

Week 1-5

Optical Properties 2

Understanding molecular spectra

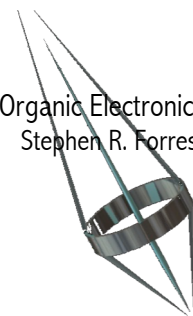
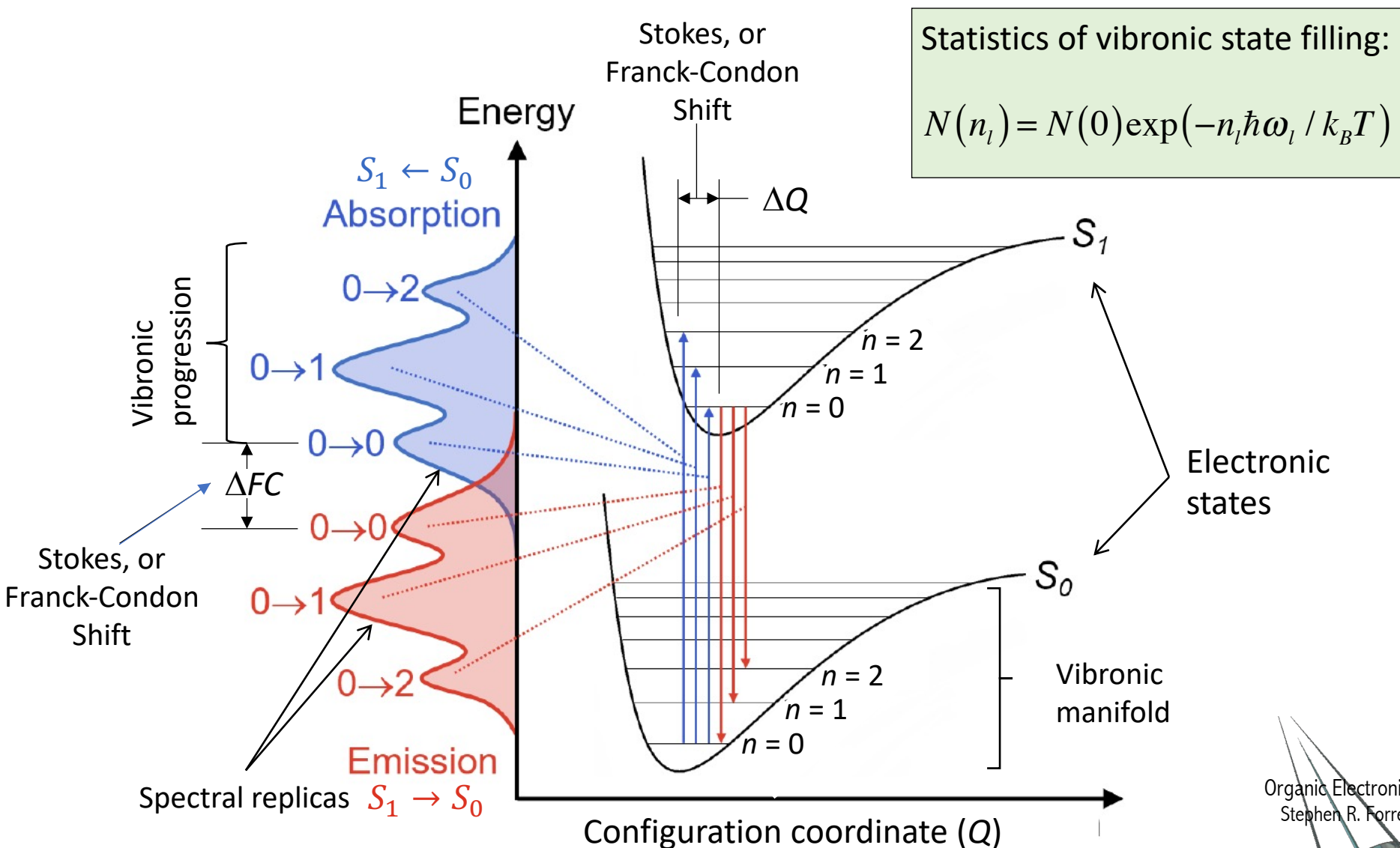
Dimers, excimers and exciplexes

Chapter 3.5.3 – 3.6.5

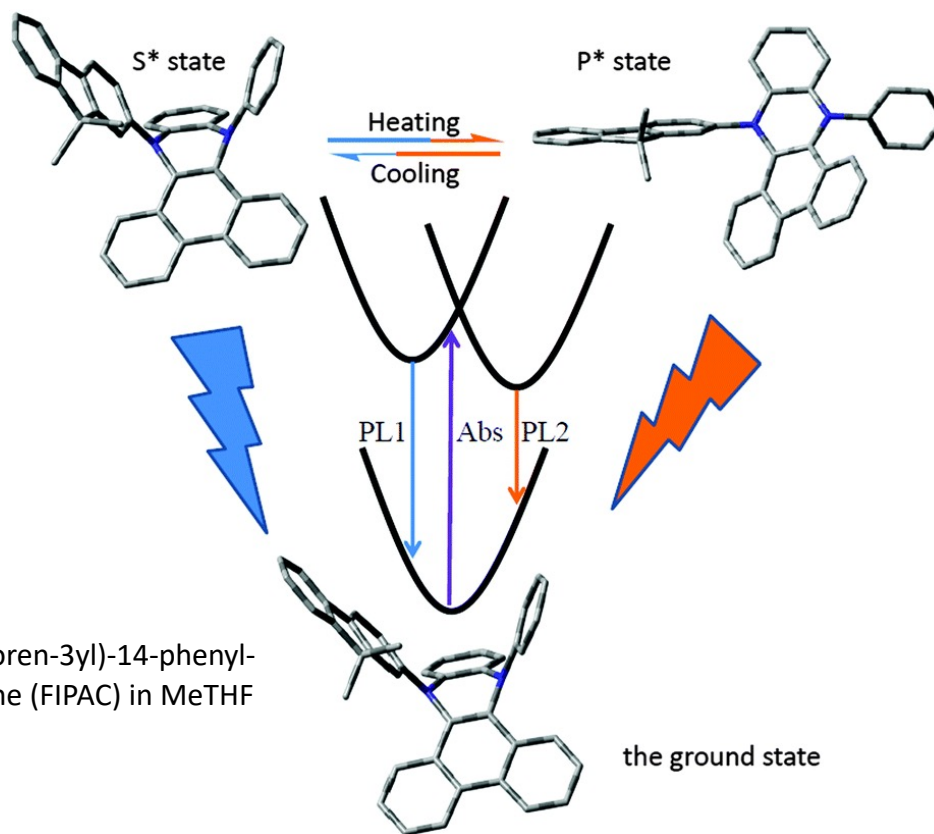


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Understanding molecular spectra



Molecular reconfiguration leads to Stokes shifts



Two excited isomers

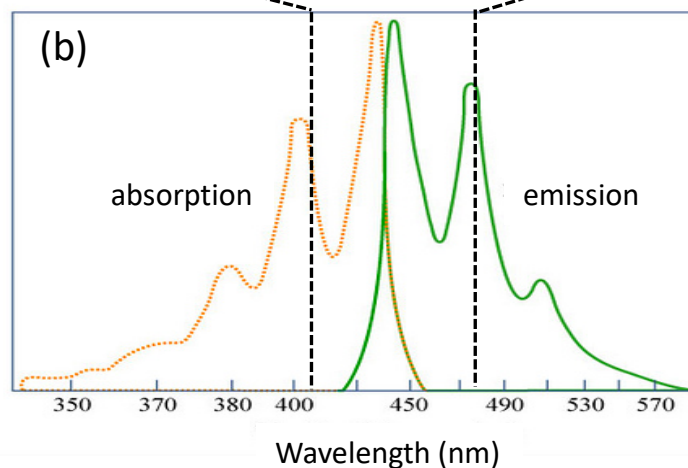
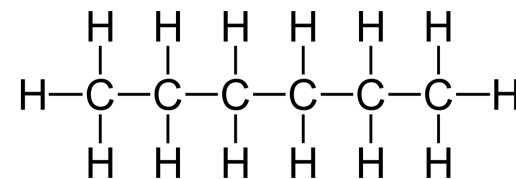
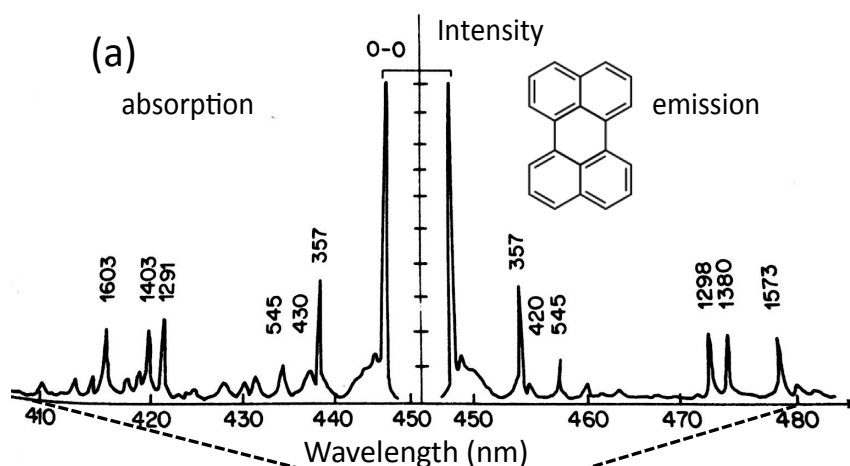
S*: saddle-like

P*: planar-like

Molecule: 9-(9,9-dimethyl-9Hfluoren-3yl)-14-phenyl-9,14-dihydrodibenzo[a,c]phenazine (FIPAC) in MeTHF (methyl tetrahydrofuran) solution

the ground state

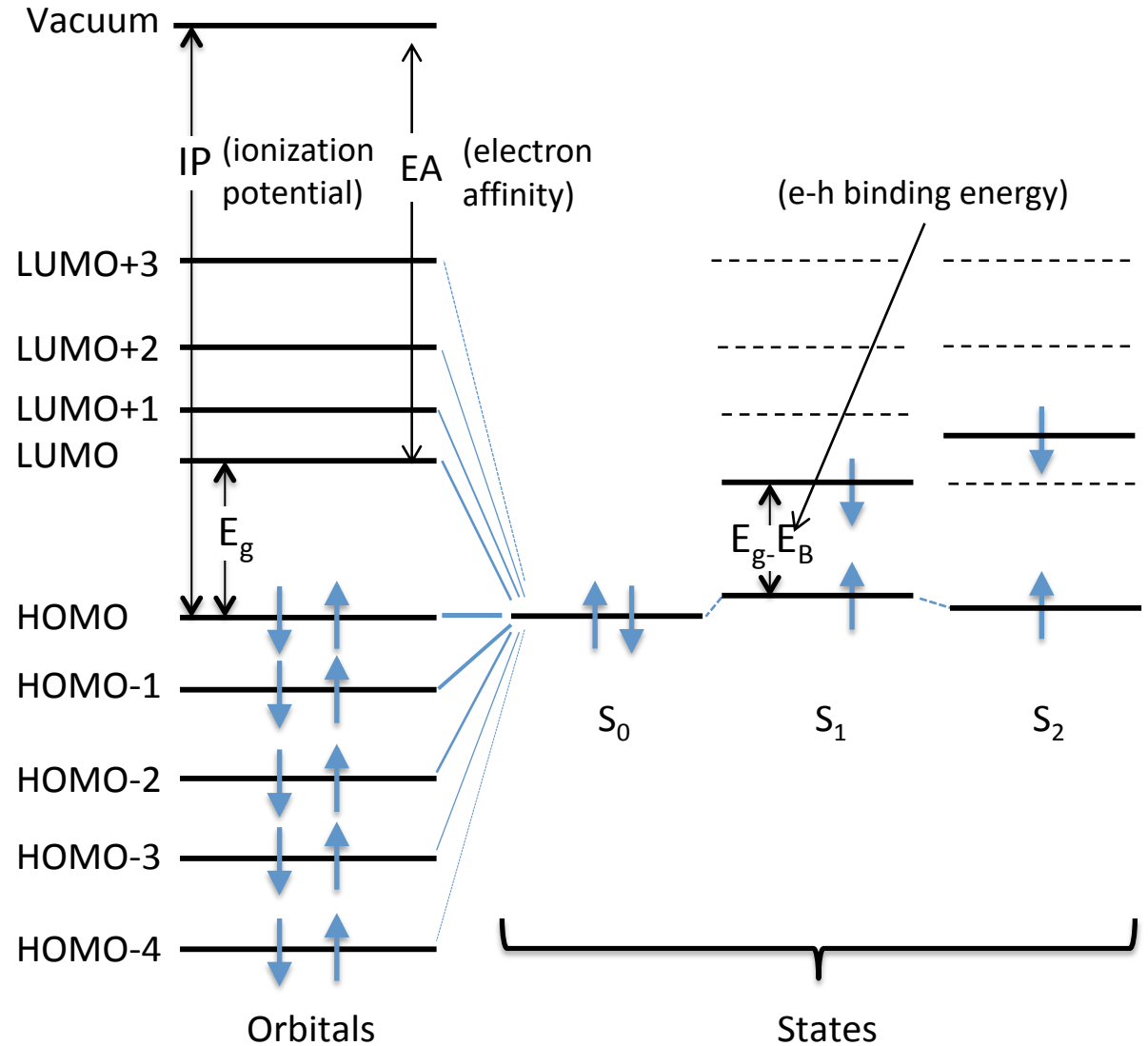
A classic spectrum at low temperature



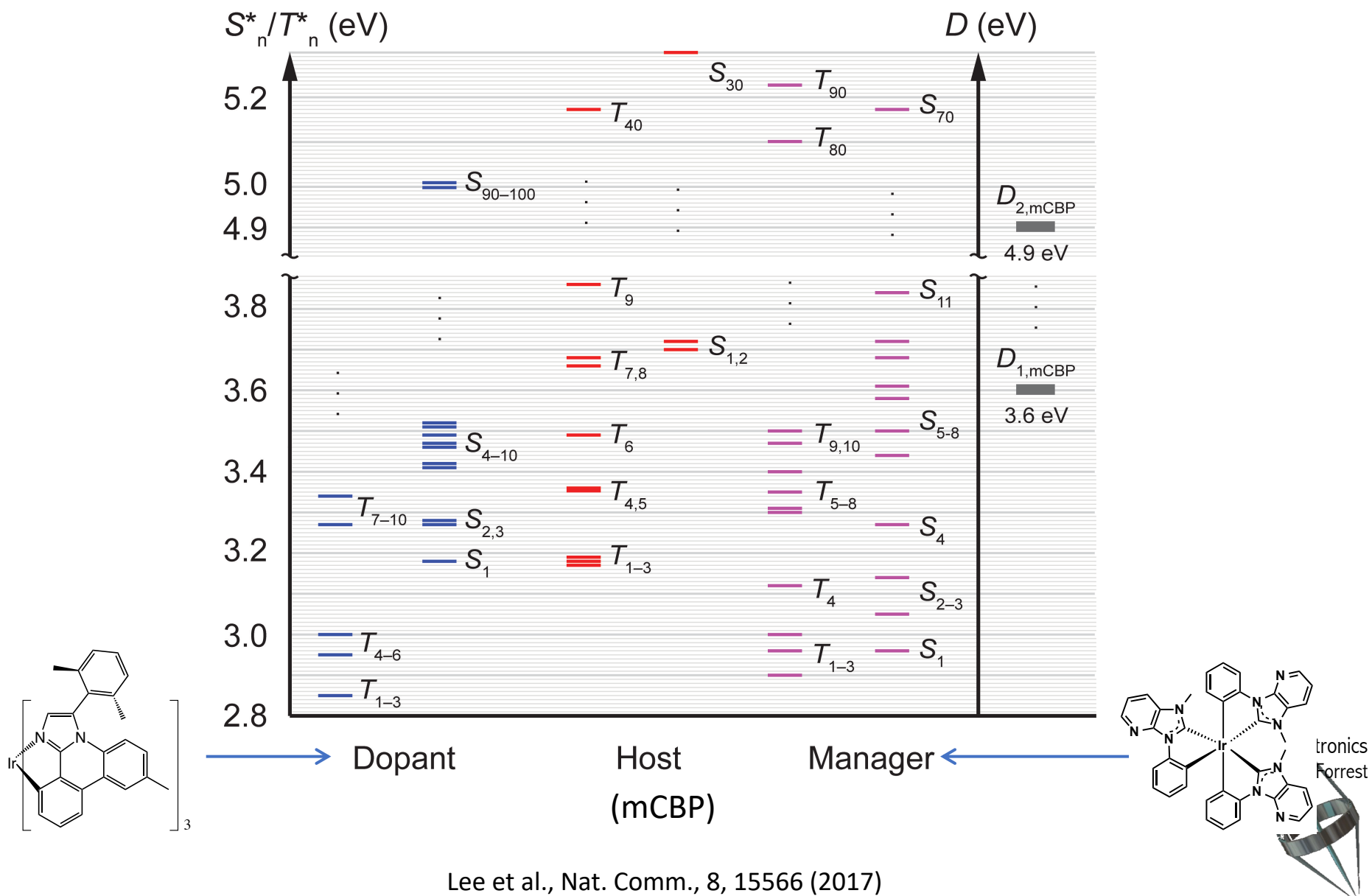
- **Perylene in *n*-hexane solution**
- Perfect replica of absorption and emission
- Homogeneously broadened phonon lines narrow as the random disorder is “frozen” out
- Numerous vibronics apparent in this progression: rotons, librions, etc...

Important distinctions between electronic *orbitals* and electronic *states*

1. Orbital energies refer to single electrons
2. Orbital energies are referenced to the vacuum level: All HOMO and LUMO energies < 0
3. State energies refer to collections of electrons: they are calculated from a linear combination of orbitals
4. State energies are referenced to each other (not vacuum)
5. States are formed after relaxation and include the electron-hole binding energy
6. States comprised of two or more electrons, and hence their spin multiplicity determines their character.
7. States and orbitals cannot co-exist meaningfully on the same diagram

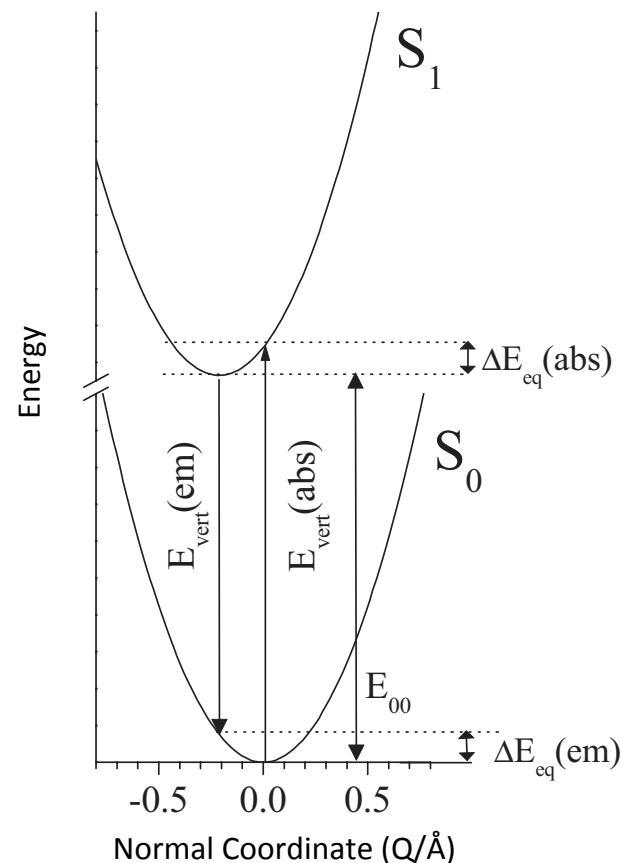
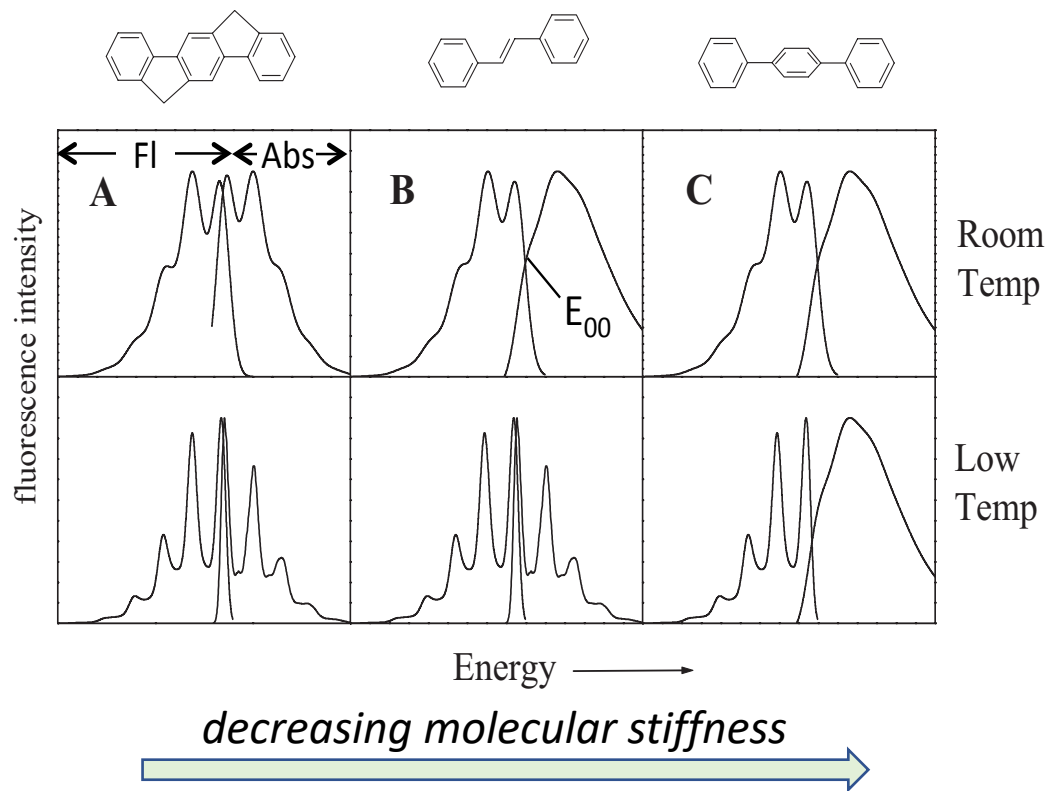


A (complicated) example of states



Spectral dependence on molecular stiffness

3 different phenylene spectra



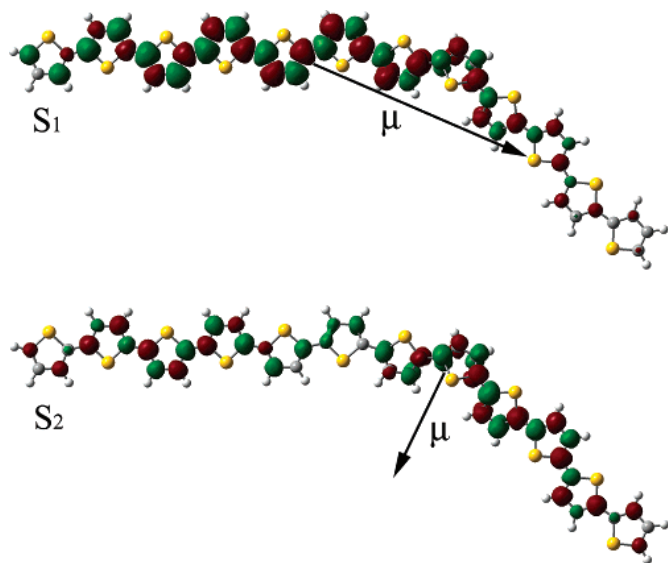
Gierschner, J., et al. 2007. *Adv. Mater.*, 19, 173. ics
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Stiffer molecules show less broadening of phonon lines at high temperatures
 E_{00} =adiabatic transition energy $\sim E_G$

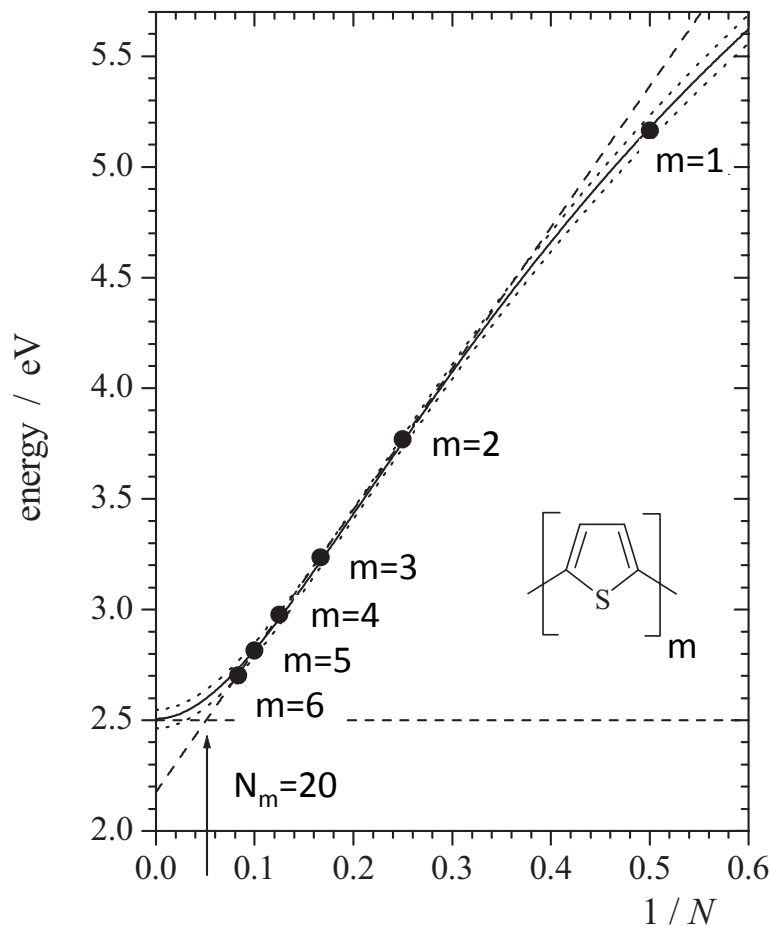
How big is the excited state?

Low energy absorption cutoff of thiophene oligomers vs. no. of monomer segments, m .

- N =number of **double bonds** in the oligomer
- Result \Rightarrow excited state is < 6 units
- Chain twists or kinks limit the extent of the electron charge distribution



dodecithiophene



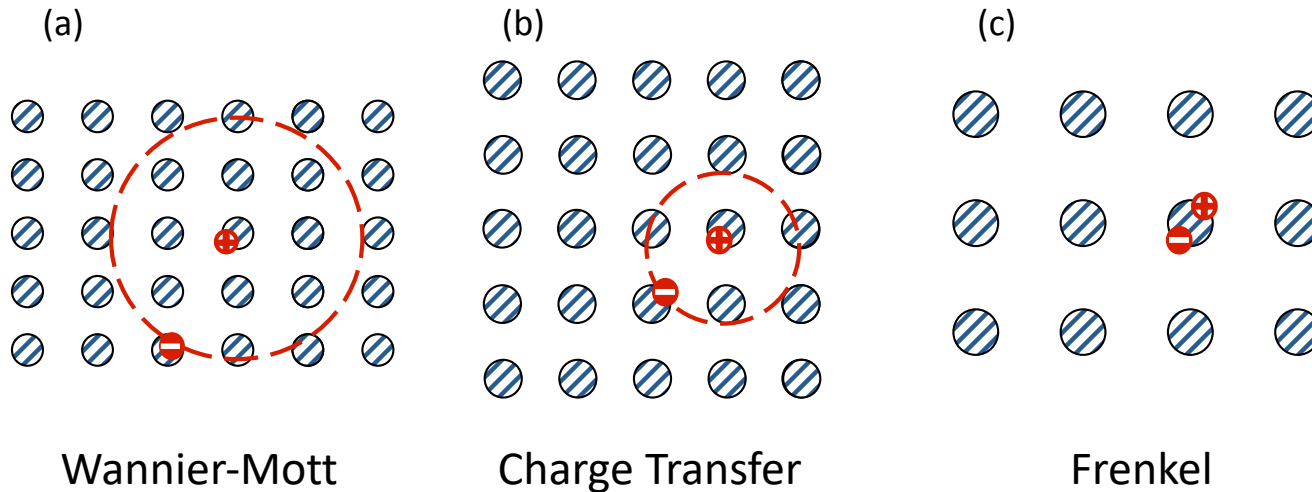
Gierschner, J., et al. 2007. *Adv. Mater.*, 19, 173.

Excitons

- Collective response of a solid to the excitation of a molecule
- Excited states that transport energy
 - But not charge, except for charged excitons
- The excited state transfers from molecule to molecule.
 - Excitons have momentum
 - Energy migration is known as *exciton diffusion*.
- Migration can happen in gas, solution and especially solids.



Three Types of Exciton



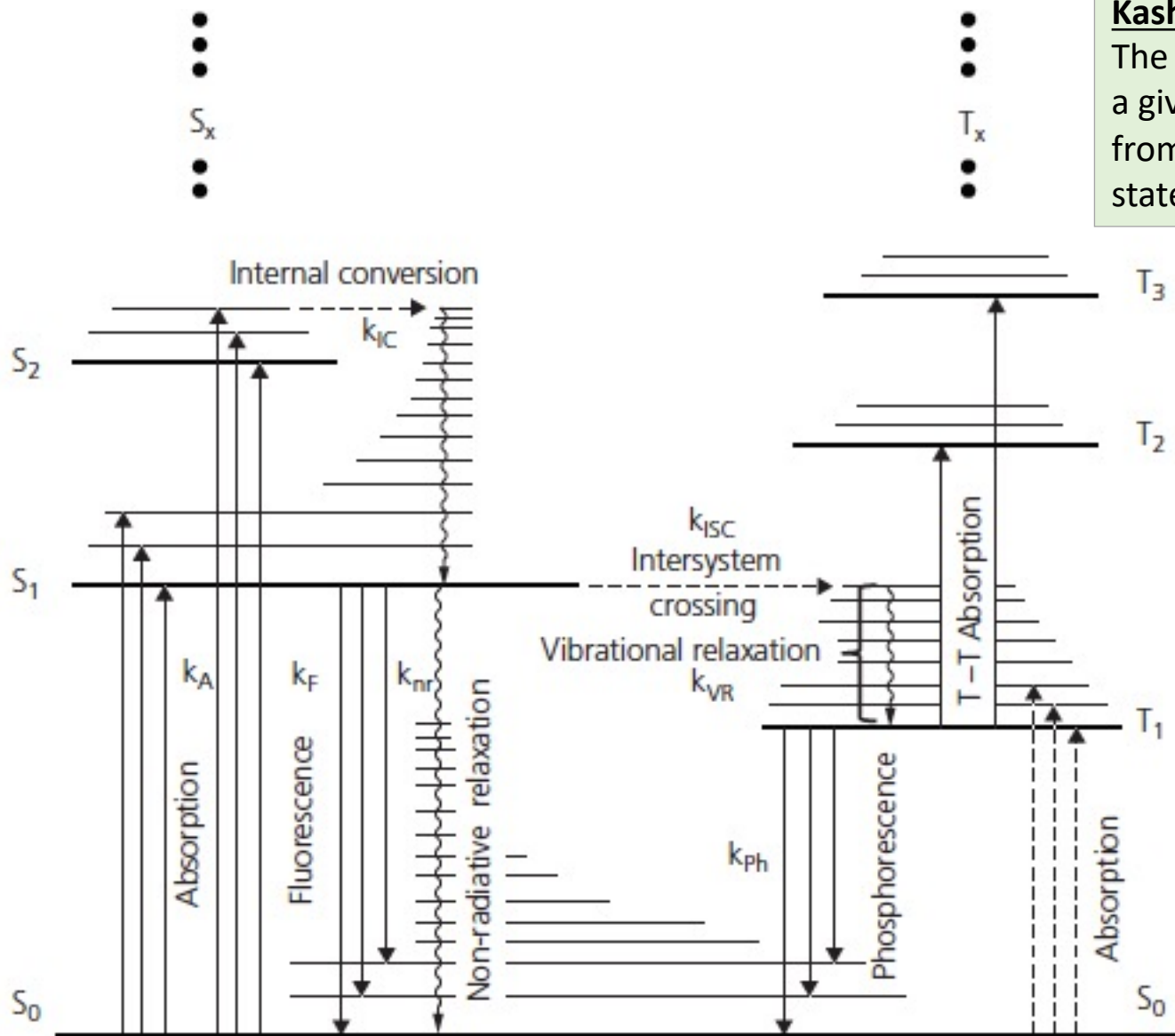
Bohr Model:

$$E_B = -\frac{q^2}{8\pi a_0 (\epsilon_r \epsilon_0)} \frac{1}{n^2}$$

$$a_0 = \frac{4\pi (\epsilon_0 \epsilon_r) \hbar^2}{m_r^* q^2}$$

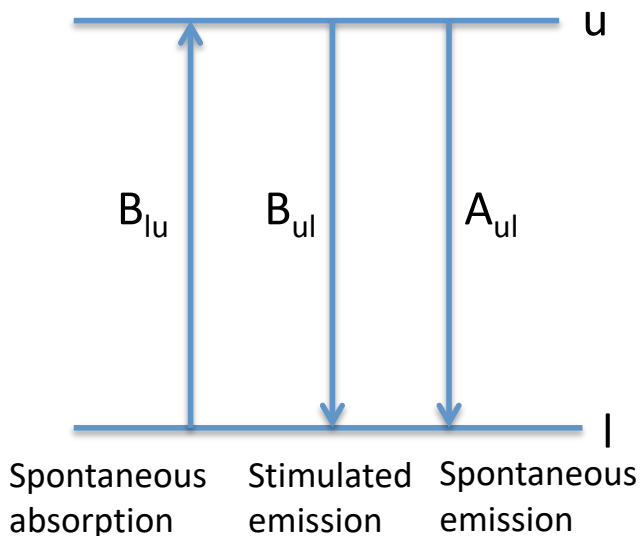
Medium	ϵ_r	m_r^* / m_e	a_0 (Å)	E_B (eV)
Vacuum (H atom)	1	1	0.5	13.6
Anthracene ^(a)	2.4-4.1	1	1.2-2.1	0.8-2.4
PTCDA ^(b)	2.0-4.4	0.14-1	2.2-7.1	0.5-0.7
ZnS ^(c)	5.2	0.4	5.2	0.2
Si ^(c)	11.9	0.14	43	0.014
GaAs ^(c)	13.1	0.07	94	0.006

Jablonski Diagrams: Life Histories of Excitons



Kasha's rule
The radiative transition from a given spin manifold occurs from the lowest excited state.

Relationships between emission and absorption: The Einstein Coefficients



$\mu_{ln,um}$ is the transition dipole from the lower to the upper state between vibronics n and m , respectively.

In terms of the transition matrix elements:

$$B_{ln,um} = \frac{\pi}{3\epsilon_0 \hbar^2} \left| \langle \phi_{ln} | H_{\text{int}} | \phi_{um} \rangle \right|^2 = \frac{\pi}{3\epsilon_0 \hbar^2} \left| \mu_{ln,um} \right|^2$$

($m, n =$ corresponding vibronic levels). And:

$$A_{um,ln} = \frac{\hbar}{\pi^2} \left(\frac{\omega n_r}{c} \right)^3 B_{ln,um}$$

But A_{ul} is simply the sum of all radiative transition rates:

$$\tau_R^{-1} = \sum_n A_{u0,ln}$$

Then in terms of frequency:

$$\tau_R^{-1} = \frac{8\pi^2 n_r^3}{3\epsilon_0 \hbar c^3} \sum_n \nu_{u0,ln}^3 \left| \mu_{u0,ln} \right|^2$$

Oscillator Strength

The *oscillator strength* is the ratio of the emission or absorption rate of the molecule to that of a classical oscillator, which is defined by:

Recall this is simply $|\mu_{if,e}|^2 FC_{if}$

$$f_{in,fn} = \frac{4\pi m_e c}{3q^2 \hbar} \langle \tilde{\nu}_{in,fn} \rangle \left| \langle \phi_{in} | H_{int} | \phi_{fn} \rangle \right|^2 = \frac{4\pi m_e c}{3q^2 \hbar} \langle \tilde{\nu}_{in,fn} \rangle |\mu_{in,fn}|^2.$$

Normalized line shape

The absorption cross section is: $\sigma_0(\omega) = \hbar\omega B_{ln,um} \gamma(\omega) / c$

This leads to more practical expressions for the oscillator strength:

$$f_{in,fn} = \frac{2m_e \epsilon_0 c}{\pi q^2 n_r} \int \sigma(\omega) d\omega = \frac{2303 m_e c^2}{N_A \pi q^2 n_r} \int \epsilon(\tilde{\nu}) d\tilde{\nu} = \frac{4.39 \times 10^{-9}}{n_r} \int \epsilon(\tilde{\nu}) d\tilde{\nu}$$

Decadic molar absorption
Coefficient [l-cm⁻¹-M⁻¹]

wavenumber = ν/c

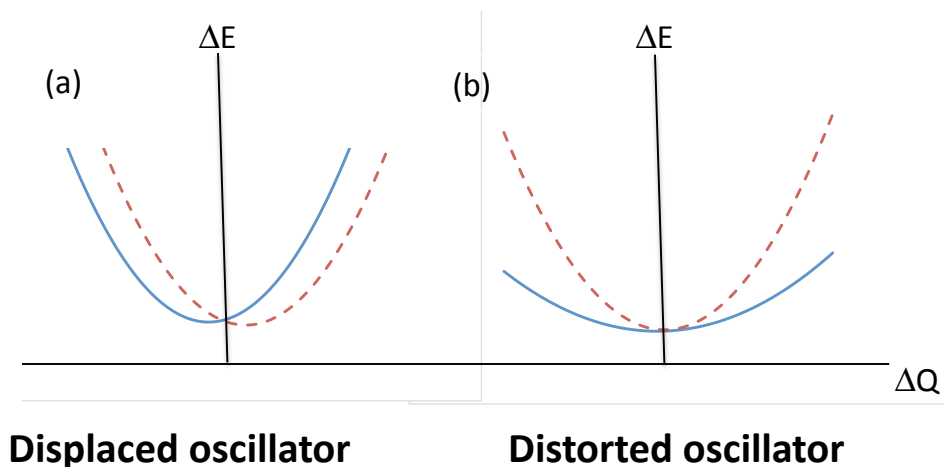
Absorption coeff't relationships: $\alpha(\nu) = \ln 10 \epsilon(\nu) C = 2.303 \epsilon(\nu) C$

C=concentration [M/l]

What is the strength of a vibronic transition?

$$\bar{f}_{in,fm} = \frac{\tilde{\nu}_{in,fm}}{\tilde{\nu}_{i0,f0}} FC_{n,m}$$

- The strength of a transition depends on the overlap between the excited and ground state vibronics, i.e. on the Franck-Condon factor $FC_{n,m}$!
- It is convenient to reference the oscillator strength to the 0-0 transition $\nu_{i0,f0}$
- Two cases to consider:



- Rigid shift of nuclear coordinates on excitation
- Vibronic progression is unaffected
- Red shift of spectrum= bathochromic shift
- Blue shift=hypsochromic

- No net shift of nuclear coordinates
- Electronic potential changes
- Energies between vibronics changes



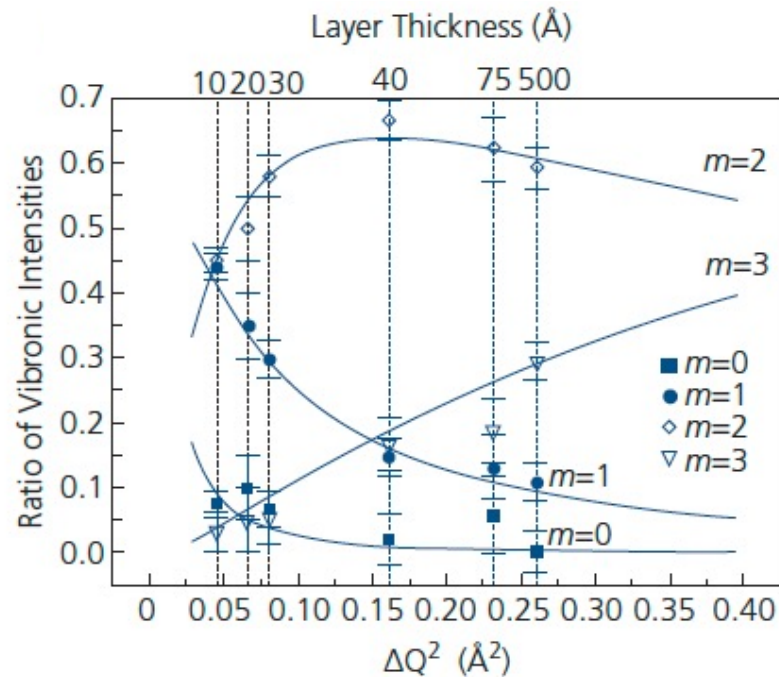
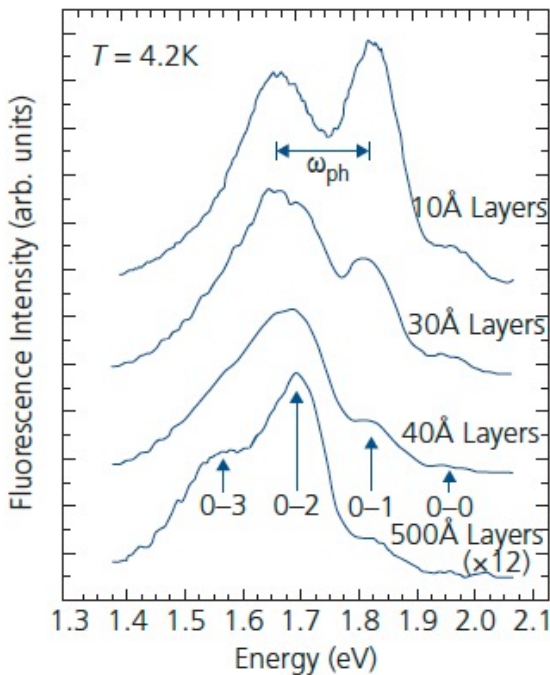
Example 1: Displaced Oscillator

- A Poisson distribution describes the overlap and state filling. Hence

- Such that: $FC_{n,m} = Z^m e^{-Z} / m!$ $Z = \text{Huang-Rhys factor}$

$$\bar{f}_{in,fm} = \frac{\tilde{\nu}_{in,fm} Z^m}{\tilde{\nu}_{i0,f0} m!} e^{-Z} \quad : \text{Ratio of vibronic intensity to that at 0-0}$$

- Where: $Z = \frac{1}{2} k \Delta Q^2 / h \tilde{\nu}_{i0,fm}$ $\Delta Q = \sqrt{\sum_p^N \Delta R_p^2}$: Sum of squares of nuclear displacements



Ultrathin PTCDA layers separated by NTCDA layers of equal thickness

Example 2: Distorted Oscillator

FC Shift for the distorted oscillator:

$$FC_{if} = (1 - \xi^2)^{1/2} \xi^m \frac{1 \cdot 3 \cdot 5 \cdots (m-1)}{2 \cdot 4 \cdot 6 \cdots m}; \quad m \text{ even}$$

$$FC_{if} = 0; \quad m \text{ odd}$$

where

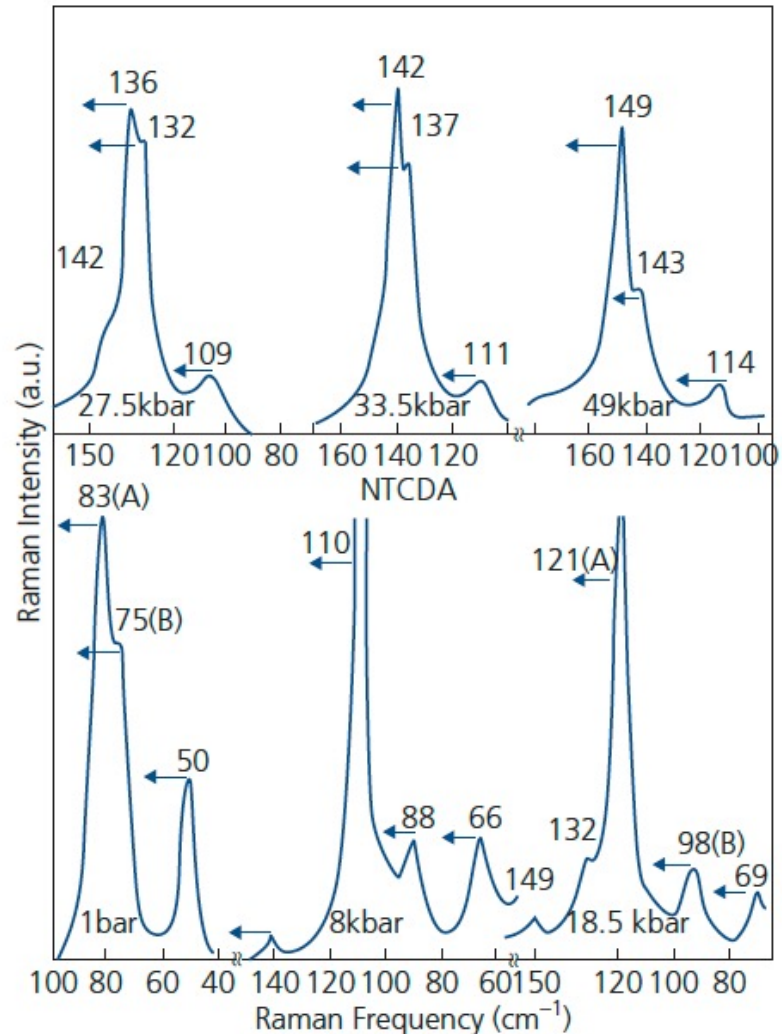
$$\xi = (\omega_{i0} - \omega_{fm}) / (\omega_{i0} + \omega_{fm}) = \Delta\omega / (\omega_{i0} + \omega_{fm})$$

Relative peak absorption intensities also scale with distortion:

$$G(\Delta\omega) = \exp(-\hbar\Delta\omega / (D-1)k_B T)$$

where

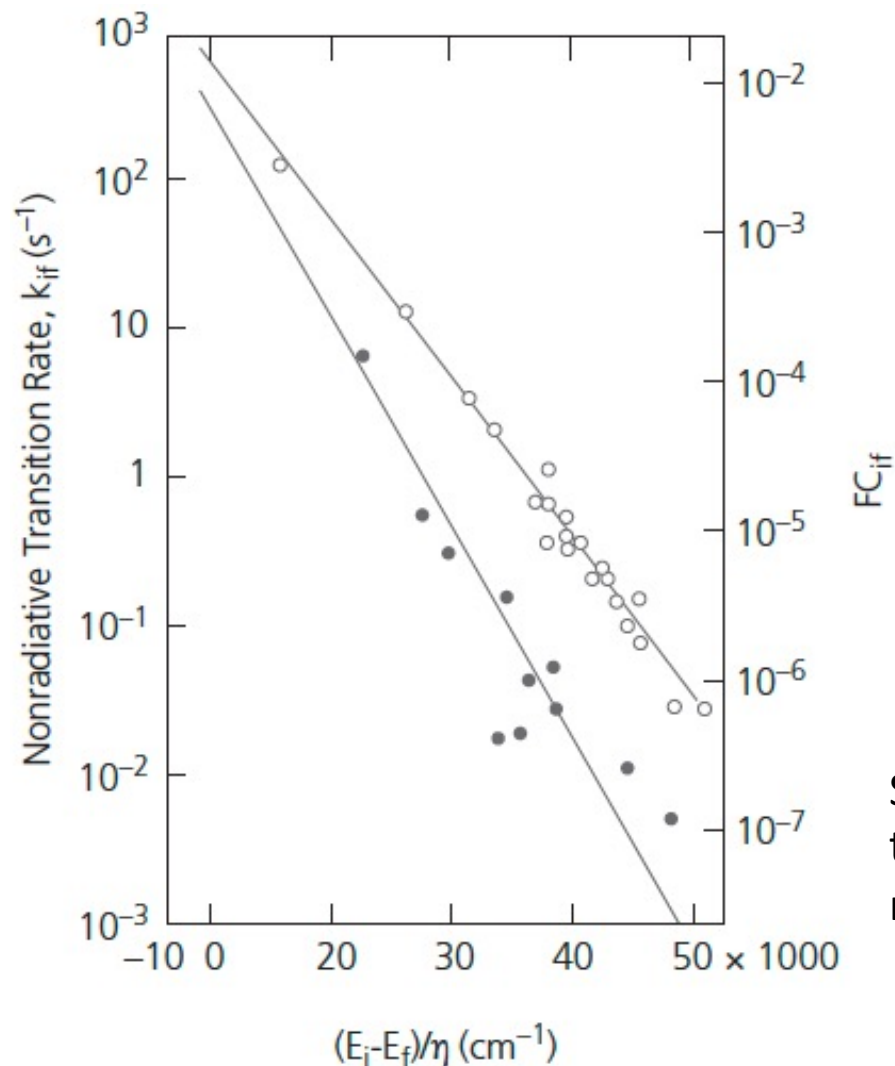
$$D = \omega_{i0} / \omega_{fm}$$



NTCDA under hydrostatic pressure
 Vibronic spacings and relative peak intensities shift
 indicating manifold distortion

Energy Gap Law

The larger the energy gap, the lower the probability for non-radiative recombination.
 ⇒ As the energy gap of a molecular species decreases, radiative transitions have a higher probability for non-radiative decay:



$$k_{if} = A \exp(-\gamma E_g / \hbar \omega_p)$$

$$\gamma = \log\left(\frac{E_g}{\Omega E_p}\right) - 1$$

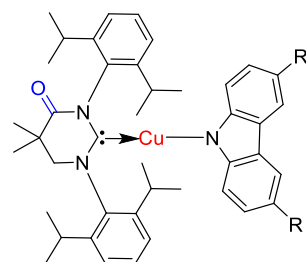
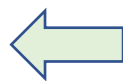
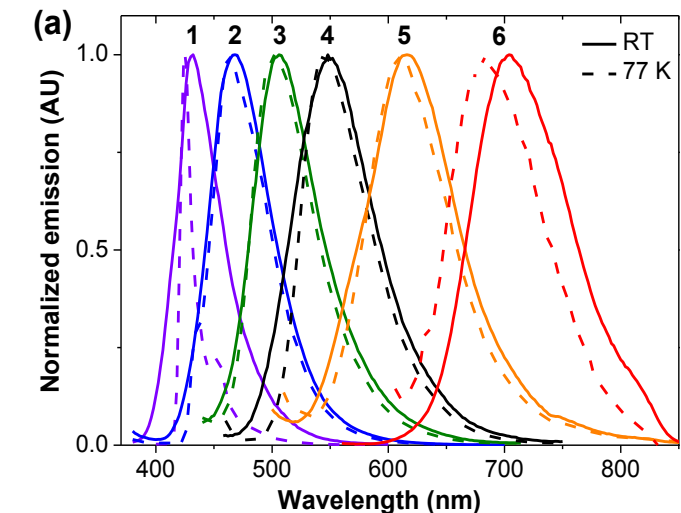
Ω = number of modes contributing to the maximum phonon energy,
 = ½ the Stokes shift.

Series of aromatic hydrocarbons and their deuterated isotopes (filled circles).
 η = relative number of H or D atoms in molecul.

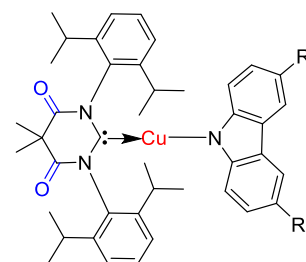
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Energy Gap Law

Example of thermally activated delayed fluorescent molecules whose energy gaps are varied via ligand substitution from deep blue to IR

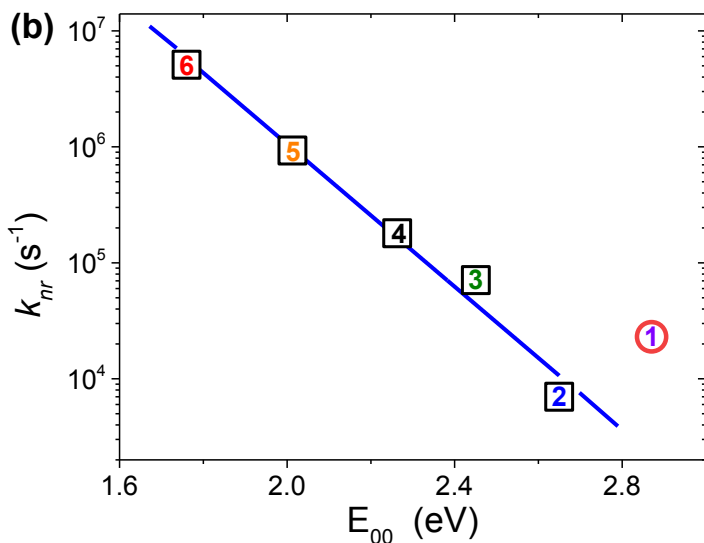


Carbene = MAC*
R, R' = CN (1)
R = CN, R' = H (2)
R, R' = H (3)

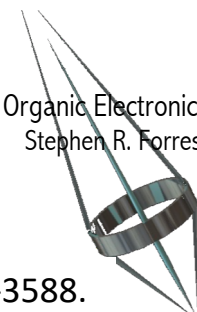


Carbene = DAC*
R, R' = CN (4)
R = CN, R' = H (5)
R, R' = H (6)

Cu-metallated, emissive TADF compounds



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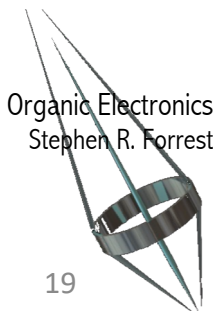


Dimers

- Interaction of an isolated pair of molecules
- First step in building up a solid: smallest possible aggregate unit
- Chemical dimer: the pair forms a bond
- Physical dimer: the pair is attracted by a bonding force, typically van der Waals
- New energy levels appear that do not exist in the individual molecules
- Treatment much like that of a H₂ molecule.
 - Ground state: $\psi_G(\mathbf{r}_1, \mathbf{r}_2) = \psi(\mathbf{r}_1)\psi_2(\mathbf{r}_2)$: $\psi(\mathbf{r}_{1,2})$ = ground state of individual molecules comprising the pair.
 - These identical molecules have identical energies: $E_1 = E_2 = E_0$
 - When interacting to form a dimer, the energy is perturbed:

$$E_I = \langle \psi_1(\mathbf{r}_1)\psi_2(\mathbf{r}_2) | H_{\text{int}} | \psi_1(\mathbf{r}_1)\psi_2(\mathbf{r}_2) \rangle$$

- With (for vdW interactions): $H_{\text{int}} = -\frac{A_{12}}{r_{12}^6}$



Normal Modes of a Dimer

Excited state 'oscillates' between the two molecules forming two normal modes:

$$\psi'_{\pm} = \frac{1}{\sqrt{2}}(\psi'_1(\mathbf{r}_1)\psi_2(\mathbf{r}_2) \pm \psi_1(\mathbf{r}_1)\psi'_2(\mathbf{r}_2))$$



Two energies associated with these normal modes:

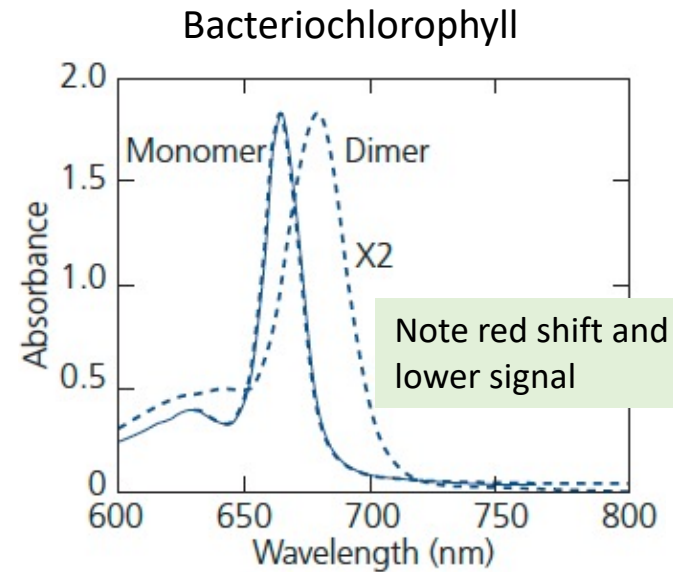
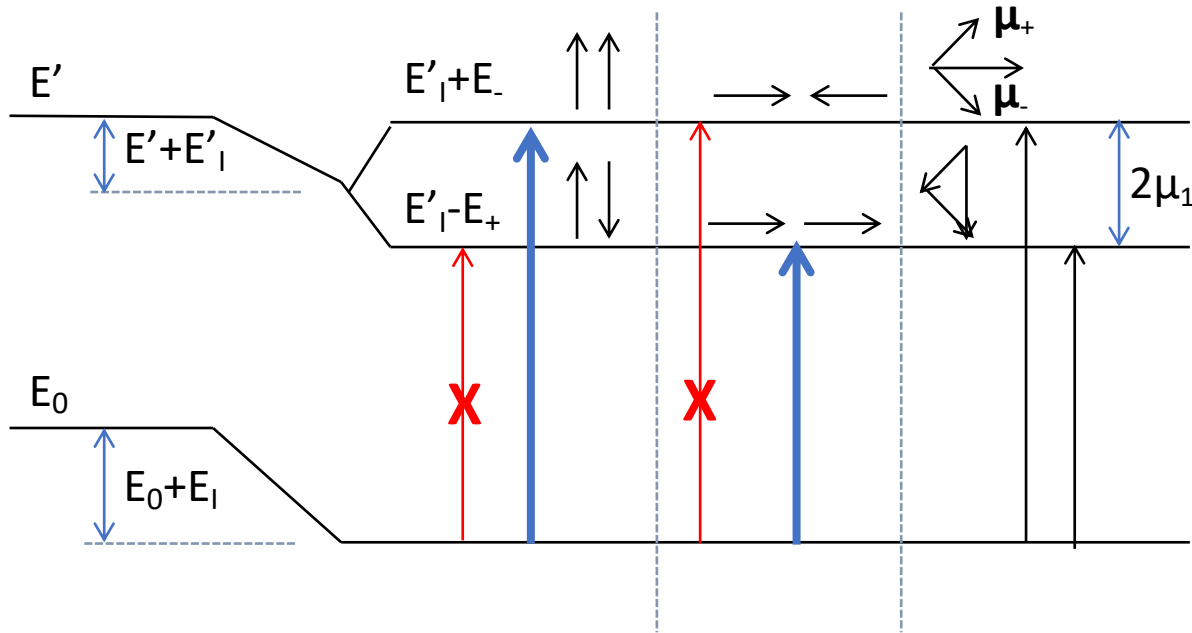
$$E'_I = \langle \psi'_1(\mathbf{r}_1)\psi_2(\mathbf{r}_2) | H_{\text{int}} | \psi'_1(\mathbf{r}_1)\psi_2(\mathbf{r}_2) \rangle \quad : \text{Coulomb energy}$$

$$E_{\pm} = \pm \langle \psi'_1(\mathbf{r}_1)\psi_2(\mathbf{r}_2) | H_{\text{int}} | \psi_1(\mathbf{r}_1)\psi'_2(\mathbf{r}_2) \rangle \quad : \text{Resonance energy}$$

Giving a total dimer energy of: $E'_T = E_0 + E' + E'_I + E_{\pm}$

=Ground state + excited state of one molecule + energies of the pair

The Dimer Spectrum



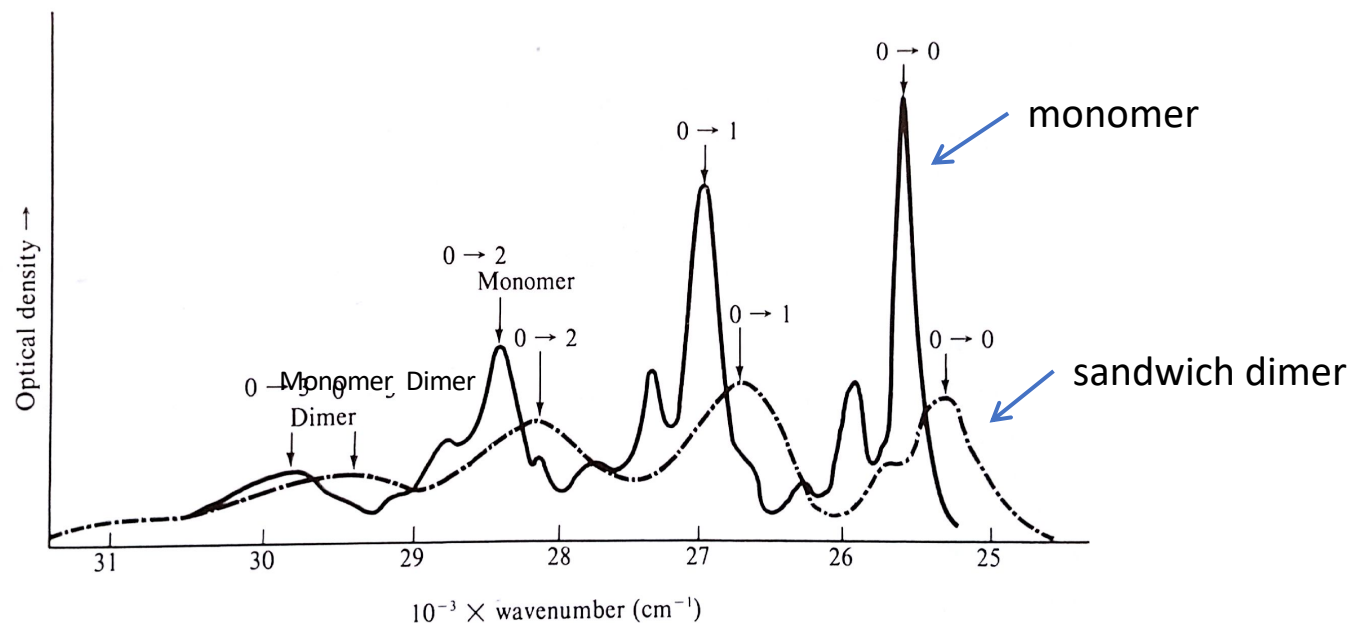
Olsen & Cox Photosynth. Res. 30, 35 (1991).

Symmetry prevents some transitions from occurring

$$\text{Transition moment: } \mu_{\pm} = -\frac{q}{\sqrt{2}} \langle \psi'_1(\mathbf{r}_1) \psi_2(\mathbf{r}_2) \pm \psi_1(\mathbf{r}_1) \psi'_2(\mathbf{r}_2) | \mathbf{r} | \psi_1(\mathbf{r}_1) \psi_2(\mathbf{r}_2) \rangle = \frac{1}{\sqrt{2}} (\mu_1 \pm \mu_2)$$



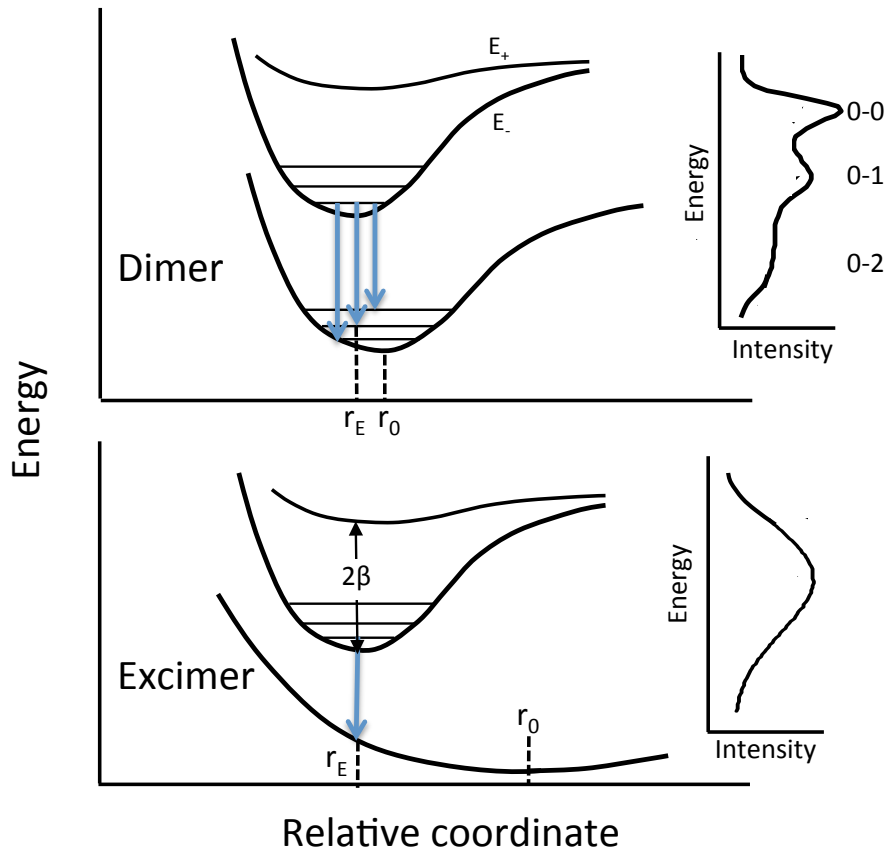
Comparison of Monomer and Dimer Spectra



- 9-chloroanthracene in cyclohexane glass
- 1400 cm^{-1} $n \rightarrow 0$ transitions labeled
- Other intramolecular transitions are apparent in the monomer spectrum

Excimers and Exciplexes

- A dimer with no ground state is an **excimer**.
- A molecular couple comprised of two different molecular species is an **exciplex**.

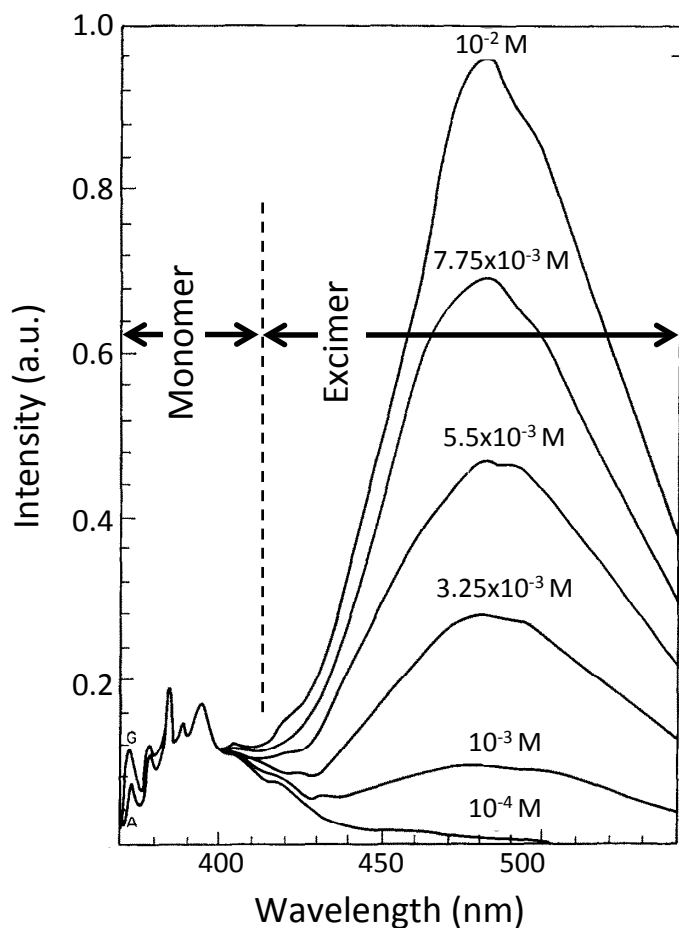


Getting to the excimer can be a multi-step process



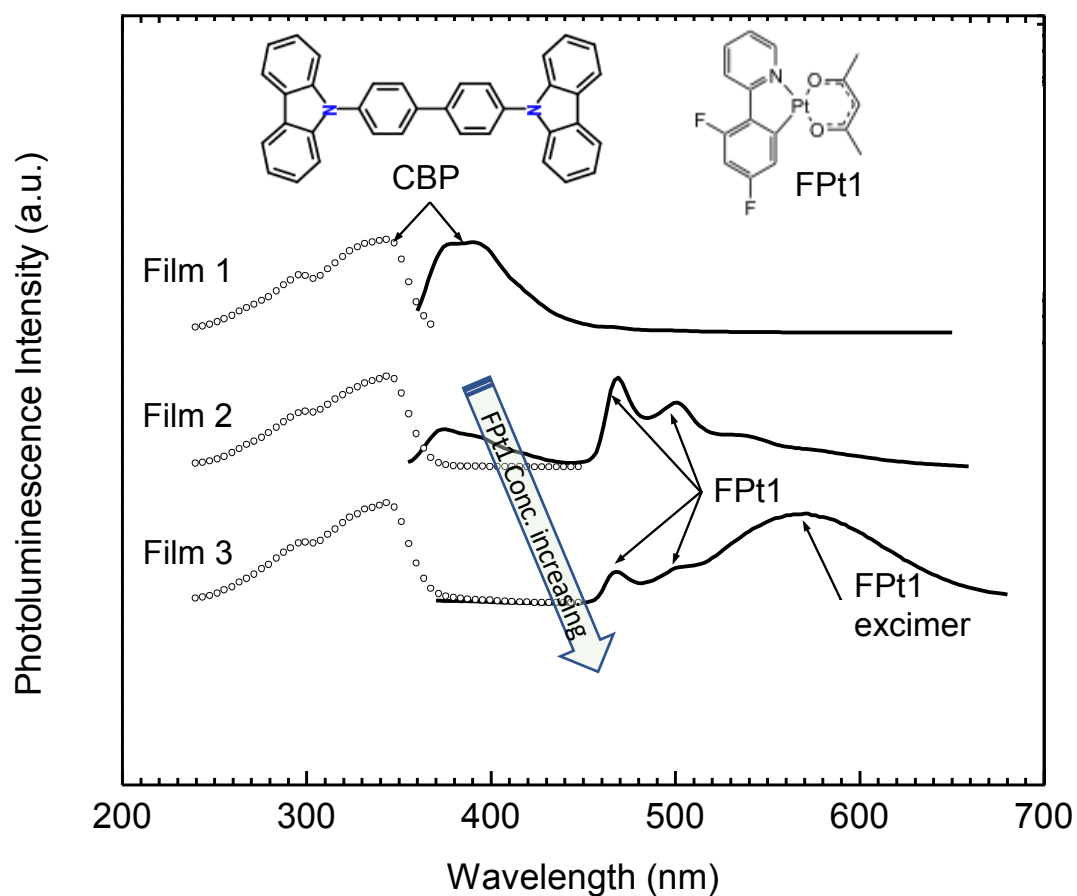
Examples of Excimer Emission in Fluorophors and Phosphors

Excimer Fluorescence: Pyrene in solution
Higher concentration=more excimer pairs



Birks & Christophorou Spectrochim. Acta, 19, 401 (1963)

Excimer Phosphorescence
Coexistence of monomer and excimer emission = white light



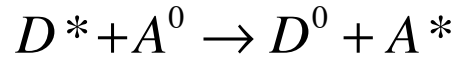
D'Andrade Adv. Mater. 14, 1032 (2002).



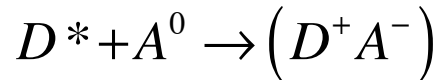
Exciplexes

- Concept of **donor** and **acceptor** molecules:

- An excitation moves from an excited donor (D^*) to a ground state acceptor (A^0)



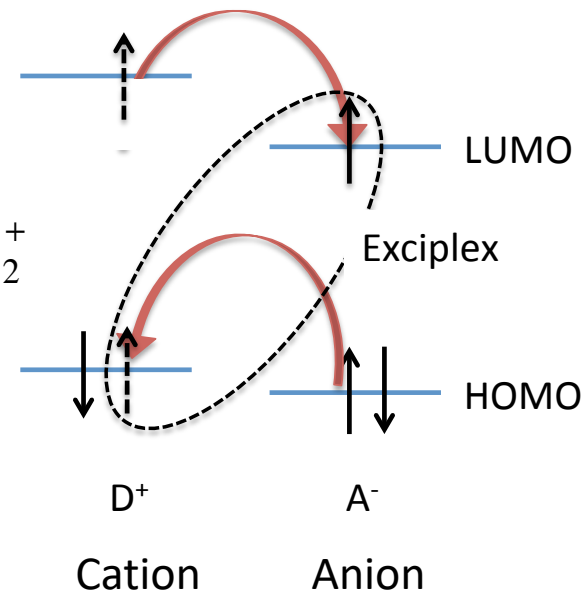
- Since there is an energy difference between D and A, an exciplex results in charge transfer (shared charge) between molecules:



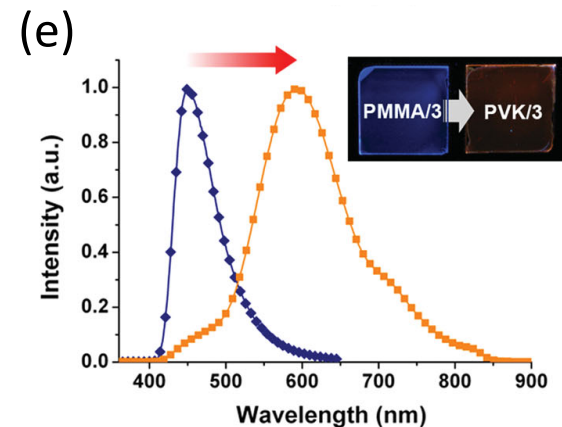
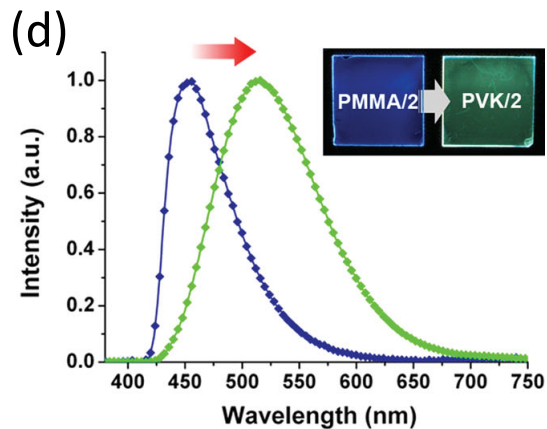
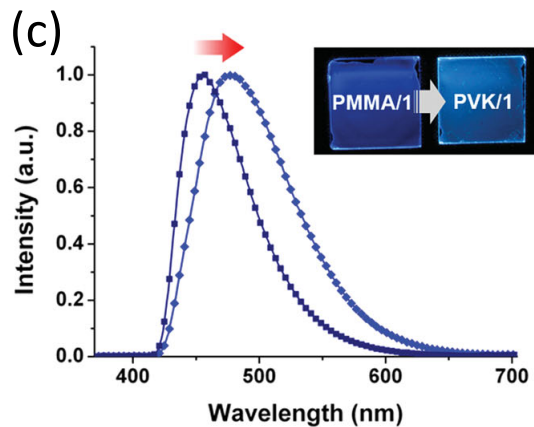
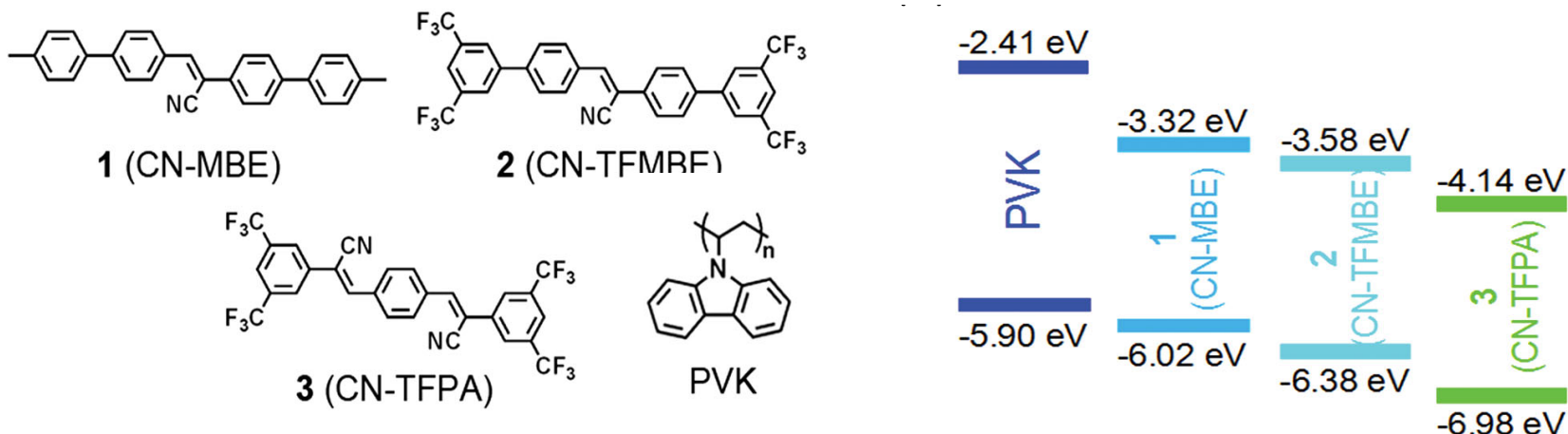
- Excitation shared by two different molecules forming a complex: the amount of charge transfer depends on energy asymmetry

$$\psi_T^0 = \alpha^0 \psi_1 \psi_2 + \gamma^0 \psi_1^+ \psi_2^- + \delta^0 \psi_1^- \psi_2^+$$

$$\psi_T' = \alpha \psi_1' \psi_2 + \beta \psi_1 \psi_2' + \gamma \psi_1^+ \psi_2^- + \delta \psi_1^- \psi_2^+$$



Example of an Exciplex



Kim et al., Adv. Functional Mater., 24, 2746 (2014).

Excited states in crystals

- **Davydov bands:** Broadening of the exciton spectrum occurs due to nearest neighbor interactions in a crystal.
- The number of branches in a crystal is equal to the number of inequivalent molecules in a basis: Davydov splitting

Crystal interaction
of N molecules:

$$H = \sum_i^N \sum_{\mu}^m H_{i\mu} + \sum_{i\mu < kv}^{N,m} V_{i\mu, kv}$$

Indiv. molec.
with basis m

Interact. between
molec. (e.g. vdW)

Wavefunctions now must be consistent with Bloch's theorem: $\Psi_{\mu} = \frac{1}{\sqrt{N}} \sum_i^N \psi'_{i\mu} \exp(i\mathbf{k} \cdot \mathbf{R}_{i\mu})$

Lattice translation vector

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Calculating Exciton Band Structure

$$E_{\pm}(\mathbf{k}) = \sum_{ik}^N \sum_{\mu}^m \langle \phi'_{i\mu} \phi_{k\mu} | V_{i\mu, k\mu} | \phi_{i\mu} \phi'_{k\mu} \rangle \exp(i\mathbf{k} \cdot \Delta\mathbf{R}_{ik, \mu})$$

$$\pm \sum_{i,k}^N \sum_{\mu \neq \nu}^m \langle \phi'_{i\mu} \phi_{k\nu} | V_{i\mu, k\nu} | \phi_{i\mu} \phi'_{k\nu} \rangle \exp(i\mathbf{k} \cdot \Delta\mathbf{R}) = E_{\mu\mu} \pm E_{\mu\nu}$$

Considering only nearest neighbors, we get the **dispersion relationship**:

$$E(\mathbf{k}) = E_0 + E' + E'_I + 2E_{\mu\mu} \cos(\mathbf{k} \cdot \Delta\mathbf{R})$$

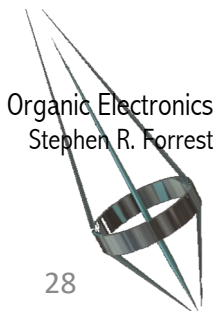
As previously: Ground + excited state of 1 molec.+interaction (Coulomb+resonance)

Lattice translation $\Delta\mathbf{R}$ restricted to distances between nearest neighbors

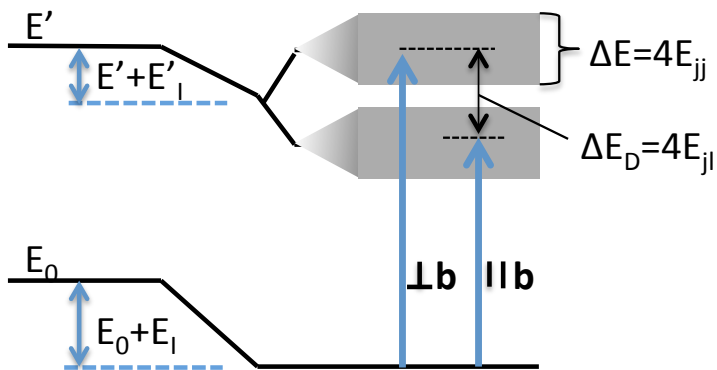
Exciton now has momentum, \mathbf{k} : It is mobile!

$$\text{Exciton bandwidth: } \Delta E = 4E_{\mu\mu}$$

Each μ gives a different Davydov Band

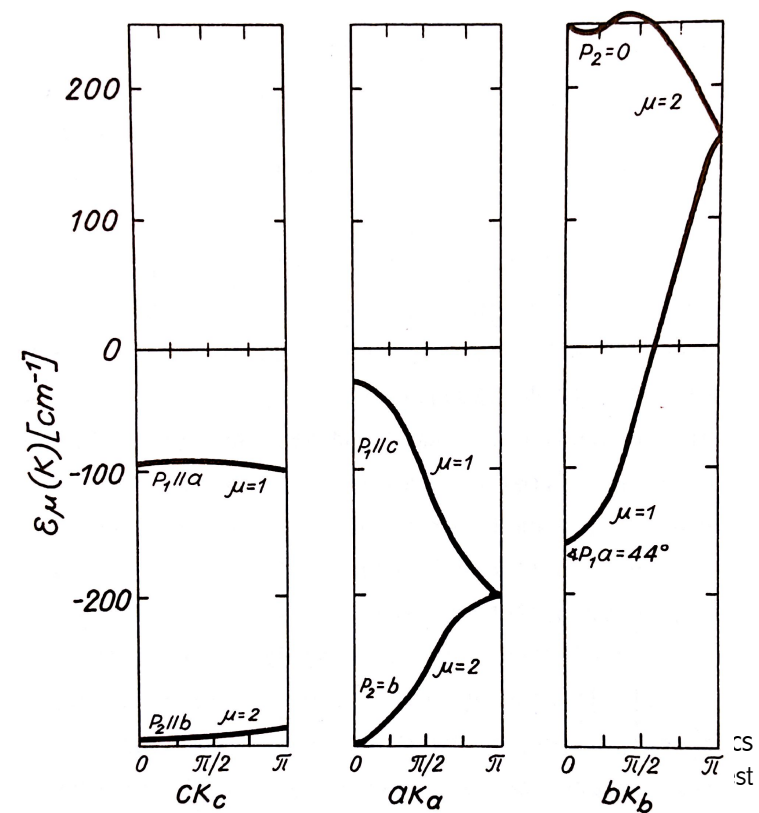
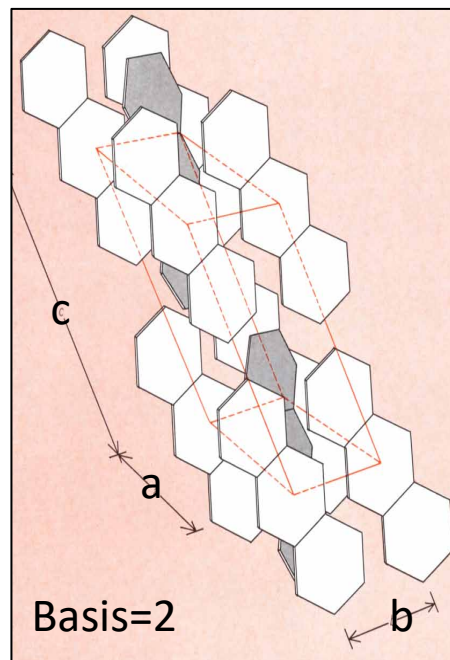
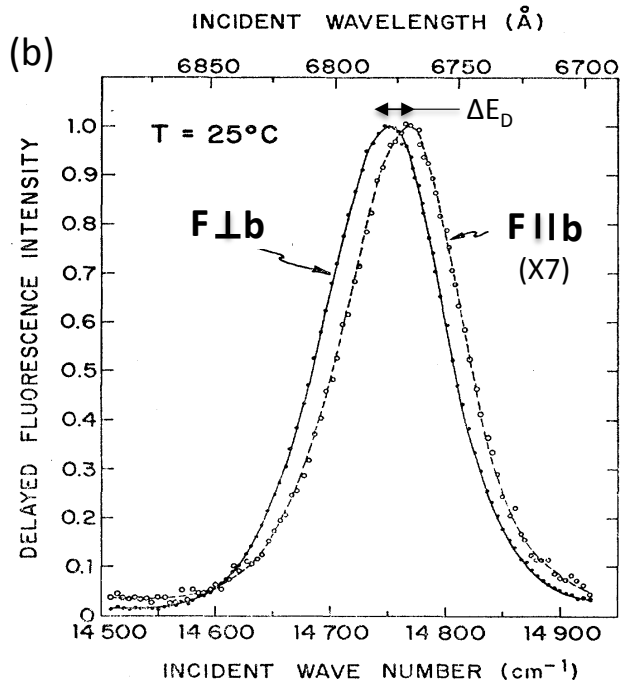


Davidov splitting in Anthracene



ΔE_D = Davidov splitting energy due to interactions between different molecules: j, l

ΔE = Davidov band energy due to interactions between like molecules on different sites: j, j



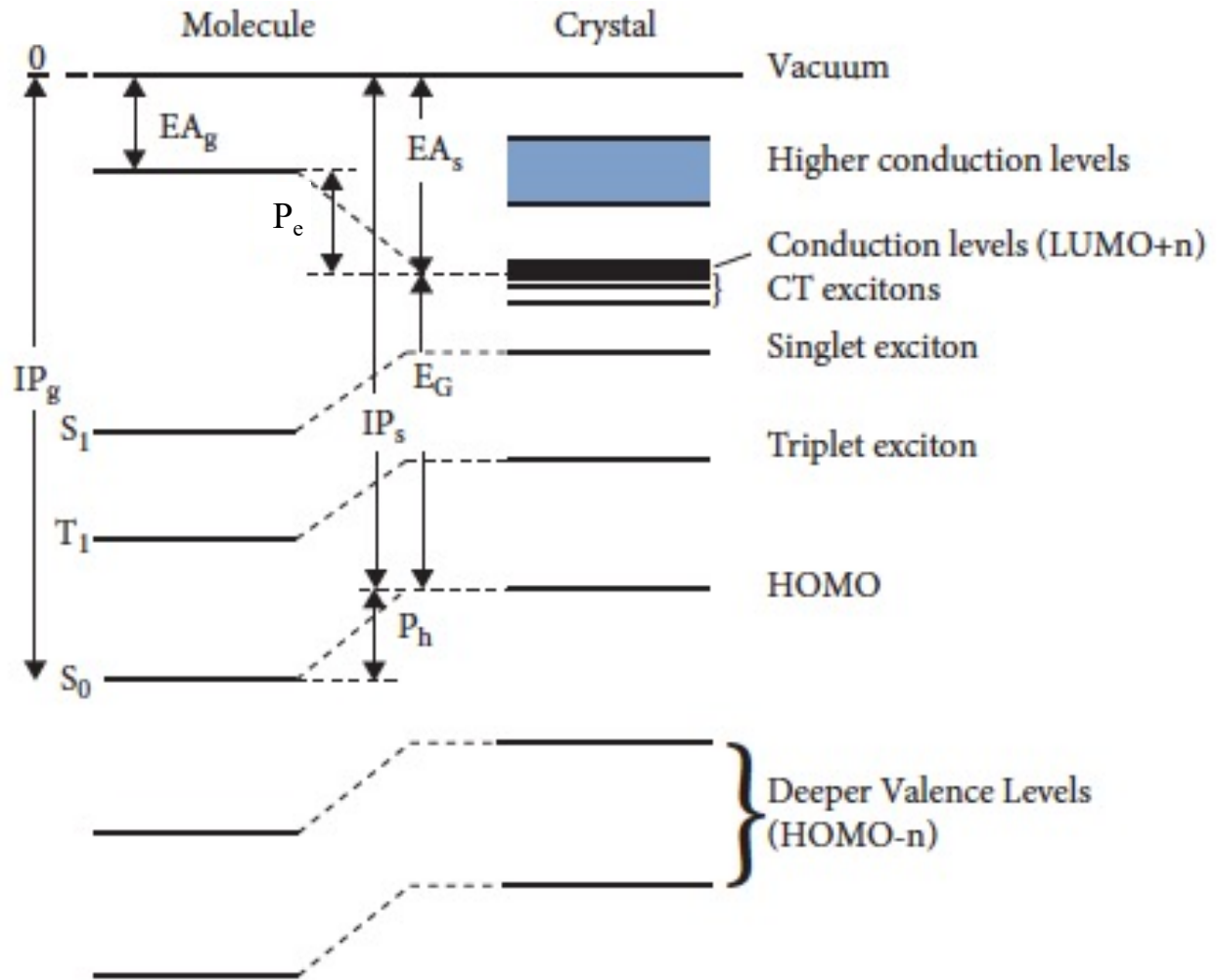
Calculated exciton bands (excited by different polarizations, p .)

Anthracene triplet splitting

Avakian et al. Phys. Rev. 165, 974 (1968)

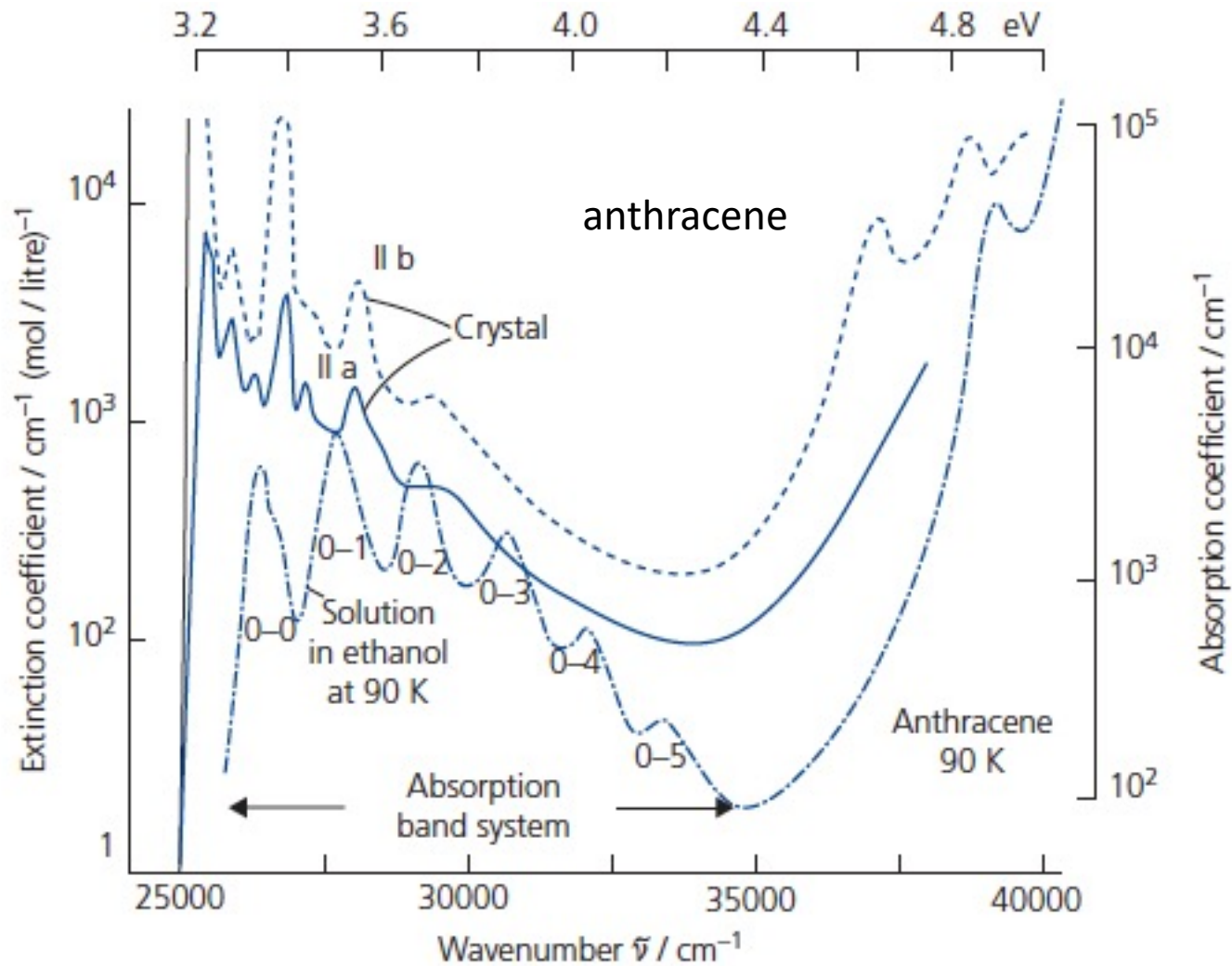
The correspondence between a molecule and a solid

- IP=ionization poten
- EA=electron affinity
- P=Polarization ener
- g,s=gas, solid



Lyons Model

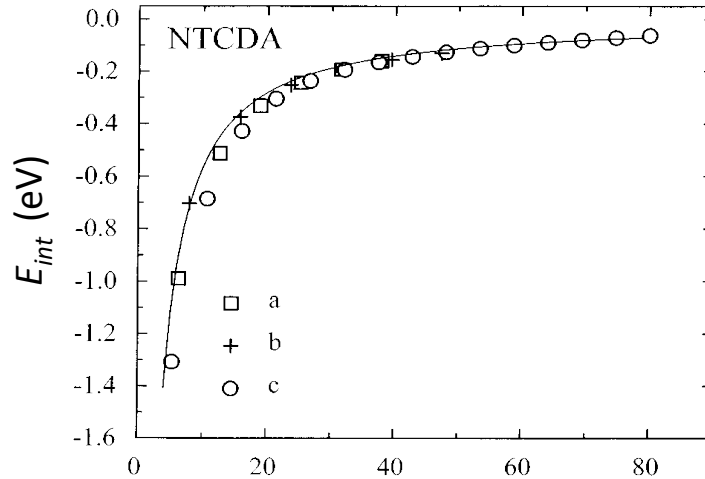
Going from molecules to solids



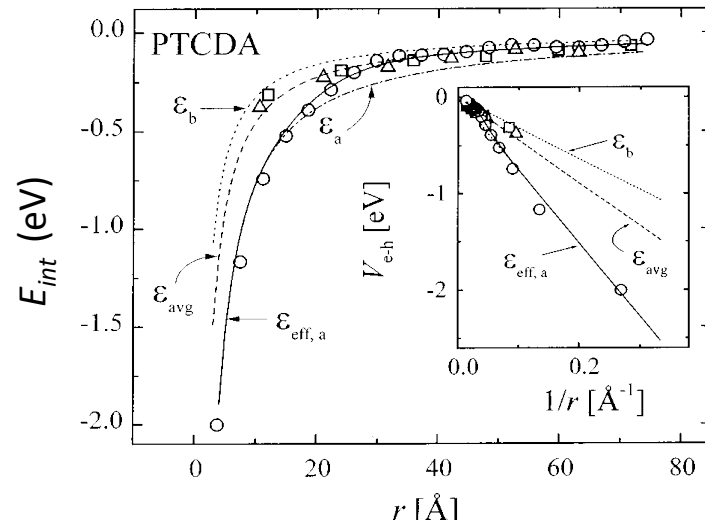
Vibronic progression loses definition in the solid: why?



How many molecules makes a solid?



One way to tell: how many molecules are needed for the dielectric constant to equal that of the bulk?



Shen, Z. & Forrest, S. R. 1997. *Phys. Rev. B*, 55, 10578.

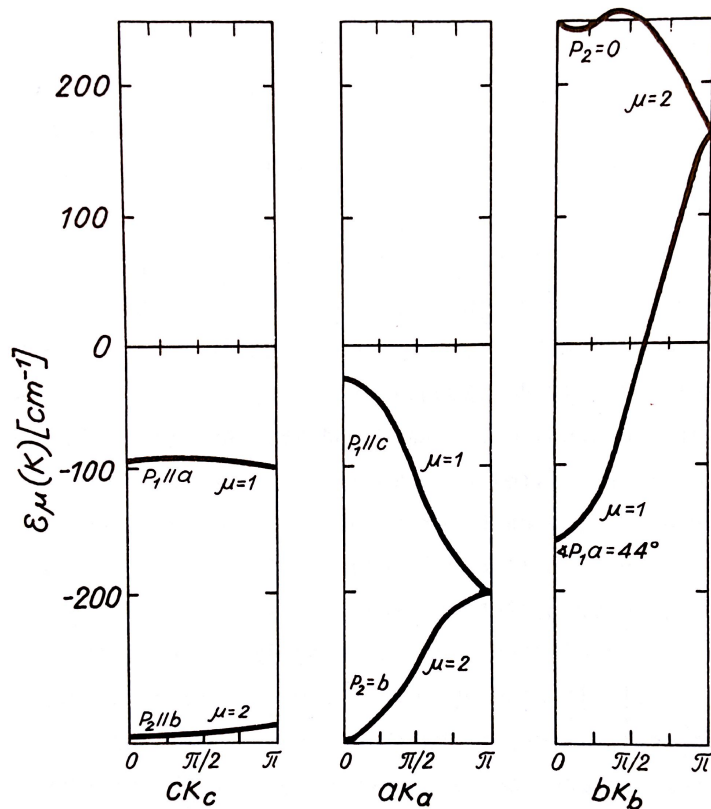
Very few!

More anisotropic media require a larger volume to become bulk-like

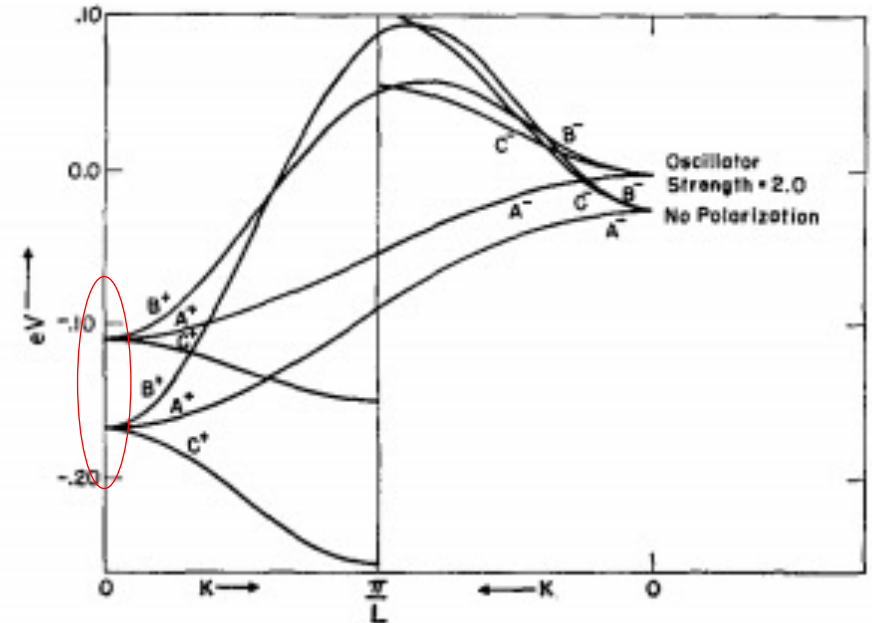
Why don't all the bands have the same value at $k=0$?

Polarization along different directions determines the dielectric constant
 \Rightarrow direction dependent exciton momentum & energy

Exciton bands in anthracene



Electron bands in anthracene



$$E_{\mu} = E_0 + E + E'_I + 4E_{\mu\mu}$$

Indiv. molecule energy

Polarization energy due to environment