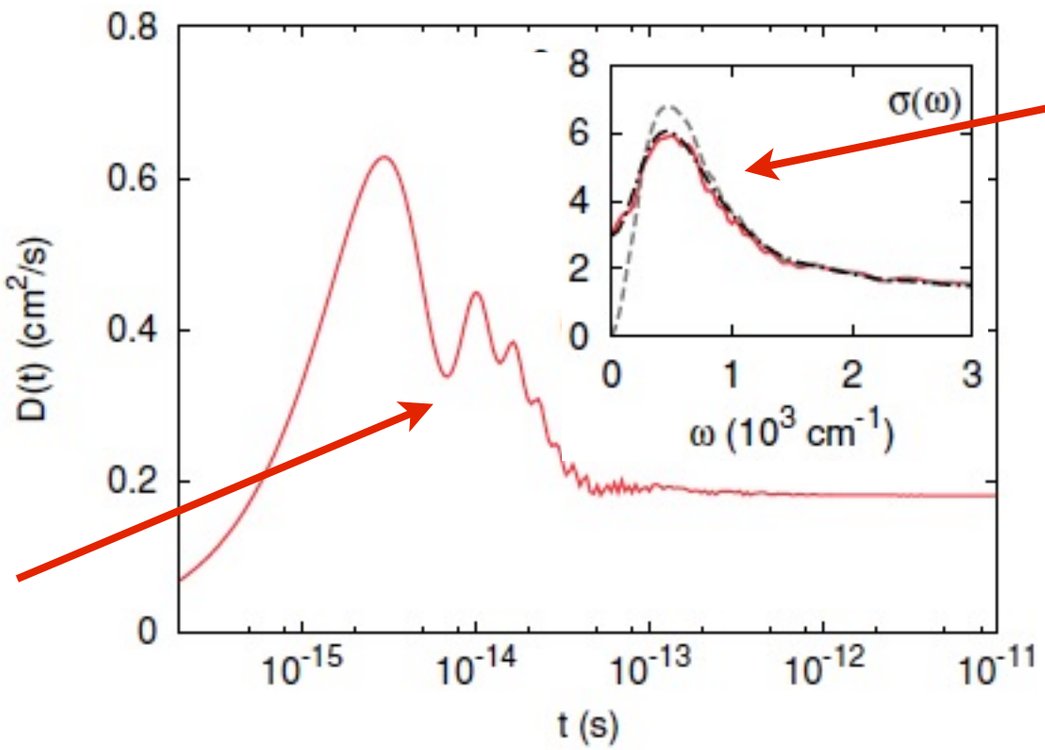
Peak in optical conductivity <=> Transient localization phenomenon

Real time dynamics from experiment

$$\Delta x^2(t) = \frac{2\hbar}{\pi e^2}\mathrm{Re}\int_0^\infty (1-e^{-i\omega t})\frac{\sigma(\omega)/n}{\omega\tanh(\beta\hbar\omega/2)}d\omega$$

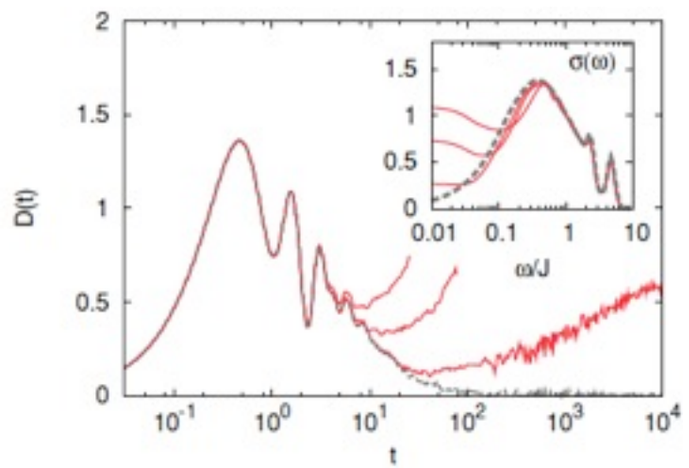
diffusivity from Fourier transform

diffusivity decreases at intermediate times: experimental proof of transient localization



Rubrene: measured optical conductivity

[Z. Q. Li, et al., PRL 99, 016403 (2007)]



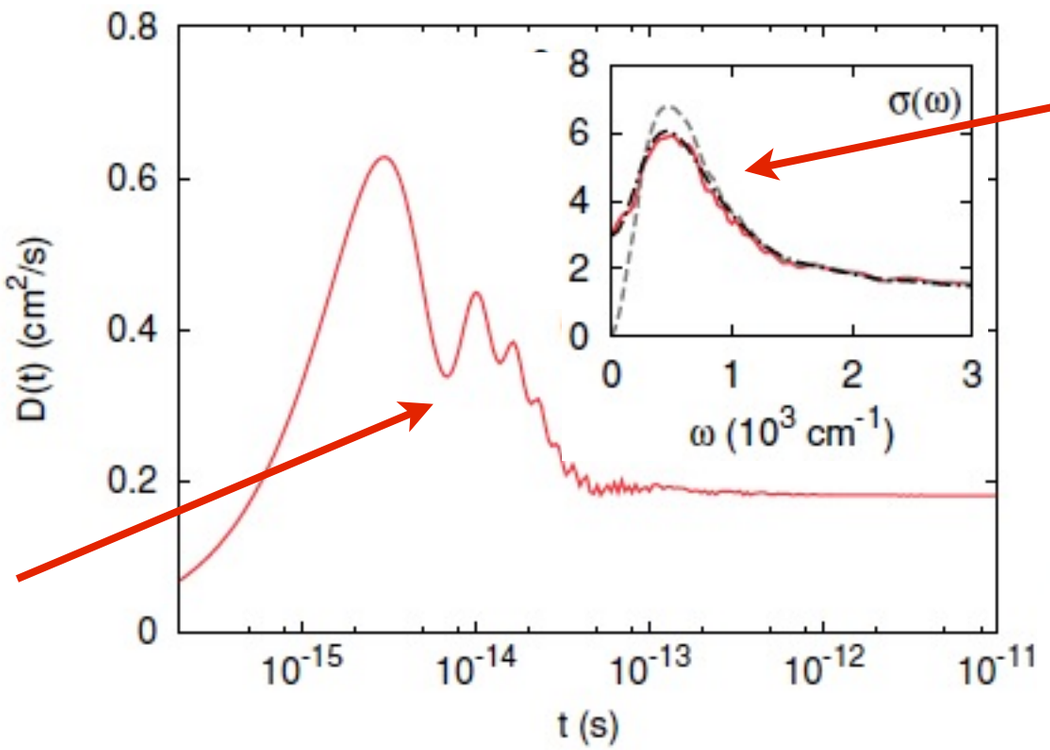
Peak in optical conductivity <=> Transient localization phenomenon

Real time dynamics from experiment

$$\Delta x^2(t) = \frac{2\hbar}{\pi e^2}\mathrm{Re}\int_0^\infty (1-e^{-i\omega t})\frac{\sigma(\omega)/n}{\omega\tanh(\beta\hbar\omega/2)}d\omega$$

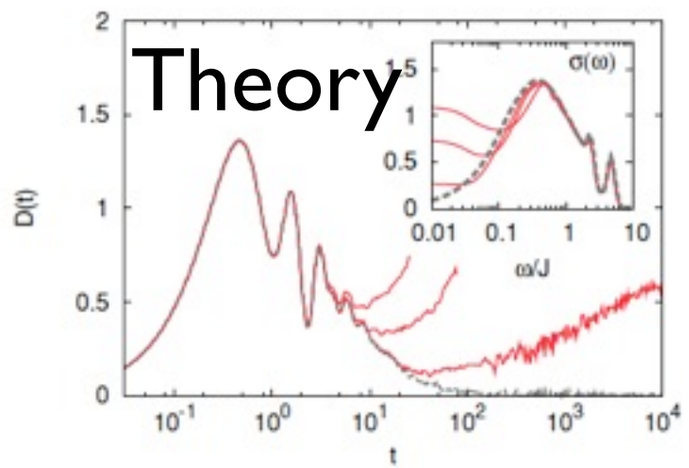
diffusivity from Fourier transform

diffusivity decreases at intermediate times: experimental proof of transient localization



Rubrene: measured optical conductivity

[Z. Q. Li, et al., PRL 99, 016403 (2007)]



Peak in optical conductivity <=> Transient localization phenomenon

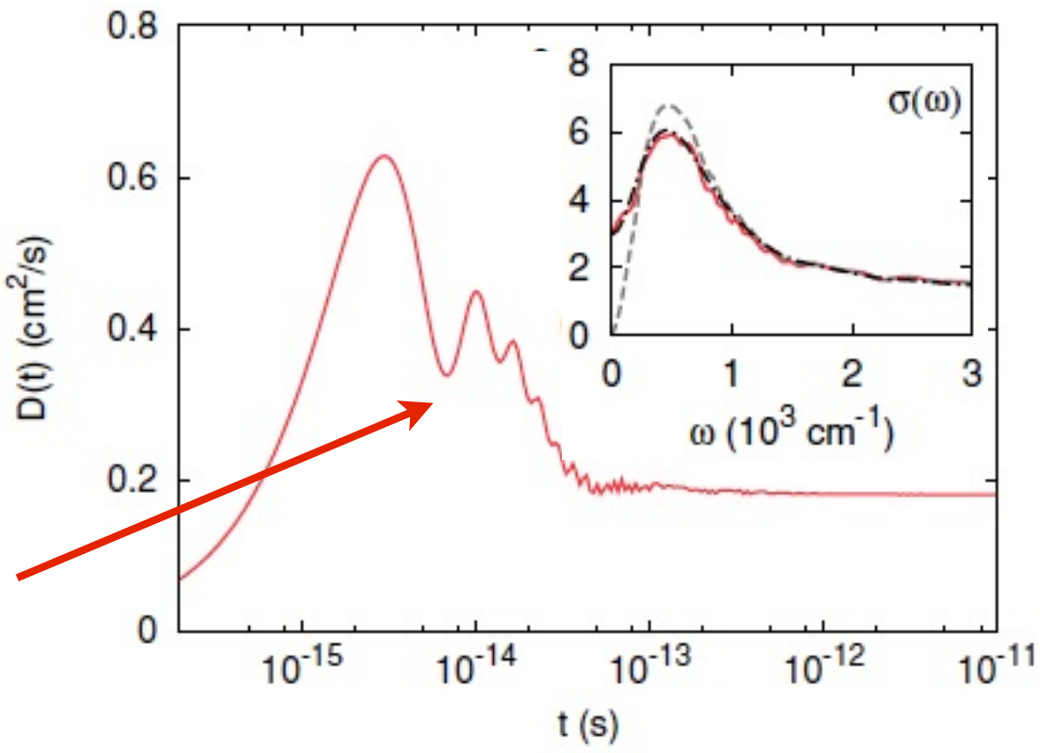
Real time dynamics from experiment

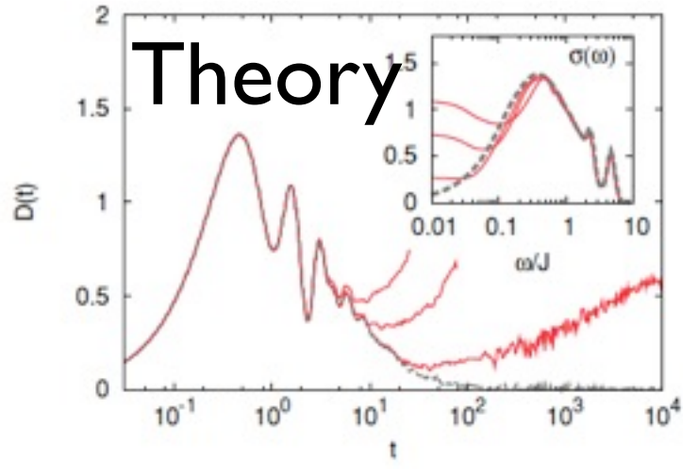
By analyzing the quantum diffusion data with the RTA we can extract:

- the inelastic time -> $\hbar/\tau_{in} = 104 cm^{-1}$ (typical inter-molecular vibrations)
- the transient localization length $L_0(1/\tau_{in}) = 2a$ (localization is important)

diffusivity from Fourier transform

diffusivity decreases at intermediate times: experimental proof of transient localization





Peak in optical conductivity <=> Transient localization phenomenon

Outline

- Introduction: something's wrong with the "common wisdom"
- ARPES:

the role of intramolecular vibrations and disorder

- Transport properties:

the role of intermolecular vibrations and the concept of transient localization

- Kubo formula revisited: carrier diffusivity from optical experiments
- Concluding remarks

Conclusions

❖ electronic band theory is not enough to describe the electronic properties of organic semiconductors (but bands are there, so molecular approaches also fail)

❖ **ARPES**: including the interaction with high frequency intramolecular vibrations and disorder provides an accurate description of the experimental photoemission spectra.

❖ **Transport**: interaction with low frequency intermolecular vibrations seems to be the crucial ingredient to understand charge transport: the dynamical disorder arising from lattice motion causes transient localization phenomena (and a breakdown of Boltzmann theory).

❖ The instantaneous diffusivity of the carriers can be extracted from optical absorption experiments via an appropriate Kubo formula.

References

[S. Ciuchi, R. C. Hatch, H. Höchst, C. Faber, X. Blase, S. Fratini PRL (2012) to appear]

[S. Ciuchi and S. Fratini Phys. Rev. Lett. 106, 166403 (2011)]

[S.Ciuchi, S. Fratini D. Mayou. Phys. Rev. B.83, 081202(R) (2011)]

[S. Fratini and S.Ciuchi Phys. Rev. Lett. 103, 266601 (2009)]