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THIRD WORKSHOP ON
THIN FILMS PHYSICS AND TECHNOLOGY
(8 - 24 MARCH 1999)
including
TOPICAL CONFERENCE ON
MICROSTRUCTURE AND SURFACE MORPHOLOGY
EVOLUTION IN THIN FILMS
(24 - 26 MARCH 1999)

"Organic thin films for electronics and photonics"
Part I

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From Molecules to Molecular Solids

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☐ Electronic states in molecules: the role of symmetry

☐ Electronic structure in cristalline organic solids ideal

- Frenkel excitons
- Charge-Transfer excitons

☐ 〃 real disorder

- Dimers
- Excimers
- Emitting traps (X-traps)

☐ Fabrication of ordered organic solids (O-MBD)
Organic Molecular Beam Deposition

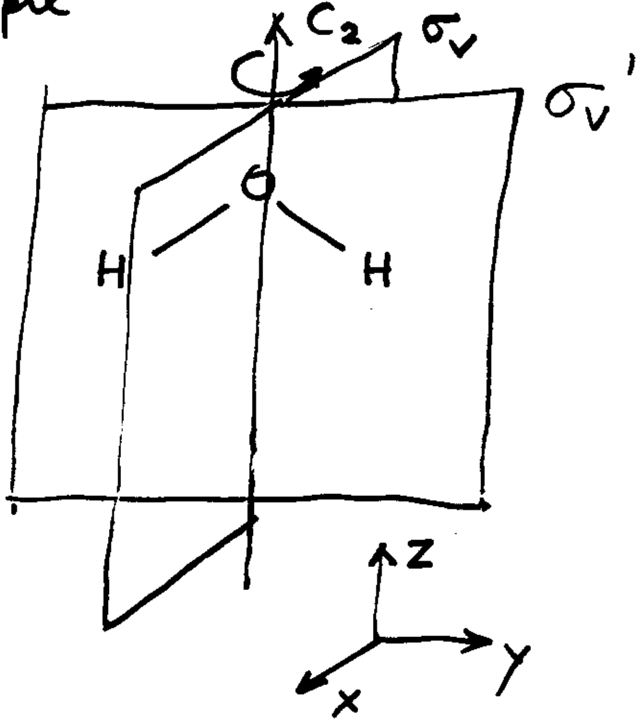
References:

1) M. Pope and C. Swenberg, Electr. Proc. in Org. Cryst. Clarendon Press, Oxford, (1982). → next new edition

2) D. P. Craig and S. H. Walmsley, Excitons in Molec. Crys. Benjamin Inc., Amsterdam (1968).

Molecular symmetry and Group theory

example H_2O



Symmetry Elements of H_2O

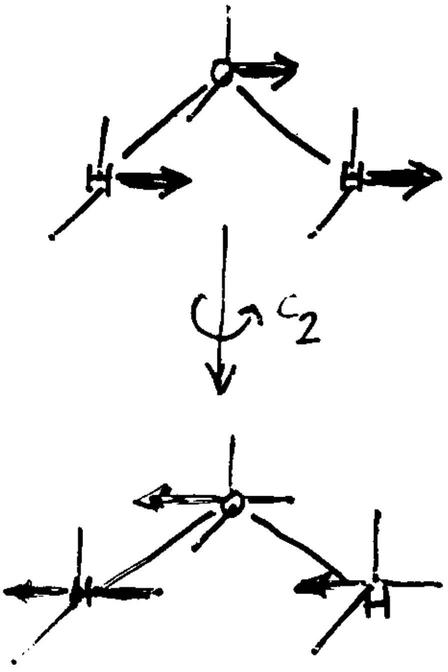
E identity

σ plane of symmet

C_2 axis of rotation

In general the symm. elem are these plus i (inversion center, S (rotation - reflection or screw rotation)

Effect of symmetry operations on molecular motions



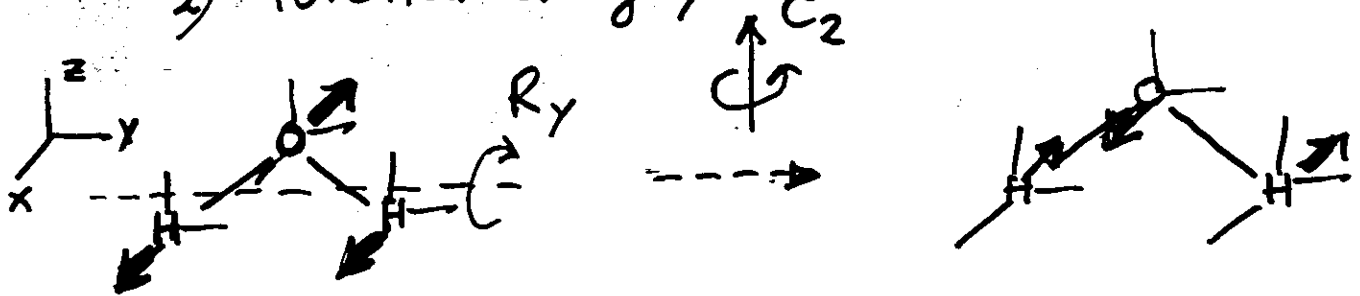
1) translation along y

C_2 reverse the molecular motion

$$C_2(T_y) = (-1)(T_y)$$

T_y is antisymmetric to the symmetry operation of C_2.

2) rotation along Y



$$C_2(R_y) = \boxed{(-1)}(R_y)$$

R_y is <u>antisymmetric</u> to C_2.

We may now built a table (transformation matrix)

	E	C_2	σ_v	σ_v'	Rotation or Translati
A_1	1	1	1	1	T_z
A_2	1	1	-1	-1	R_z
B_1	1	$\boxed{-1}$	1	-1	R_y, T_x
B_2	1	$\boxed{-1}$	-1	1	R_x, T_y

A ≡ the transformation is symmetric w.r.t. the principal axis of symmetry

B ≡ idem antisymmetric

Molecular motions (T_i, R_j) as well as the varios electronic orbitals transform like rows of this table the operations corresponding to the symmetry elements E, C_2, σ_v, and σ_v' form a group.

Properties of a group:

1) Combining any two elements of the group forms an element of the group

   i.e. $E \times C_2 \rightarrow C_2$; $C_2 \times \sigma_v \rightarrow \sigma_v'$ etc.

2) associative law holds

3) the set of elements contains the identity → E. $E \times C_2 = C_2 \times E = C_2$

4) Every element of the group has an inverse which is an element of the group.

   i.e. $C_2 \times C_2 = E$
   $\sigma_v \times \sigma_v = E$ ....

⇒ the transformation matrices form representations of the group.

There are an infinite number of representations

$$\text{Representations} \begin{cases} \nearrow \text{reducible} \\ \searrow \text{irreducibles} \end{cases}$$

⇒ A reducible representation can be broken down to a set of irreducible representations point group

C_{2v}	E	C_2	σ_v	σ_v'	
A_1	1	1	1	1	T_z
A_2	1	1	−1	−1	R_z
B_1	1	−1	1	−1	R_y , T_x
B_2	1	−1	−1	1	R_x , T_y

irreducible representations

character table

→ Electronic states are classified according to the irreducible representations of the molec. point group.

→ the electronic ground state is invariant under all symmetry operations
it is therefore "totally symmetric" (i.e. A_1)

Absorption of electromagnetic radiation occurs if one of the integrals is $\neq 0$:

$$\int \psi_0 \mu_x \psi_1 \, d\tau \; ; \; \int \psi_0 \mu_y \psi_1 \, d\tau \; ; \; \int \psi_0 \mu_z \psi_1 \, d\tau$$

→ μ_x transform like T_x ; $\mu_y \dashrightarrow T_y$; $\mu_z \dashrightarrow T_z$

$$\begin{tikzcd} & A_1 \rightarrow \text{Allowed transition} \\ \Rightarrow \quad A_1 \otimes T_i \otimes \Gamma_1 \arrow[ur] \arrow[dr] & \\ & \neq A_1 \rightarrow \text{Forbidden} \;\;'' \end{tikzcd}$$

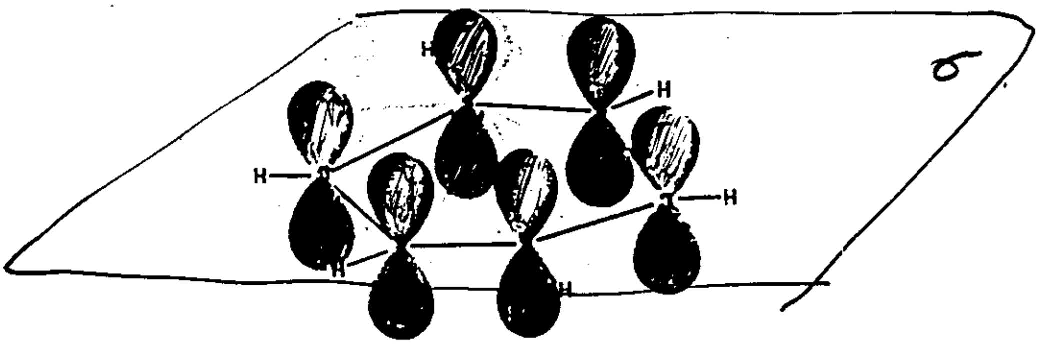
i.e. for T_x:

$A_1 \otimes \underbrace{B_1 \otimes B_1}_{A_1} \rightarrow A_1$ allowed $A_1 \rightarrow B_1$

$A_1 \otimes B_1 \otimes A_2 \rightarrow B_2$ forbidden $A_1 \rightarrow A_2$

the benzene electronic states

→ prototype of conjugated aromatic molecules limit to treat $2p_\pi$ electrons



→ the electronic wf must conform to the symmetry of the molecule.

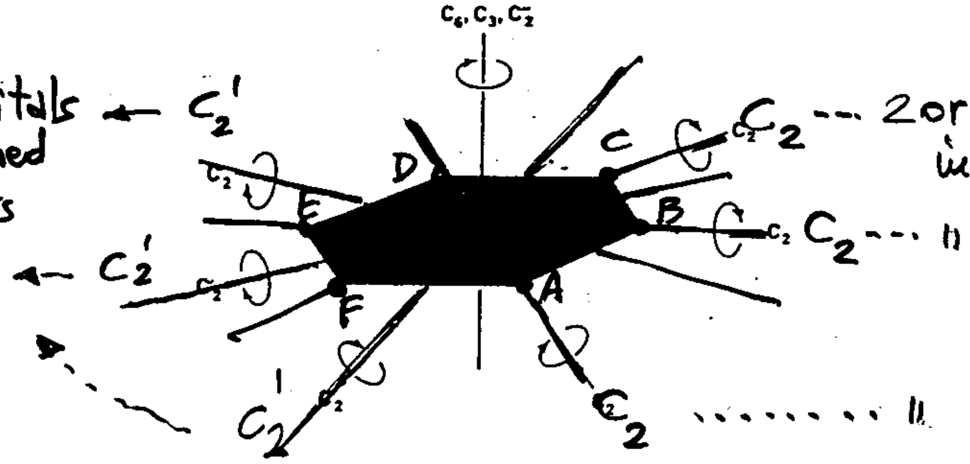
→ the point group of benzene is D_{6h}. For simplicity we ignore the plane σ.

TABLE 11-5 The D_6 Character Table

D_6	E	$2C_6$	$2C_6^2$	C_6^3	$3C_2$	$3C_2'$	
A_1	1	1	1	1	1	1	
A_2	1	1	1	1	−1	−1	T_z
B_1	1	−1	1	−1	1	−1	
B_2	1	−1	1	−1	−1	1	
E_1	2	1	−1	−2	0	0	T_x, T_y
E_2	2	−1	−1	2	0	0	

→ the six $2p_\pi$ atomic orbitals form a basis for the irreducible representation of the group.

FIG. 11-6 The symmetry elements of the D_6 point group. Note that, unlike the case for the D_{6h} point group, symmetry with regard to the plane of the molecule is not considered.



all orbitals transformed in others ← C_2'

C_2 --- 2 orbitals transform into itself

C_2 --- 〃

C_2 .... 〃

→ E (identity) transforms each $2p_\pi$ into itself

$$E\begin{pmatrix} p^A \\ p^B \\ p^C \\ \vdots \end{pmatrix} = \begin{pmatrix} \boxed{1} & 0 & 0 & 0 & 0 & 0 \\ 0 & \boxed{1} & 0 & 0 & 0 & 0 \\ 0 & 0 & \boxed{1} & 0 & 0 & 0 \\ \cdots & & & & & \cdot \\ - & - & - & - & & \cdot \end{pmatrix}\begin{pmatrix} p^A \\ p^B \\ p^C \\ \vdots \end{pmatrix}$$

— character = 6

→ C_2 transform into itself only two orbitals

$$C_2\begin{pmatrix} p^A \\ p^B \\ p^C \\ p^D \\ \vdots \end{pmatrix} = \begin{pmatrix} \boxed{1} & 0 & 0 & 0 & 0 & 0 \\ 0 & \boxed{0} & 0 & 0 & 0 & 1 \\ 0 & 0 & \boxed{0} & 0 & 1 & 0 \\ 0 & 0 & 0 & \boxed{1} & 0 & 0 \\ 0 & 0 & 1 & 0 & \boxed{0} & 0 \\ 0 & 1 & 0 & 0 & 0 & \boxed{0} \end{pmatrix}\begin{pmatrix} p^A \\ p^B \\ p^C \\ p^D \end{pmatrix}$$

character = 2

	E	$2C_6$	$2C_6^2$	C_6^3	$3C_2$	$3C_2'$
Reducible Representation	6	0	0	0	2	0

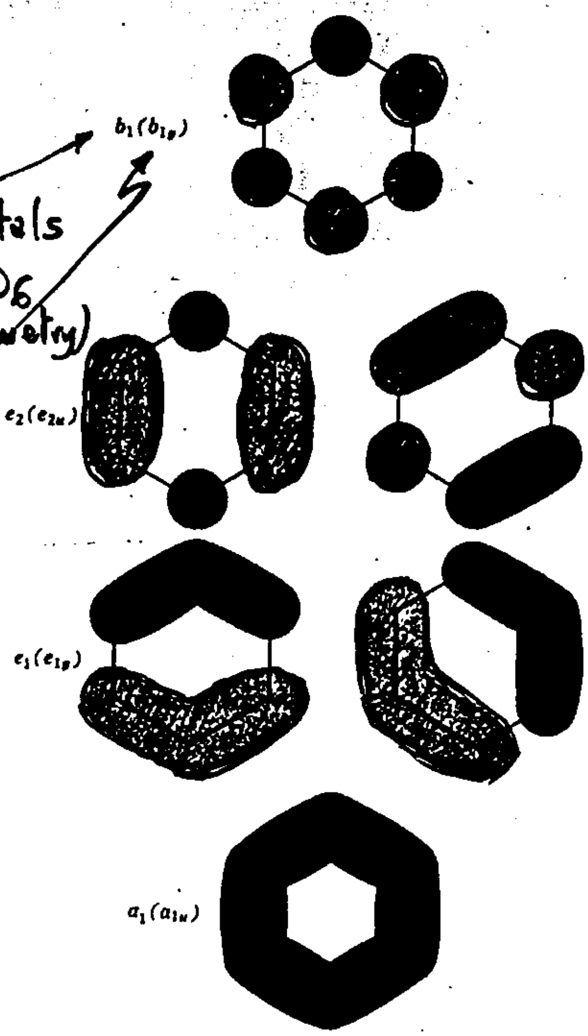
$= A_1 + B_1 + E_1 + E_2$

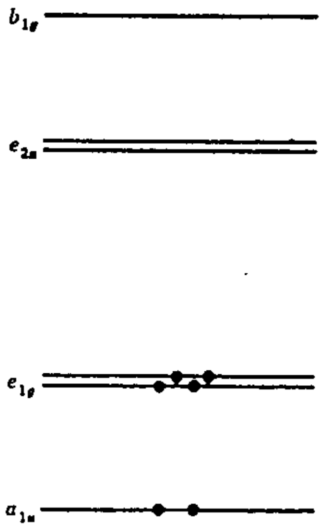
molecular orbitals according to D_6 (simplified symmetry)

idem according to D_{6h}

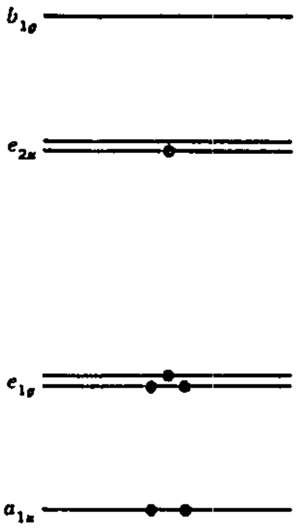
▨ negative wf.

● positive wf.





Ground-state configuration



Excited-state configuration

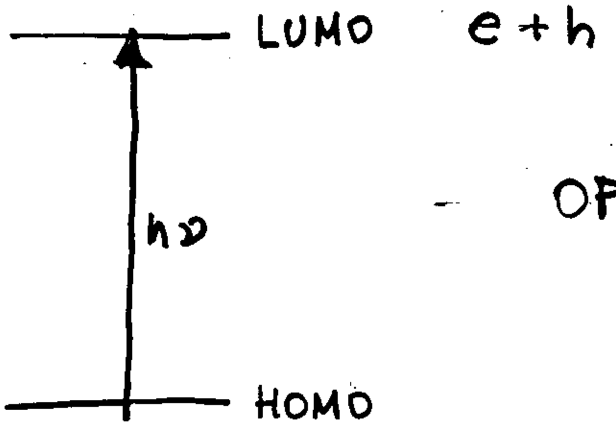
closed-shell configuration

$a_{1u}^2 \; e_{1g}^4$

$a_{1u}^2 \; e_{1g}^3 \; e_{2u}$

one electron description (no e-e correlation)

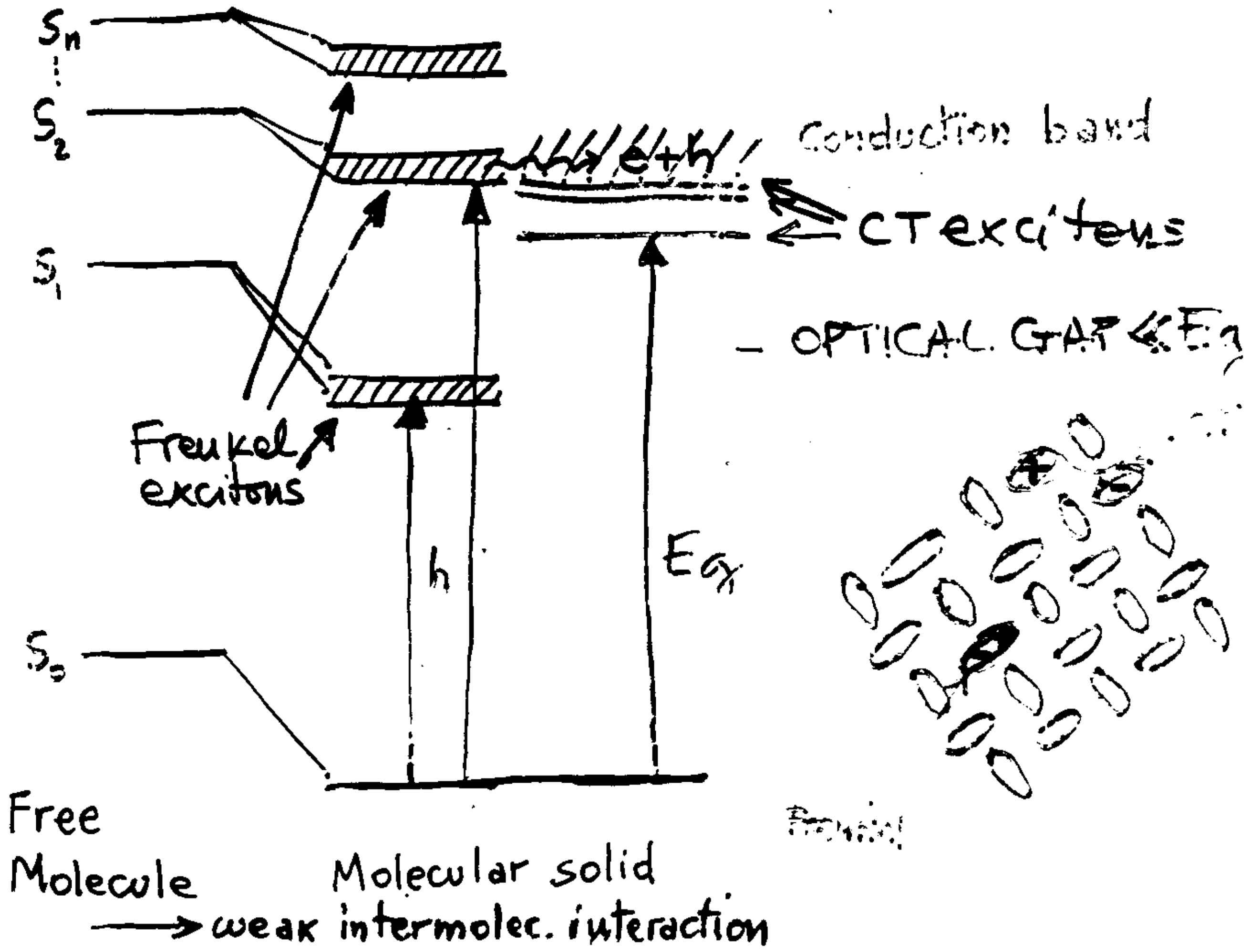
molec. orbitals



– OPTICAL GAP ≡ E_g

many electron description (e-e correlation)

many e states



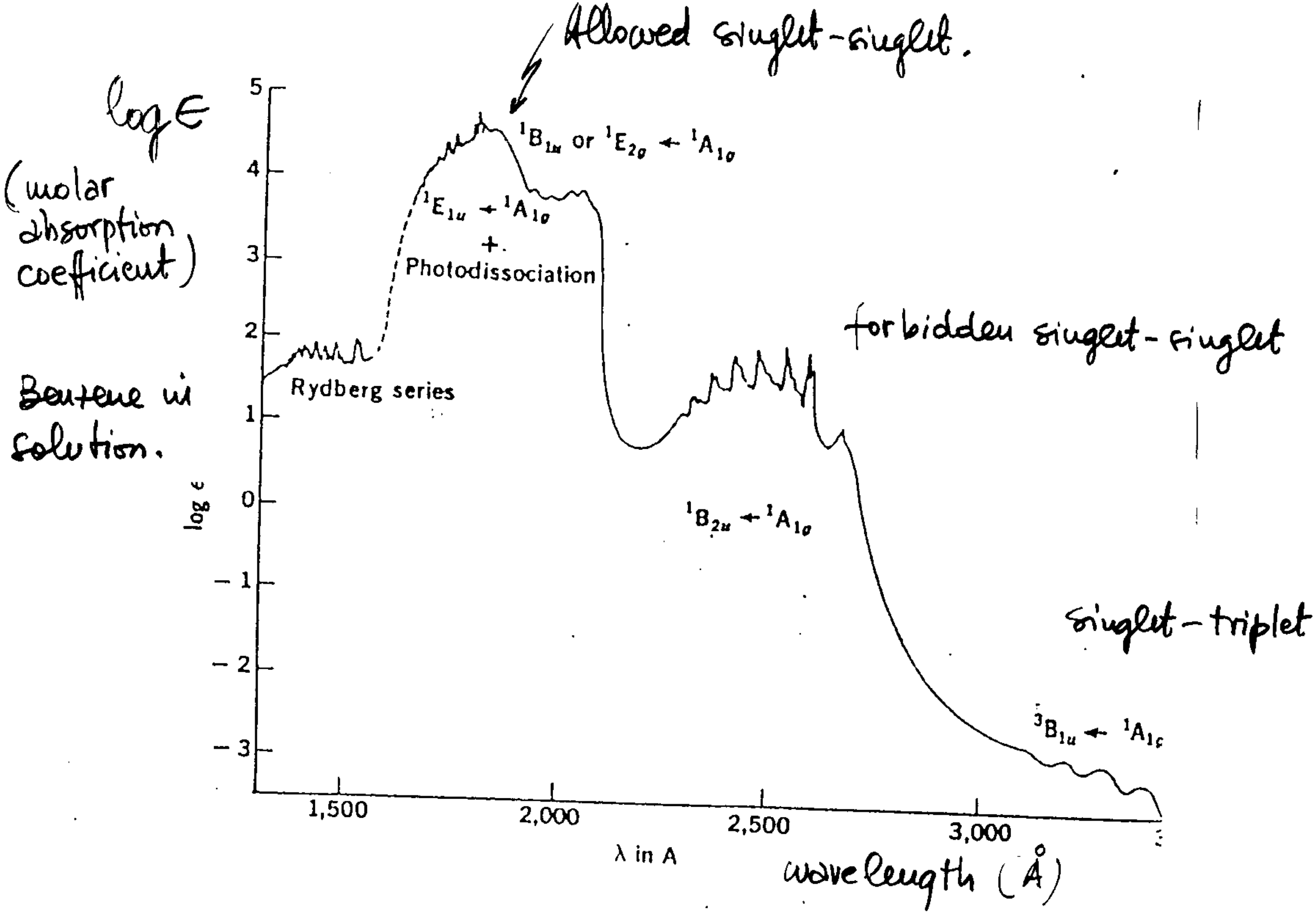
the excited configuration $a_{1u}^2 \, e_{1g}^3 \, e_{2u}$ gives rise to the states of symmetry that belong to the reducible representation obtained by the product:

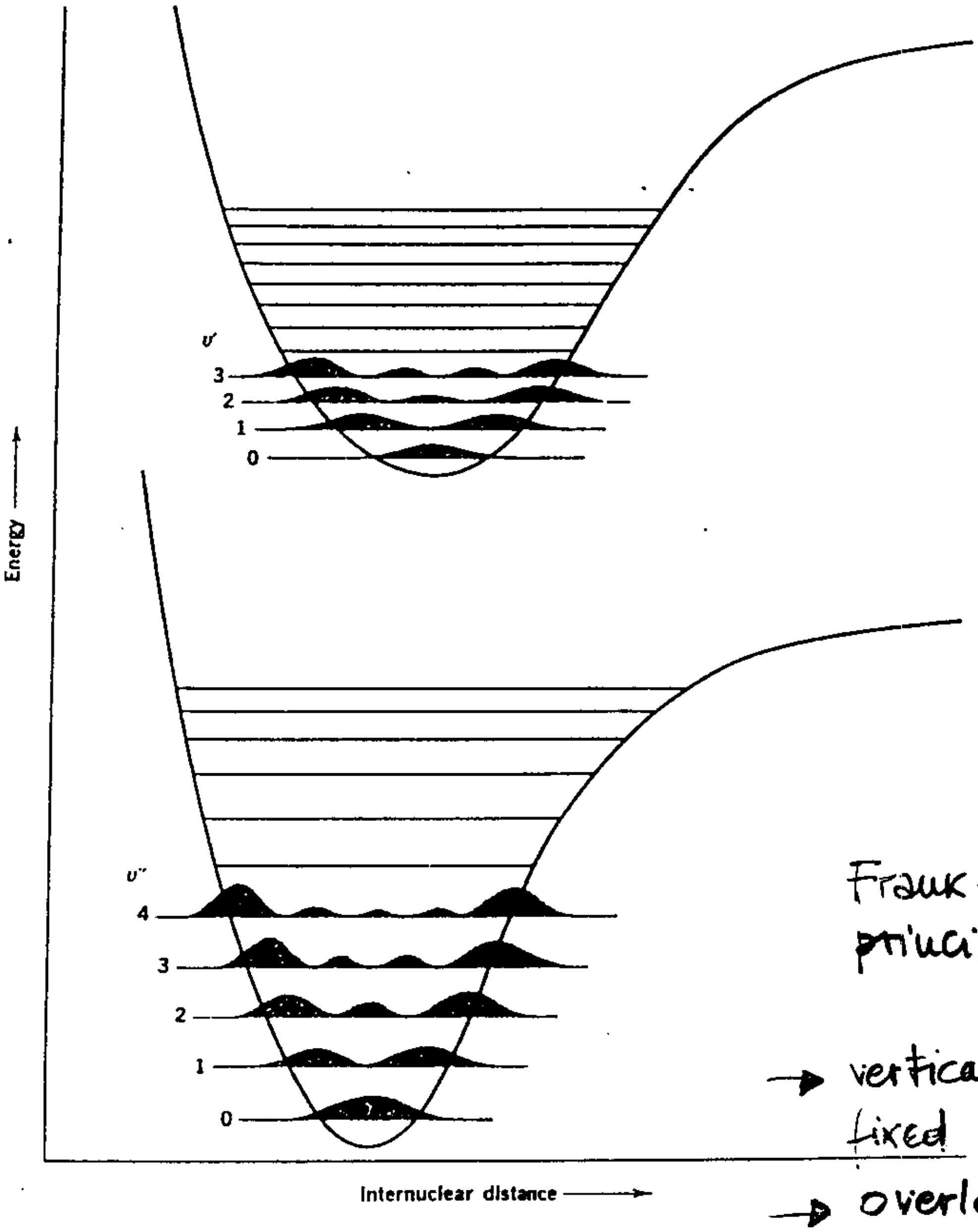
$$e_{1g} \otimes e_{2u}$$

TABLE 11-7 The D_{6h} Character Table

D_{6h}	E	$2C_6$	$2C_6^2$	C_6^3	$3C_2$	$3C_2'$	σ_h	$3\sigma_v$	$3\sigma_d$	$2S_6$	$2S_3$	i	
A_{1g}	1	1	1	1	1	1	1	1	1	1	1	1	
A_{1u}	1	1	1	1	1	1	−1	−1	−1	−1	−1	−1	
A_{2g}	1	1	1	1	−1	−1	1	−1	−1	1	1	1	
A_{2u}	1	1	1	1	−1	−1	−1	1	1	−1	−1	−1	T_z
B_{1g}	1	−1	1	−1	1	−1	−1	−1	1	1	−1	1	
B_{1u}	1	−1	1	−1	1	−1	1	1	−1	−1	1	−1	
B_{2g}	1	−1	1	−1	−1	1	−1	1	−1	1	−1	1	
B_{2u}	1	−1	1	−1	−1	1	1	−1	1	−1	1	−1	
→ E_{1g}	2	1	−1	−2	0	0	−2	0	0	−1	1	2	
E_{1u}	2	1	−1	−2	0	0	2	0	0	1	−1	−2	T_x, T_y
E_{2g}	2	−1	−1	2	0	0	2	0	0	−1	−1	2	
→ E_{2u}	2	−1	−1	2	0	0	−2	0	0	1	1	−2	
	4	−1	1	−4	0	0	4	0	0	−1	1	−4	

$$E_{1g} \otimes E_{2u} = \underbrace{B_{1u} + B_{2u}}_{\text{forbidden}} + \underbrace{E_{1u}}_{\text{allowed}}$$

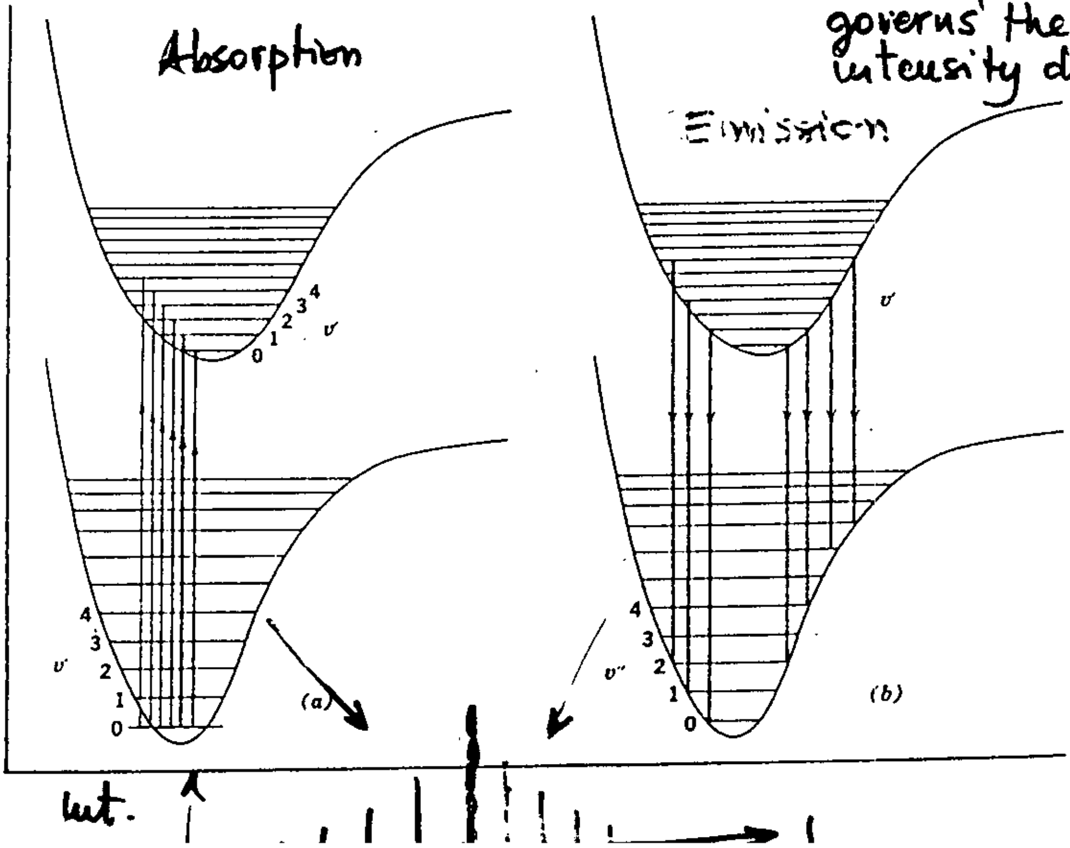

Allowed singlet-singlet.
log ∈
(molar absorption coefficient)
Benzene in solution.
5
4
3
2
1
0
− 1
− 2
− 3
log ε
$^1B_{1u}$ or $^1E_{2g}$ ← $^1A_{1g}$
$^1E_{1u}$ ← $^1A_{1g}$ + Photodissociation
Rydberg series
forbidden singlet-singlet
$^1B_{2u}$ ← $^1A_{1g}$
singlet-triplet
$^3B_{1u}$ ← $^1A_{1g}$
1,500
2,000
2,500
3,000
λ in A
wavelength (Å)



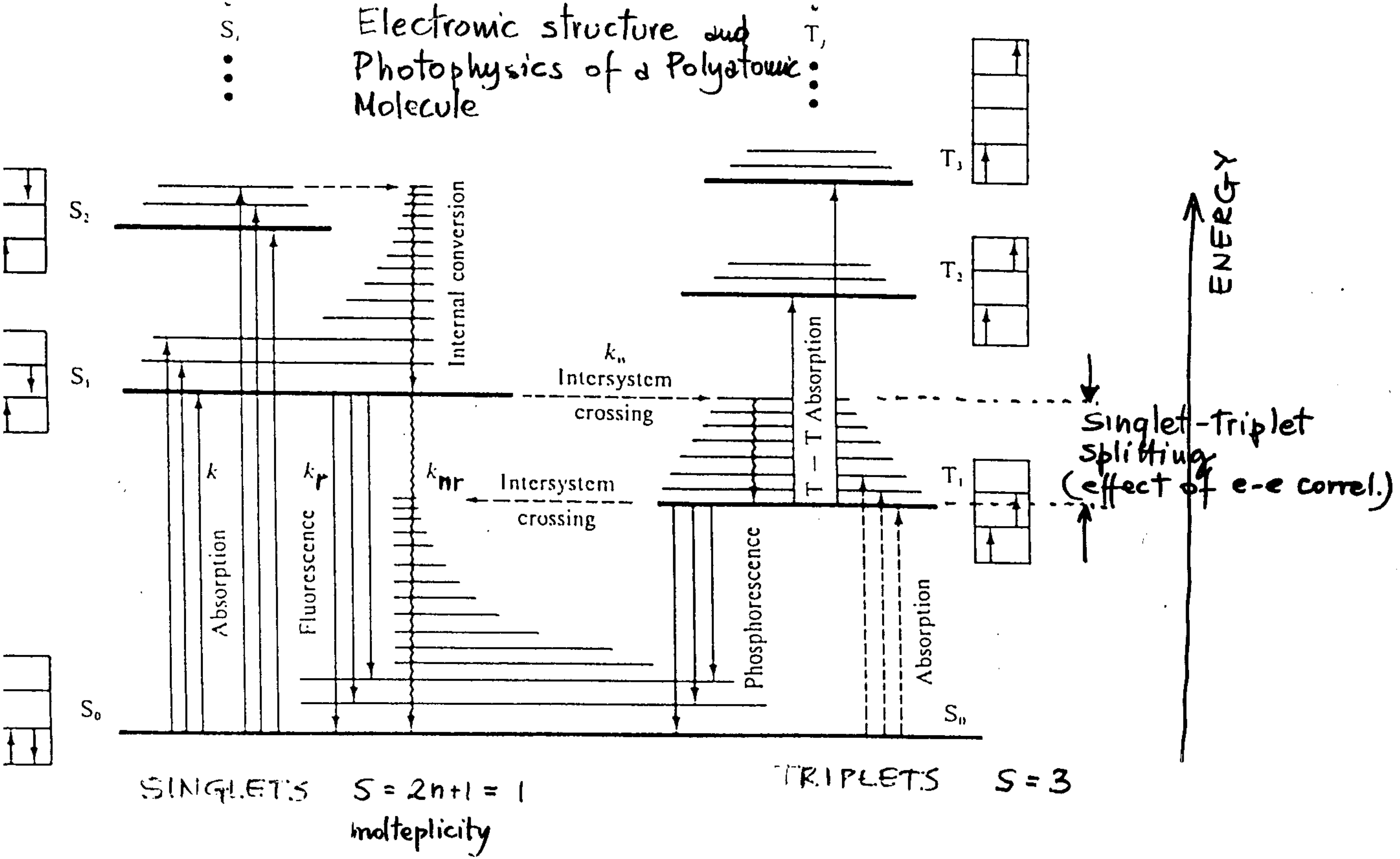
Frank-Condon principle

→ vertical transition
fixed nuclei

→ overlap integral governs the vibroni intensity distributi

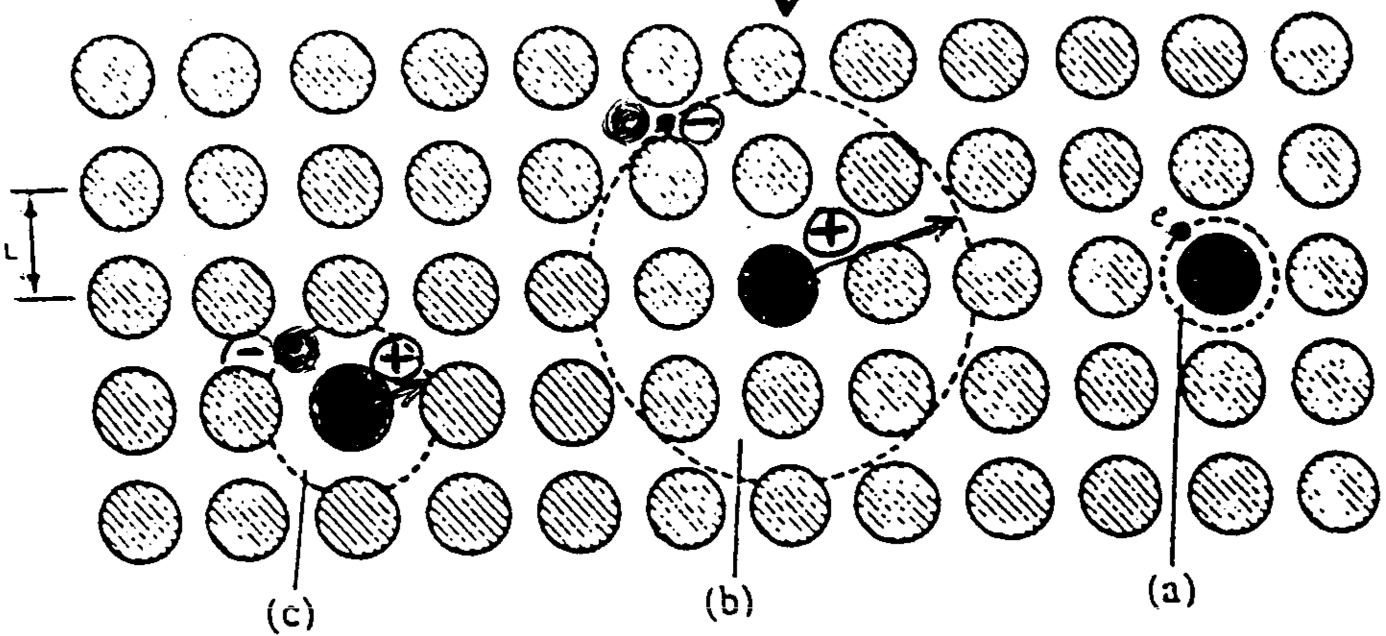


Electronic structure and Photophysics of a Polyatomic Molecule



Different Classes of "Excitons"

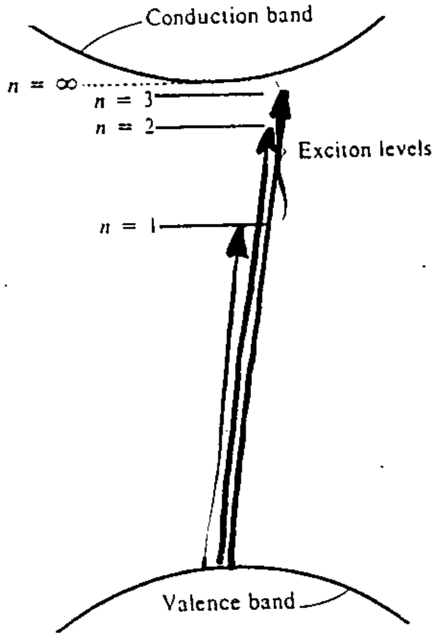
Wannier exciton
weakly bound
large radious

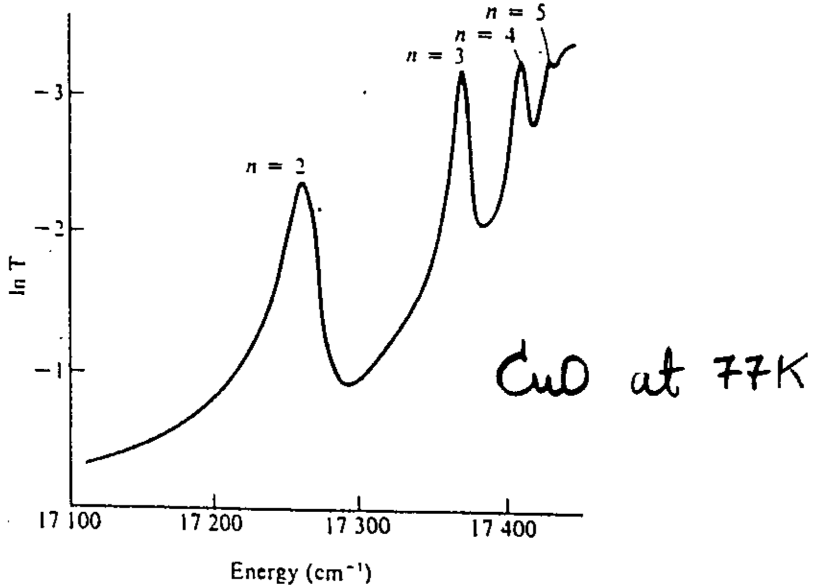


Charge-Transfer
exciton
- short radious
- intermolecular

Frenkel exciton
- tightly bound
- intramolecular

Wannier excitons





$$E = E_G - \frac{G}{n^2} \qquad n = 1, 2 \ldots$$

G = exciton binding energy

E_G = solid ionization energy

Frenkel excitons

- non interacting oriented molecules N
- perturbation due to the intermolecular potential V
- rigid lattice of molecules

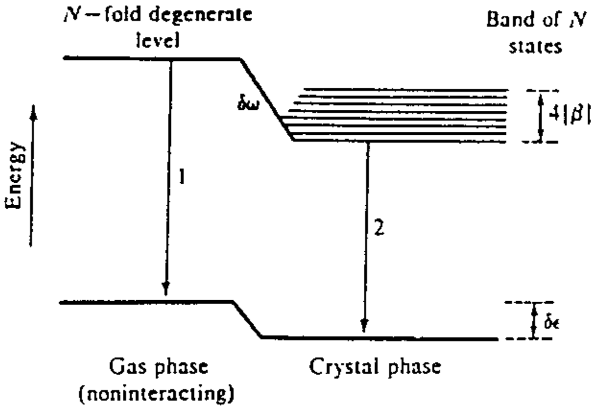
$$\left(\sum_{n=1}^{N} \underset{\substack{\uparrow \\ \text{molecular}}}{H_n} + \sum_{n<m} V_{mn}\right)\Phi = E\,\Phi$$

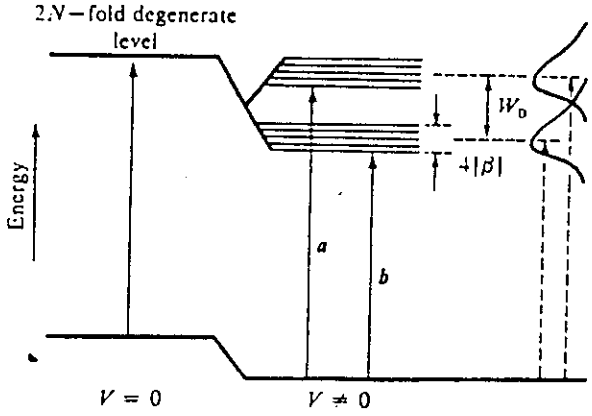
Ground state $\Phi_G = \prod_{n=1}^{N} \varphi_n$

Excited state $\Phi_i' = \varphi_i' \prod_{n\neq i} \varphi_n^0$

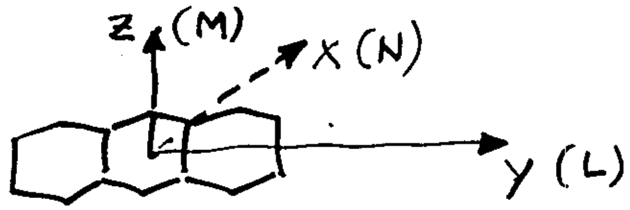
The problem may be simplified by using the crystalline symmetry:

- traslational operation on the unit cell form the entire crystal.
  wf are expressed in term of K (wave vector)
- for optical spectroscopic applications $K \simeq 0$
- cristalline wf are classified according to the cristalline symmetry (not the molecular symmetry). factor group.


N − fold degenerate level
Band of N states
δω
4|β|
Energy
1
2
δε
Gas phase (noninteracting)
Crystal phase


2N − fold degenerate level
W_D
4|β|
Energy
a
b
V = 0
V ≠ 0

Anthracene molecule



	E	C_2^z	C_2^y	C_2^x	i	iC_2^z	iC_2^y	
A_g	1	1	1	1	1	1	1	
A_u	1	1	1	1	−1	−1	−1	
B_{1g}	1	−1	−1	1	1	−1	−1	
→ B_{1u}	1	−1	−1	1	−1	1	1	(M) T_z
B_{2g}	1	−1	1	−1	1	−1	1	
→ B_{2u}	1	−1	1	−1	−1	1	−1	(L) T_y
B_{3g}	1	1	−1	−1	1	1	−1	
→ B_{3u}	1	1	−1	−1	−1	−1	1	(N) T_x

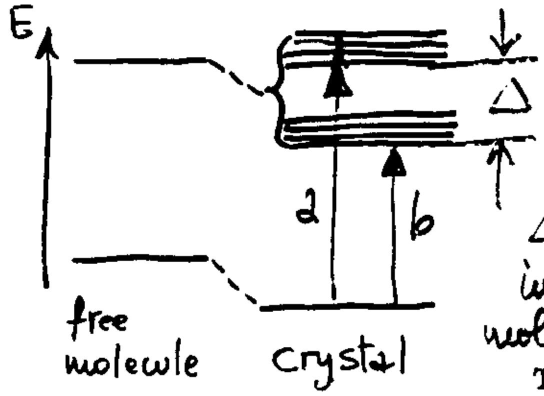
[a] The conventions in this Table conform with the recommendations of the J Commission for Spectroscopy, *J. Chem. Phys.*, 23, 1997 (1955). Two other sets conventions as well as these are in common use.

Allowed electronic transitions

$$\Phi_1^r = \frac{1}{\sqrt{2}}(\phi_1^r + \phi_2^r)\ (ac)$$

$$\Phi_2^r = \frac{1}{\sqrt{2}}(\phi_1^r - \phi_2^r)\ (b)$$

C_{2h} group (factor)

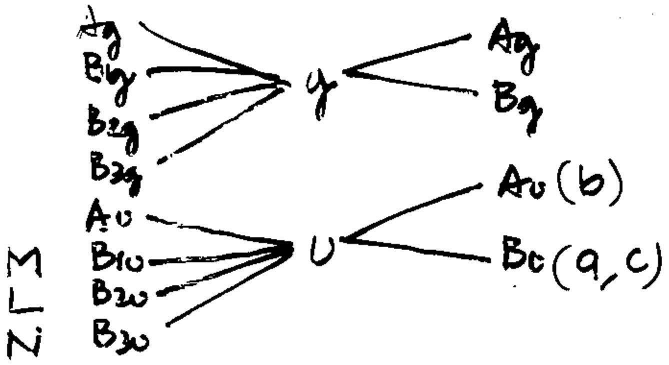


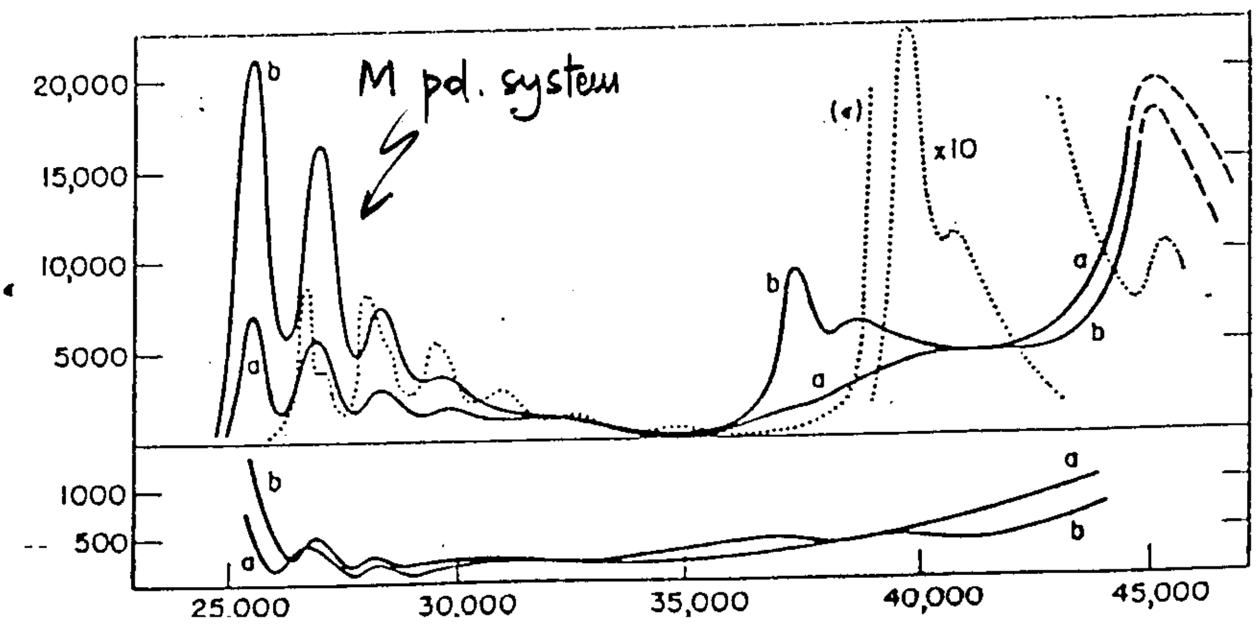
2 molecules in the unit cell.

Δ = Davydov splitting interaction between mol I and all mol. II.

THE REPRESENTATIONS OF GROUP C_{2h}

	E	C_2	σ_h	i
A_g	1	1	1	1
$A_u(b)$	1	1	−1	−1
B_g	1	−1	−1	1
$B_u(a,c)$	1	−1	1	−1



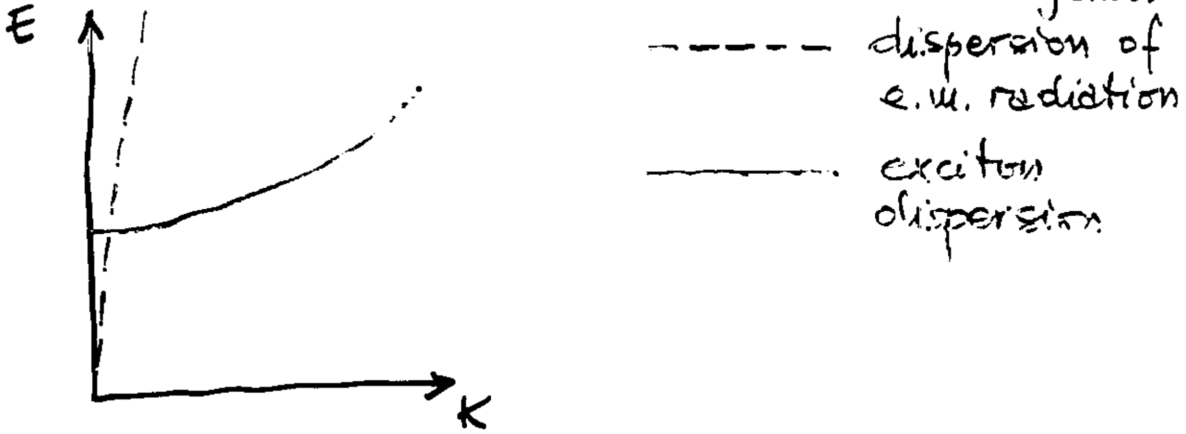


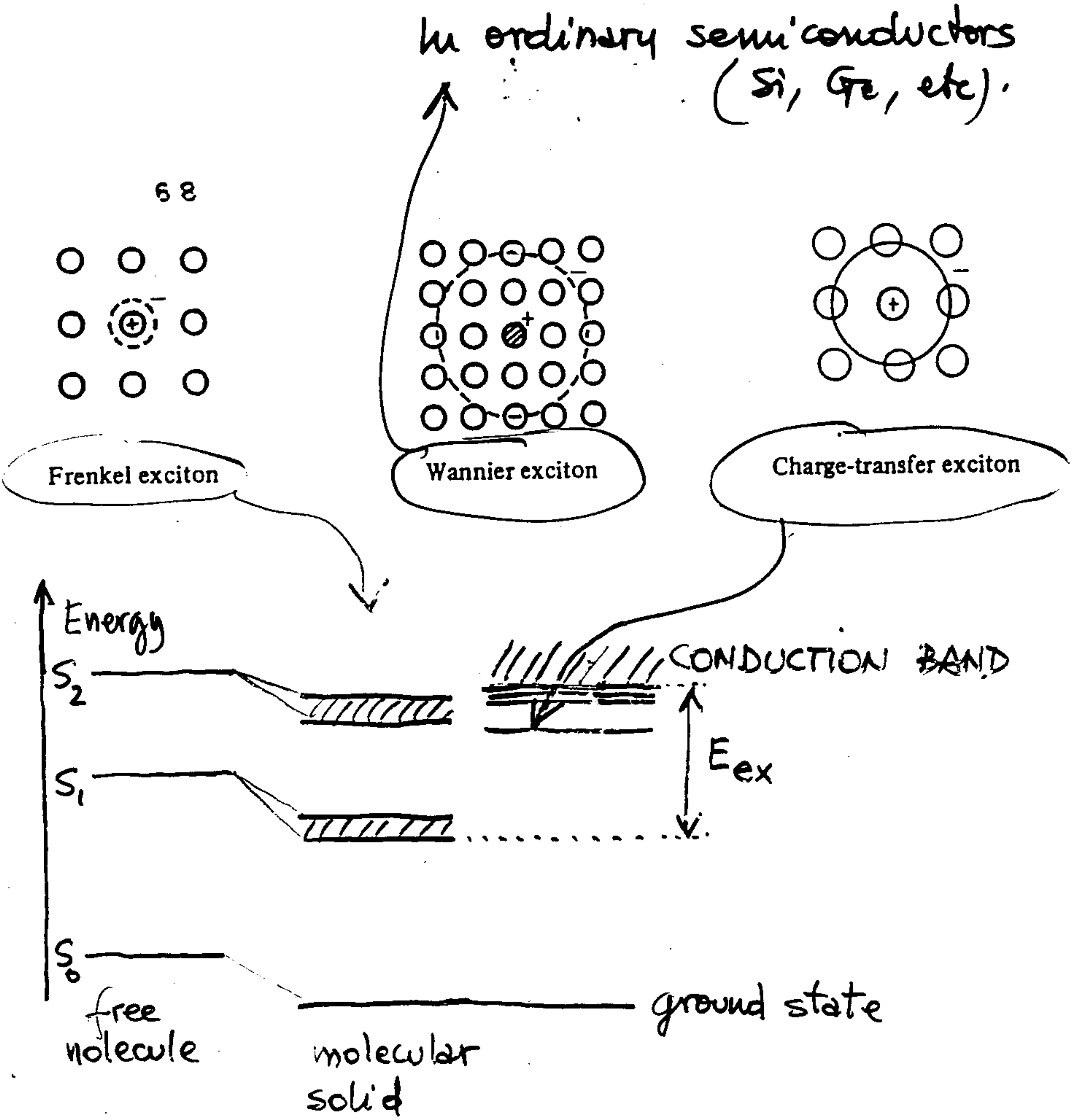
Exciton in molecular solids.

- collective excitation in the cristalline solid that travels coherently in a fixed direction (k)
- phonons or impurity scatter the exciton to a different direction (k)
- coherence length is the distance between scattering events

If the coherent length is ~ to the lattice const. It is convenient to visualize the excited state as a localized exciton hopping stockastica from one molecule to another.

- Interaction with light at $k \approx 0$ in perfect crystals.




In ordinary semiconductors (Si, Ge, etc).

Exciton binding Energy (E_{ex}) → small → Wannier Exc. (few meV)

→ large → Frenkel Exc. (up to 2eV)

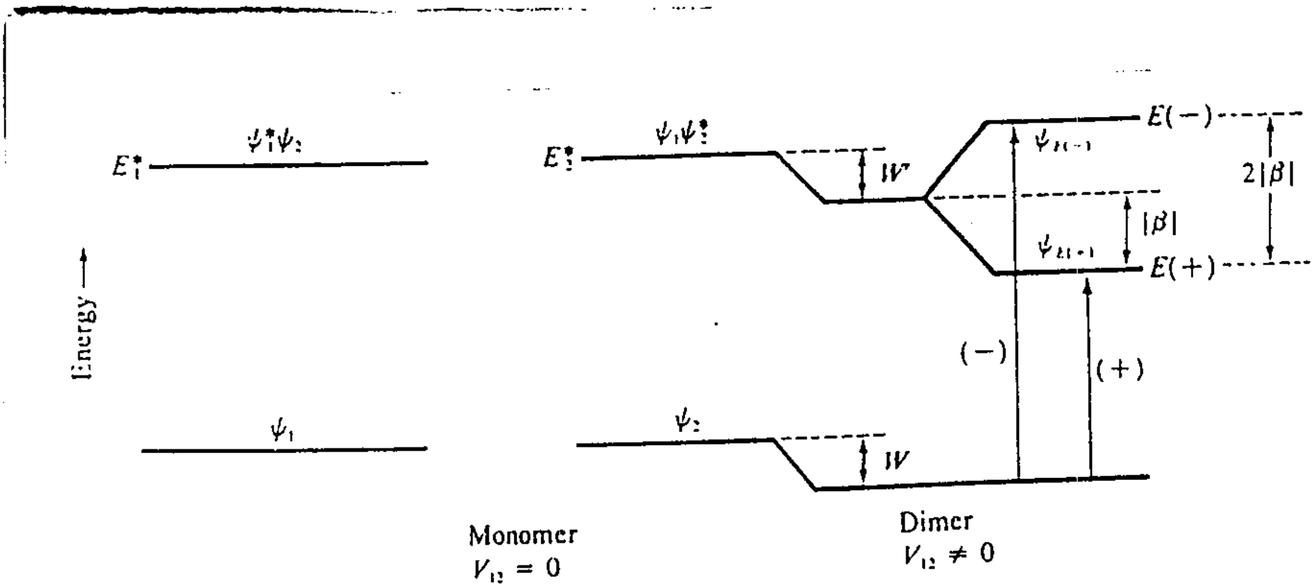


Fig. I.D.2. Exciton band splitting and energy shift for a physical dimer. The dimer state $\psi_{E(+)}$ is of lower energy when $\beta < 0$. Also illustrated are the two possible dimer optical transitions. See text for definition of symbols. (Adapted from Kasha 1976, p. 345)

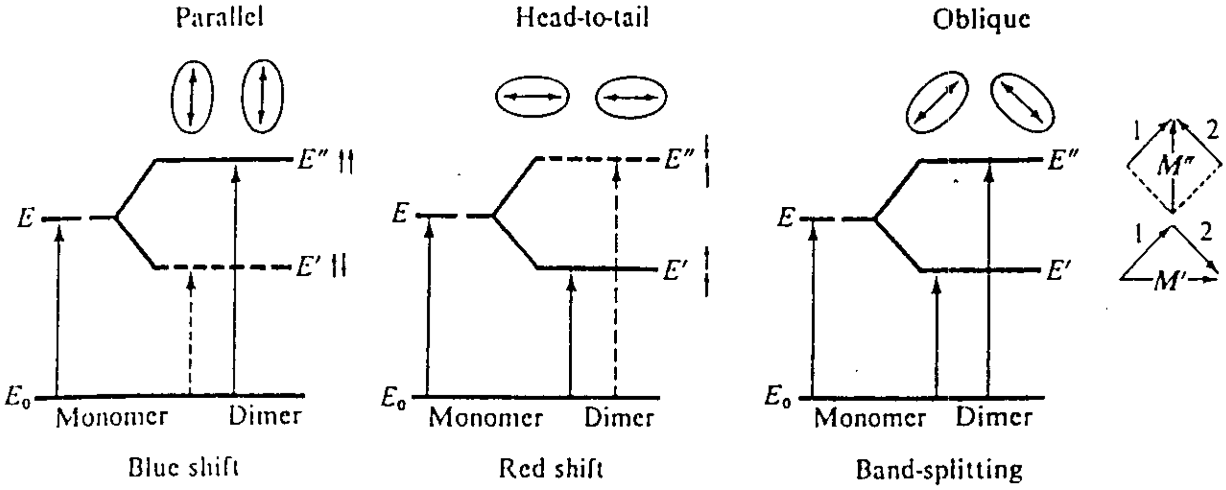
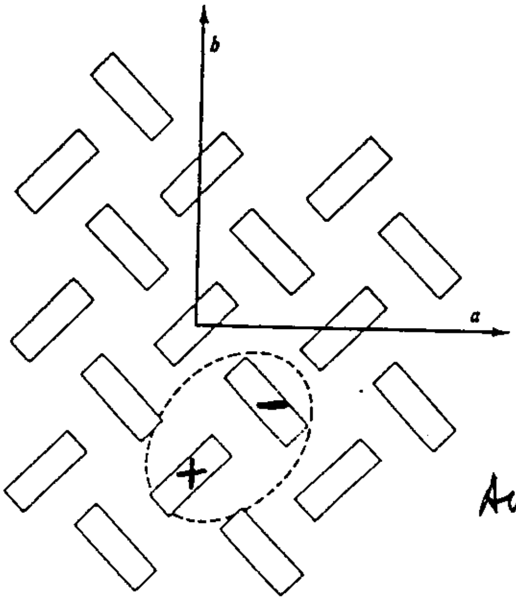
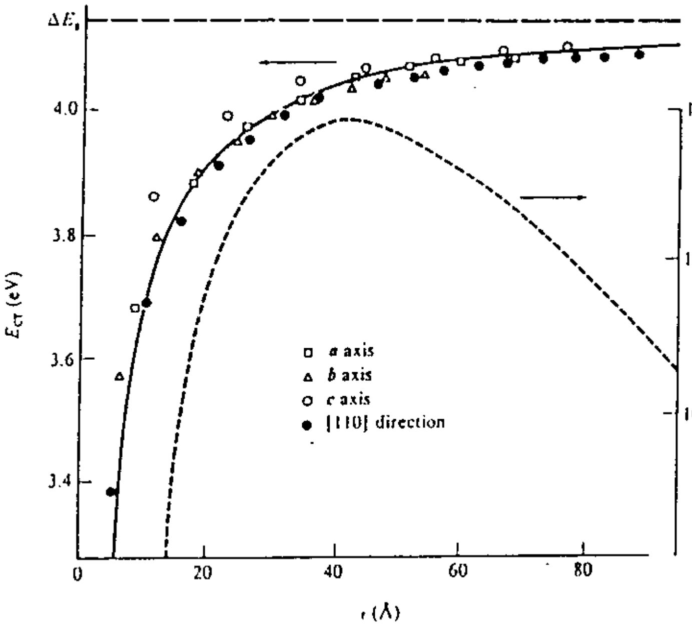


Fig. I.D.3. Exciton splitting in dimers of various geometries. Solvent energy shifts have been neglected. Orientations of monomer transition dipoles are represented by short arrows. Dipole-forbidden transitions are denoted by dotted lines. (From Kasha 1976, p. 346)

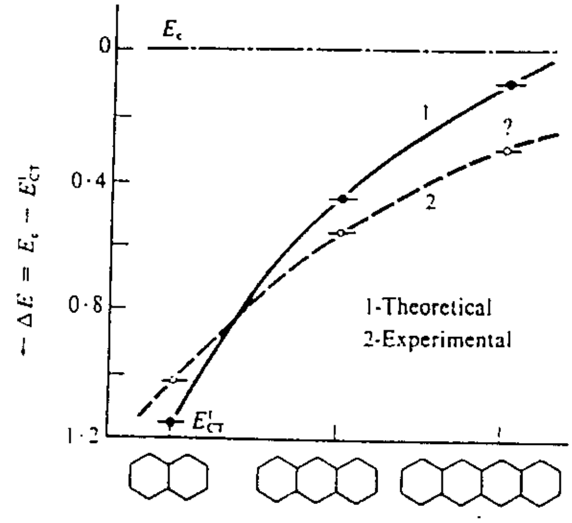
Charge-Transfer
Exciton



Anthracene



$$E = E_G - \frac{e^2}{4\pi\epsilon\epsilon_0 r_{CT}}$$

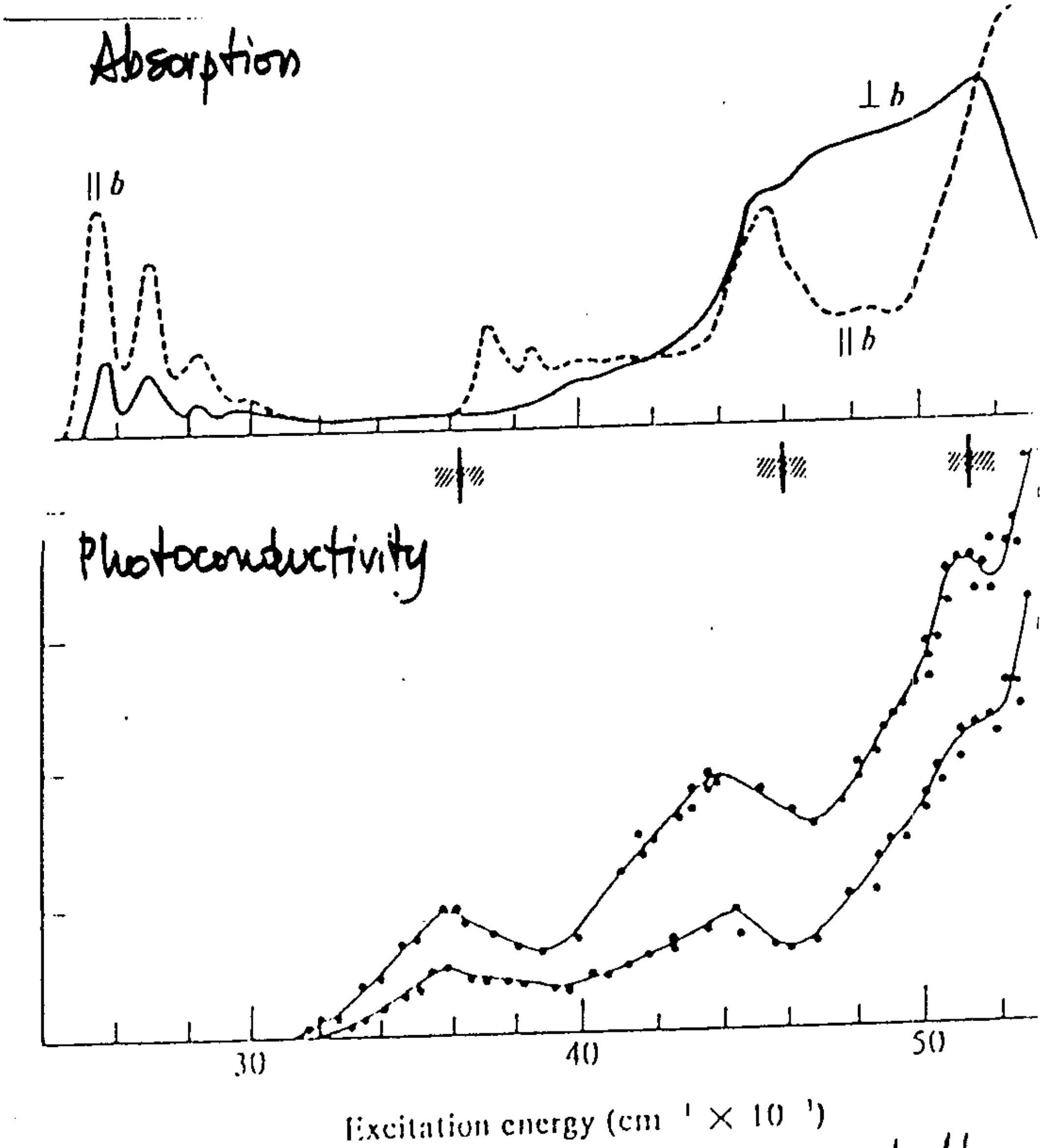


Experimental values for energy
of CT exciton

Naphthalene	4.38 eV (a)
Anthracene	3.45 eV (a)
Tetracene	2.7–2.9* eV (b)

*These energies depend on value for f

Fig. II.C.5. Energy differency ΔE from the first CT state E_{CT} to the electron conductivity level E_c for naphthalene, anthracene, and tetracene crystals. (From Silin *et al.* 1974). Listed to the right of the figure are the experimental values for the



Anthracene

eV

X-traps

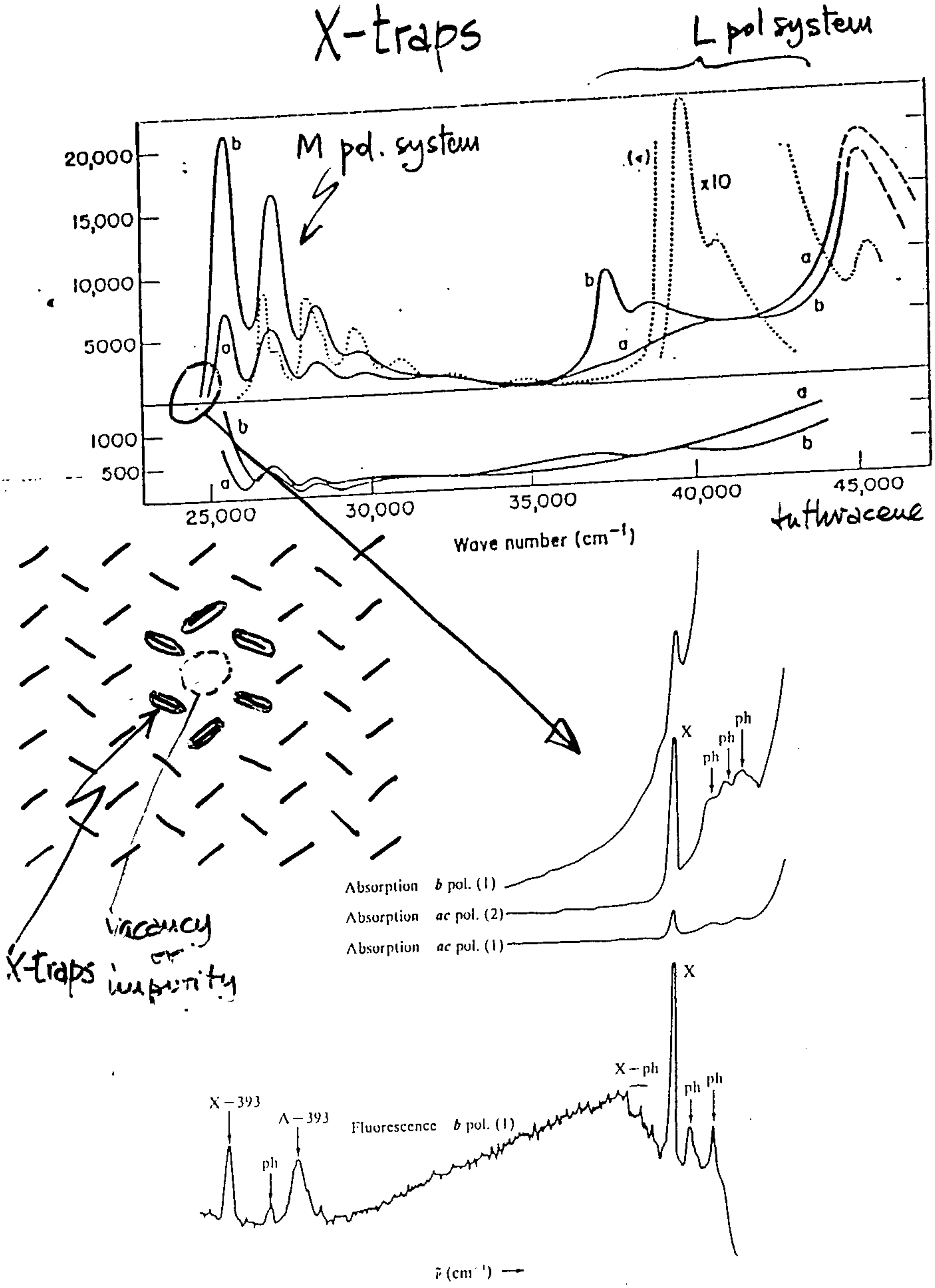


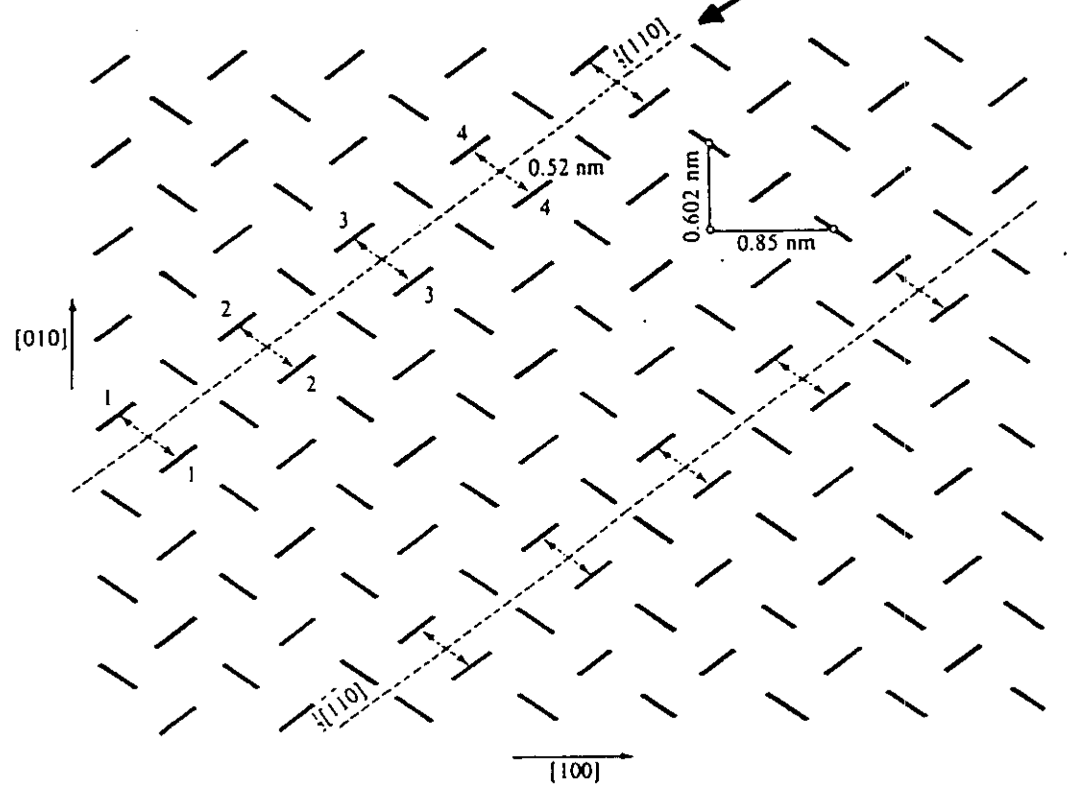
Fig. I.D.37. X-trap fluorescence (lower) and absorption (upper) for pyrene-induced X-traps in anthracene single crystals at ≈ 6 K in a lightly doped (1) and a more heavily doped crystal (2). The fluorescence peaks on the high-frequency side of the trap emission marked X are completely polarized satellites built on the host origin (A) at

coincides with the X fluorescence, is stronger in *b*

Dimers

Anthracene (ab plane)

slip dislocation



Absorption

9 Cl Anthracene in glass.

monomer

dimer

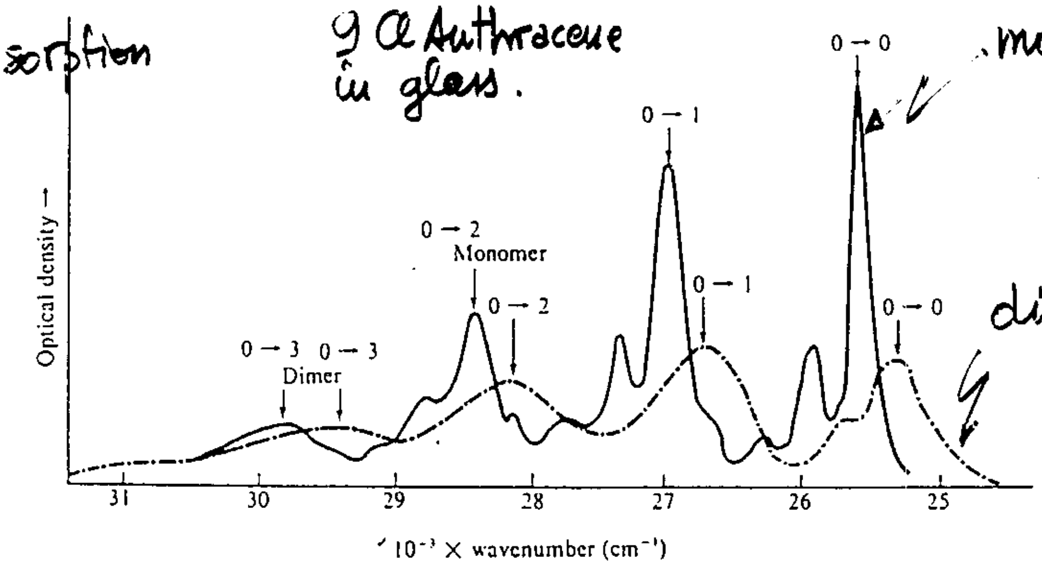


Fig. I.D.6. Absorption spectra of the sandwich dimer (dashed line) and monomer (solid line) of 9-chloroanthracene in methyl cyclohexane glass. The 1400-cm^{-1} vibrational mode progression is labeled 0 → n. Additional structure in the spectrum is due to other intramolecular vibrational modes. (Chandross and Ferguson 1966)

Excimer

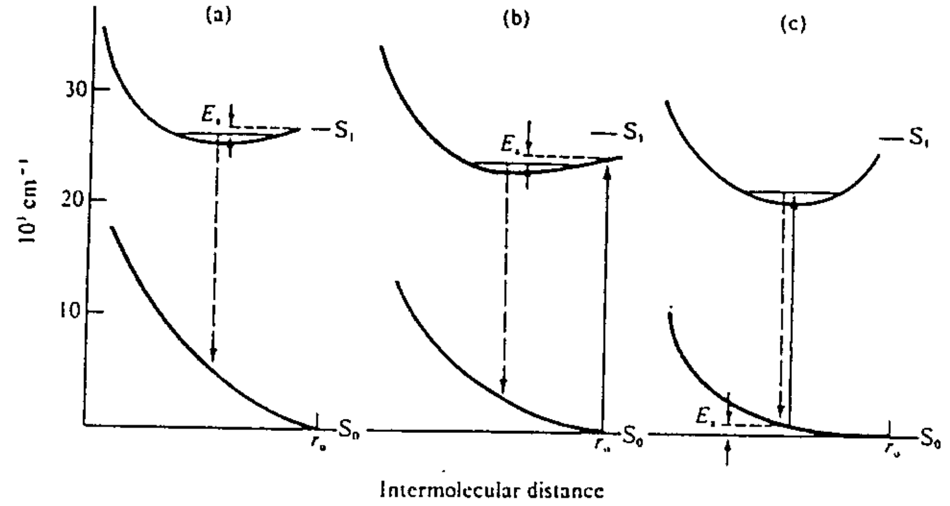
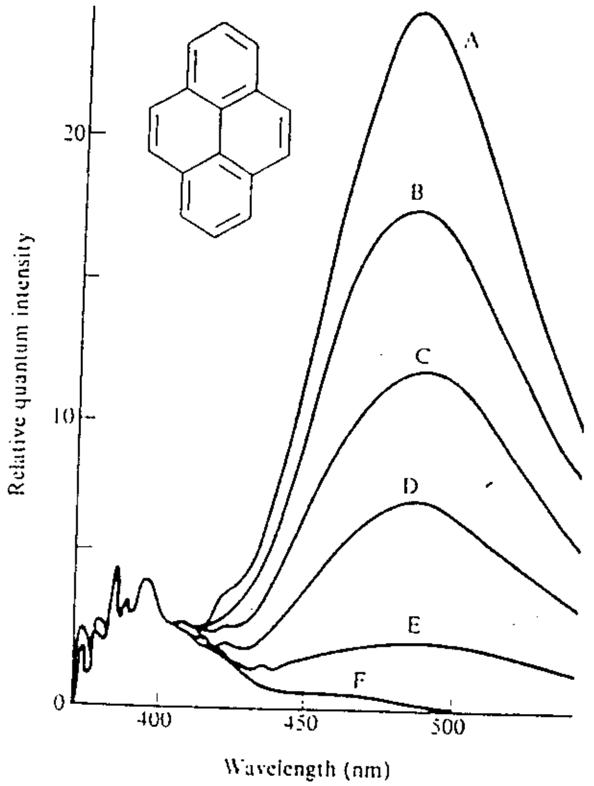


Fig. I.D.12. Diagrammatic view of excimer and ground-state potentials for different mechanisms of excimer–exciton transport. E_1 = activation energy for excimer–exciton hopping; r_0 is the ground-state intermolecular separation between the two molecules. Possible ground-to-excimer absorption is indicated by solid arrows. Dashed arrows indicate excimer fluorescence; their length corresponds to the experimentally measured maximum. (From Fischer, Naundorf, and Klöpffer 1973)

Pyrene PL in soln. at different concentrations



higher concentration

Fig. I.D.7. Fluorescence spectra of pyrene solutions in cyclohexane. Intensities are normalized to a common value of the molecular fluorescence quantum yield. Concentrations: A, 10^{-2} M; B, 7.75×10^{-3} M; C, 5.5×10^{-3} M; D, 3.25×10^{-3} M; E, 10^{-3} M; F, 10^{-4} M. (From Birks and Christophorou 1963)

Summary

electronic structure 1) molecule
manifold of singlet
and Triplet states
(vibronic bands)

2) molecular solid
Frenkel exciton bands of ↓ 〃
(small – intermediate V)

Splitting (Davidov)
(vibronic bands + lattice (inter molec.
vibrations ≡ phonons))