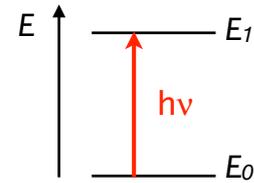


1.3 Radiation and molecular orbitals

Conditions for light absorption leading to an electronic excited state

- 1) The energy of the photon must correspond to that of an electronic transition

$$h\nu = E_1 - E_0$$



- 2) The **transition dipole moment** \mathcal{M} must be non-zero

$$\mathcal{M}_{1 \leftarrow 0} \neq 0 \Rightarrow \text{transition is allowed} \quad , \quad \mathcal{M}_{1 \leftarrow 0} = 0 \Rightarrow \text{transition is forbidden}$$

$$\mathcal{M}_{1 \leftarrow 0} = \langle \psi_1 | \hat{R} | \psi_0 \rangle = \langle \varphi_1 | \hat{R} | \varphi_0 \rangle \cdot \langle S_1 | S_0 \rangle \cdot \langle \eta_1 | \eta_0 \rangle$$

ψ_0 and ψ_1 are the electronic wave-functions of the ground- and excited states, respectively. \hat{R} is the operator of the transition dipolar moment.

$$\langle \varphi_1 | \hat{R} | \varphi_0 \rangle \neq 0 \quad \text{electronic transition dipolar moment (orbitals symmetry)}$$

$$\langle S_1 | S_0 \rangle \neq 0 \quad \text{electronic spin overlap integral (magnetic moment)}$$

$$\langle \eta_1 | \eta_0 \rangle \neq 0 \quad \text{nuclear wave-functions overlap integral}$$

\Rightarrow selection rules

21

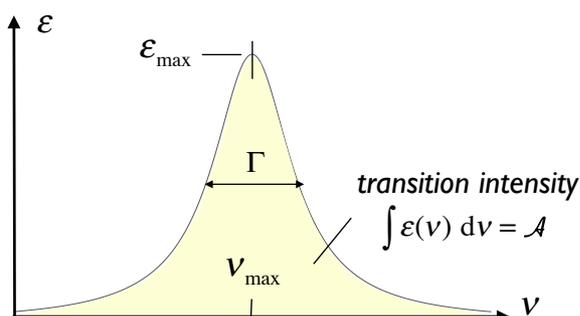
The transition oscillating strength $f_{1,0}$

Polarizability p is the tendency of a charge distribution in an atom or molecule to be distorted by an external electric field, such as the oscillating field associated with radiation.

The **transition oscillating strength** $f_{1,0}$ is defined as being the ratio of the electronic polarizability p of an atom or molecule to that of a free electron in the vacuum p_0 .

$$f_{1,0} [-] = \frac{p}{p_0}$$

$$f_{1,0} = \frac{4 \epsilon_0 \cdot m_e \cdot c^2 \cdot \ln(10)}{N_A \cdot e^2} \cdot \int_{\text{band}} \epsilon(\nu) d\nu$$



Single-peak Lorentzian absorption band

$$\epsilon(\nu) = \epsilon_{\max} \cdot \frac{\frac{1}{2} \cdot \Gamma}{(\nu - \nu_{\max})^2 + (\frac{1}{2} \cdot \Gamma)^2}$$

$$\mathcal{A} = \int_{\text{band}} \epsilon(\nu) d\nu = \frac{\pi}{2} \cdot \epsilon_{\max} \cdot \Gamma$$

$$f_{1,0} = 6.78 \cdot 10^{-9} \cdot \epsilon_{\max} \cdot \Gamma$$

$[\text{mol} \cdot \text{l}^{-1} \cdot \text{cm}^2]$ $[\text{mol}^{-1} \cdot \text{l} \cdot \text{cm}^{-1}]$ $[\text{cm}^{-1}]$

22

Transition oscillating strength $f_{1,0}$ and dipole moment $\mathcal{M}_{1,0}$

$$f_{1,0} = \frac{8\pi^2 \cdot m_e \cdot c}{3h \cdot e^2} \cdot \bar{\nu}_{\max} \cdot \mathcal{M}_{1,0}^2$$

Example

Dipole moment: $\mu = \Delta q \cdot r$ $\Delta q = e$, $r = 1 \text{ \AA} \Rightarrow \mu = 1.602 \cdot 10^{-19} \text{ C} \cdot 10^{-10} \text{ m}$
 $\mu = 1.6 \cdot 10^{-29} \text{ C} \cdot \text{m} = 4.8 \text{ D}$

Allowed transition: $f_{1,0} \approx 1$, $\bar{\nu}_{\max} = 4 \cdot 10^4 \text{ cm}^{-1}$ ($\lambda = 250 \text{ nm}$)
 $\Rightarrow \mathcal{M} = 2.3 \cdot 10^{-29} \text{ C} \cdot \text{m} = 7 \text{ D} \Rightarrow r = 1.5 \text{ \AA}$

the transition leads in this example to a charge separation in the excited state corresponding to the displacement of 1 electron over 1.5 Å.

Note for $f_{1,0}$ constant: $r \propto \frac{1}{\sqrt{\bar{\nu}_{\max}}}$ or $\bar{\nu}_{\max} \propto \frac{1}{r^2}$

the shorter the displacement distance r , the larger the excitation energy $\bar{\nu}_{\max}$!

23

Molecular orbitals

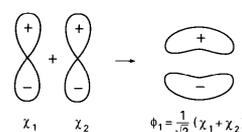
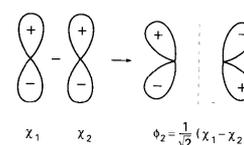
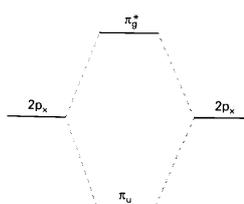
Absorption by molecules of a radiation of wavelength $100 \text{ nm} < \lambda < 1.2 \text{ }\mu\text{m}$ leads to electronic transitions between various molecular orbitals. In Hückel's (HMO) theory, the latter result from a linear combination of the orbitals of the atoms constituting the molecules.

A symmetric combination of atomic wave-functions yields low-energy **bonding** molecular orbitals, each occupied by two electrons of anti-parallel spins. Anti-symmetric combination of atomic orbitals leads to **anti-bonding** molecular orbitals of higher energy.

In organic molecules, axial overlap of two s or p atomic orbitals yields a σ (or σ^* , for an anti-symmetric combination) molecular orbital. Lateral overlap of two p orbitals yields π (respectively π^*) orbitals. Atomic orbitals that do not combine with any other in the molecule are called **non-bonding** orbitals.

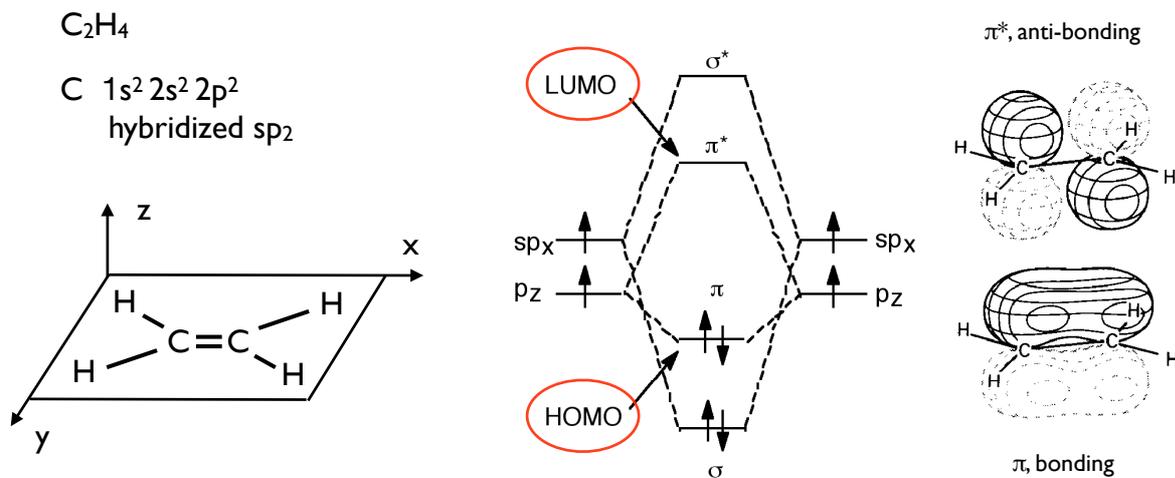


Erich Hückel
(1896-1980)



24

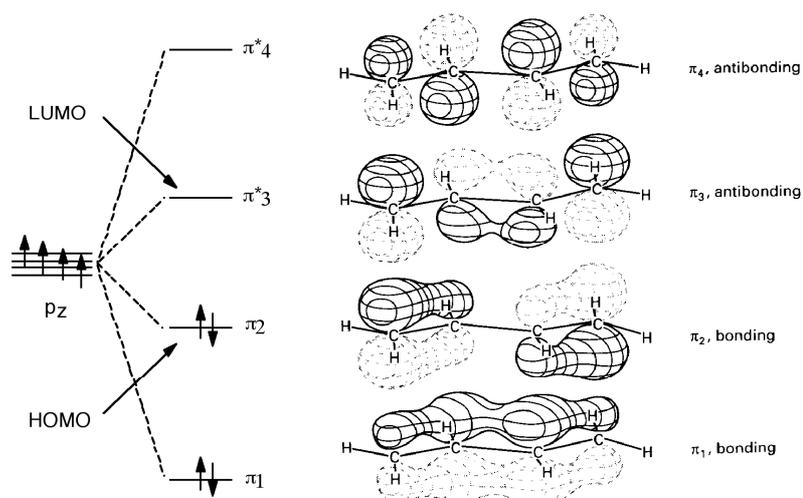
Example of the ethene molecule



The **highest occupied molecular orbital (HOMO)** and **lowest unoccupied molecular orbital (LUMO)** play a very important role in photochemistry, as the electronic transition of the lowest energy (**HOMO-LUMO transition**) will take place between these two particular levels.

25

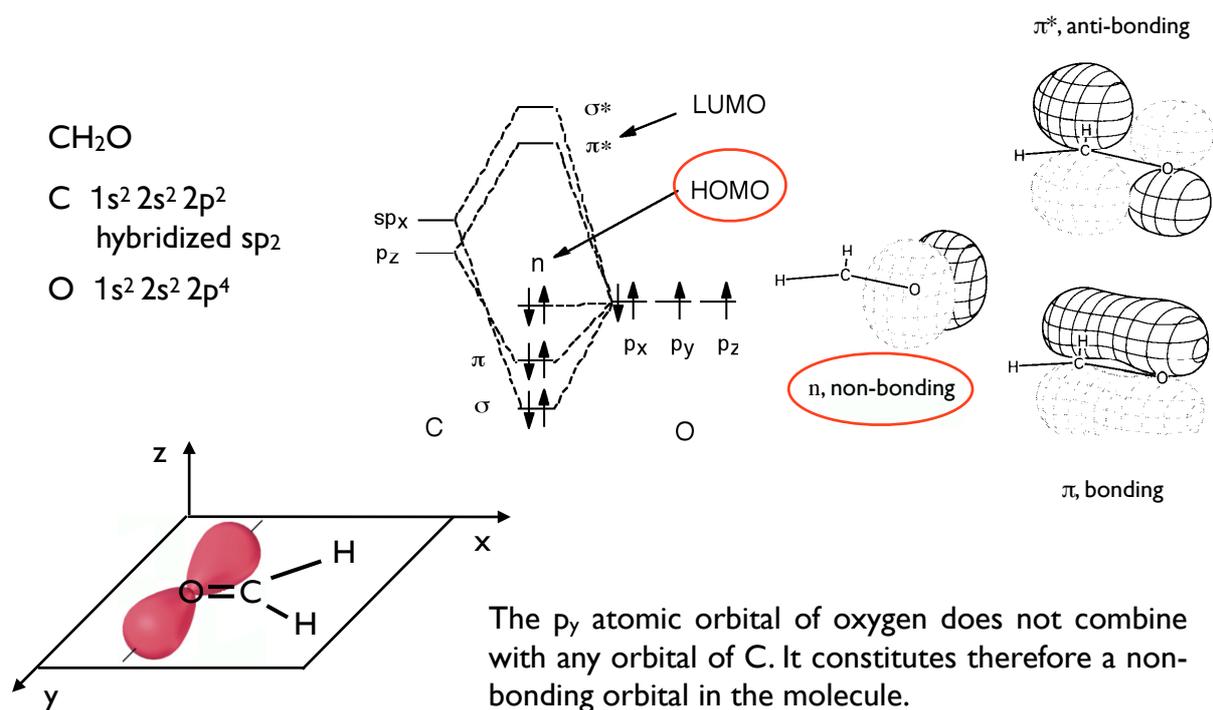
Example of the butadiene molecule



The same result can be obtained by correlating respectively π and π^* molecular orbitals of two ethene molecules. This shows that the HOMO-LUMO transition in the conjugation-extended butadiene molecule requires less energy than in ethene.

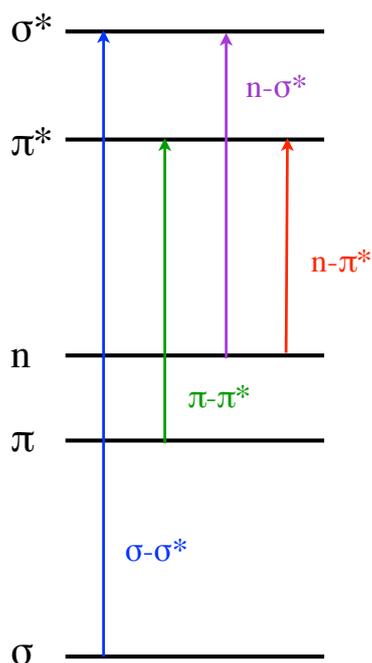
26

Example of the formaldehyde molecule



27

HOMO-LUMO transitions in organic molecules



n-π*

compounds containing hetero-atoms
 carbonyl derivatives, thicarbonyl, nitro-,
 azo-, imine ...

π-π*

alkenes, alkynes, aromatic compounds

n-σ*

amines, alcohols, halo-alkanes

σ-σ*

alkanes

28

Transition oscillating strength and selection rules

We shall see later that the violation of symmetry and spin selection rules, rather than leading to completely forbidden transitions, can be partially overcome. Very weak absorption results however in these cases.

$n\text{-}\sigma^*$ and $n\text{-}\pi^*$ transitions, for example, imply a change in the molecular orbital symmetry. These transitions are, therefore, forbidden. Compared to fully allowed transitions, their oscillating strength is reduced at least by a factor of 1,000-10,000.

Violation of the spin conservation rule has even more severe consequences, as $f_{1,0}$ decreases in that case by 6-7 orders of magnitude.

Allowed transition

$$f_{1,0} \approx 1 \quad \Gamma = 3,000 \text{ cm}^{-1} \Rightarrow \epsilon_{max} = 5 \cdot 10^4 \text{ mol}^{-1} \cdot \text{l} \cdot \text{cm}^{-1}$$

Forbidden transition (symmetry selection rule)

$$f_{1,0} \approx 2 \cdot 10^{-4} \quad \Gamma = 3,000 \text{ cm}^{-1} \Rightarrow \epsilon_{max} = 10 \text{ mol}^{-1} \cdot \text{l} \cdot \text{cm}^{-1}$$

Forbidden transition (spin selection rule)

$$f_{1,0} \approx 2 \cdot 10^{-7} \quad \Gamma = 3,000 \text{ cm}^{-1} \Rightarrow \epsilon_{max} = 10^{-2} \text{ mol}^{-1} \cdot \text{l} \cdot \text{cm}^{-1}$$

29

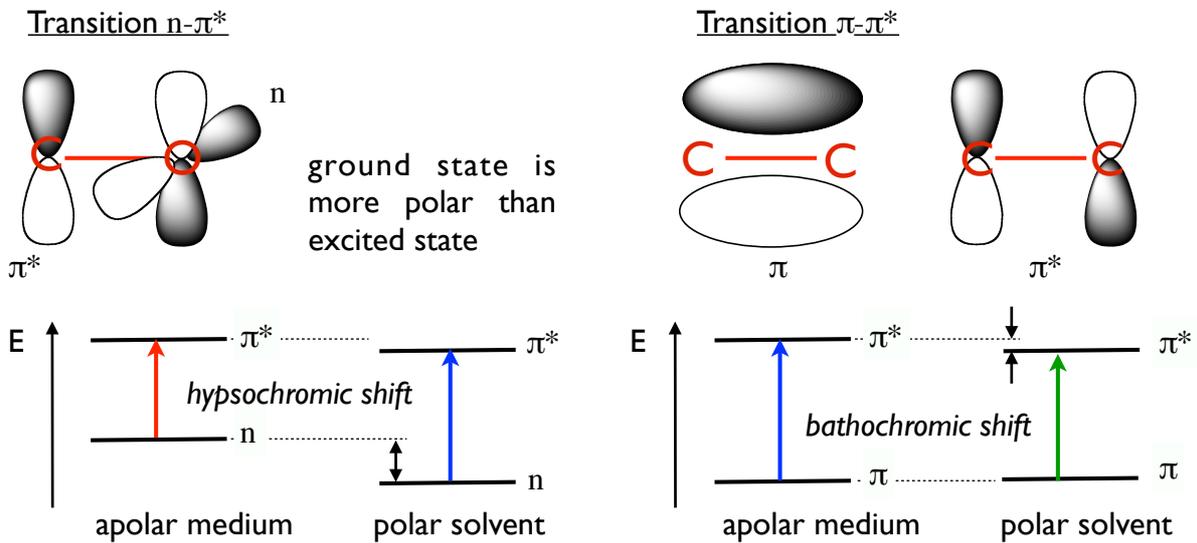
HOMO-LUMO transitions in organic molecules

Chromophore	Transition	$\lambda_{max} / \text{nm}$	$\epsilon_{max} / \text{mol}^{-1} \cdot \text{l} \cdot \text{cm}^{-1}$
N=O	$n\text{-}\pi^*$	~ 660	200
C=S	$n\text{-}\pi^*$	~ 520	100
N=N	$n\text{-}\pi^*$	~ 350	100
C=C-C=O	$n\text{-}\pi^*$	~ 350	30
C=O	$n\text{-}\pi^*$	~ 280	20
NO ₂	$n\text{-}\pi^*$	~ 270	20
C≡N	$n\text{-}\pi^*$	~ 260	150
S=O	$n\text{-}\pi^*$	~ 210	$1.5 \cdot 10^3$
benzene ring	$\pi\text{-}\pi^*$	~ 260	200
C=C-C=O	$\pi\text{-}\pi^*$	~ 220	$2 \cdot 10^5$
C=C-C=C	$\pi\text{-}\pi^*$	~ 220	$2 \cdot 10^5$
C=C	$\pi\text{-}\pi^*$	~ 180	$1 \cdot 10^5$
C-C	$\sigma\text{-}\sigma^*$	< 180	$1 \cdot 10^5$
C-H	$\sigma\text{-}\sigma^*$	< 180	$1 \cdot 10^3$

30

Solvatochromism

The **solvatochromic effect** refers to a dependence of absorption and emission spectra with the solvent polarity. If polarities of the ground and excited state of a chromophore are different, a change in the solvent polarity will lead to differential stabilization of both states, and thus, to a change in the energy gap between these electronic levels.



31

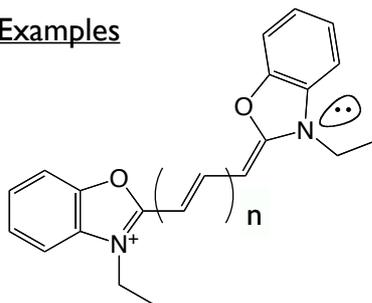
Charge-transfer transitions

Charge-transfer transitions are arbitrarily defined as transitions implying a large transition dipole moment $m_{1\leftarrow 0}$.

$$\text{As } m_{1\leftarrow 0}^2 \propto \frac{f_{1,0}}{\bar{\nu}_{\max}} \Rightarrow \bar{\nu}_{\max} \propto \frac{1}{r^2} \quad (\text{see p. 19}),$$

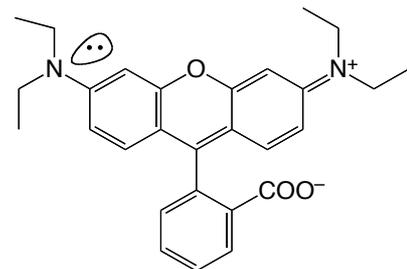
a large value of $m_{1\leftarrow 0}$ implies absorption of photons of longer wavelengths, extending to the visible light domain. All dye molecules, in particular, are characterized by charge transfer transitions.

Examples



oxa-n-carbocyanine

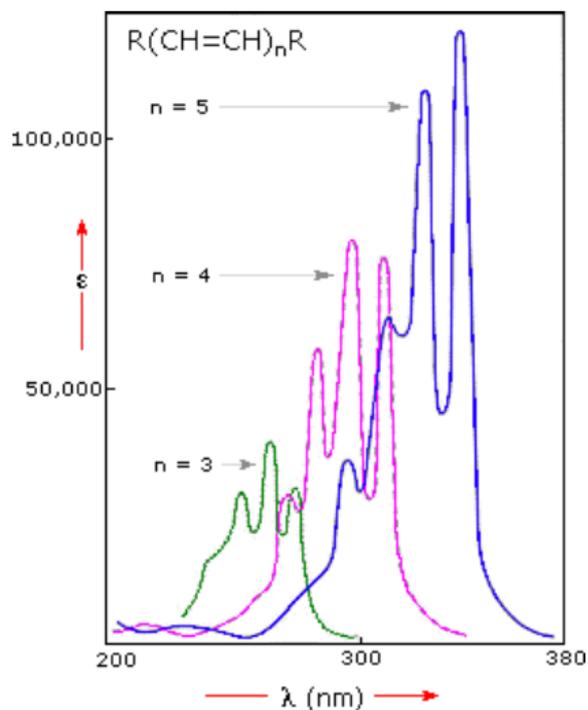
n	$\Delta E_{0,0}$ [eV]
0	3.32
1	2.58
2	2.16
3	1.81



rhodamine B

32

Bathochromic/ hyperchromic shift

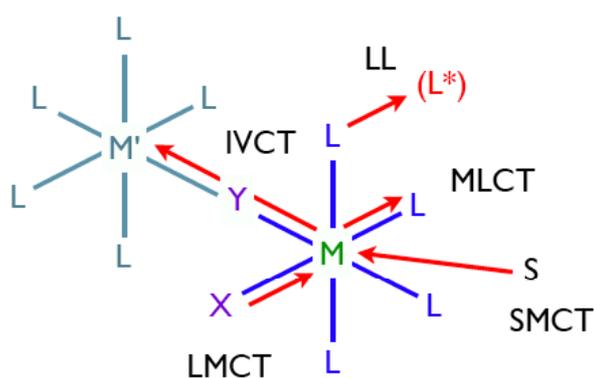


Increase of the dimensions of the conjugation domain yields a larger extinction coefficient (**hyperchromic** effect), due to an increase of the effective cross section for light absorption.

Concomitantly, a wider one-dimensional quantum box implies an increased transition dipole moment and a lower transition energy. As a result, a **bathochromic shift** of the absorption spectrum is observed (move of the absorption band to longer wavelengths).

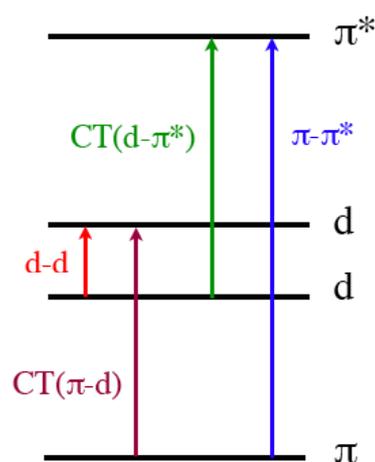
33

Electronic transitions in metal complexes



- MLCT ($d-\pi^*$): metal-to-ligand charge transfer
- LMCT ($\pi-d$): ligand-to-metal charge transfer
- LL ($\pi-\pi^*$): ligand-ligand
- IVCT ($d-d'$): intervalence charge transfer
- SMCT ($n-d$): solvent-to-metal charge transfer

...



34