Excitons – Types, Energy Transfer

- Wannier exciton
- Charge-transfer exciton
- Frenkel exciton

- Exciton Diffusion
- Exciton Energy Transfer (Förster, Dexter)

Handout (for Recitation Discusssion):
J.-S. Yang and T.M. Swager, J. Am. Chem. Soc. 120, 5321 (1998)
Q. Zhou and T.M. Swager, J. Am. Chem. Soc. 117, 12593 (1995)

looe @ MIT

Exciton

In some applications it is useful to consider electronic excitation as if a quasi-principle, capable of migrating, were involved. This is termed as exciton. In organic materials two models are used: the band or wave model (low temperature, high crystalline order) and the hopping model (higher temperature, low crystalline order or amorphous state). Energy transfer in the hopping limit is identical with energy migration.

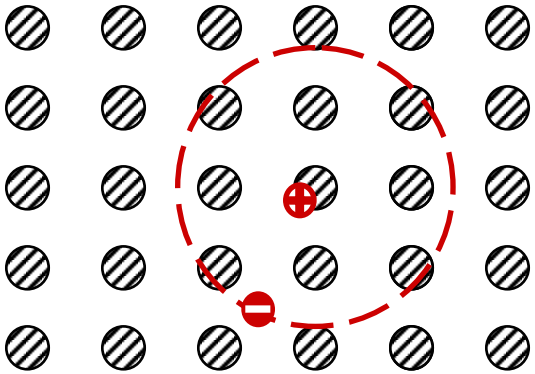
Caption from IUPAC Compendium of Chemical Terminology compiled by Alan D. McNaught and Andrew Wilkinson (Royal Society of Chemistry, Cambridge, UK).

Excitons
(bound electron-hole pairs)

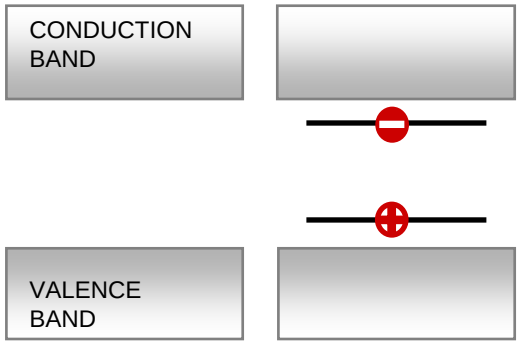
treat excitons as chargeless particles capable of diffusion,

also view them as excited states of the molecule

Wannier exciton
(typical of inorganic semiconductors)



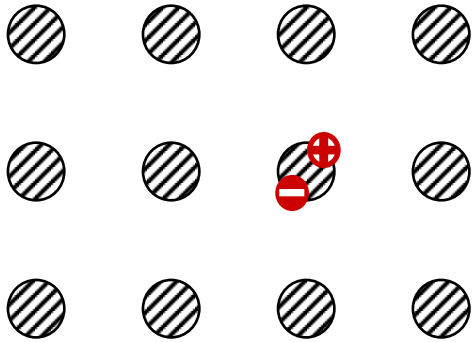
SEMICONDUCTOR PICTURE



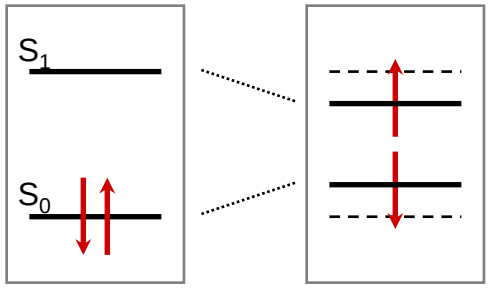
GROUND STATE WANNIER EXCITON

binding energy ~10meV
radius ~100Å

Frenkel exciton
(typical of organic materials)



MOLECULAR PICTURE



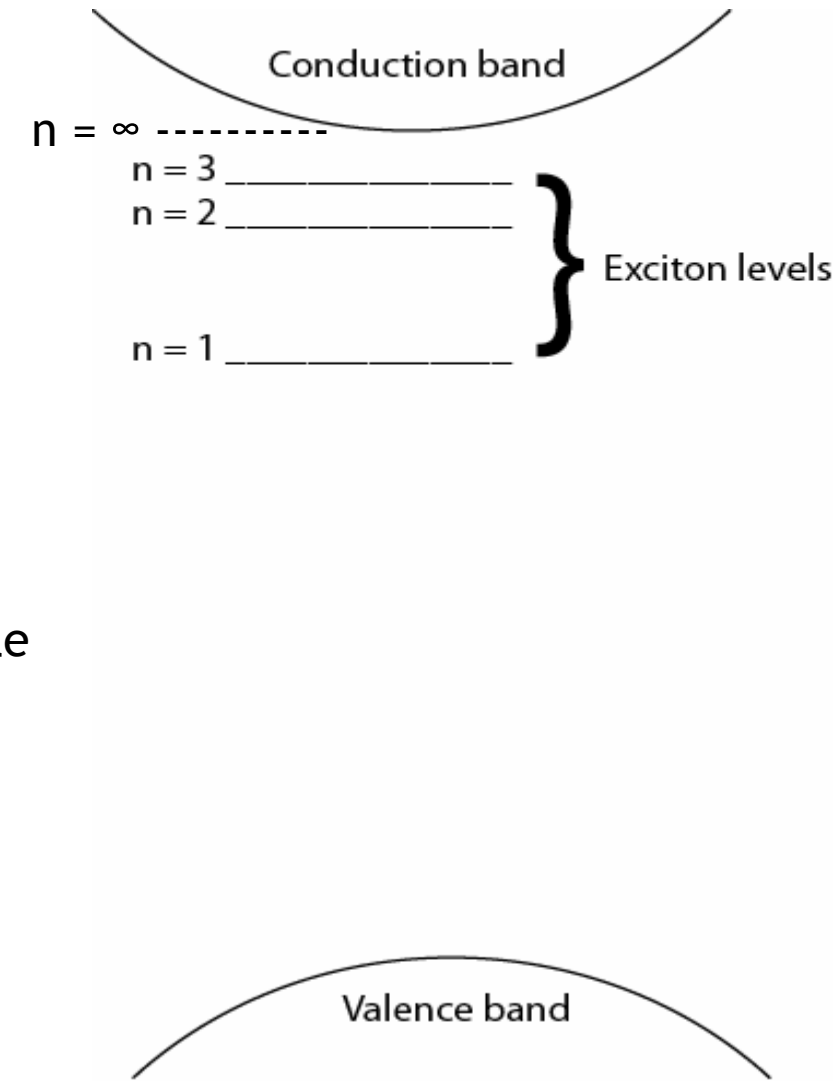
GROUND STATE FRENKEL EXCITON

binding energy ~1eV
radius ~10Å

Charge Transfer (CT) Exciton
(typical of organic materials)

Electronic Processes in Organic Crystals and Polymers by M. Pope and C.E. Swenberg

Wannier-Mott Excitons



Columbic interaction between the hole and the electron is given by

$E_{EX} = -e^2/\in r$

The exciton energy is then

$E = E_{ION} - E_{EX}/n^2$, n = 1,2, …

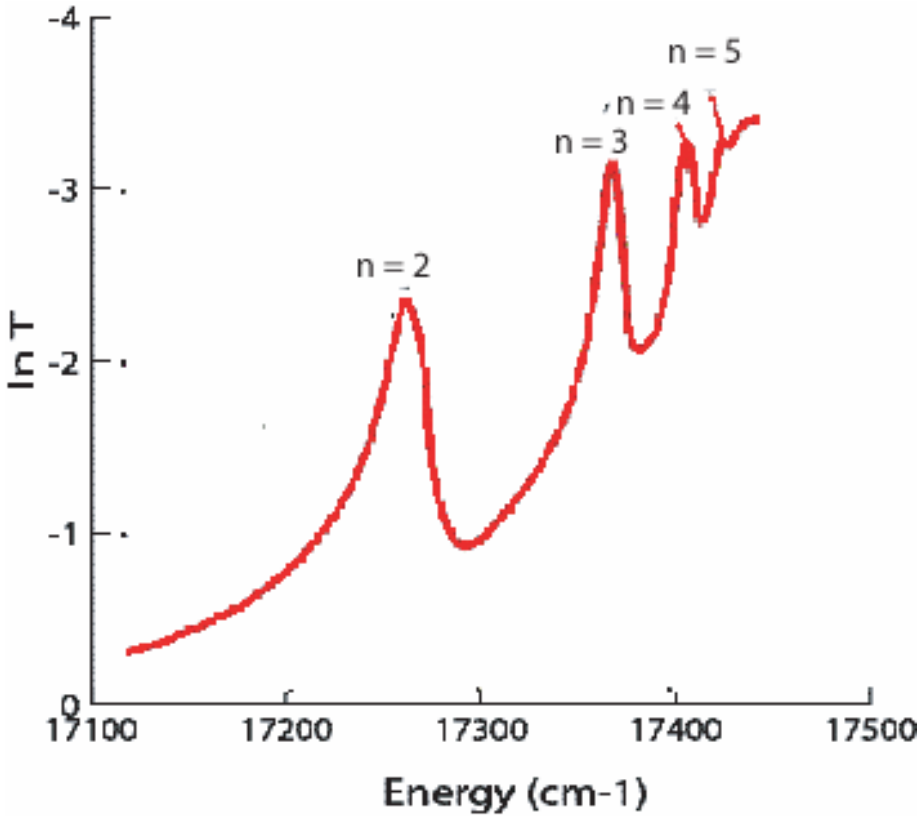
E_{ION} – energy required to ionize the molecule
n – exciton energy level

$E_{EX} = 13.6\ eV\ \mu/m\in$

μ- reduced mass = $m_e m_h / (m_e+m_h)$

Adapted from Electronic Processes in Organic Crystals and Polymers by M. Pope and C.E. Swenberg

An Example of Wannier-Mott Excitons



exciton progression
fits the expression

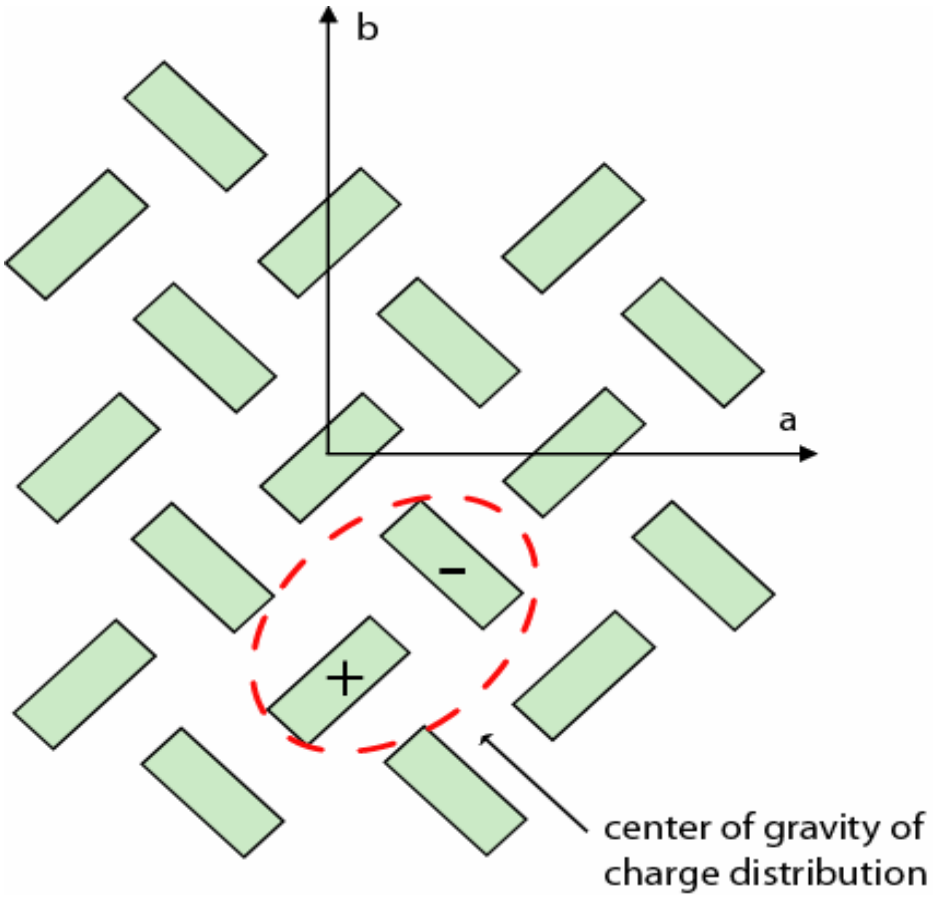
ν[cm-1] = 17,508 – 800/n²

corresponding to
μ = 0.7 and $\in$ = 10

The absorption spectrum of Cu_2O at 77 K, showing the exciton lines corresponding to several values of the quantum number *n*. (From Baumeister 1961).

Quoted from Figure I.D.28. Electronic Processes in Organic Crystals and Polymers by M. Pope and C.E. Swenberg

Charge Transfer Excitons



The lowest CT exciton state in the *ab* plane of an anthracene crystal with two inequivalent molecules per unit cell; the plus and minus signs refer to the center of gravity of charge distribution. The Frenkel exciton obtains when both (**+**) and (**–**) occupy essentially the same molecular site.

Crystalline Organic Films

CHARGED CARRIER MOBILITY INCREASES WITH INCREASED π–π ORBITAL OVERLAP

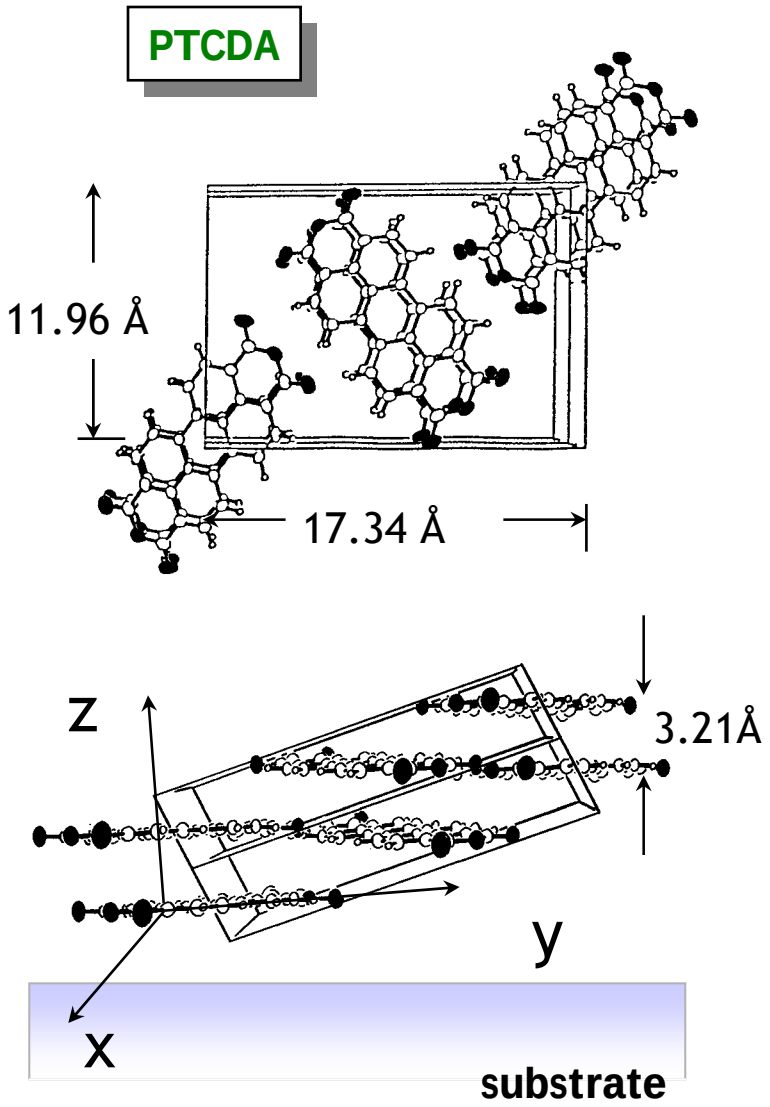
GOOD CARRIER MOBILITY IN THE STACKING DIRECTION

μ = 0.1 cm^2/Vs – stacking direction
μ = 10^{-5} cm^2/Vs – in-plane direction

Highest mobilities obtained on single crystal

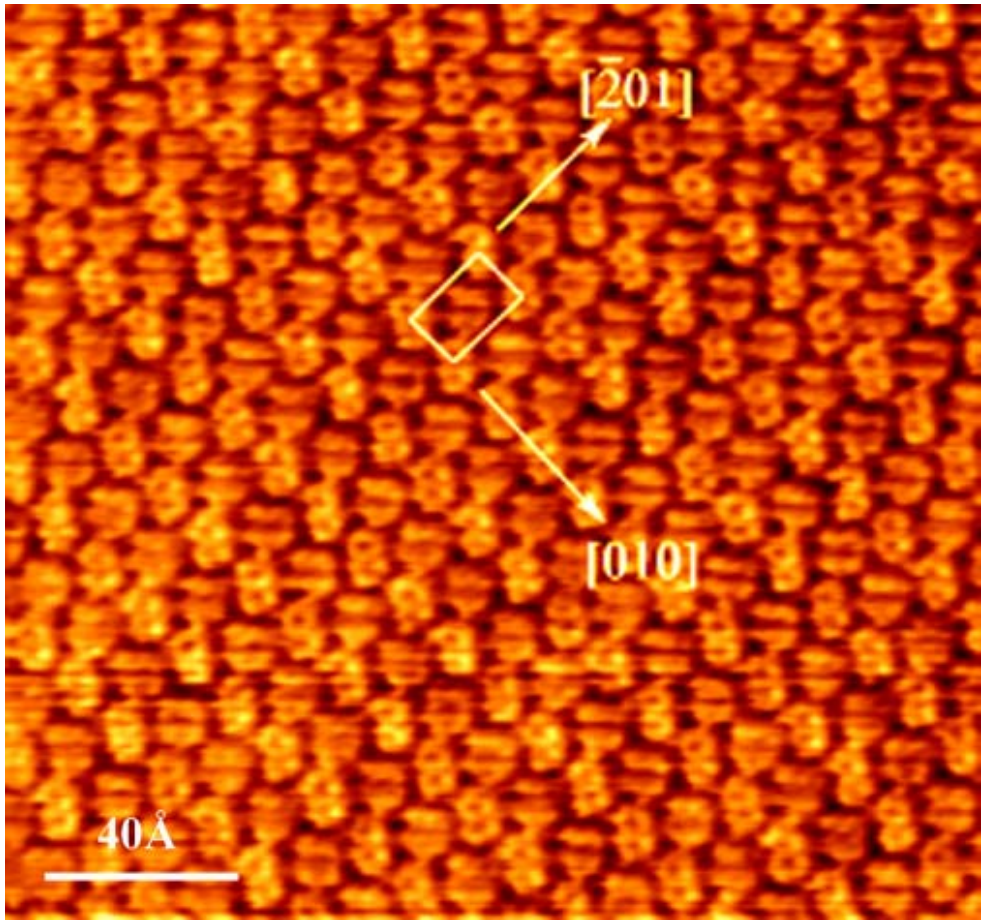
pentacene μ = 10 ^{5} cm^2/Vs at 10K
tetracene μ = 10 ^{4} cm^2/Vs at 10K

(Schön, *et al.*, Science 2000).

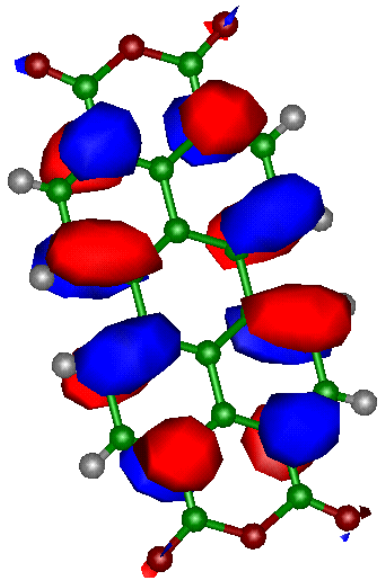


Organic Semiconducting Materials

Van der Waals-BONDED
ORGANIC CRYSTALS
(and amorphous films)

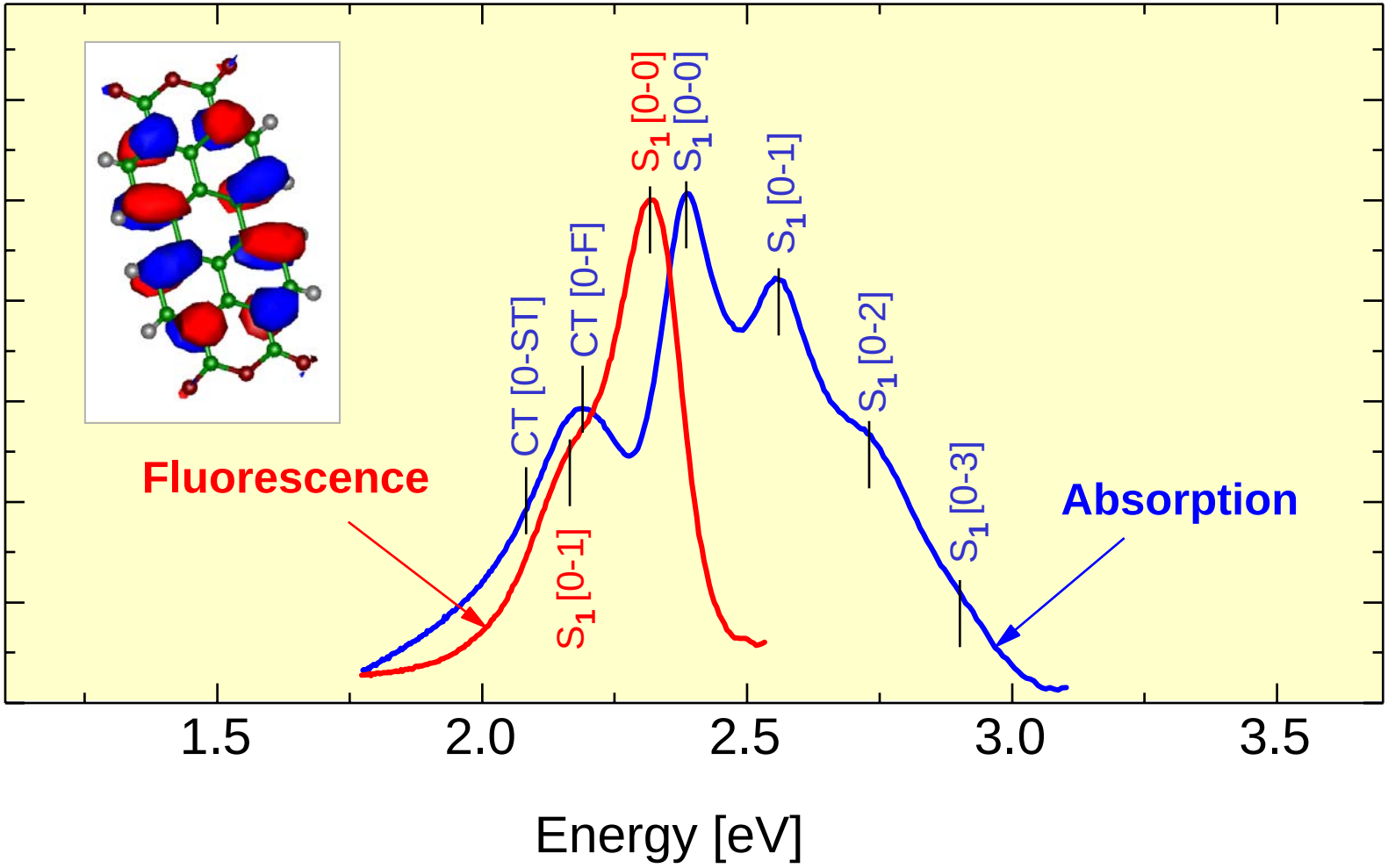


PTCDA monolayer on HOPG
(STM scan)

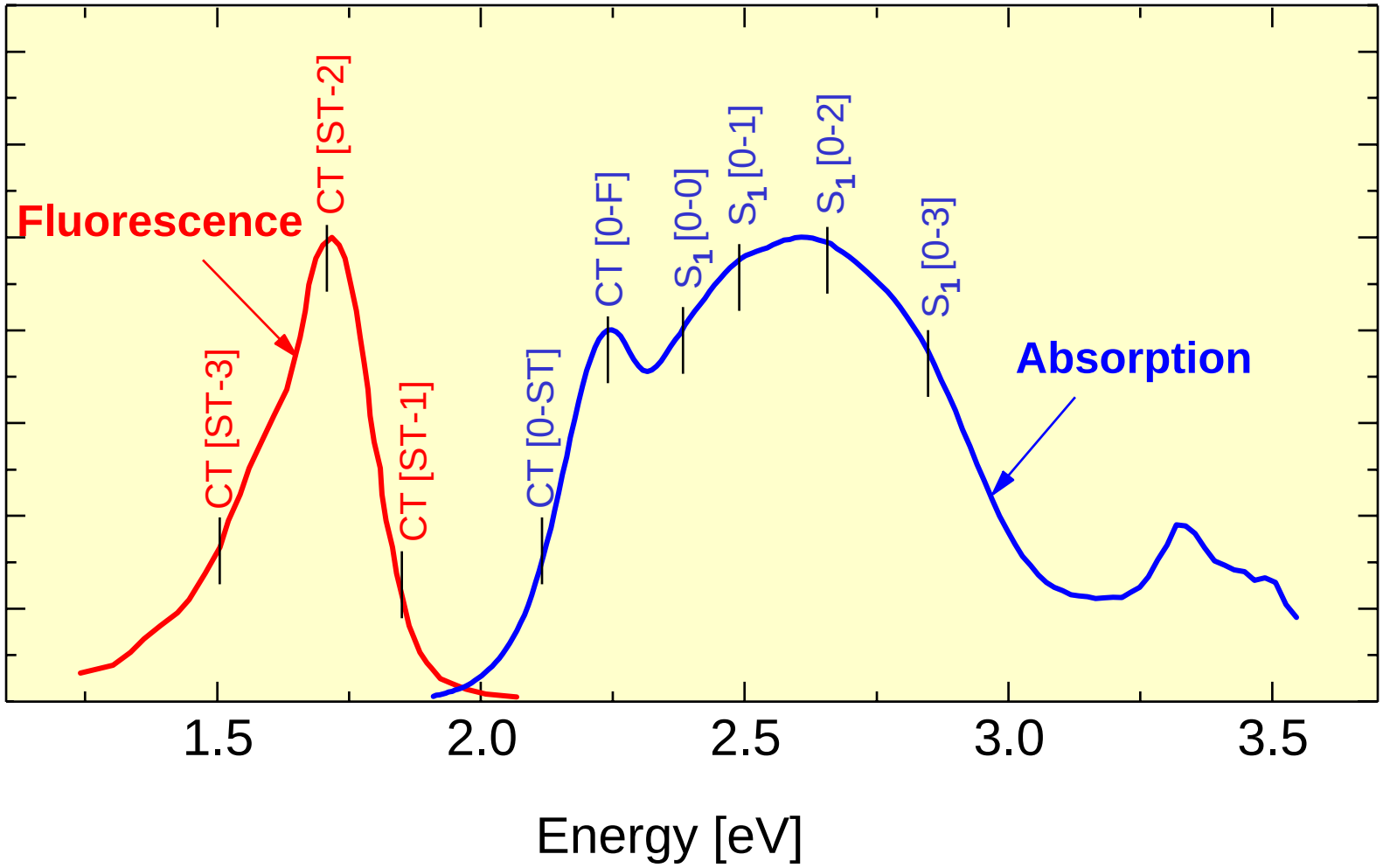


HOMO of
3,4,9,10- perylene tetracarboxylic dianhydride

PTCDA Solution (~ 2μM in DMSO)



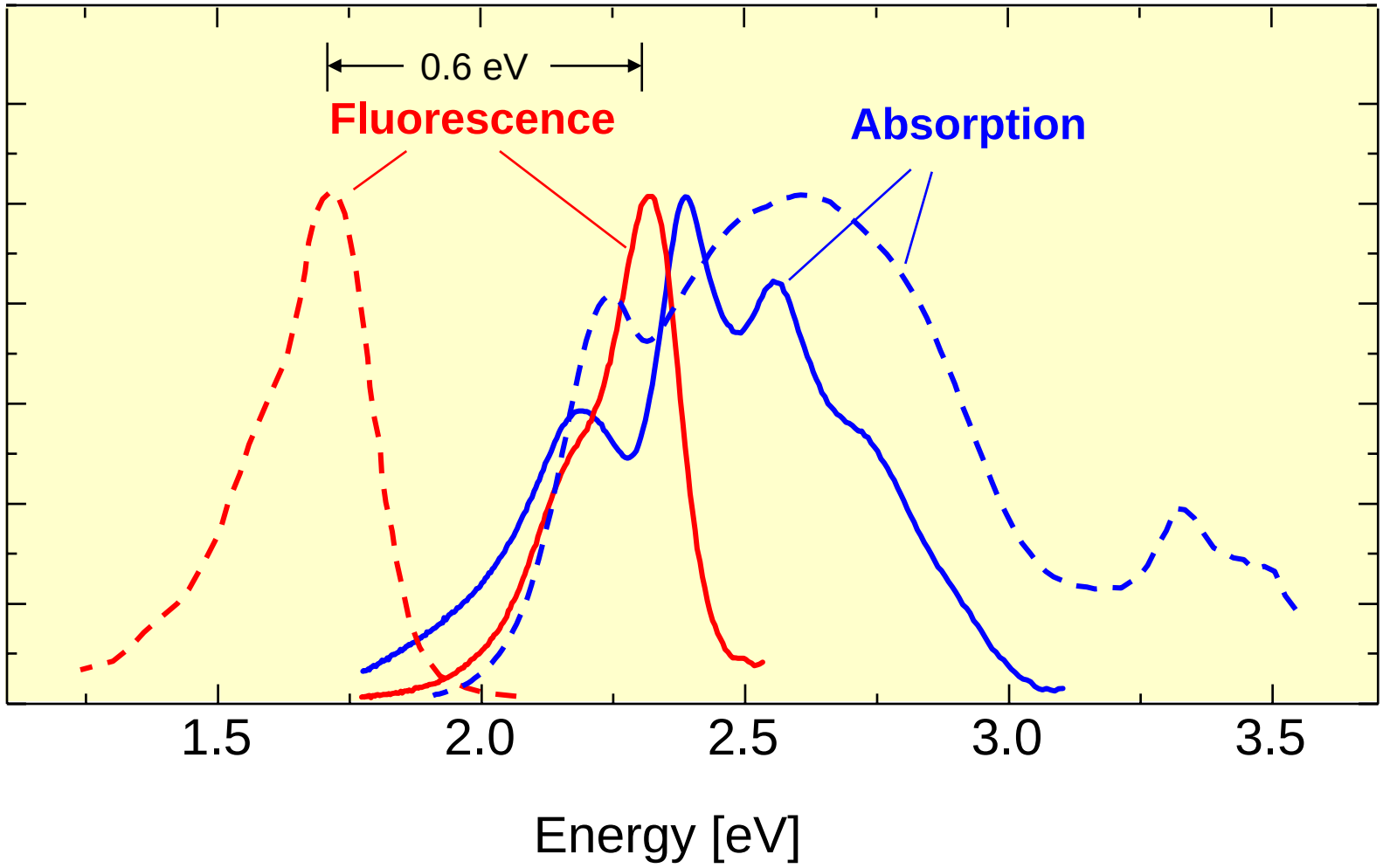
PTCDA Thin Film



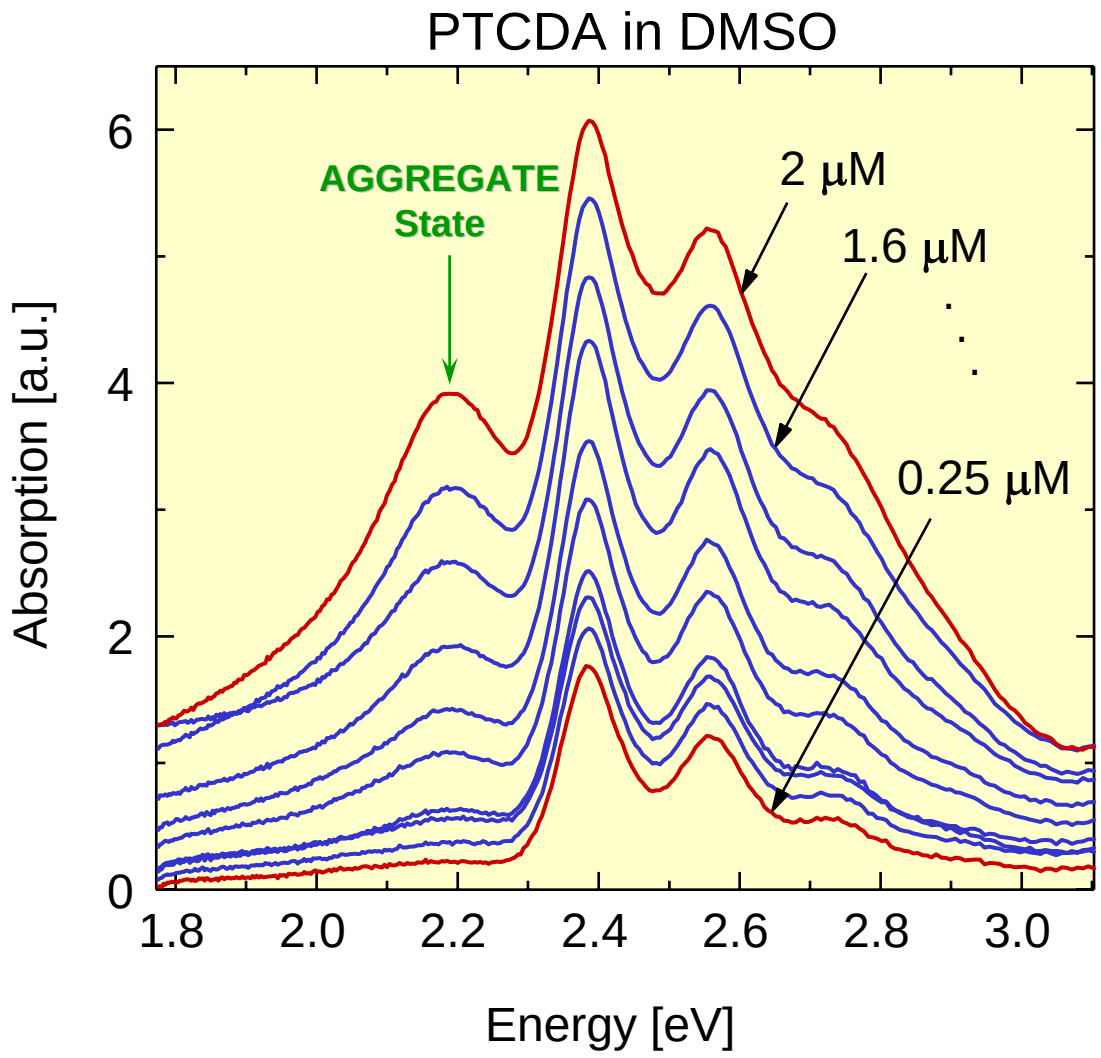
PTCDA Solution

PTCDA Thin Film

(~ 2μM in DMSO)

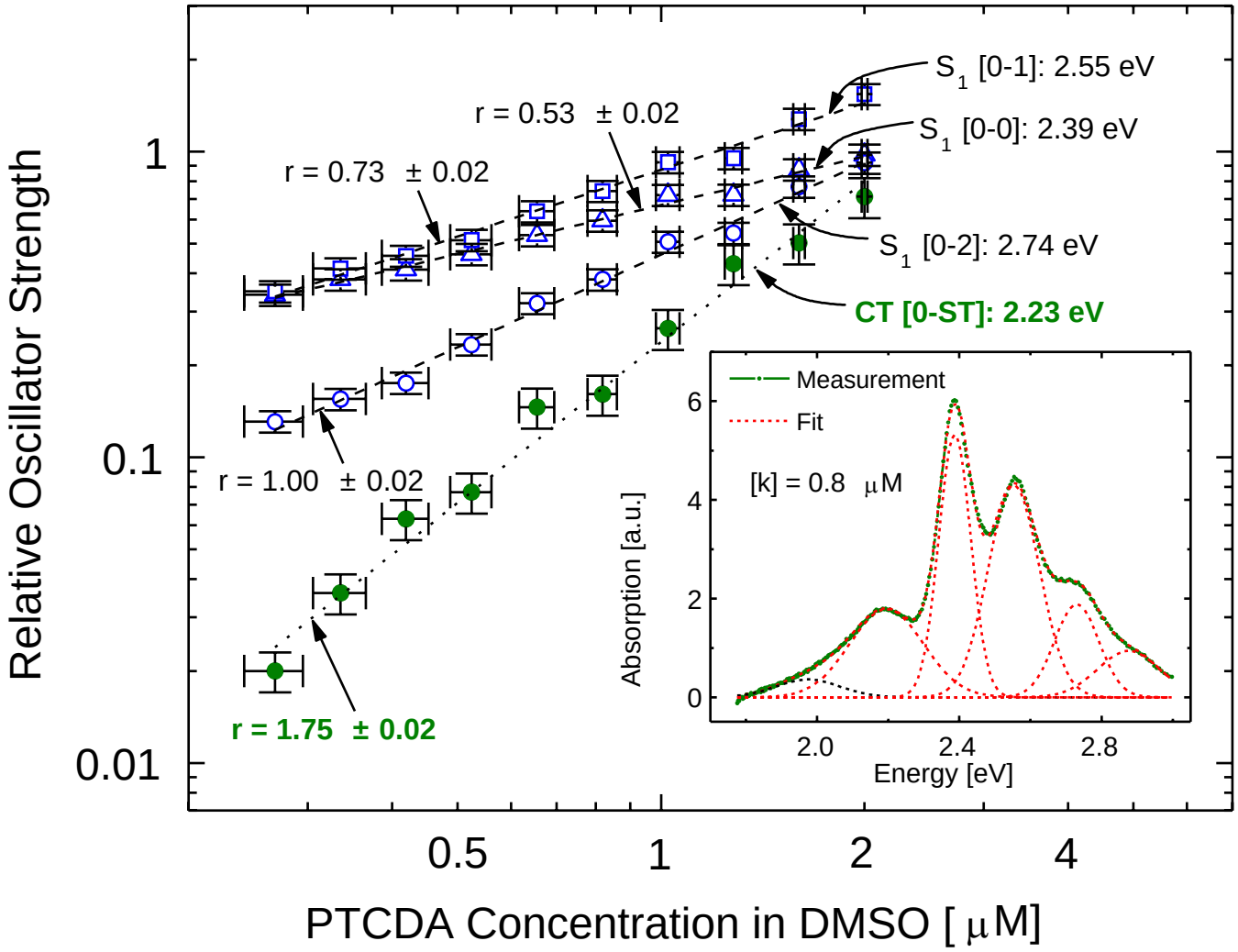


Solution Absorption

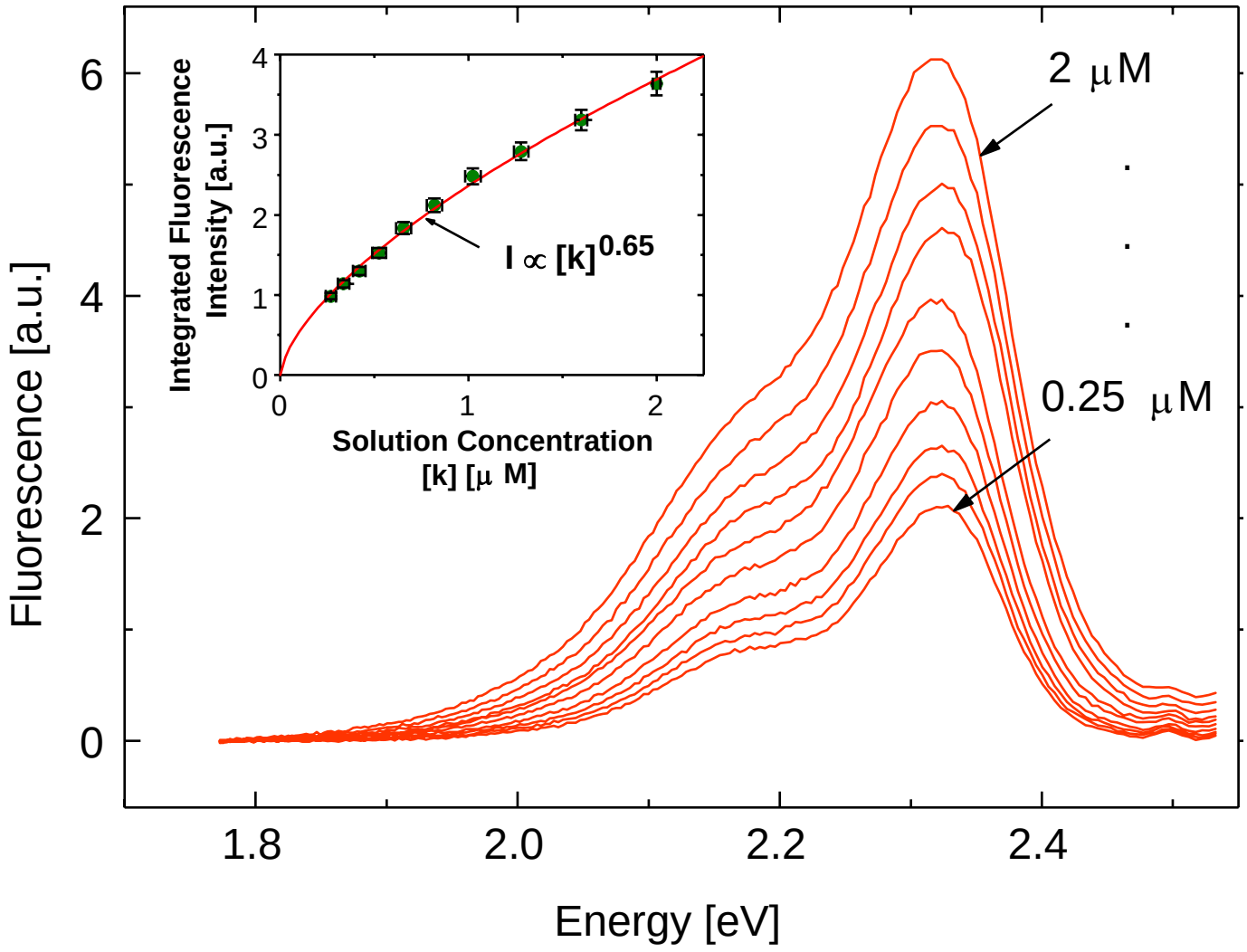


AGGREGATE STATE ABSORPTION increases with PTCDA solution concentration

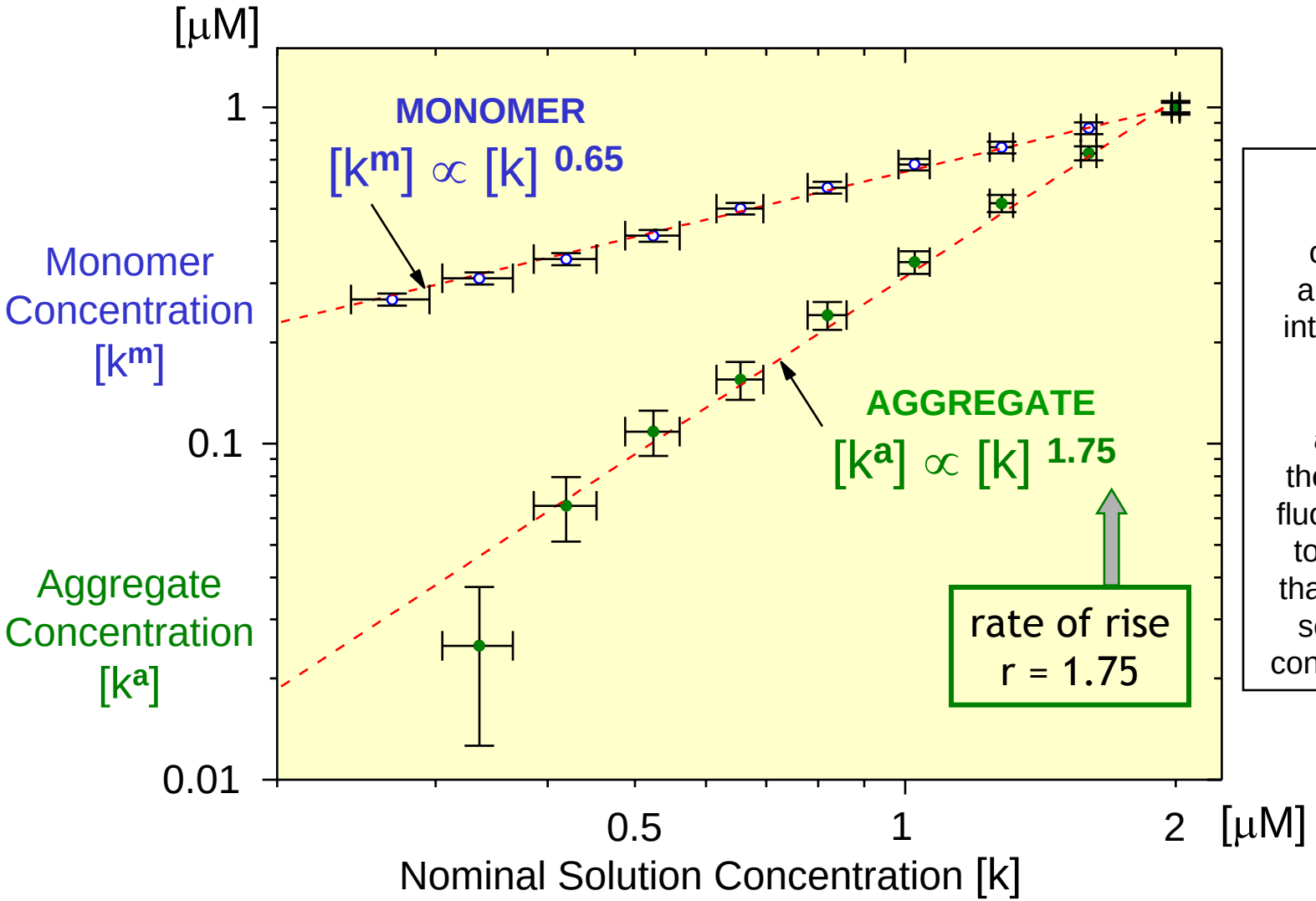
Absorption of Vibronic Transitions
– Change with Solution Concentration



Solution Luminescence

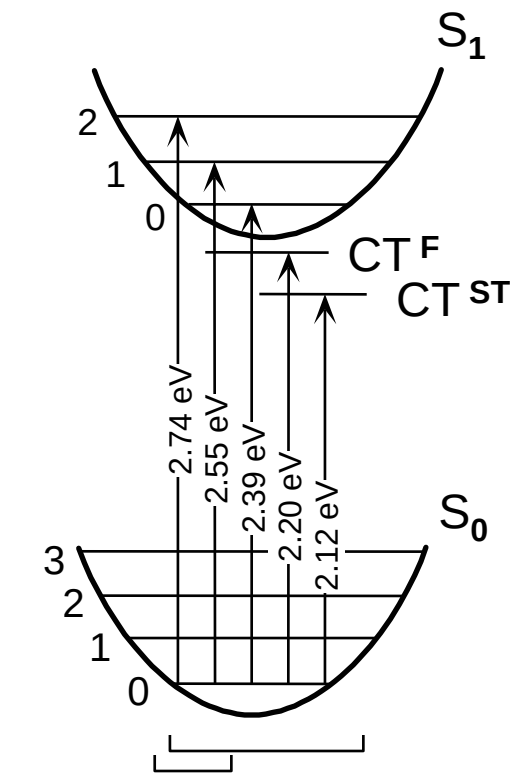


Monomer and Aggregate Concentration in Solution

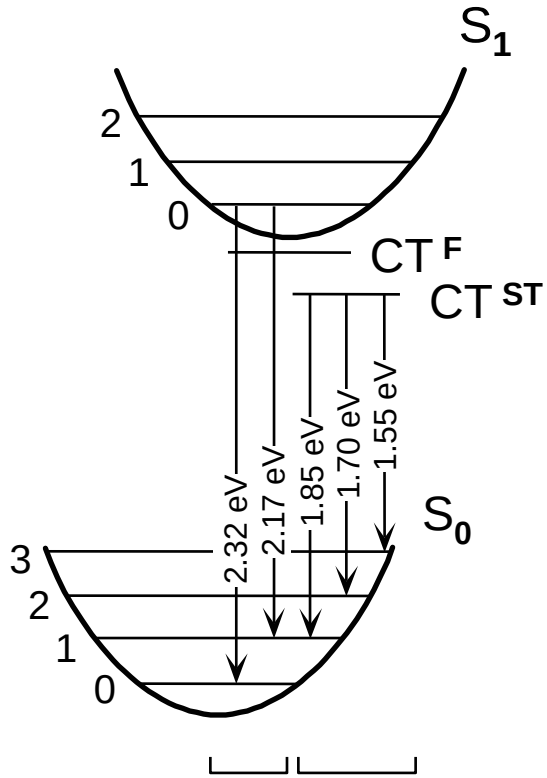


Monomer and Aggregate concentrations are derived from integrated solution fluorescence efficiency by assuming that the 2.3 eV solution fluorescence is due to monomers and that the most dilute solution primarily contains monomers.

PTCDA Electron Energy Structure



Absorption

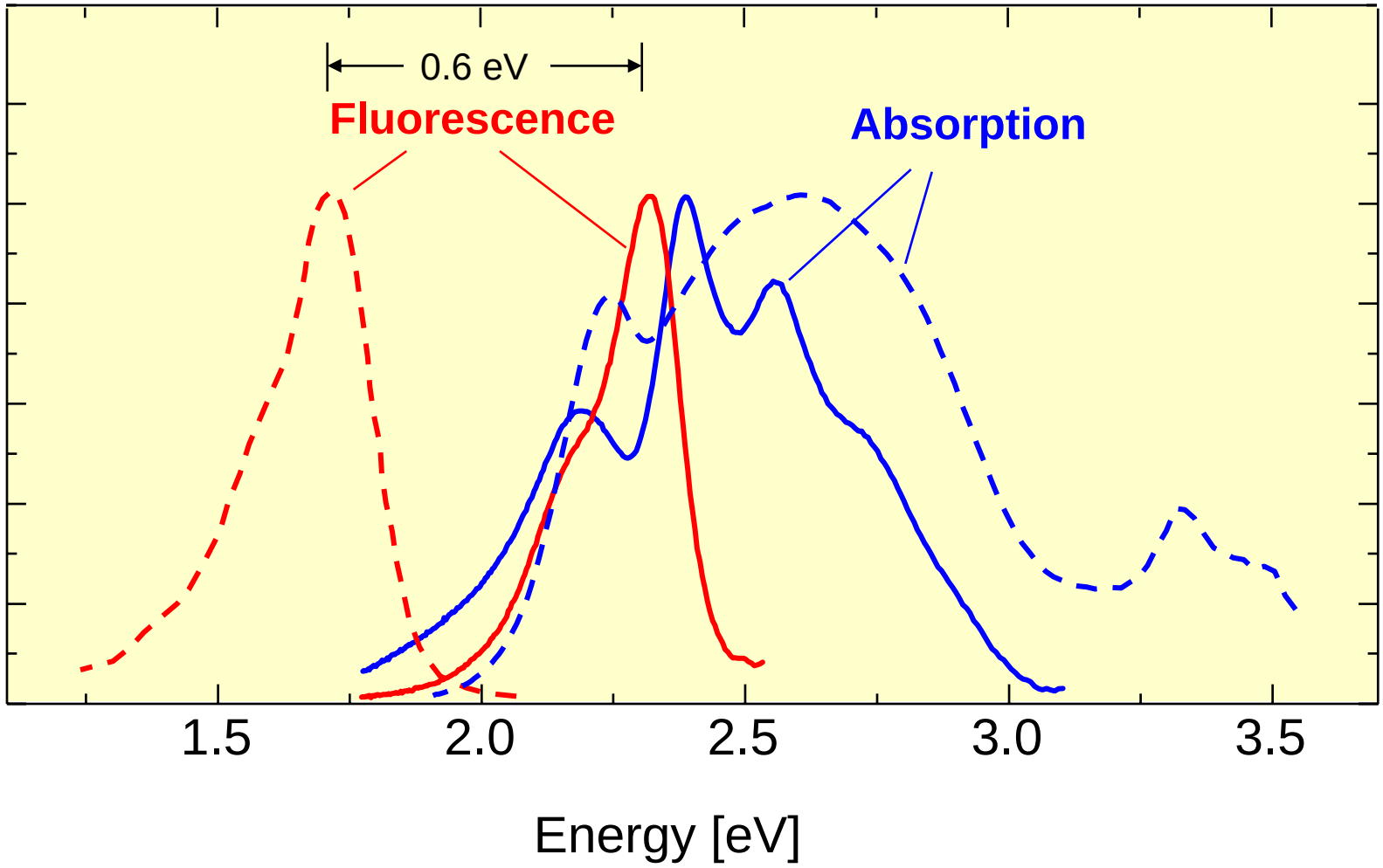


Luminescence

PTCDA Solution

PTCDA Thin Film

(~ 2μM in DMSO)

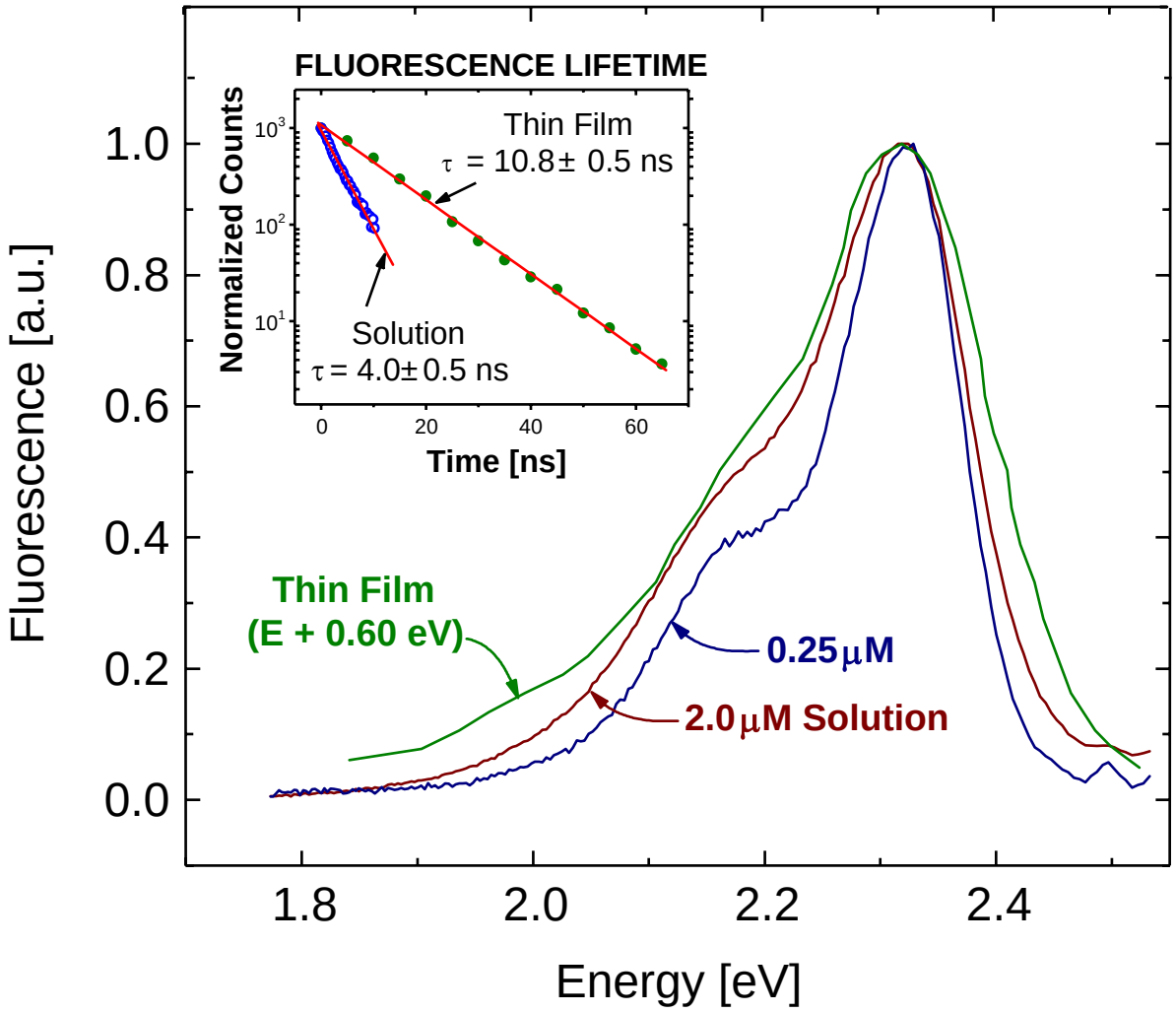


Solution and Thin Film Fluorescence

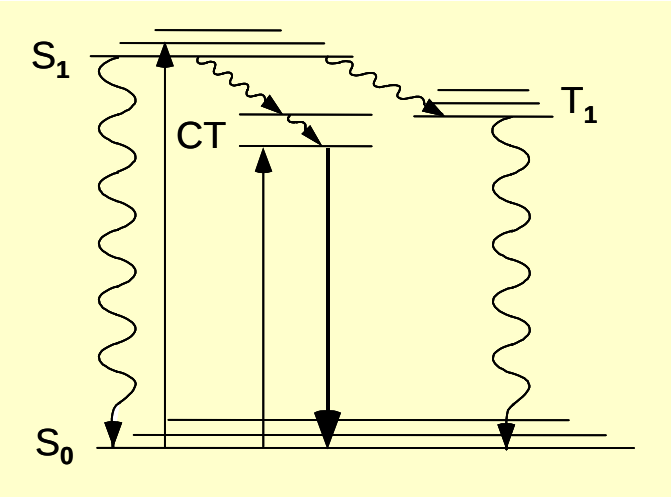
* Thin film fluorescence is red-shifted by 0.60 eV from solution fluorescence

* Minimal fluorescence broadening due to aggregation

* Fluorescence lifetime is longer in thin films

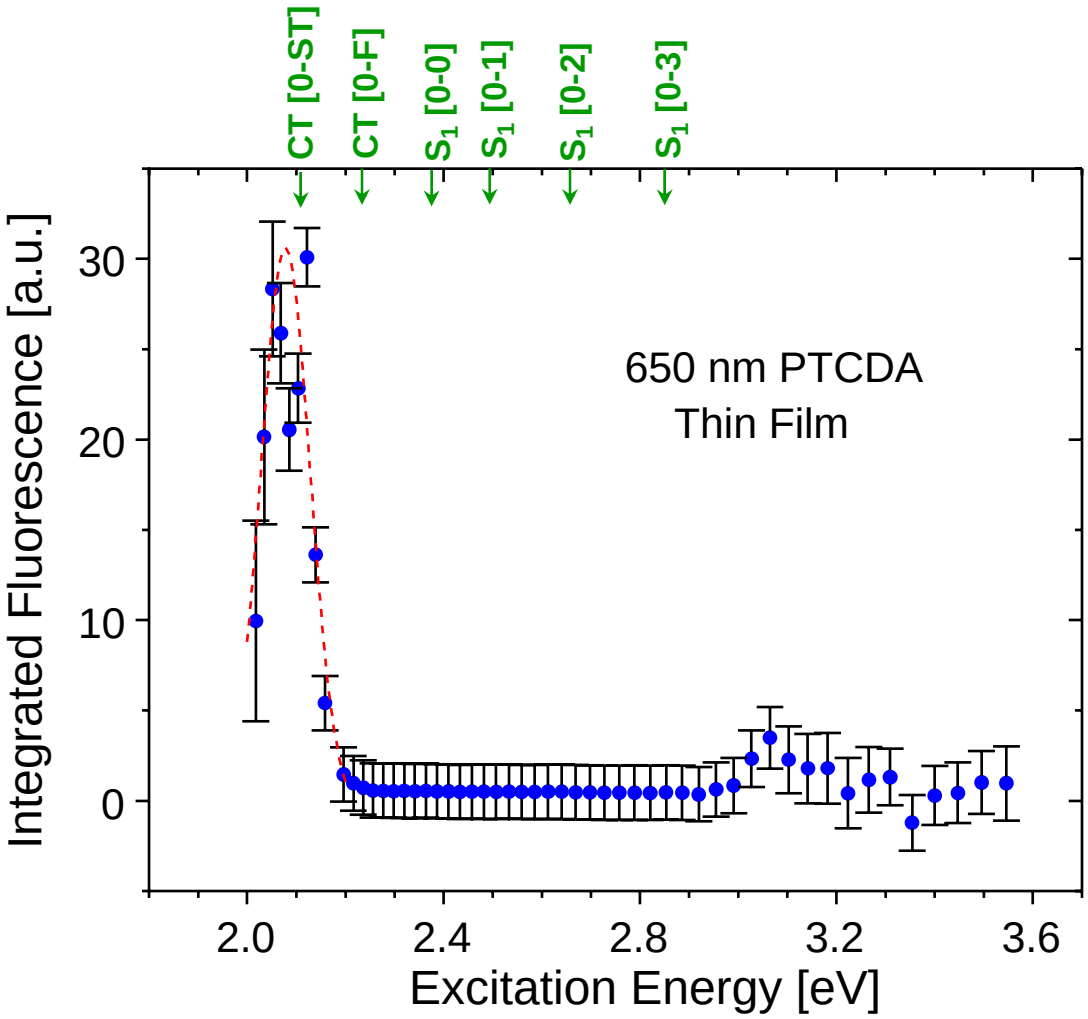


Thin Film Excitation Fluorescence



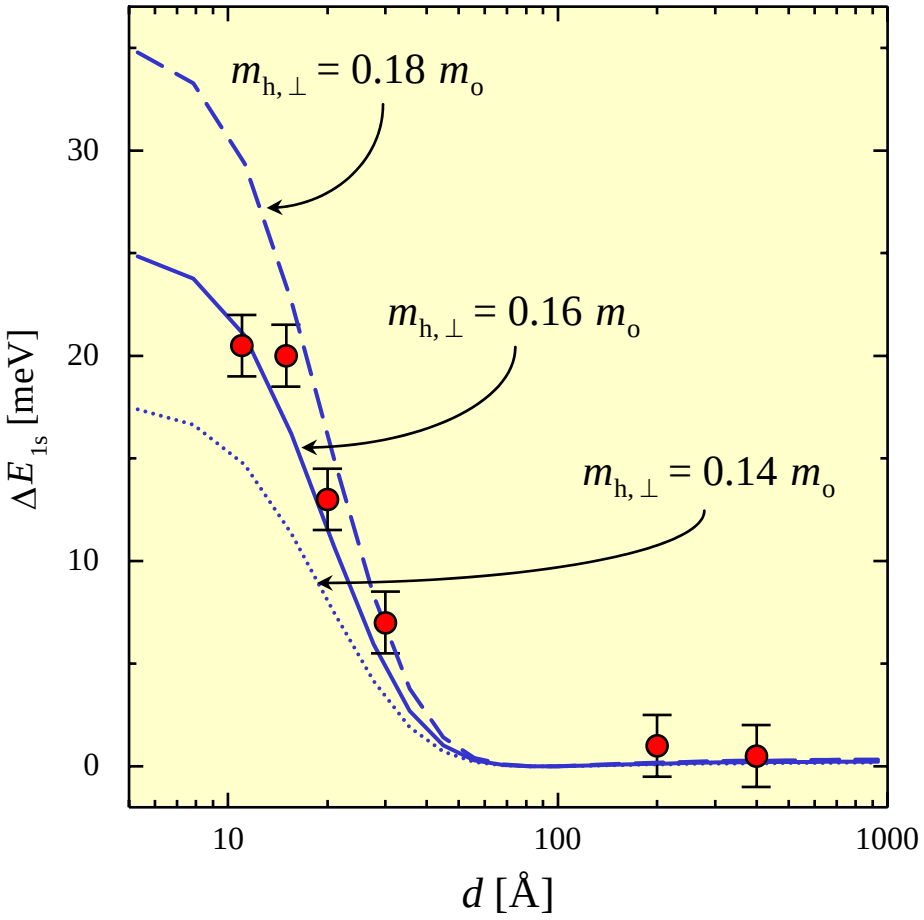
* Fluorescence energy and shape is not affected by the change in excitation energy

* Fluorescence efficiency increases when exciting directly into CT state

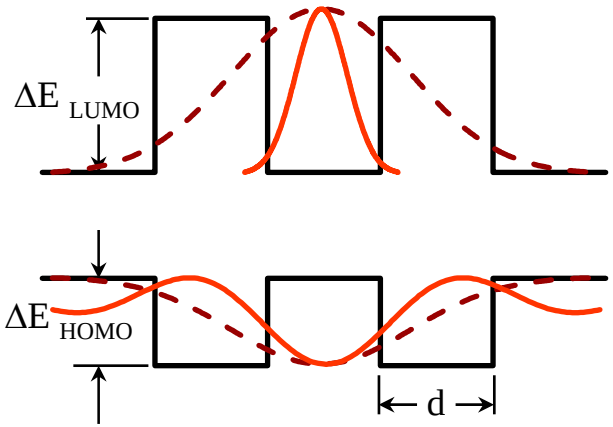


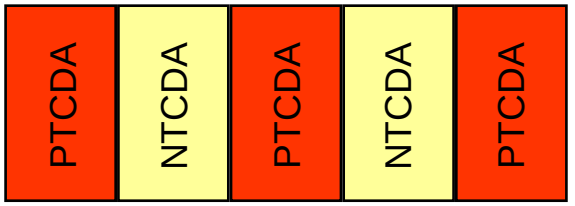
Exciton Quantum Confinement in Multi Quantum Wells

So and Forrest, *Phys. Rev. Lett.* 66, 2649 (1991).
Shen and Forrest, *Phys. Rev. B* 55, 10578 (1997).



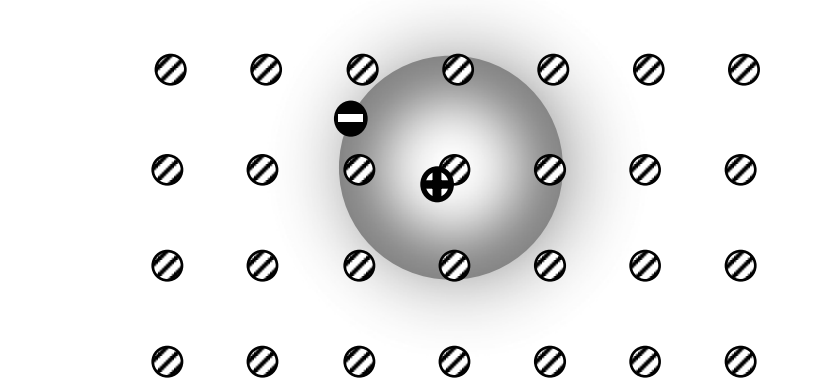
Exciton radius = 13 Å

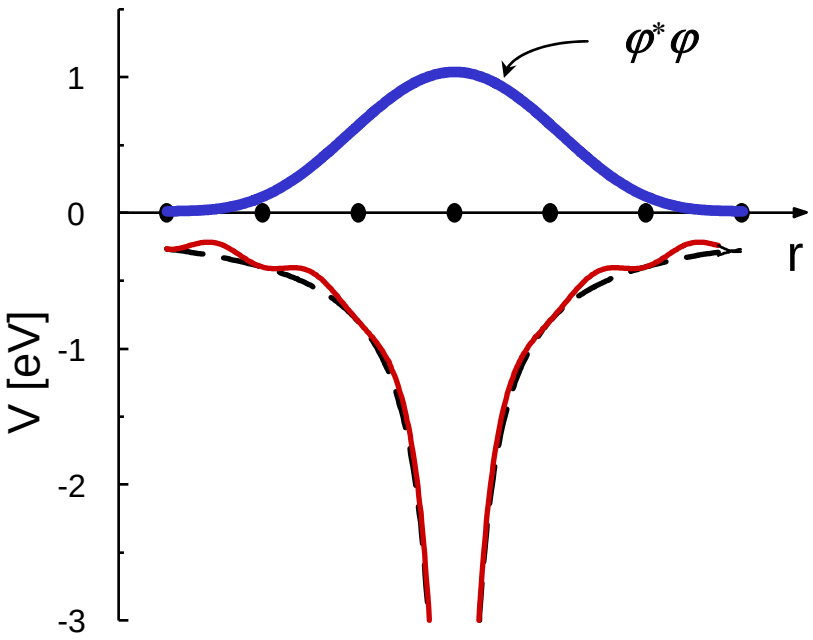




(a) Delocalized CT Exciton

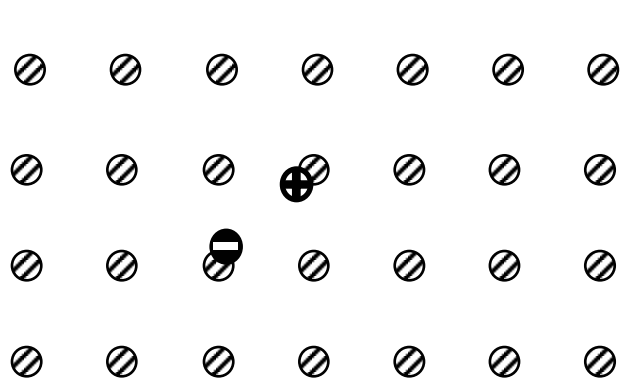
Bandwidth >> V_{PSEUDO}

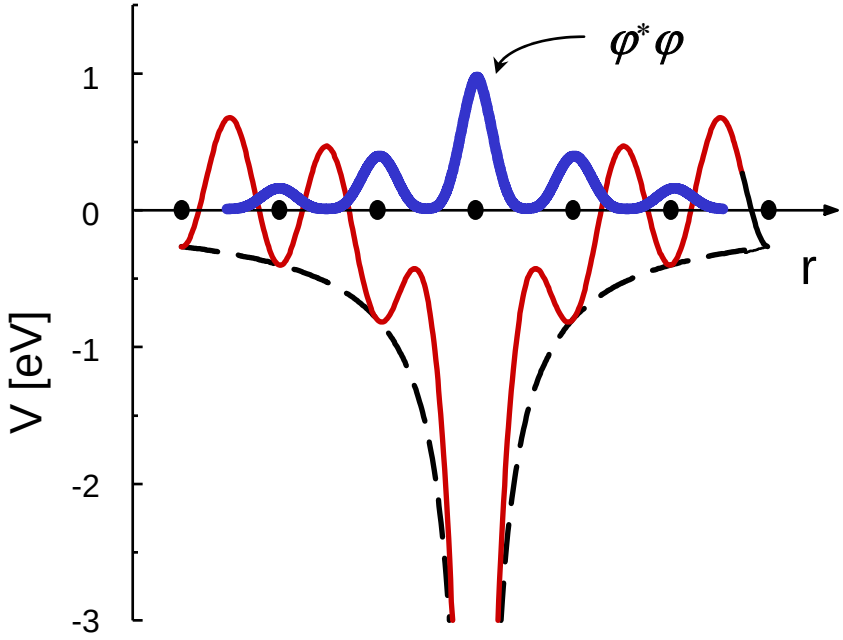




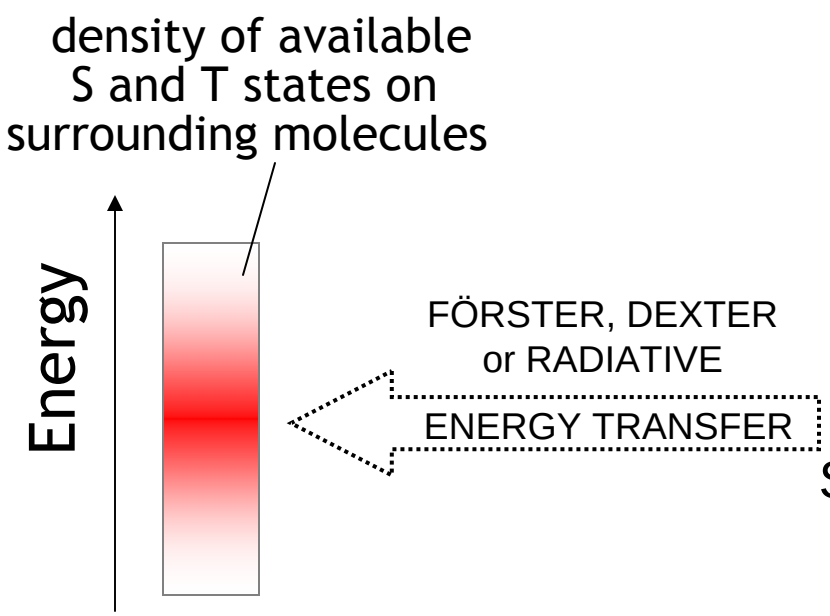
(b) Localized CT Exciton

Bandwidth << V_{PSEUDO}

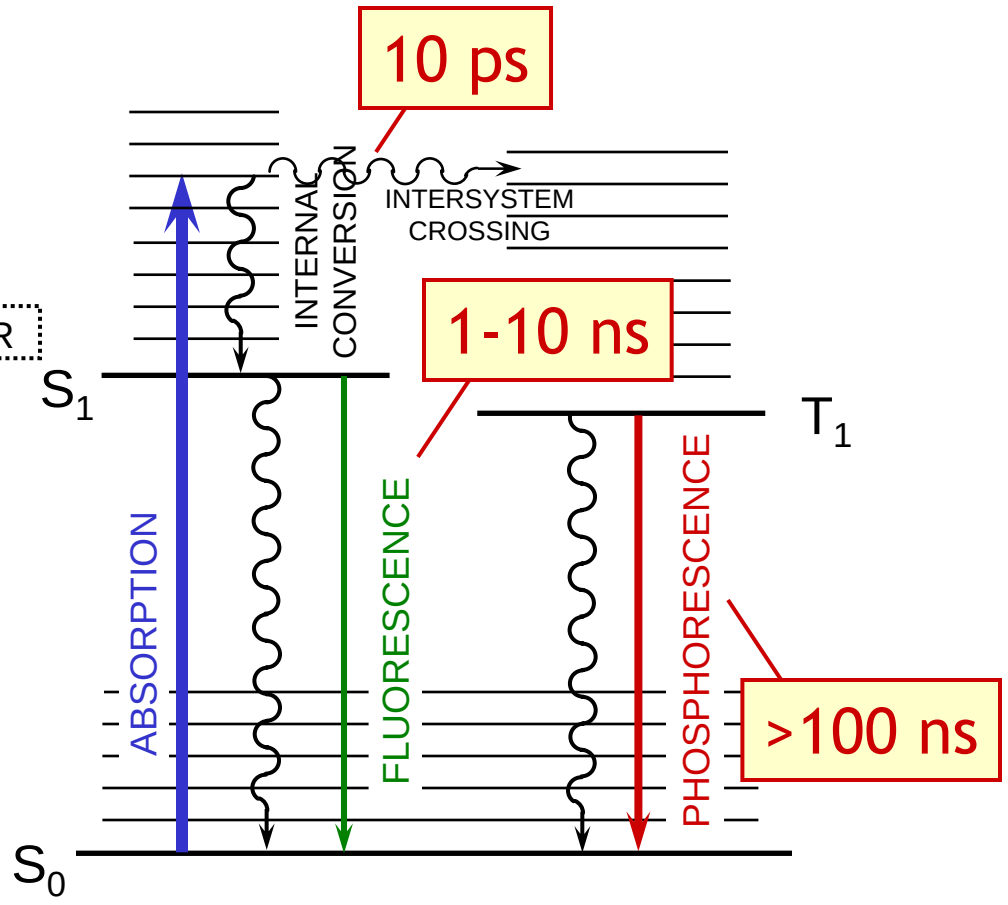




Electronic Processes in Molecules

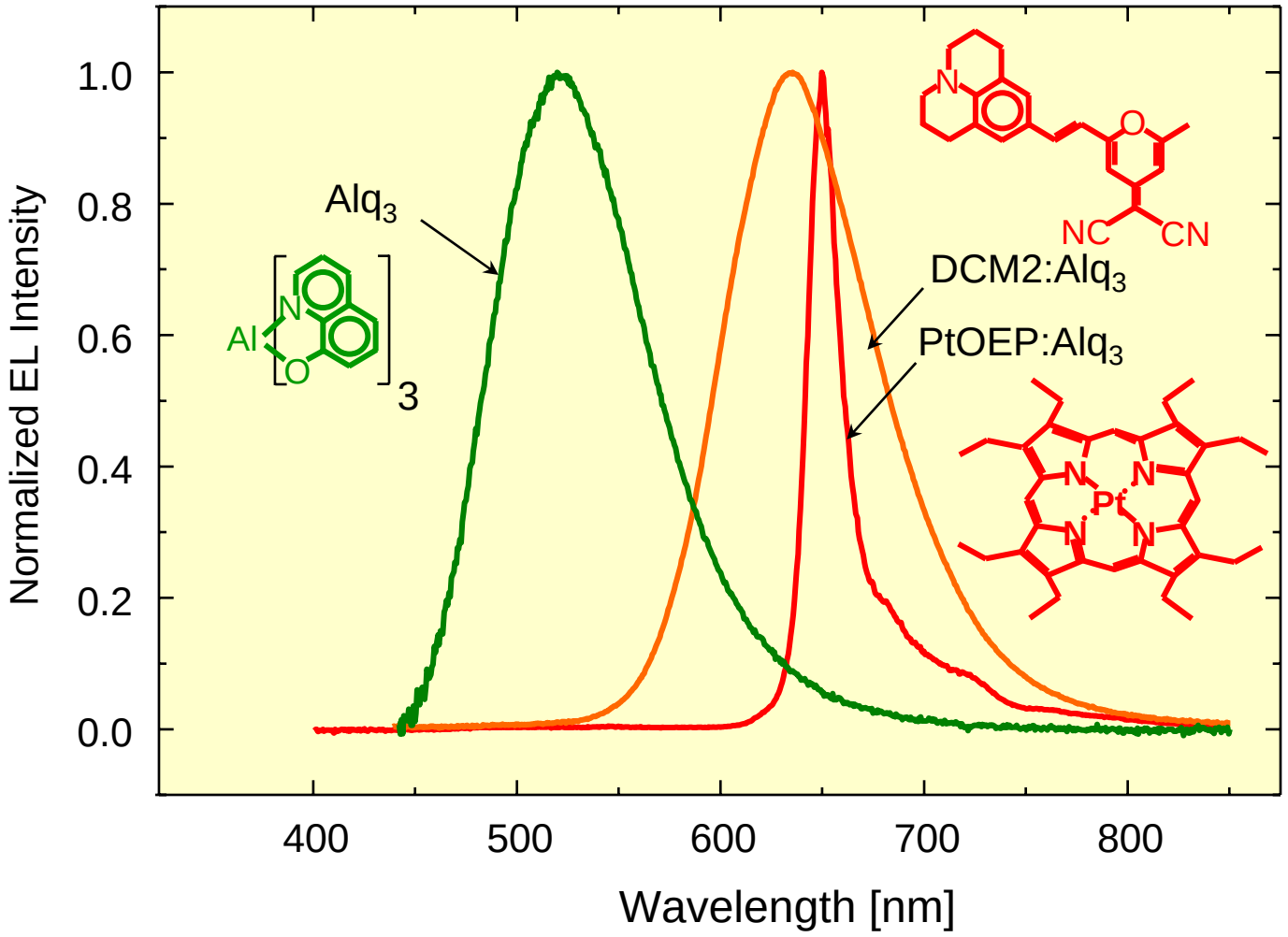


JABLONSKI DIAGRAM

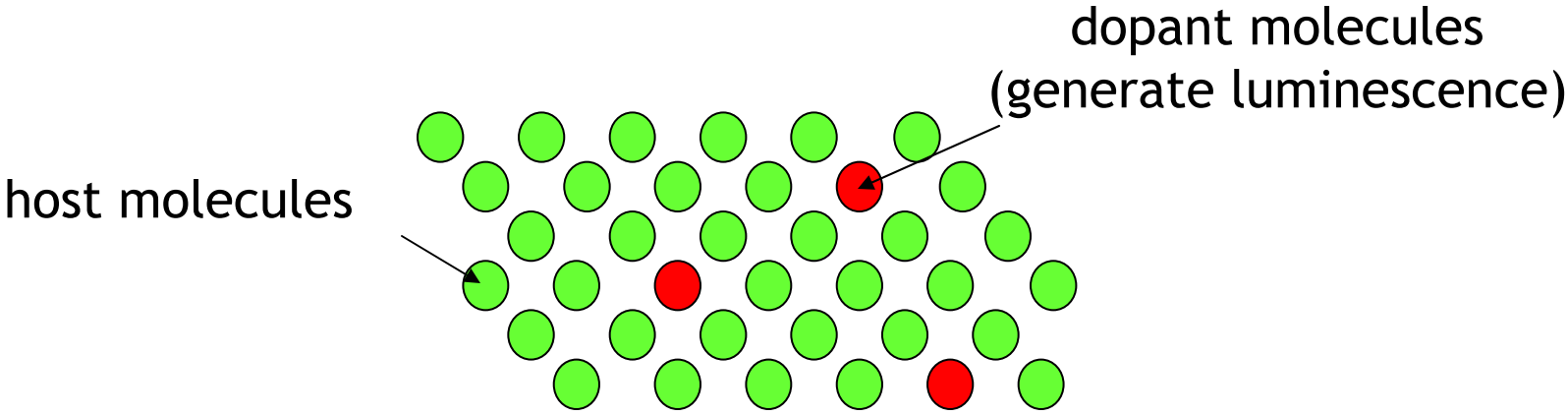


S: spin=0 (singlet) states
T: spin=1 (triplet) states

Effect of Dopants on the Luminescence Spectrum



Nonradiative Energy Transfer



How does an exciton in the host transfer to the dopant?

Energy transfer processes:

1. Radiative transfer

2. Förster transfer

3. Dexter transfer