# Exciton transfer in the optical cycle of α-PTCDA

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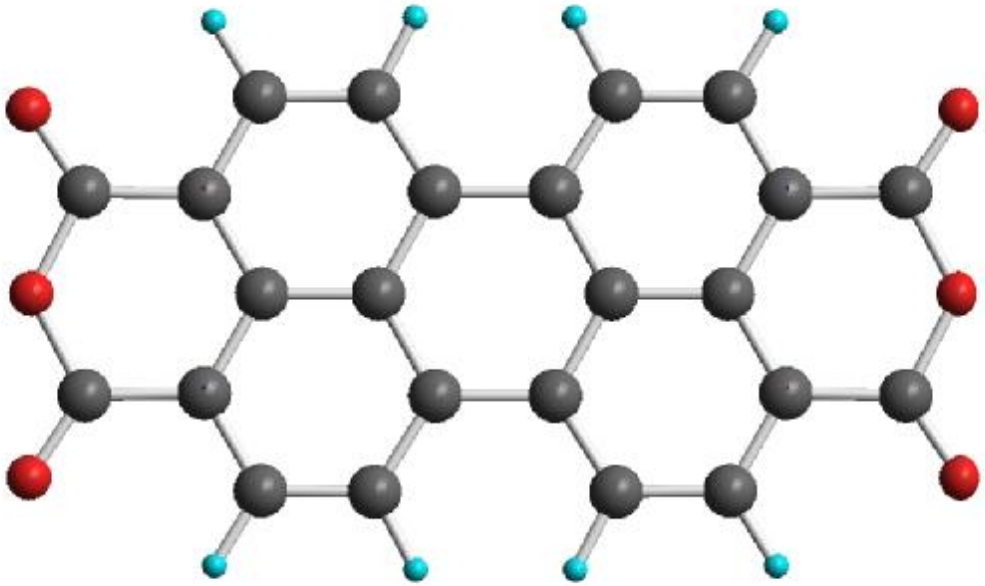
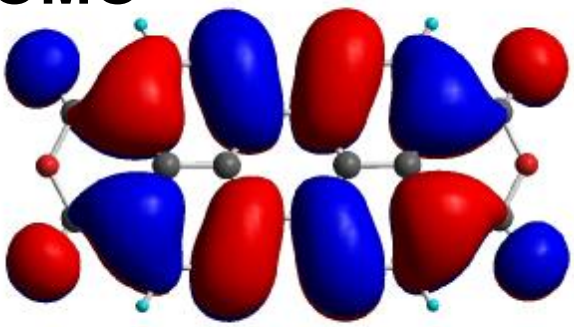
CoPhen04, Dresden, 16 June 2004

# PTCDA

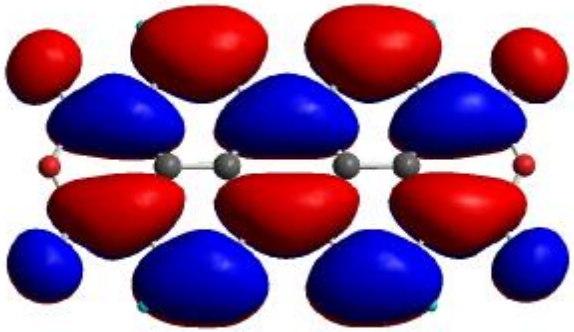
## 3,4,9,10,-Perylene TetraCarboxylic DiAnhydride ($C_{24}H_8O_6$)



HOMO



LUMO



# *Outline*

- Motivation: Material, experimental techniques
- Photoluminescence: Early results
- Time-resolved PL results on α-**PTCDA** single crystals
- Theoretical calculations of excitons in α-**PTCDA** crystals
  - ***Monomer:*** relaxed excited state, resonant Raman
  - ***Frenkel excitons:*** absorption, low-temperature PL
  - ***Time-dependent DFT for molecular dimers:***
    red shift in crystalline phase, slow PL channels
  - ***Configuration interaction of singles (CIS), Møller-Plesset (MP2)***
    self-trapping of excimer along stack direction
- Summary

# Motivation

- **PTCDA**
  prototypic organic material
  ***short stacking distance* (3.21 Å)**
  ***large $\pi$-overlap*** between stack neighbours
  grows on most substrates in rather ***well-ordered*** films
  absorbs ***in the visible***
  ***high mobility*** for organic semiconductors **(1 $cm^2V^{-1}s^{-1}$)**

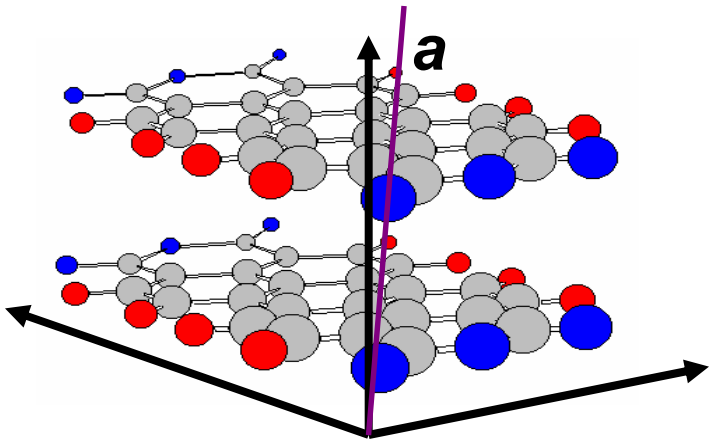
- **Time-resolved photoluminescence**
  information about ***relaxed excited states***
  ***complementary information*** with respect to absorption
  ***thermalization and relaxation*** of excitons
  ***PL quenching***: non-radiative recombination channels

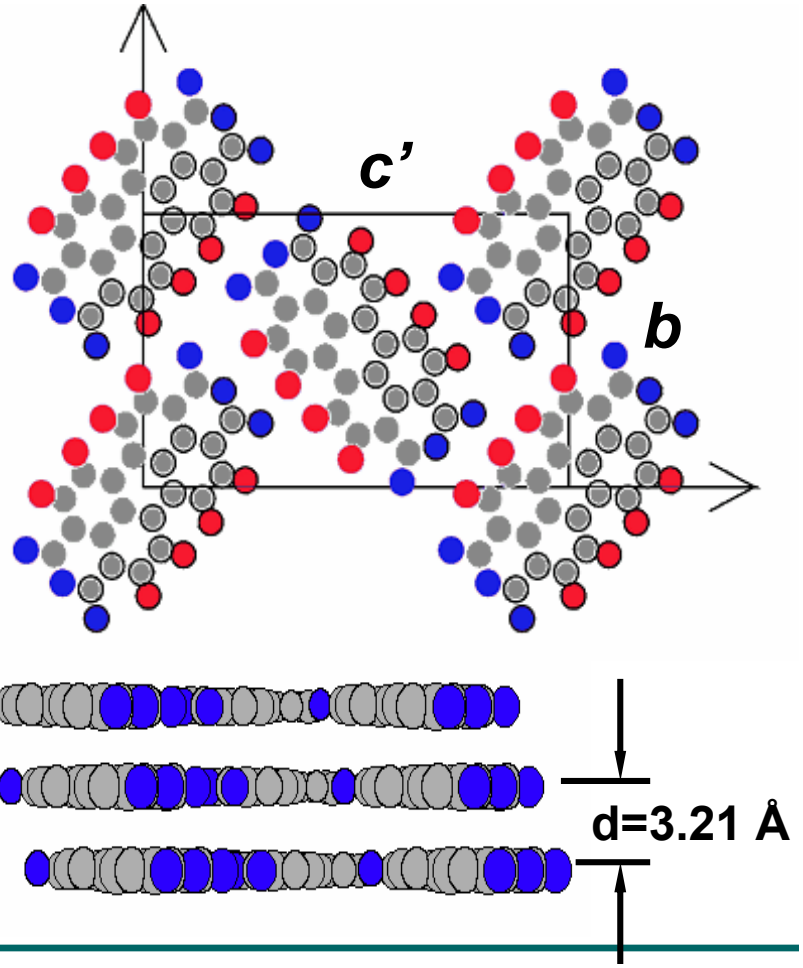
- **Theory**
  microscopic understanding of ***energetics*** and ***decay times***

# PTCDA crystal structure

## 3,4,9,10,-Perylene TetraCarboxylic DiAnhydride ($C_{24}H_8O_6$)

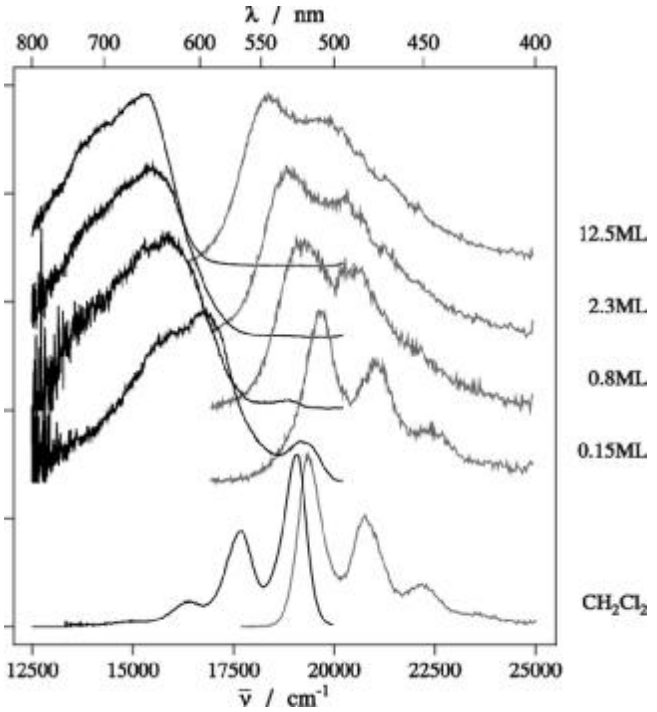
- Monoclinic structure
- $C_{2h}$ symmetry space group
- 2 molecules per unit cell
- $\alpha$- and $\beta$- phases

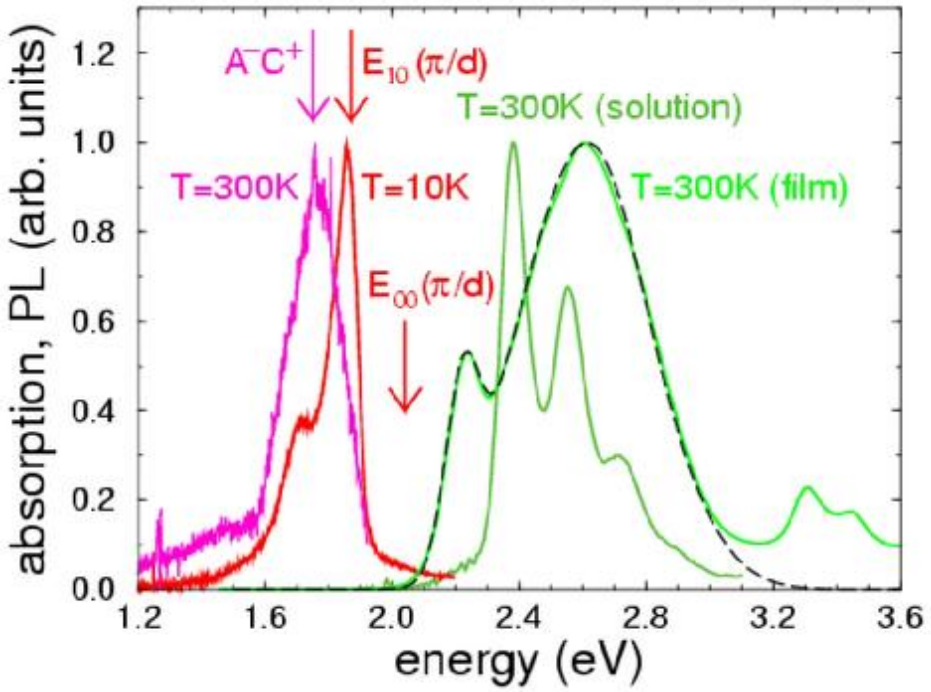


# *Photoluminescence: Early results*

U. Gómez, M. Leonhardt, H. Port, and H.C. Wolf, Chem. Phys. Lett. **268**, 1 (1997)
A.Yu. Kobitski, G. Salvan, H.P. Wagner, D.R.T. Zahn, Appl.Surf.Sci. **175-76**, 363 (2001)

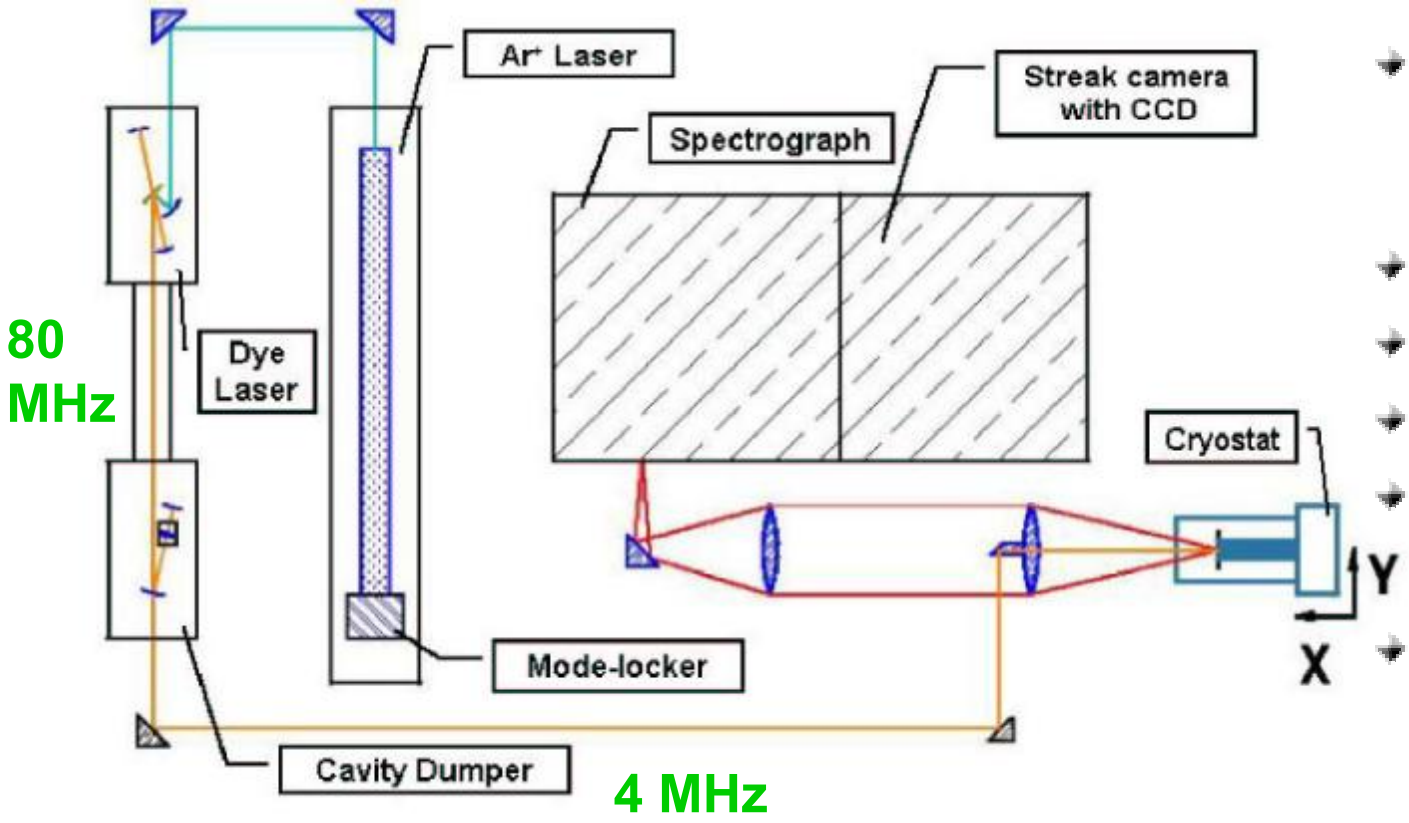



**Interpretation:** R. Scholz, I. Vragović, A.Yu.Kobitiski, G. Salvan, T.U. Kampen, MS, D.R.T.Zahn, Proc. of Int. School of Physics *E. Fermi*, course CXLIX (2001): ***Organic nanostructures: Science and applications***, ed. by V.M. Agranovich and G.C. La Rocca

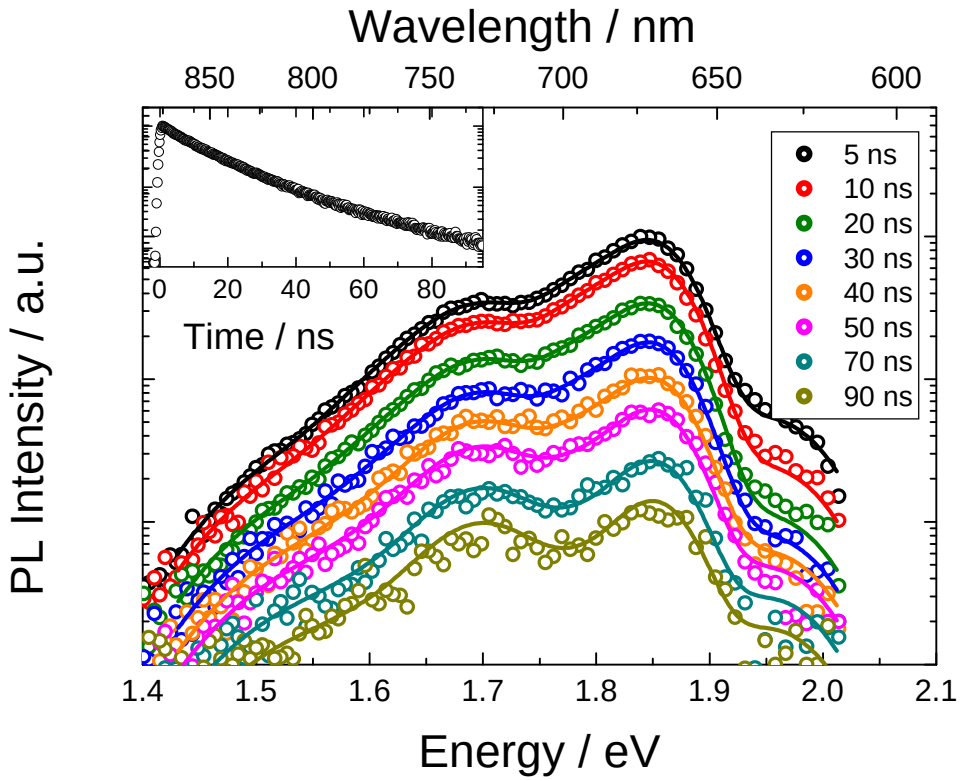
# *Experimental set-up*

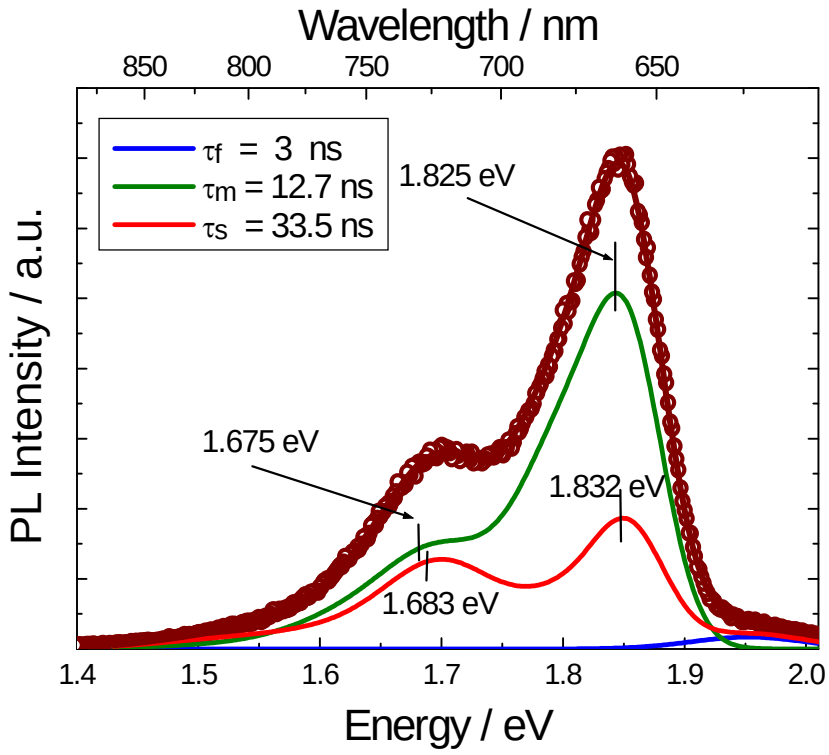
for time-resolved photoluminescence at different temperatures




- **excitation:** 2.14 – 2.18 eV (570 - 580 nm)
- laser pulse: 20 ps
- **pulse rate: 4 MHz**
- delay: **100 ns**
- **cutoff filter:** 2.10 eV (590 nm)
- **T = 10 – 300 K**

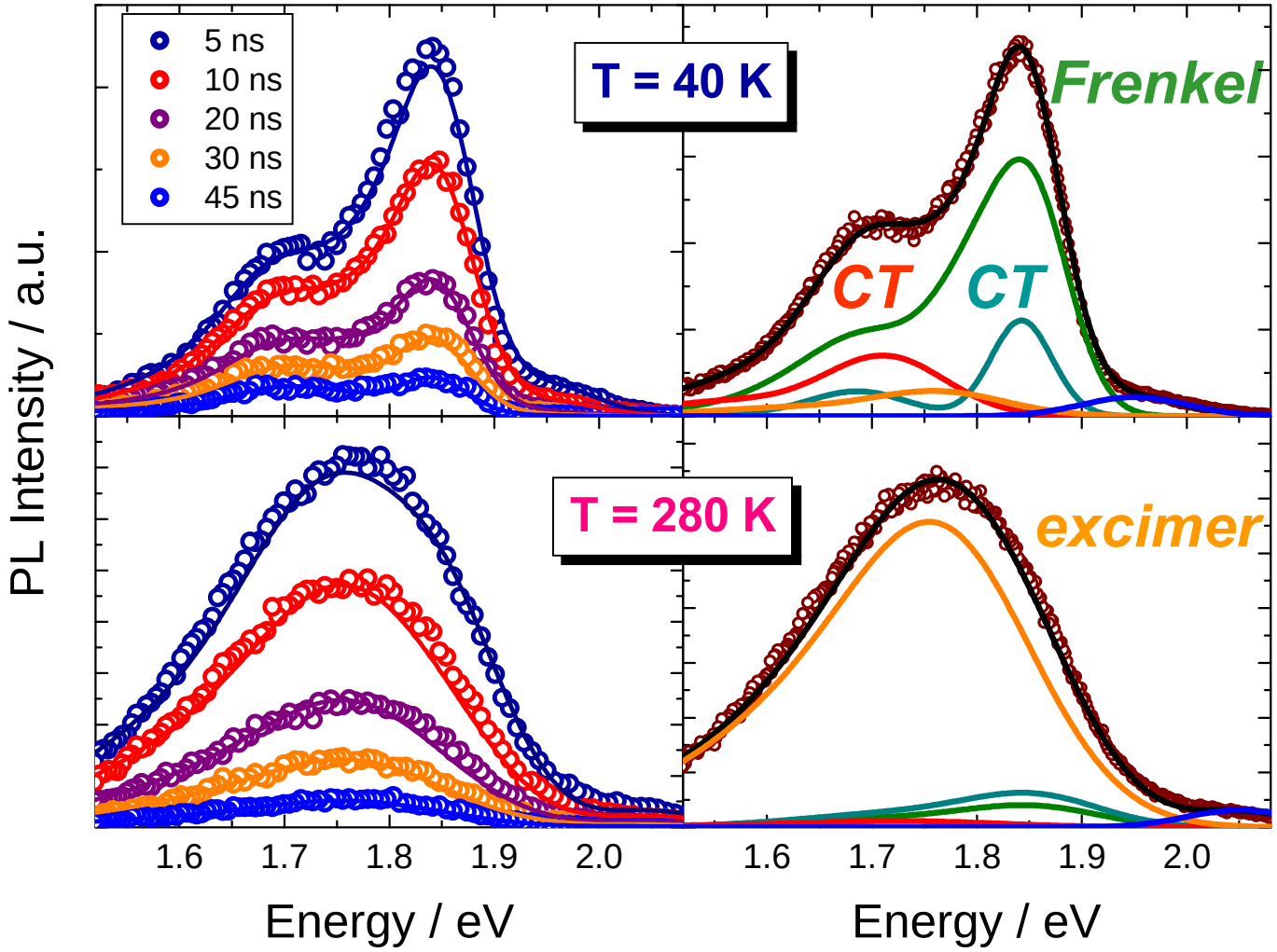
# PL components at low temperature




- $\tau_m$ is due to ***Frenkel excitons*** [R. Scholz, et al., phys. stat. sol. (b) **234**, 402 (2002)]
- $\tau_s$ is related to ***anion-cation pairs*** and ***excimers*** [R.Scholz et al., ICPS26]
- ***higher temperatures:*** distinction between ***three slow PL channels***

# PL spectra at higher temperatures




A. Yu. Kobitski, R. Scholz, H.-P. Wagner, D.R.T. Zahn, PRB **68**, 155201 (2003)

# Exciton kinetics: decay times

$$\frac{1}{\tau(T)} = \frac{1}{\tau^{rad}} + \gamma^{nrad} \exp\left(-\frac{\Delta^{nrad}}{k_B T}\right)$$

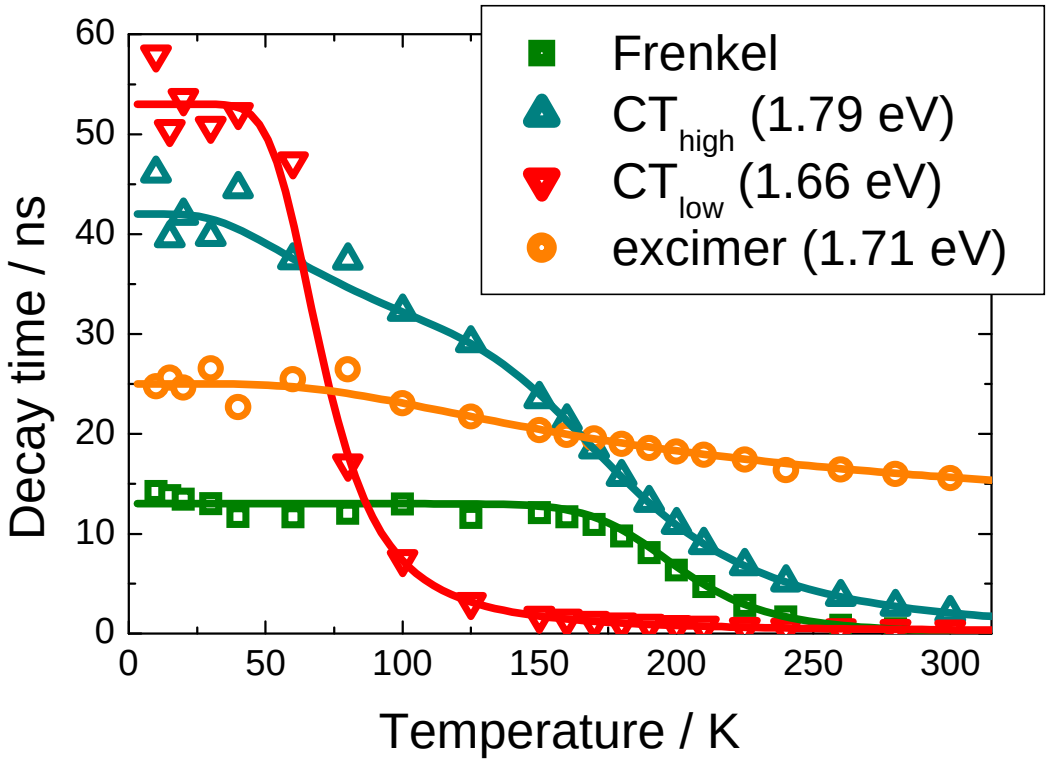
**Radiative decay times**

$$\tau_{CT_{high}} = 42\,\text{ns}$$

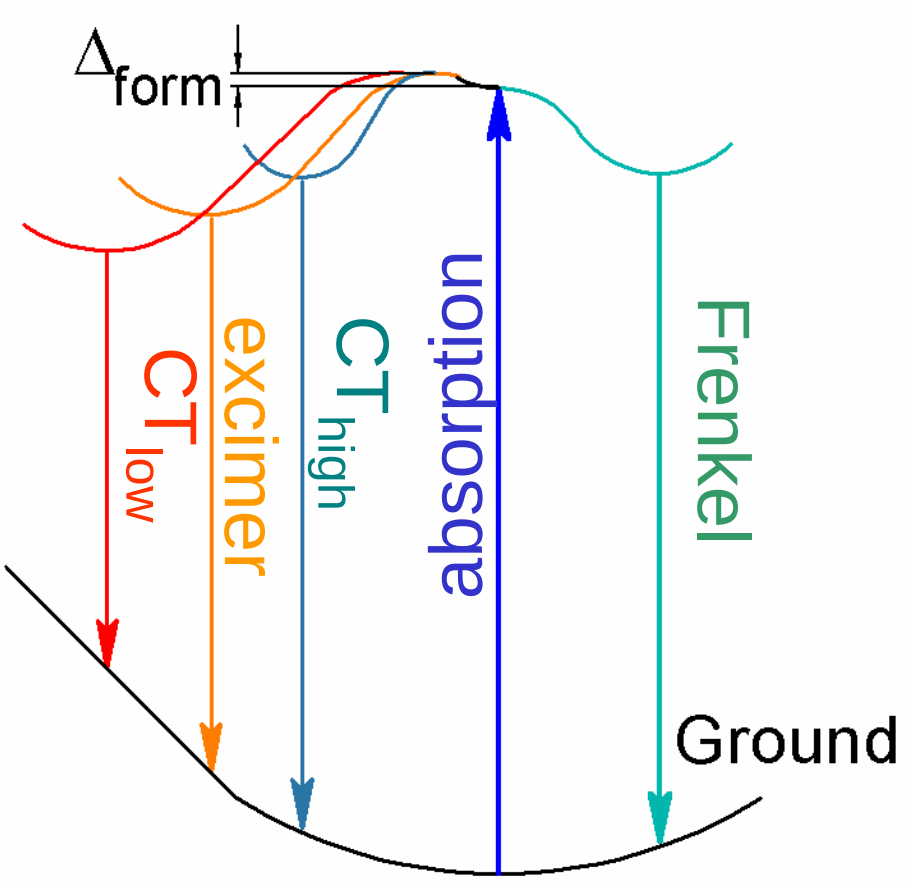
$$\tau_{CT_{low}} = 53\,\text{ns}$$

$$\tau_{Exc} = 25\,\text{ns}$$

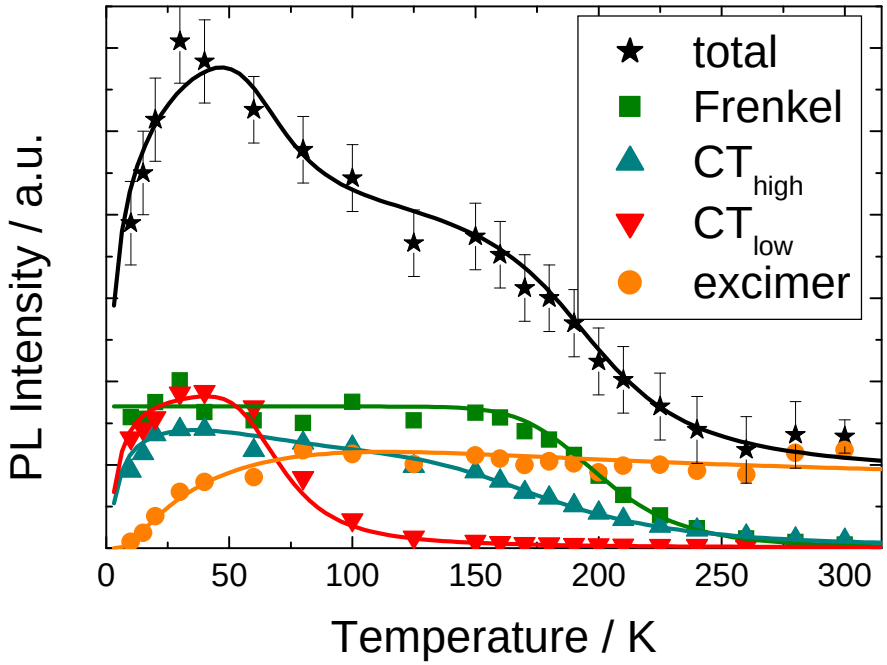
$$\tau_{F} = 13\,\text{ns}$$



# PL recombination scenario in PTCDA

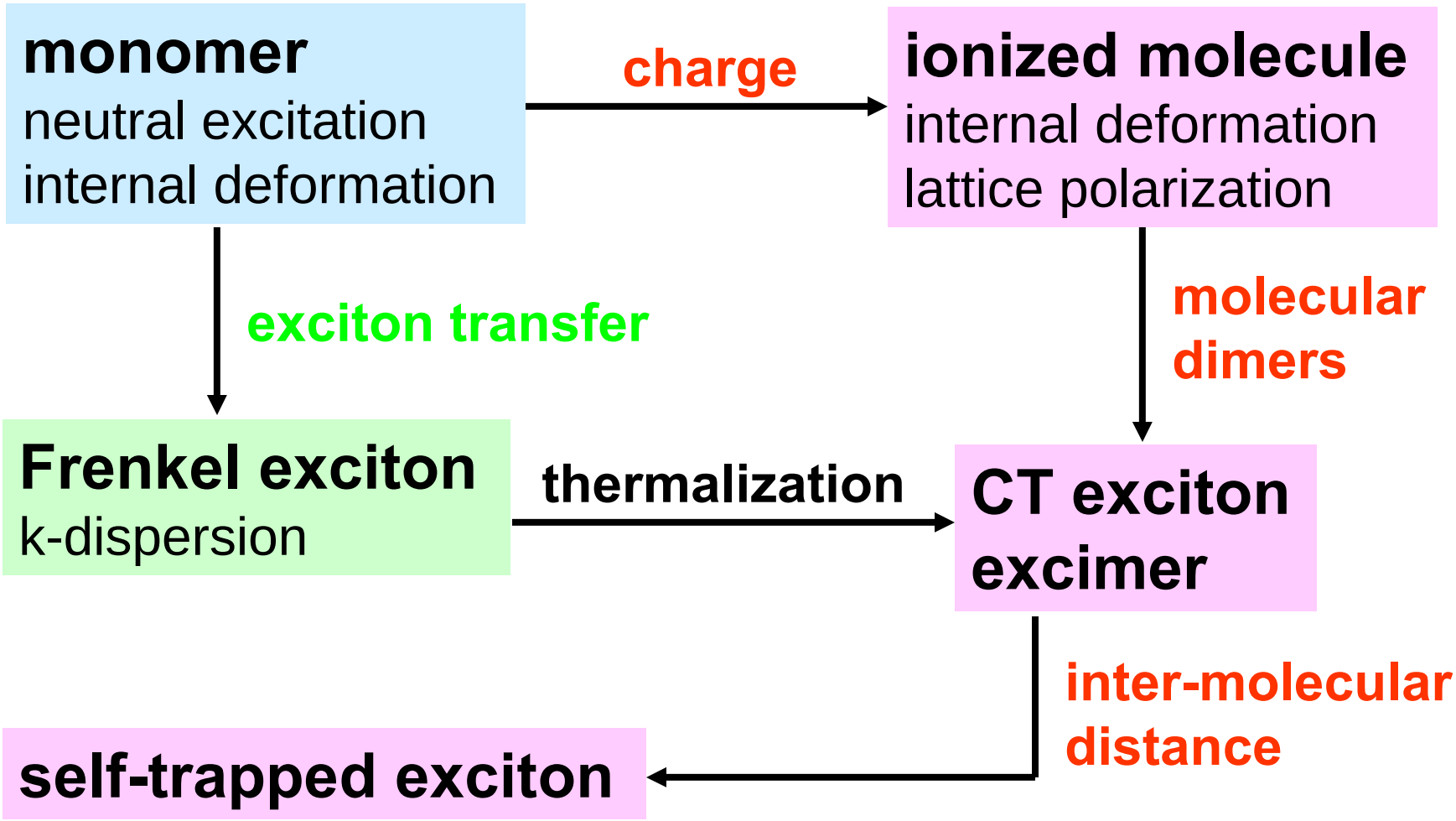



$$I(T) = I_0 \cdot \exp\left(-\frac{\Delta_{form}}{k_B T}\right) \cdot \frac{\tau(T)}{\tau^{rad}}$$




$\Delta_{CT\ high}$ = 0.3 meV $\Delta_{CT\ low}$ = 0.3 meV $\Delta_{Excimer}$ = 2.7 meV

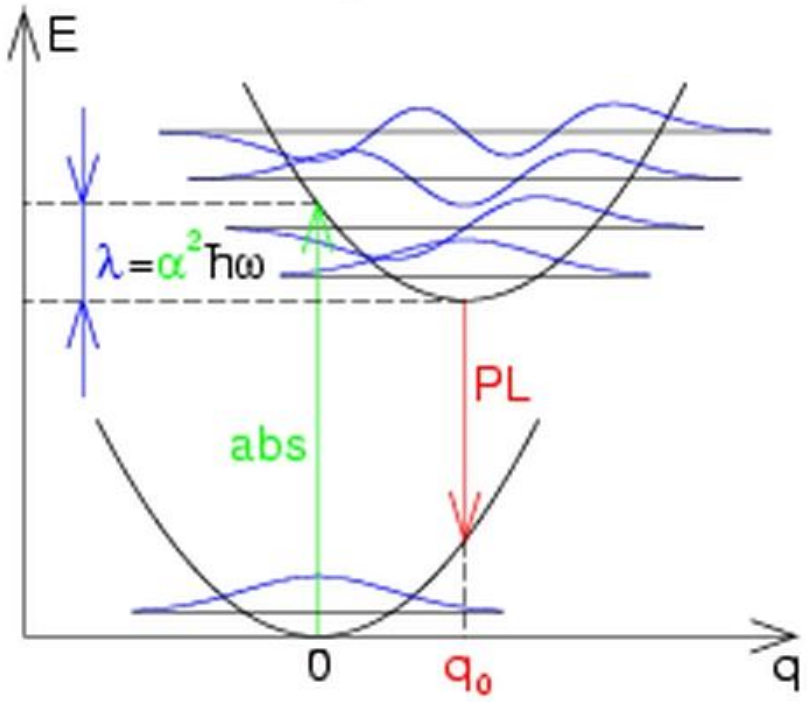
# *Strategy for microscopic models*



# *Theory: Monomer*

- **geometry in relaxed excited state**
- **linear absorption, resonant Raman**

# Displaced Harmonic Oscillator




Reorganization energy:

$$\lambda = |\alpha|^2 \hbar\omega = \frac{m\omega^2}{2} q_0^2$$

$$H_g = \frac{p^2}{2m} + \frac{m\omega^2}{2} q^2$$

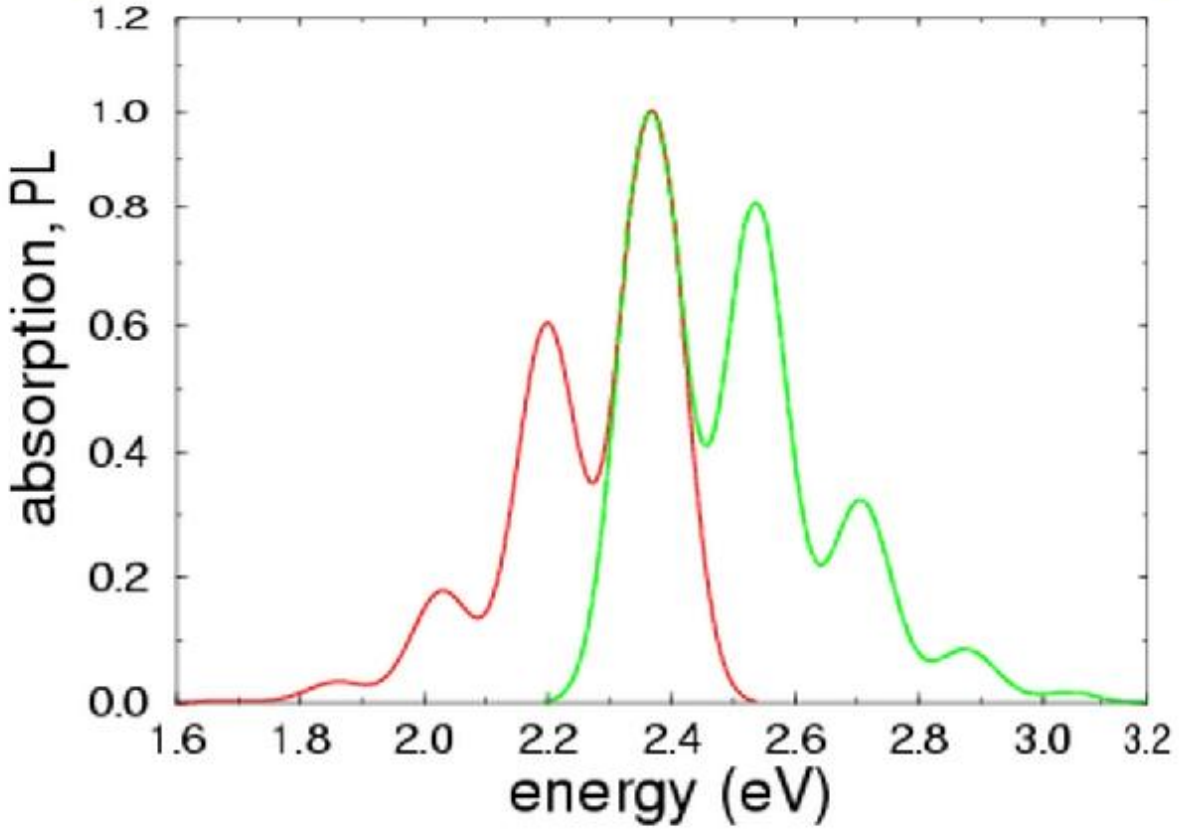
$$H_e = \frac{p^2}{2m} + \frac{m\omega^2}{2} (q - q_0)^2$$

Transition probability:

$$P(|0_g\rangle \to |n_e\rangle) = P(|0_e\rangle \to |n_g\rangle) \quad = e^{-|\alpha|^2} \frac{(|\alpha|^2)^n}{n!}$$ Poisson

Stokes Raman: $\sigma_R(E_L) \propto \alpha^2 (\hbar\omega)^2 [1 + n_{th}(\hbar\omega, k_B T)]$

# Displaced harmonic oscillator: Absorption, PL




$E_{00} = 2.38$ eV

$\hbar\omega = 0.17$ eV

$\alpha^2 = 0.75$

$$\Gamma(|0_e\rangle \rightarrow |n_g\rangle) = \frac{e^2|\mathbf{r}_{12}|^2\omega_n^3}{3\pi\epsilon_0\hbar c^3} P_n(\alpha^2)$$

# Geometry of relaxed excited state

## Density functional:

Perdew-Burke-Ernzerhof, gradient corrected

## Variational basis:

minimal basis of compressed Slater orbitals

‘‘Density-Functional Tight-Binding, DFTB‘‘

T. Frauenheim. G. Seifert, M. Elstner, Z. Hajnal, G. Jungnickel, D. Porezag, S. Suhai, R. Scholz, phys. stat. sol (b) **217**, 41 (2000)

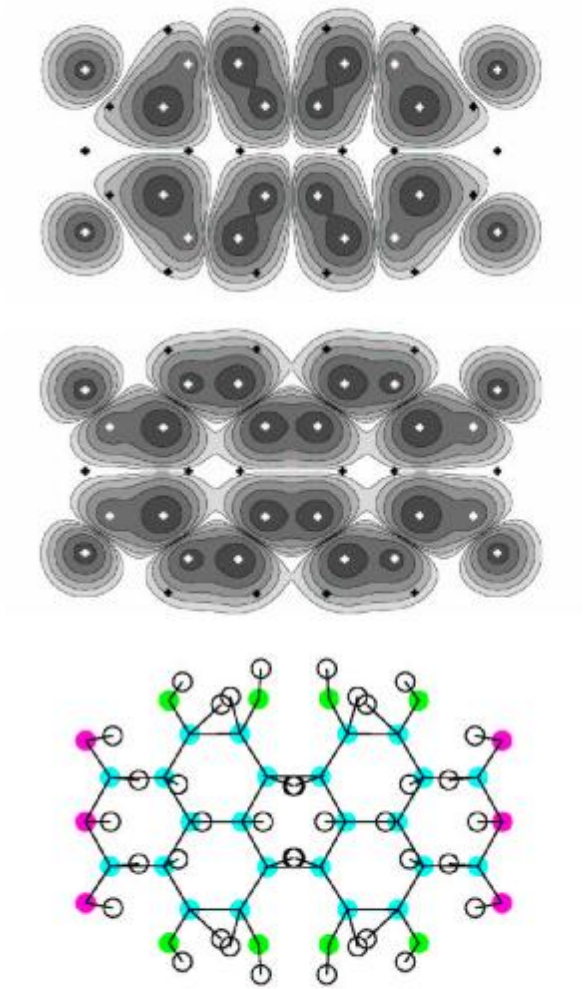
## Short-range repulsive energy semi-empirical:

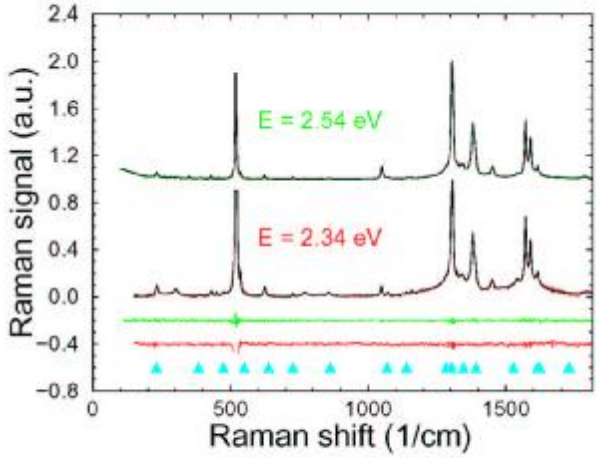
correct slope for bond length of diamond, $C_6H_6$

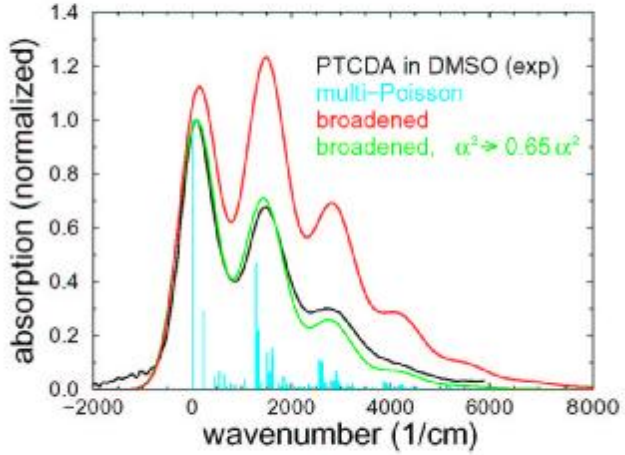
curvature: C-C stretching mode frequencies of $C_6H_6$

keep $n_{HOMO}=n_{LUMO}=1$ fixed

# OPTICAL PROPERTIES, RESONANT RAMAN

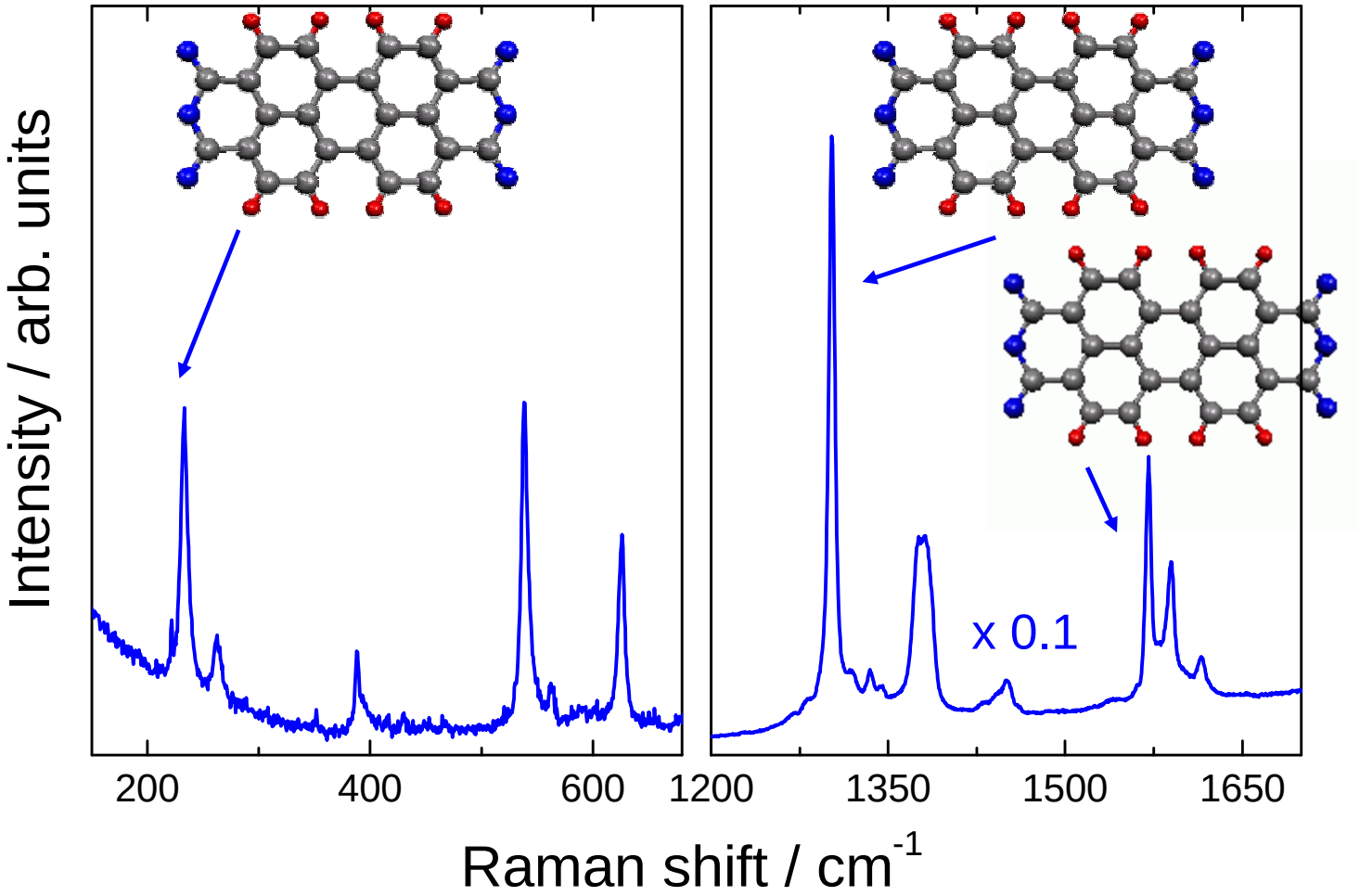




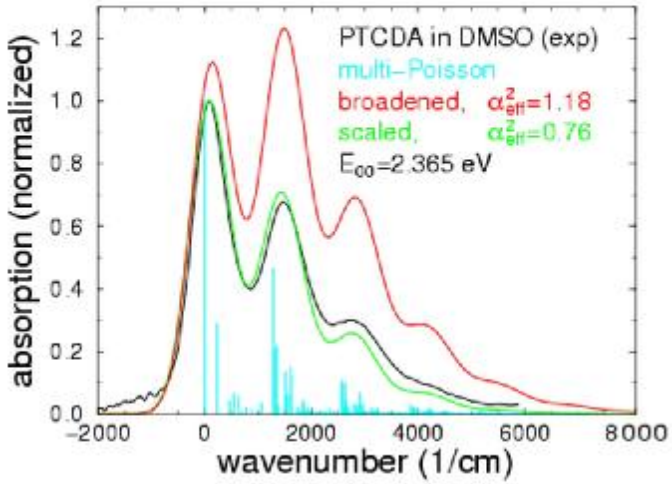

**HOMO-LUMO transition ⇒ deformation ⇒ elongation $A_g$ modes**

# Raman Spectrum of a PTCDA Crystal



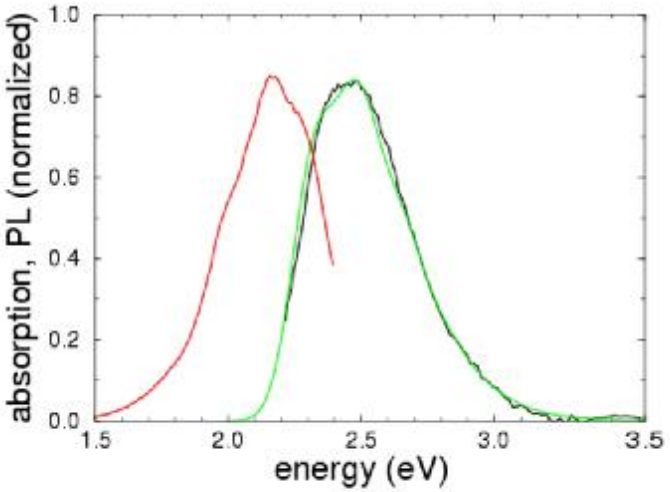
# Scaling of internal deformation

PTCDA dissolved in dimethyl sulfoxide:
$\epsilon(0) = 46, \quad \epsilon(\hbar\omega = 0.17\ \text{eV})$ unknown
scaling: $\alpha^2_{\text{eff}} = 1.18 \rightarrow \alpha^2_{\text{eff}} = 0.76$




broadening: FWHM = 850 $\text{cm}^{-1}$

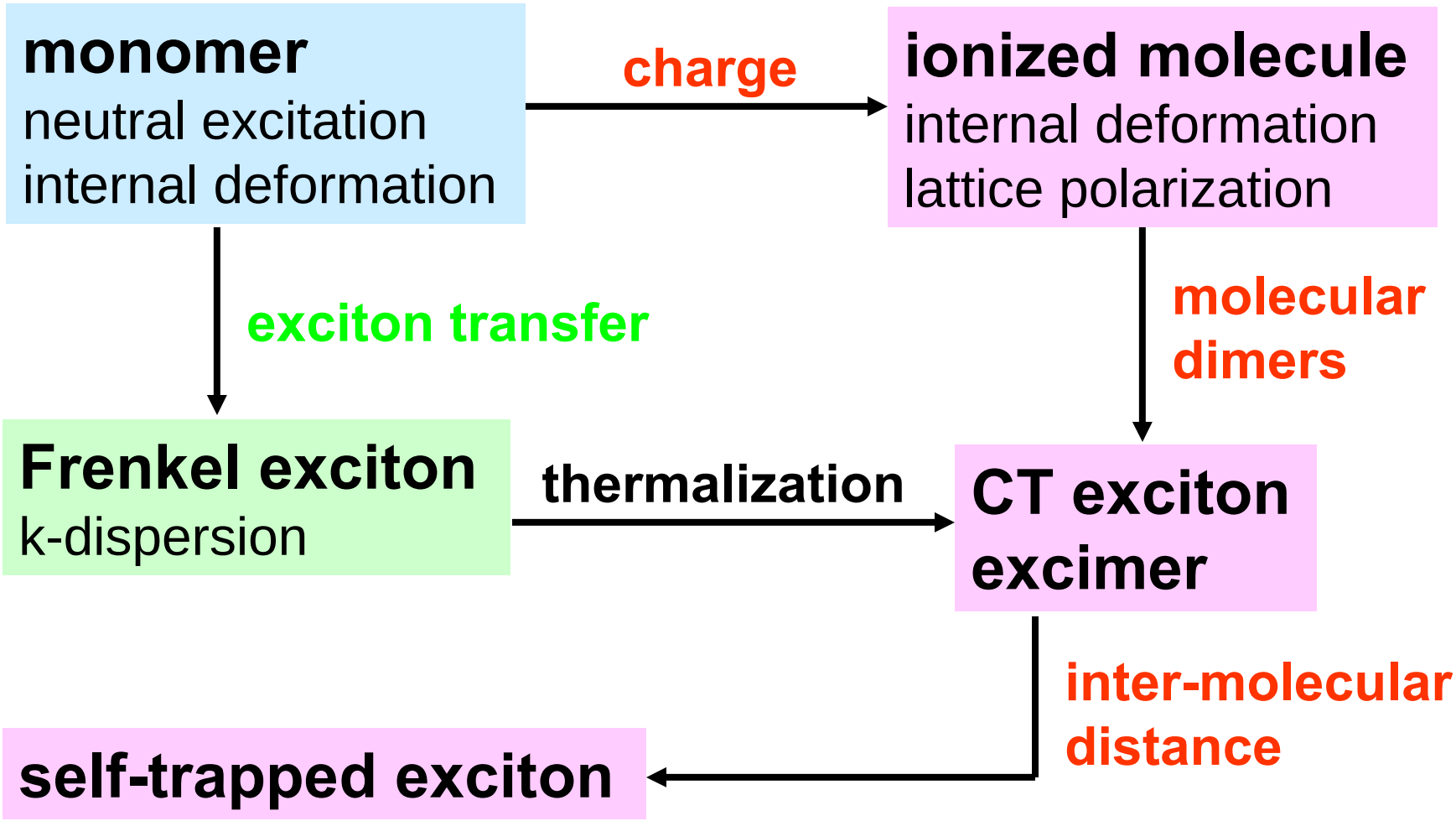
PTCDA in quartz glass matrix (H. Fröb):
$\epsilon(0) = 3.9, \quad \epsilon(\hbar\omega = 0.17\ \text{eV}) = 1$
no scaling: $\alpha^2_{\text{eff}} = 1.18$ as calculated




broadening: FWHM = 1500 $\text{cm}^{-1}$

PTCDA crystal: $\epsilon_{||}(0) = \epsilon_{||}(\hbar\omega = 0.17\ \text{eV}) = 4.07$
$\Rightarrow$ assume $\alpha^2_{\text{eff}} = 1.0$

# *Strategy for microscopic models*



# *Microscopic models for exciton transfer*

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*Michael Schreiber*

*CoPhen04, Dresden, 16 June 2004*

# Model Hamiltonian

$$H = \sum_{i\alpha\nu} \Delta_\nu b^+_{i\alpha\nu} b_{i\alpha\nu} + \sum_{i\alpha\nu} \sum_{j\beta\mu} t_{i\alpha\nu;j\beta\mu} b^+_{i\alpha\nu} b_{j\beta\mu}$$

$b^+_{i\alpha\nu}$ creates Frenkel exciton (Pauli-operator)

$b_{i\alpha\nu}$ annihilates Frenkel exciton

- in unit cell $i$
- on molecule $\alpha$
- in vibronic state $|\nu_e\rangle$

$\Delta_\nu$ transition energy, $\Delta_\nu = \Delta_0 + \nu\hbar\omega$

$t_{i\alpha\nu;j\beta\mu}$ transfer matrix element

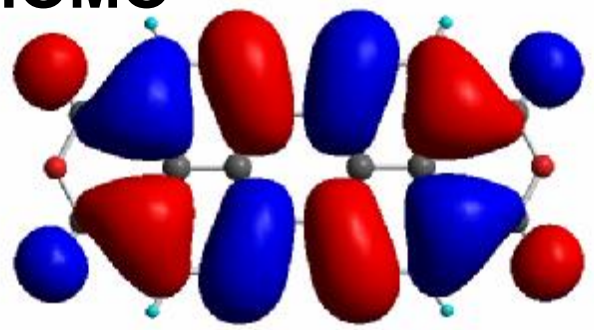
# Exciton transfer

**due to interaction between HOMO-LUMO transition dipoles**

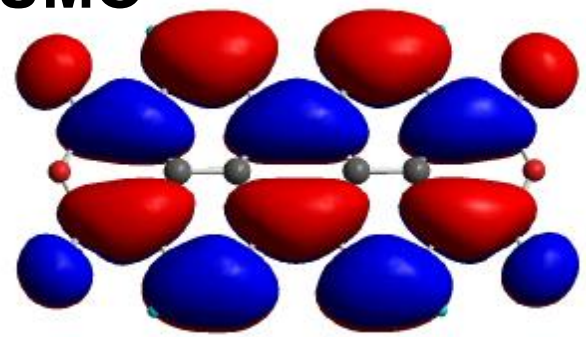
$$\langle \chi_{HOMO} | er | \chi_{LUMO} \rangle = \sum_i q_i R_i$$

⌘ **replace transition dipole by distribution of overlap charges**

**HOMO**



**LUMO**

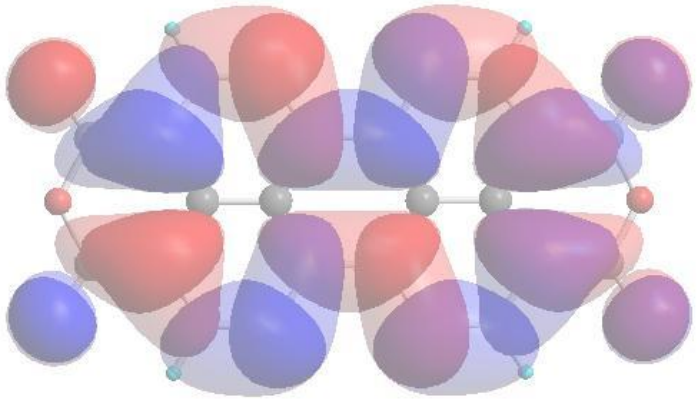


# Exciton transfer

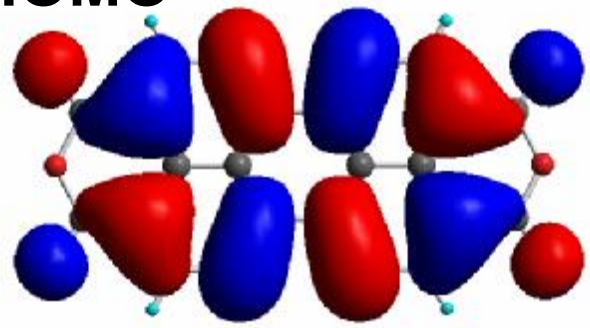
**due to interaction between HOMO-LUMO transition dipoles**

$\langle \boxtimes_{HOMO} | er | \boxtimes_{LUMO} \rangle = \blacklozenge_i \, q_i R_i$

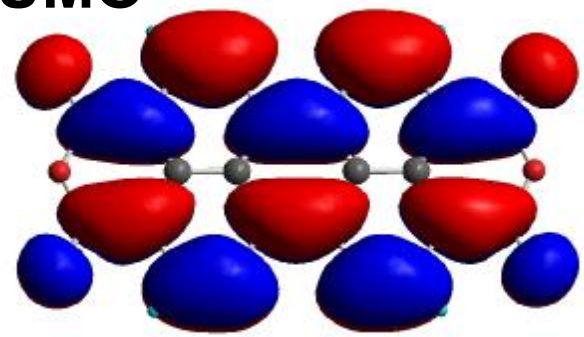
⌘ **replace transition dipole by distribution of overlap charges**



**HOMO**



**LUMO**



# *Related model calculations*

**single 1-dim stack**, **Frenkel** and **CT** excitons:
M. Hoffmann, K. Schmidt, T. Fritz, T. Hasche, V.M. Agranovich, and K. Leo, Chem. Phys. **258**, 73 (2000)

**two molecules** per unit cell, only **Frenkel** exciton:
**absorption:** I. Vragović, R. Scholz, M. Schreiber, Europhys. Lett. **57**, 288 (2002)
**photoluminescence:** R. Scholz, I. Vragović, A. Yu. Kobitski, M. Schreiber, H.-P. Wagner, and D.R.T. Zahn, phys. stat. sol. (b) **234**, 402 (2002);
I. Vragović, RS, PRB **68**, 155202 (2003)

**Frenkel** and **CT excitons**, spreading of **vibronic cloud**:
M. Hoffmann and Z.G. Soos, Phys. Rev. B **66**, 024305 (2002)

**Frenkel** and **CT excitons**, applied to **electro-absorption**:
G. Mazur, P. Petelenz, and M. Slawik, J. Chem. Phys. **118**, 1423 (2003)

# *Diagonalization:*

## Fourier transform to k-space

**Different points in the Brillouin zone decouple**

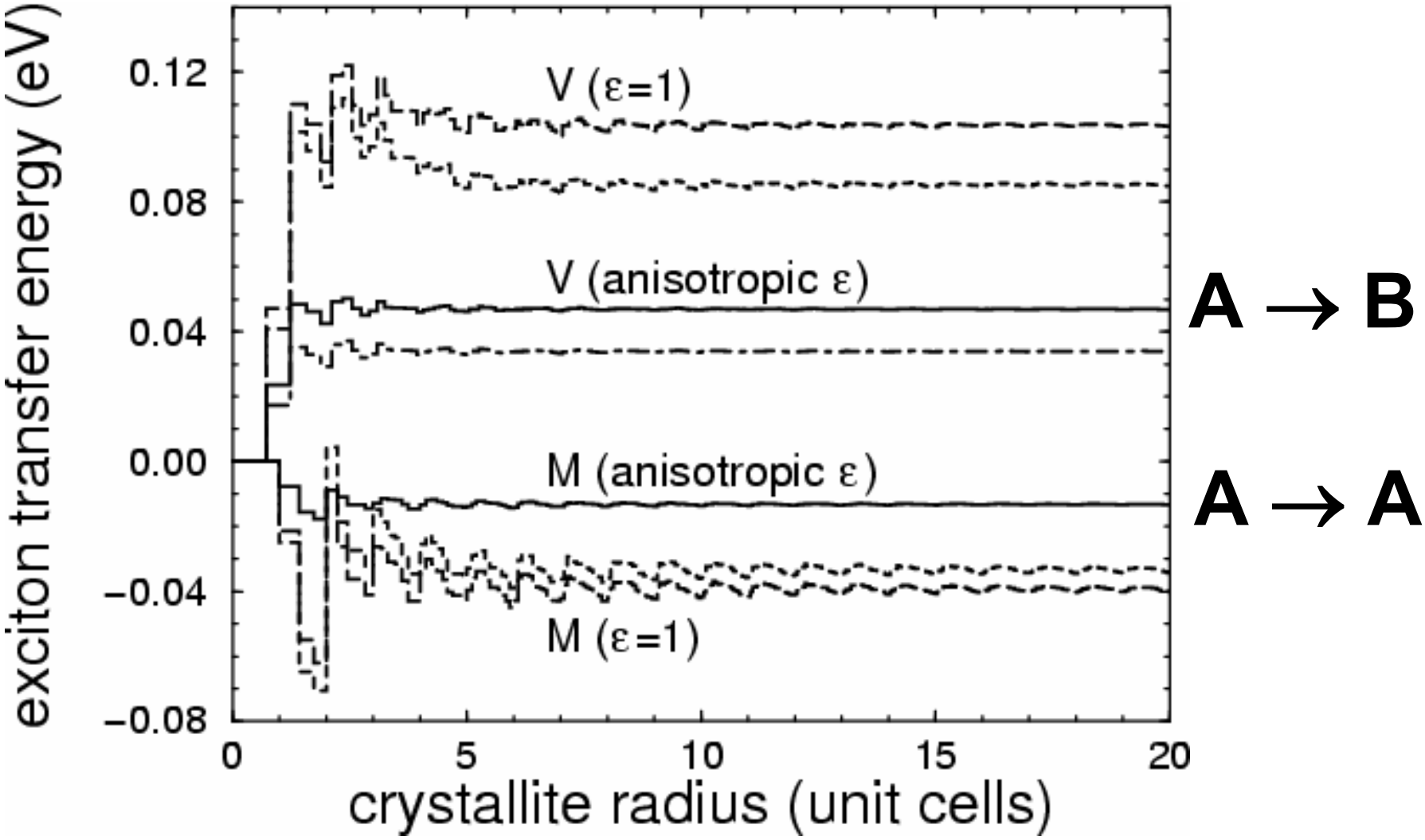
## Optical excitation:

**vertical excitation (photon wave vector: k=0)**
**creates Frenkel exciton at Γ-point of Brillouin zone**

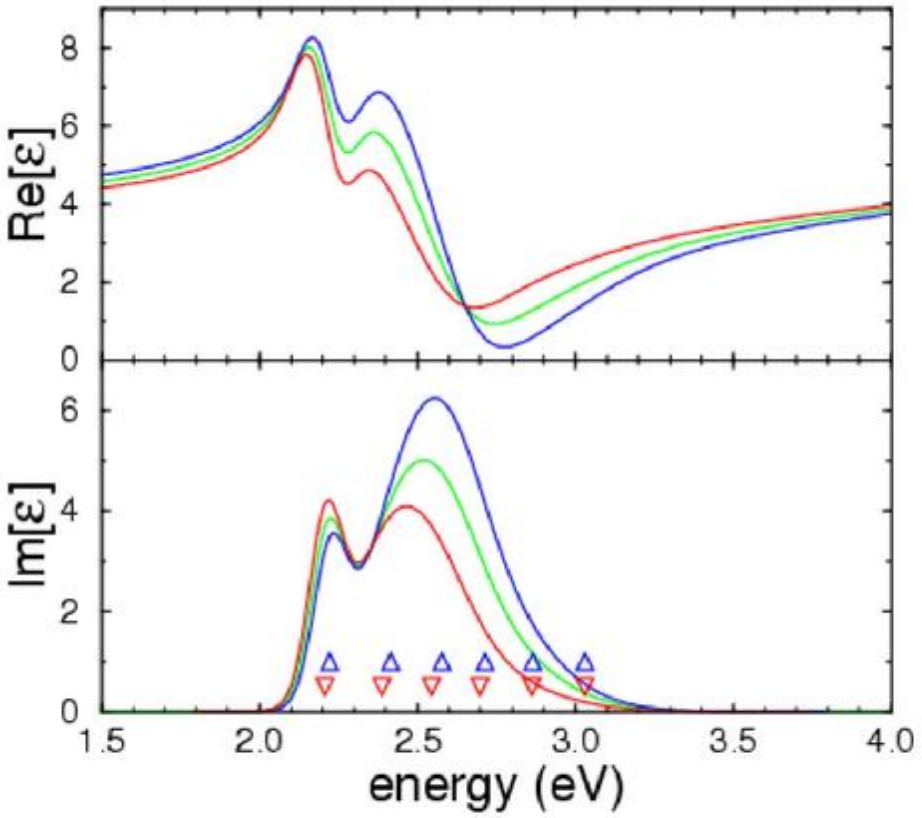
## Transfer matrix elements:

**Fourier transform of exciton transfer in real space**
**for optical excitation (Γ-point):**
**sum of all transfer matrix elements**

# Transfer matrix elements for absorption



# Anisotropic dielectric function




$\hbar\omega = 0.17$ eV

$\alpha^2 = 1.0$

$\Delta_0 = 2.18$ eV

$d_0 = 6.45$ Debye

$T_{AA} = 150$ meV

$= 2 \times 82$ meV

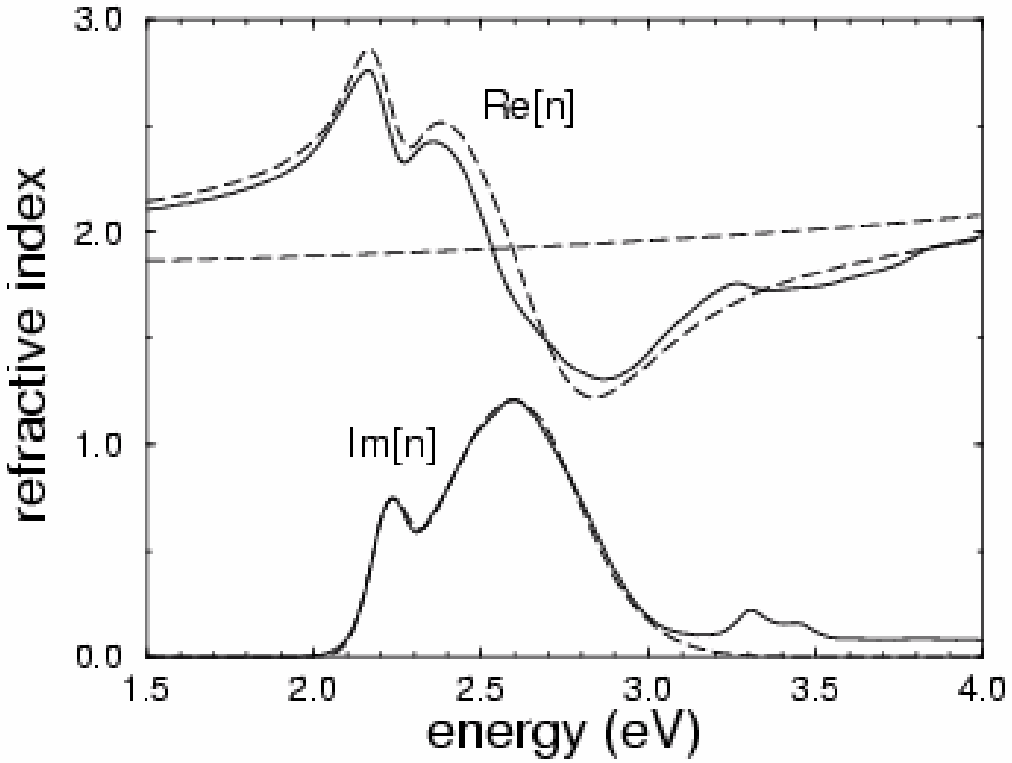
$-14$ meV

$T_{AB} = 47$ meV

$\epsilon_{xx}(\omega)$ $\epsilon_{yy}(\omega)$ $\frac{1}{2}[\epsilon_{xx}(\omega) + \epsilon_{yy}(\omega)]$

I. Vragović, RS, M. Schreiber, Europhys. Lett. **57**, 288 (2002).

# Optical properties of poly-crystalline thin films

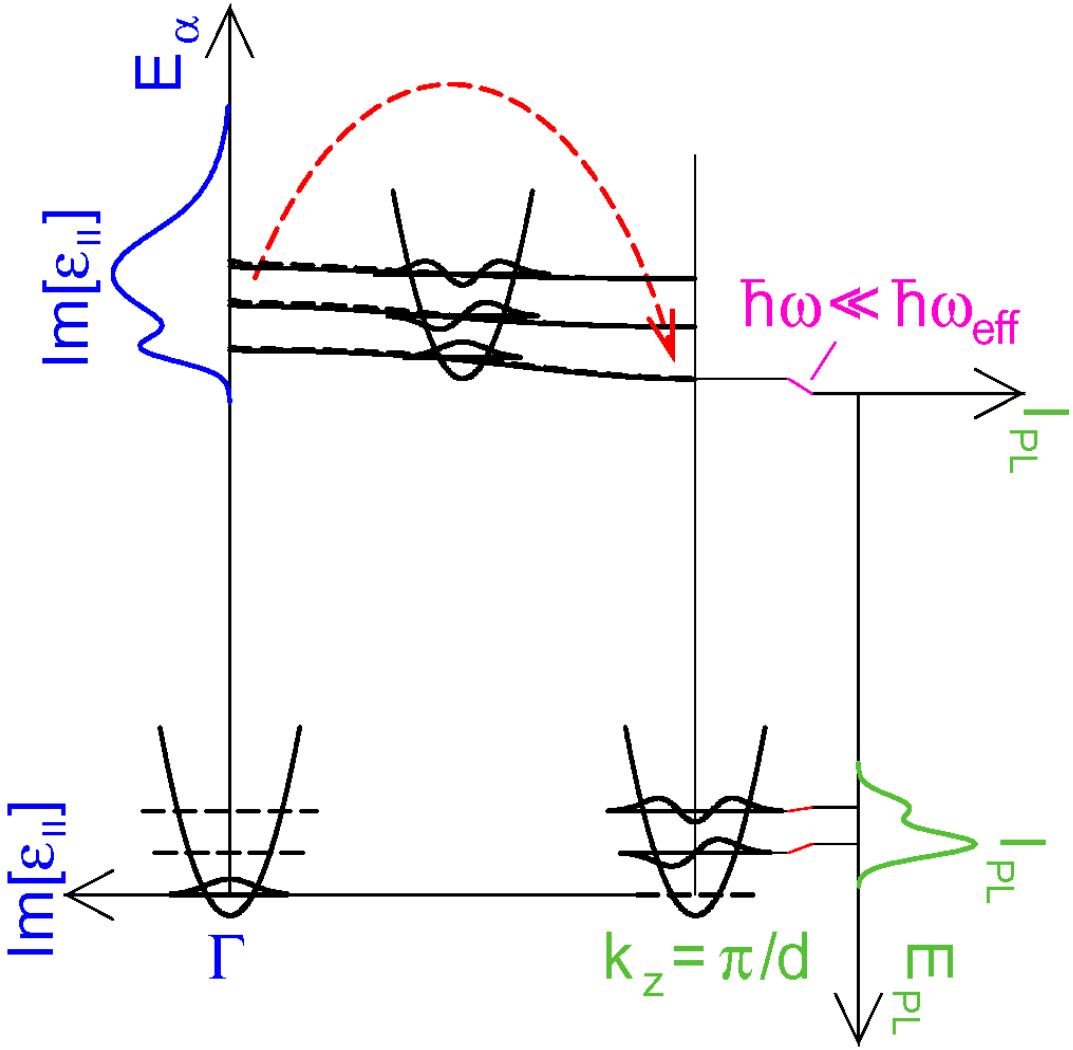



exp (—) A. Djurišić, T. Fritz, and K. Leo, Opt. Commun. **183**, 123 (2000).

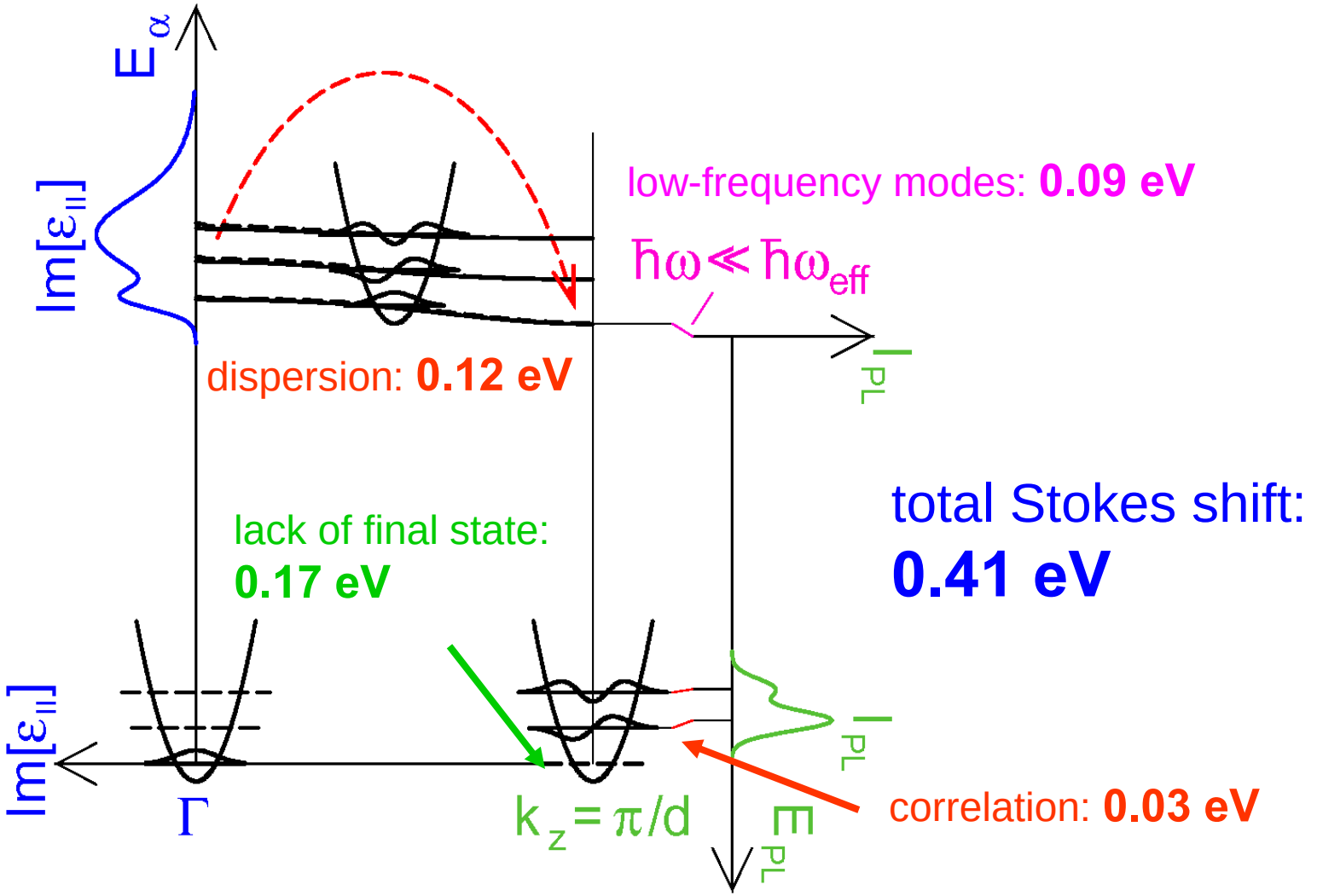
th (- - -) I. Vragović, R.S., M. Schreiber, Europhys. Lett. **57**, 288 (2002).

model parameters fitted to extinction coefficient Im[$n$]

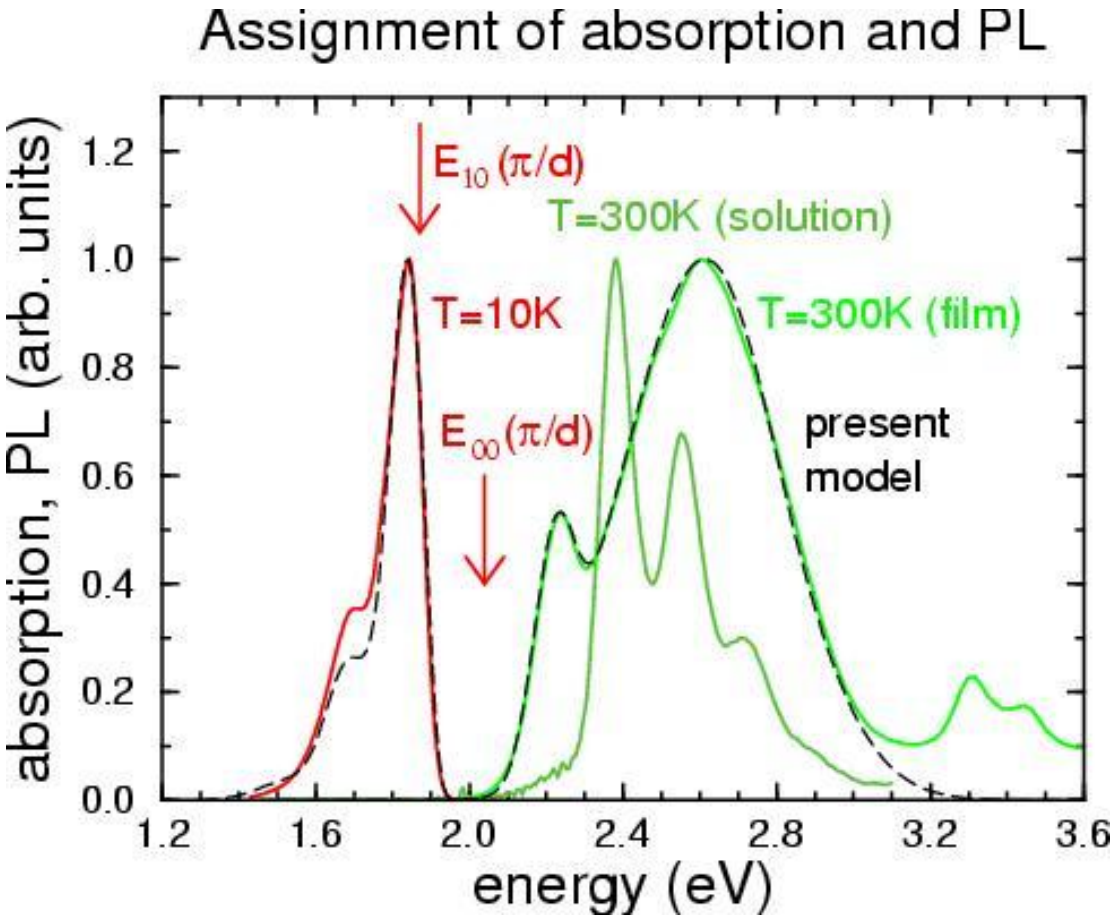
# *Frenkel* exciton: optical cycle



# *Frenkel* exciton: optical cycle

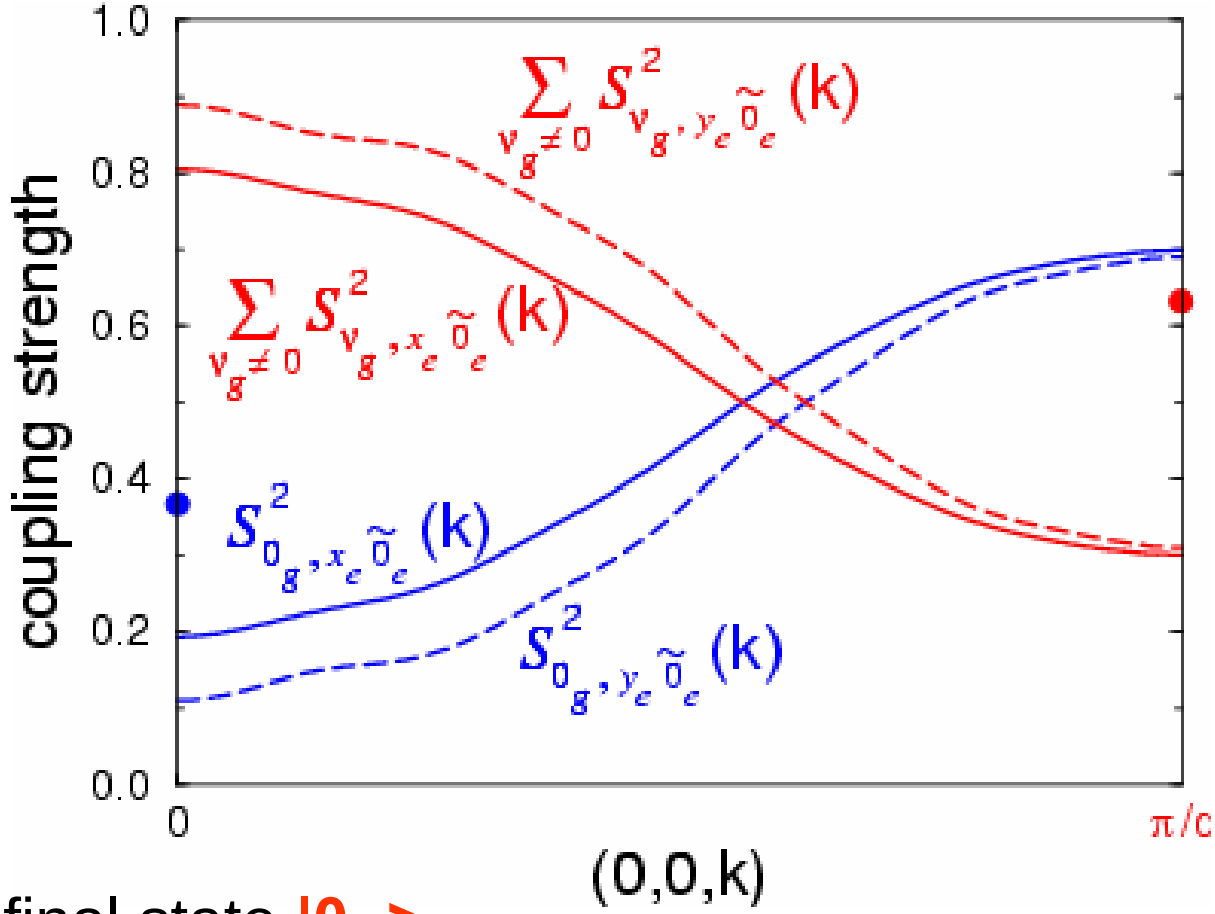


# *Frenkel exciton: lineshapes*




radiative lifetime: **τ = 13±2 ns** (exp), **13 ns** (model)

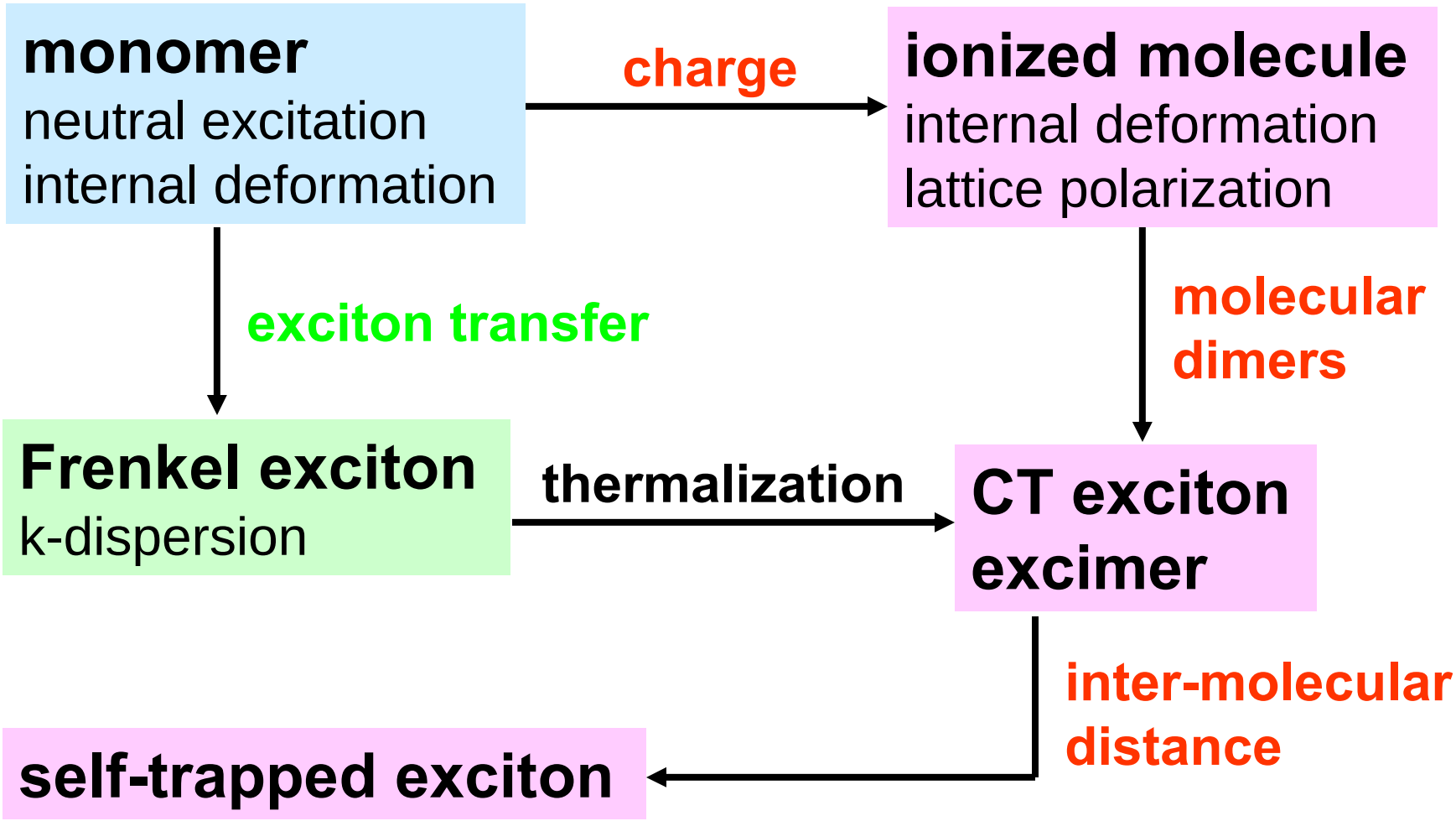
# Why is the recombination so slow?




lack of final state $|0_g\rangle$

monomer radiative lifetime ($\tau$ = 4 ns) slows down to $\tau$ = 13 ns

# *Strategy for microscopic models*



# *Time-dependent DFT: Monomer*

- **Monomer, experimental**
  **PTCDA in superfluid He nanodroplets: $E_{00}$ = 2.60 eV**
  Wewer, Stienkemeier, Phys. Rev. B **67**, 125901 (2003)
  **PTCDA in DMSO $E_{00}$ = 2.38 eV (all modes: 2.365 eV)** Forrest'97
  **Frenkel exciton model $E_{00}$ = 2.18 eV (all modes: 2.125 eV)**

- **Free molecule $E_{00}$ = 2.60 eV vs. crystal $E_{00}$ = 2.125 eV**
  **evidence for red-shift in crystalline phase: 0.475 eV**

- **Monomer, TD-DFT (B3LYP, 3-21G)**
  vertical transition energy: $E_{00} + \lambda$ = 2.56 eV
  estimate for reorganization energy: $\lambda$ = 0.22 eV
  gives $E_{00}$ = 2.34 eV: underestimate of $E_{00}$ by 0.26 eV

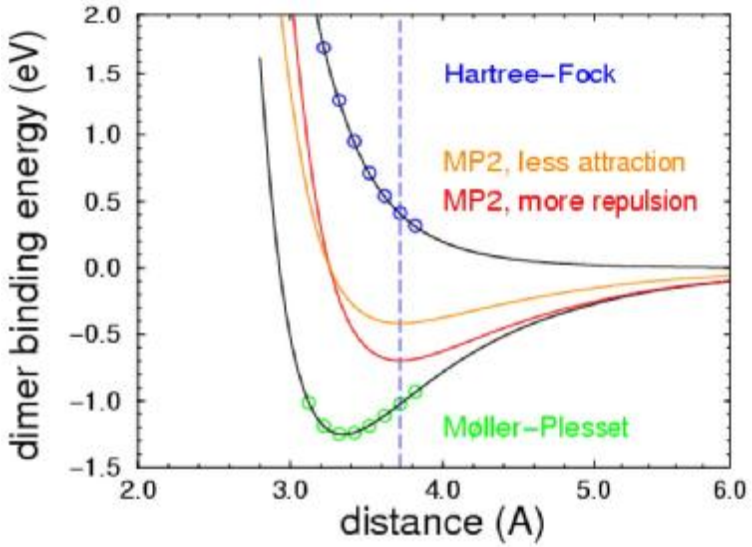
# Dimers: Total energy calculations

***binding energy per molecule:***

Hartree-Fock (HF)

B3LYP

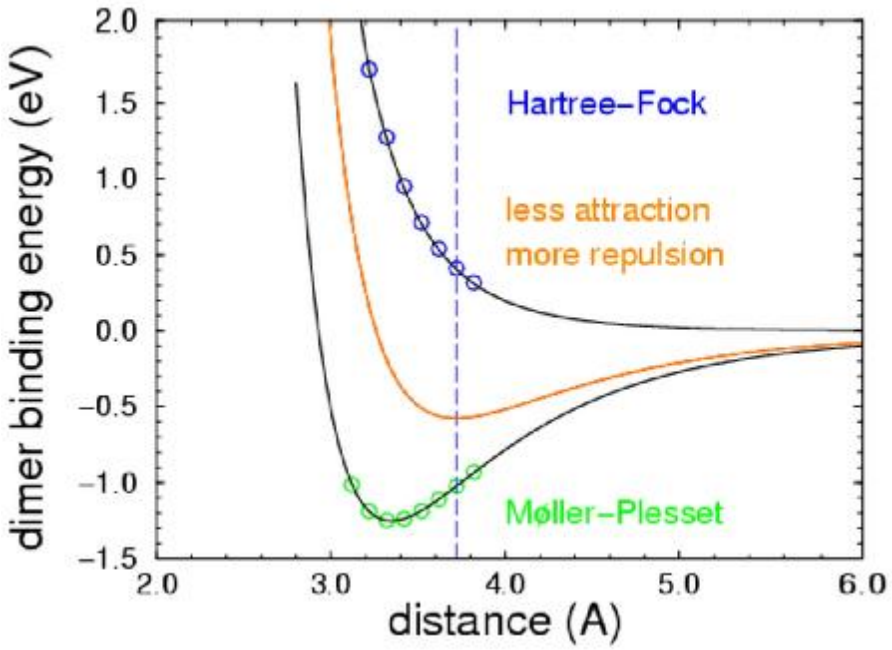
Møller-Plesset (MP2)



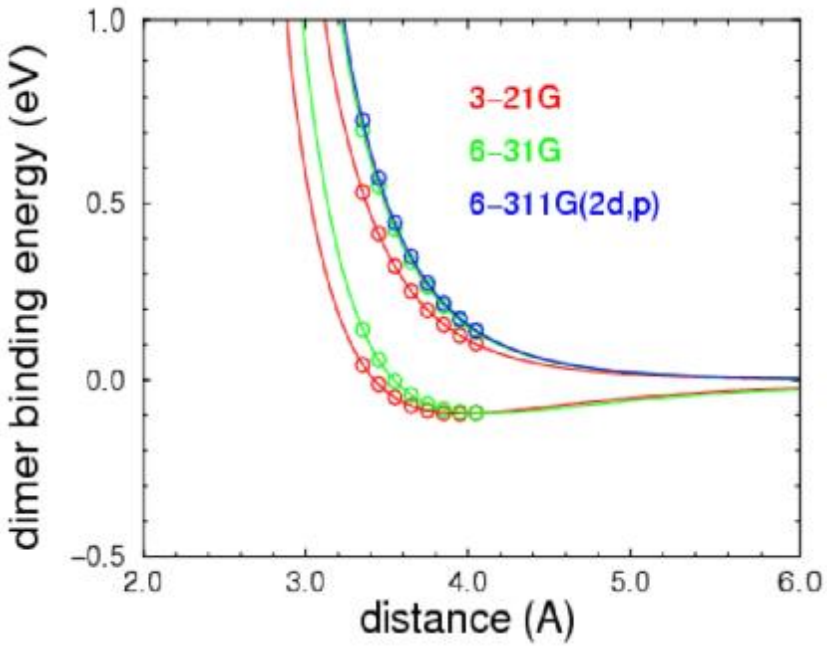

| dimer | sites | HF | B3LYP | MP2 |
|---|---|---|---|---|
| coplanar, equivalent (b-axis) | 2 | - 0.25 | - 0.26 | - 0.25 |
| coplanar, non-equivalent | 4 | - 0.20 | - 0.23 | - 0.25 |
| non-coplanar, equivalent (a) | **2** | **+ 0.21** | **+ 0.10** | **- 0.51** |
| non-coplanar, non-equivalent | 4 | - 0.04 | - 0.07 | - 0.10 |
| non-coplanar, non-equivalent | 4 | - 0.01 | - 0.02 | - 0.01 |
| **total** | **16** | **- 1.08** | **- 1.57** | **- 2.94 eV** |

# Improved potential along stack

***PTCDA dimer 3-21G***



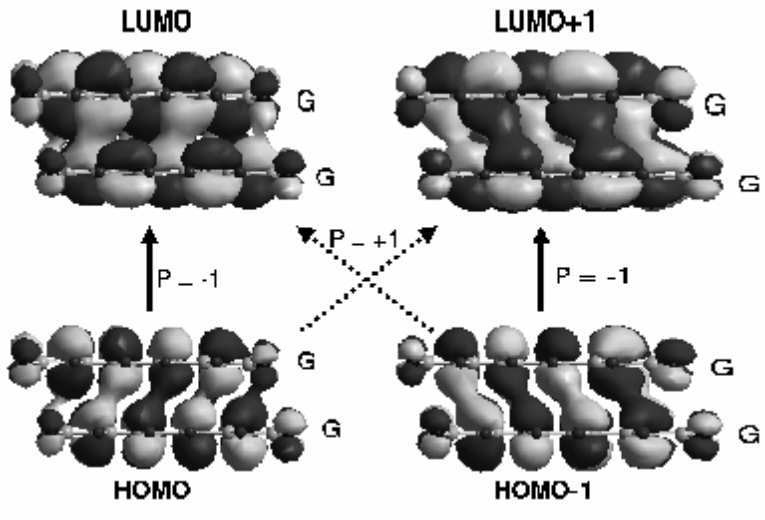

***benzene dimer***




**3-21G basis: too low repulsion ⇒ increase by 1.38**

**3-21G basis: too strong attraction ⇒ reduce by 0.83**

# *Dimer calculations: red shift in crystal*




Excited states:

**2.73 eV (*f* = 0.93)**

**2.43 eV (*f* = 0)**

**2.19 eV (*f* = 0.02)**

**2.16 eV (*f* = 0)**

$$H = \begin{pmatrix} F & W & t_e & t_h \\ W & F & t_h & t_e \\ t_e & t_h & CT & V \\ t_h & t_e & V & CT \end{pmatrix}$$

➢ $W \neq 0$, $V \neq 0$, $F_{vertical}$ = 2.58 eV

| dimer | ΔE per dimer / eV | neighbours | ΔE / eV |
|---|---|---|---|
| coplanar, equivalent (b-axis) | - 0.011 | 2 | - 0.022 |
| coplanar, non-equivalent | - 0.015 | 4 | - 0.060 |
| non-coplanar, equivalent (a) | **- 0.078** | **2** | **- 0.156** |
| non-coplanar, non-equivalent | - 0.013 | 4 | - 0.052 |
| non-coplanar, non-equivalent | - 0.002 | 4 | - 0.008 |
| **gas-to-crystal: ΔE = - 0.475 eV** | | **$\Delta E_{total}$ =** | **- 0.298 eV** |

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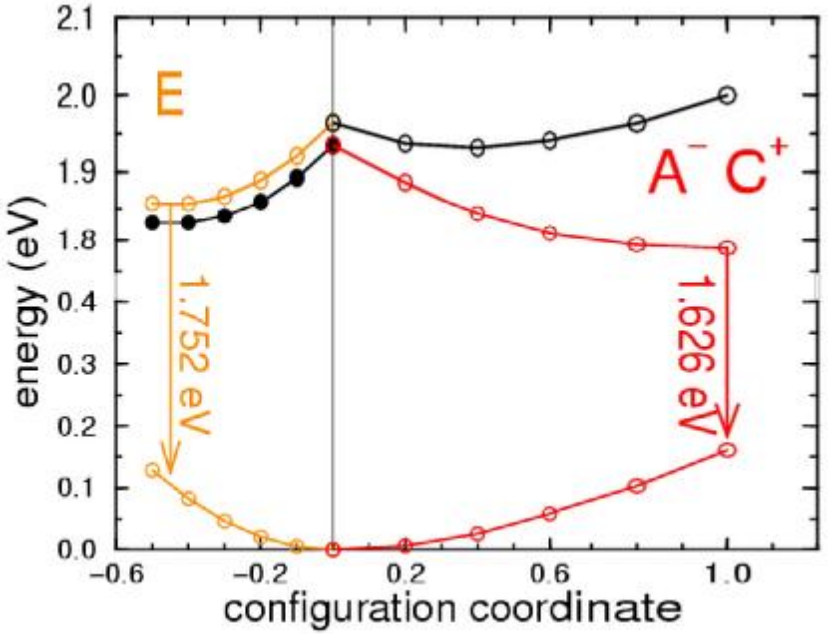
*Michael Schreiber*

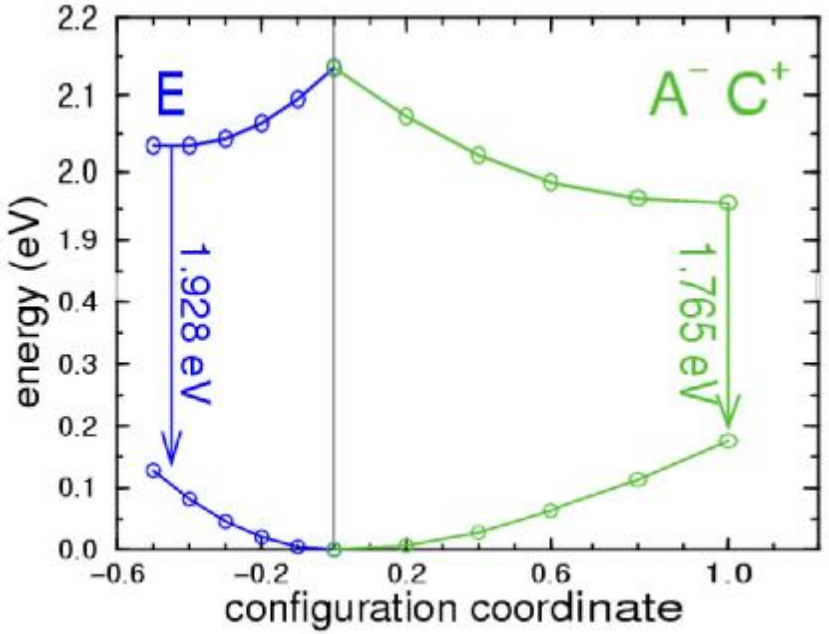
*CoPhen04, Dresden, 16 June 2004*

# *Dimer calculations: slow PL channels*

vertical stack




non-coplanar, non-equivalent

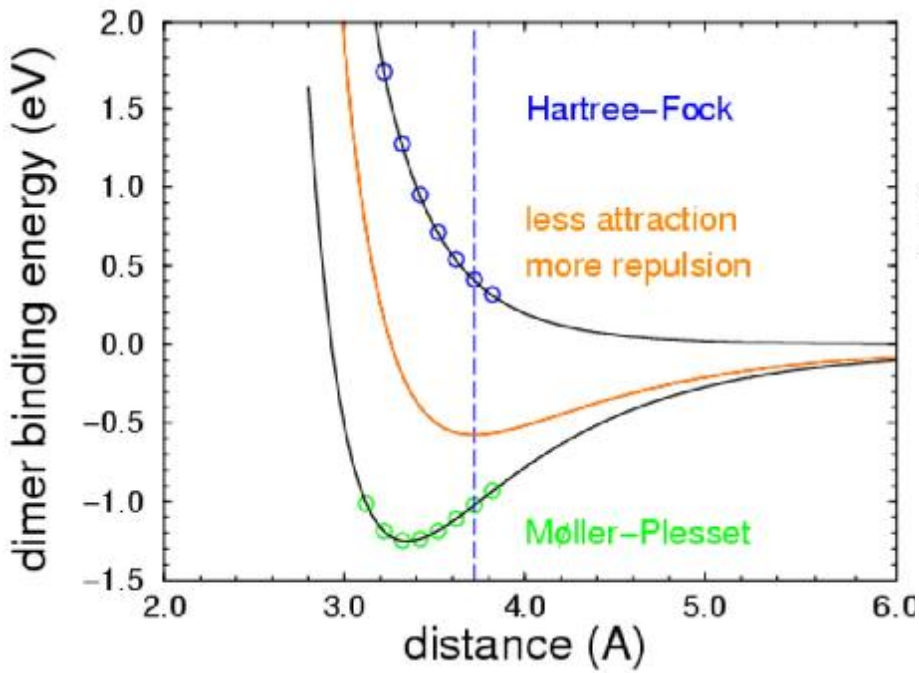


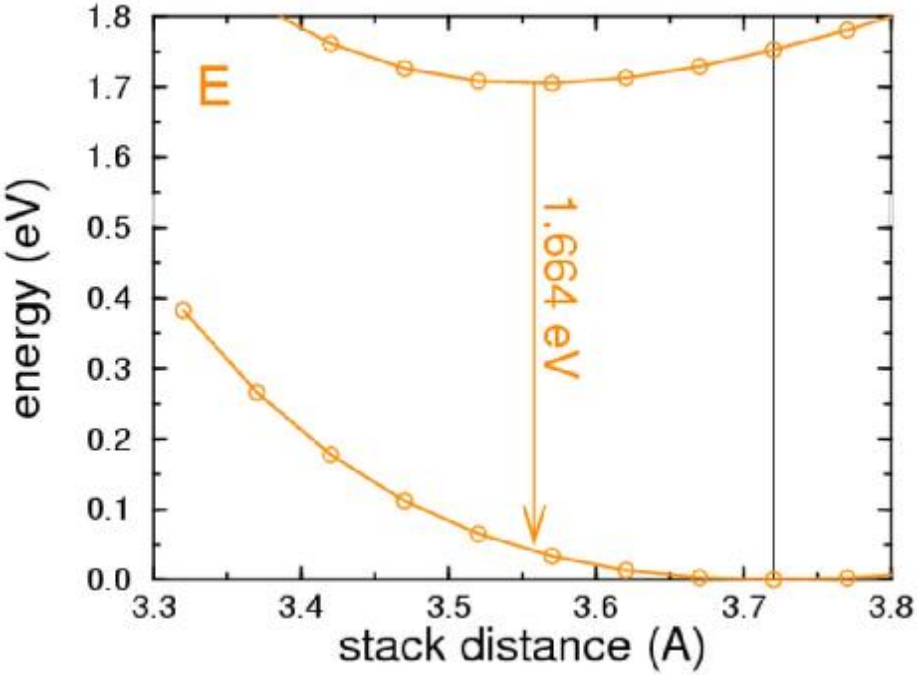

**PL:** stack excimer: **1.72 eV** non-coplanar excimer: **1.93 eV**

anion-cation stack: **1.67 eV** anion-cation pair: **1.78 eV**

⇒ good agreement with observed PL, but **TOO SLOW**

# *Self-trapping* of excimer along stack



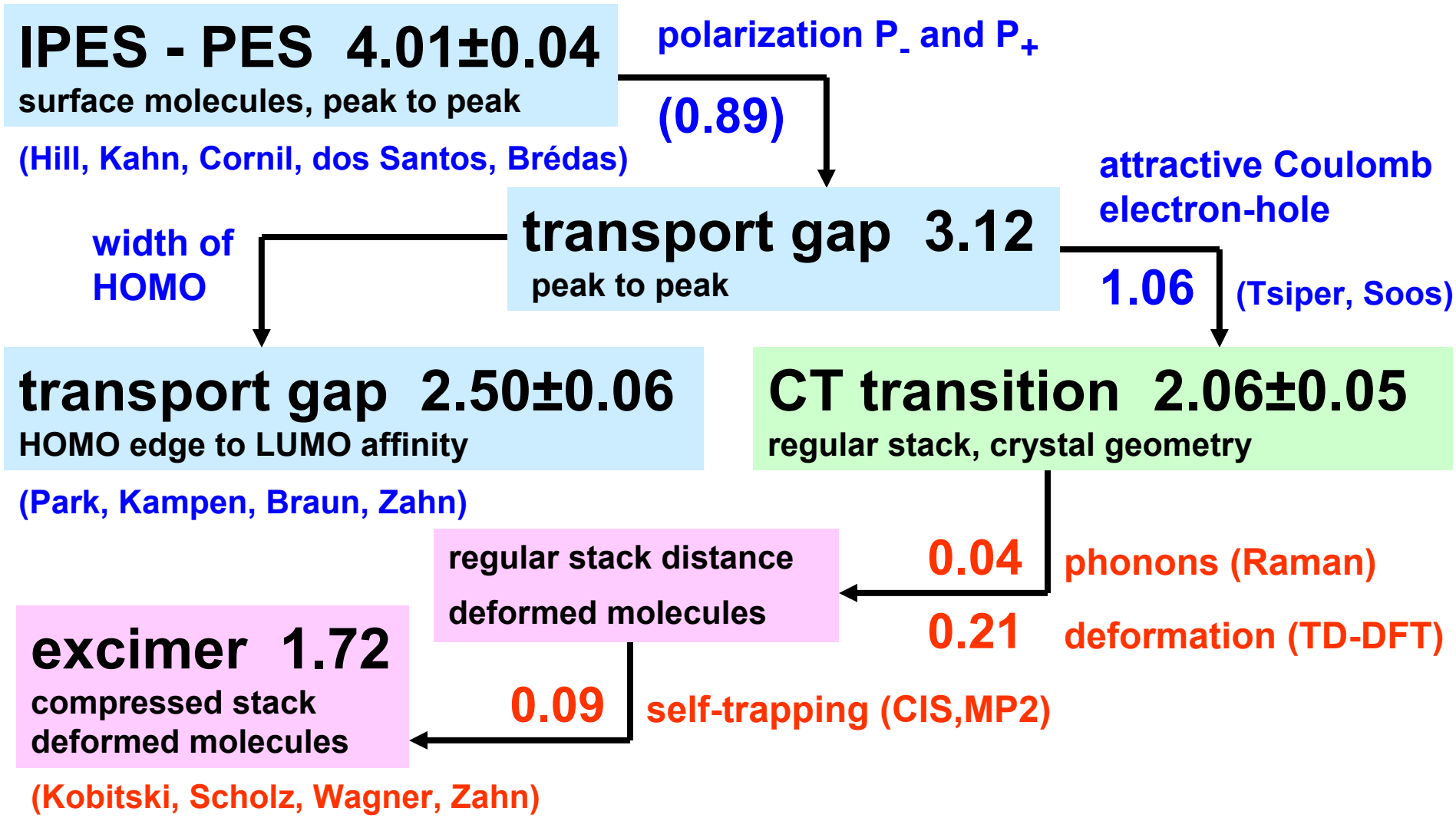



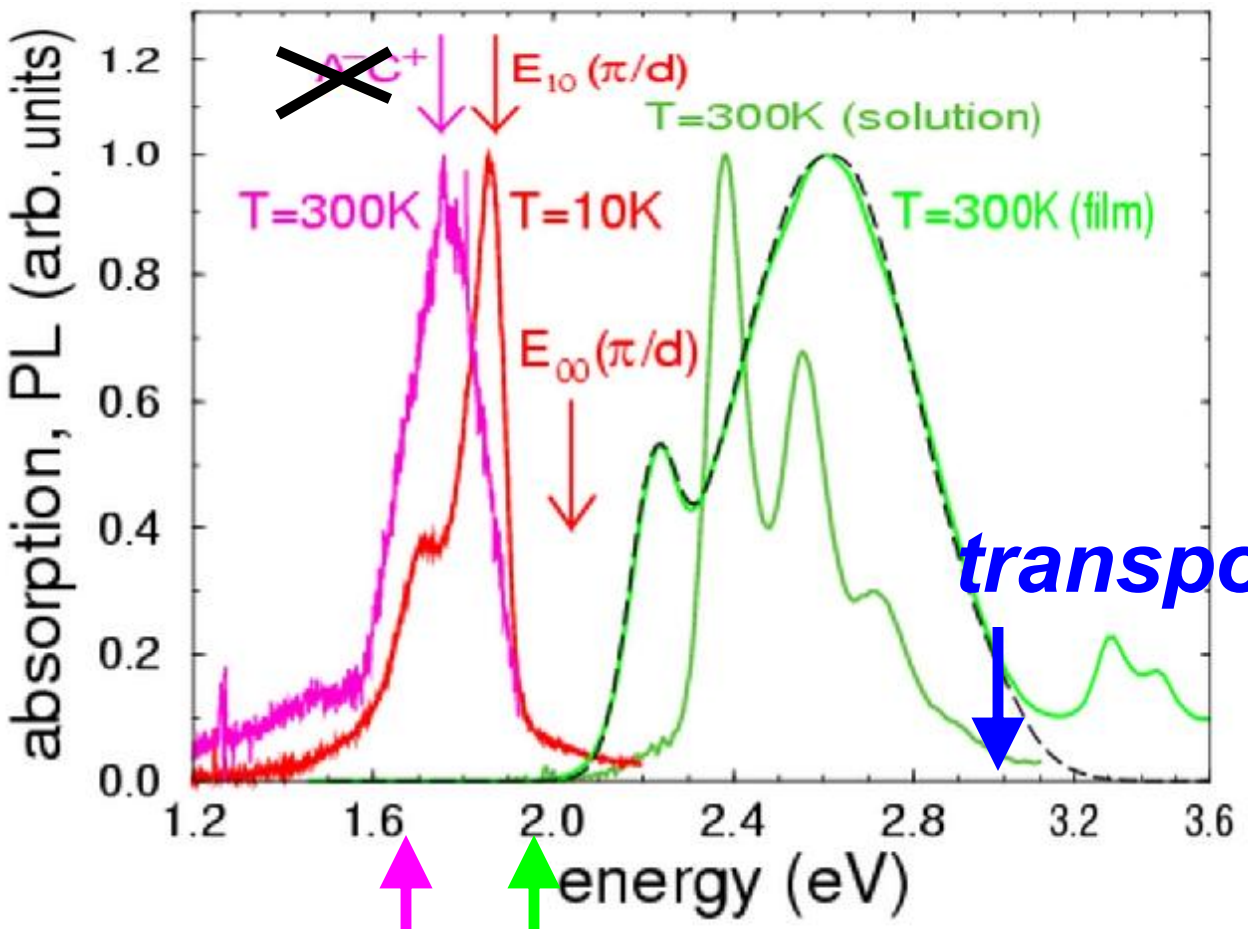

***Method:*** ***configuration interaction of singles (CIS), MP2***

***Stokes shift*** ***of excimer:***

**0.09 eV self-trapping, 0.21 eV internal deformation**

# Transition energies and transport gap






***transport gap***

***excimer (stack)*** ***CT (undeformed stack)***

# Conclusion

- **α-PTCDA**
  *large π-overlap* ⇒ *large variety* of relaxed excited states

- **Time-resolved photoluminescence**
  - *low T: Frenkel exciton*,radiative decay in *13 ns*
  - *2 slower CT bands*
  - *excimer* dominating at *T > 220 K*
  - *efficient activated PL quenching* at higher T
  - self-trapped precursor states involve a *formation barrier*

- **Theoretical methods**
  - *k-dispersion* of *Frenkel* exciton
  - *absorption* at Γ*-point*, *minimum* at surface of BZ gives *PL*
  - *dimer calculations* **(TD-DFT/B3LYP, CIS, MP2)**
    for *self-trapped localized exciton* states

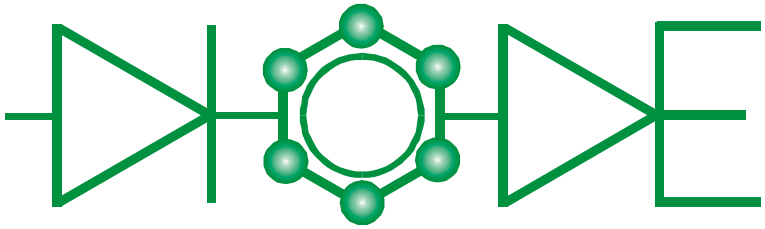
# *Outlook*

- **Single molecule**
  - ***geometry: routine task*** **(HF, DFT, B3LYP)**
  - ***transitions: routine task*** **(CIS, TD-DFT)**

- **Inter-molecular transitions (CIS, TD-DFT)**
  - ***feasible, energy offsets difficult to assess***
  - ***time consuming*** **($N^3$)**
  - ***convergence problems***

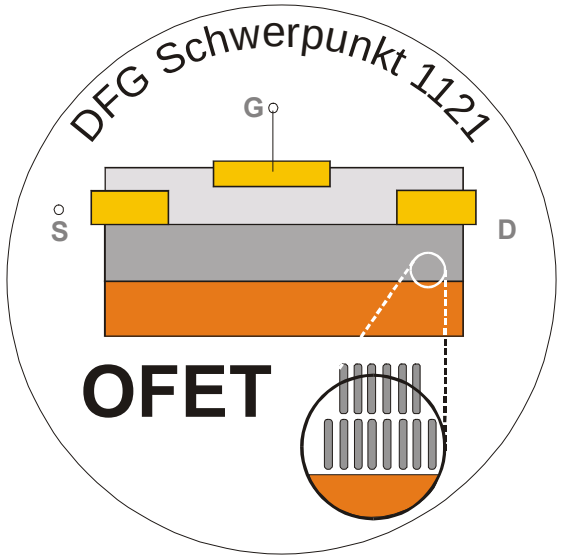
- **Inter-molecular binding, adsorbates, doping**
  - ***geometry: challenging***
  - ***hierarchy of methods*** **(HF, DFT, B3LYP ($N^3$), MP2 ($ON^4$))**
  - ***time-consuming, convergence problems***
  - ***transitions: feasible*** **(CIS, TD-DFT)**

***Thanks:*** **Igor Vragović (Alicante) DFG**
**Andrei Yu Kobitski (Ulm) DFG**
**Georgeta Salvan DIODE**
**Thorsten U Kampen (FHI Berlin)**
**Hans-Peter Wagner (Cincinnati)**
**Dietrich RT Zahn, Reinhard Scholz**



EU funded research Training Network DIODE
(Contract No.: HPRN-CT-1999-00164)

Deutsche Forschungsgemeinschaft DFG



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**M. Wewer, F. Stienkemeier (Uni Bielefeld)**
**M.I. Alonso, M. Garriga, J.O. Osso (UA Barcelona)**

**H. Port (Uni Stuttgart)**
**M. Knupfer (IfW, Dresden)**

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