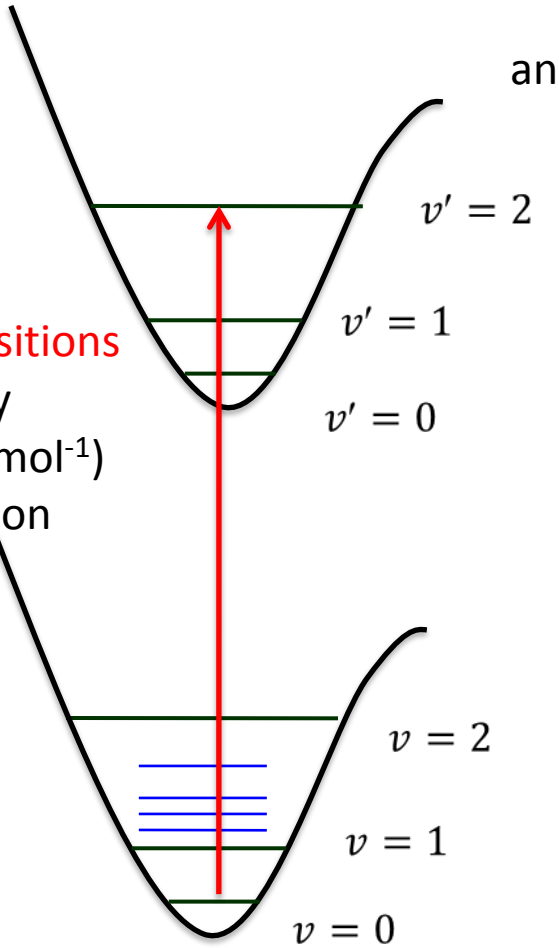
05.07.12 lecture PCIII (Lehramt)

molekulare elektronische Übergänge

Pics are taken from www.kcbirdingwalks and www.birdcapemay.org

Molecular transitions - outline



electron transitions
higher energy
(100 - 10^4 kJ mol^{-1})
UV-vis radiation

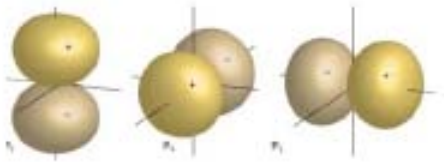
Grundzustand

molecular vibrations/rotations
medium /lower energy
(1 - 120 kJ mol^{-1}), (0.01 - 1 kJ mol^{-1})
IR/MW radiation

Molecular term symbols: diatomic molecules

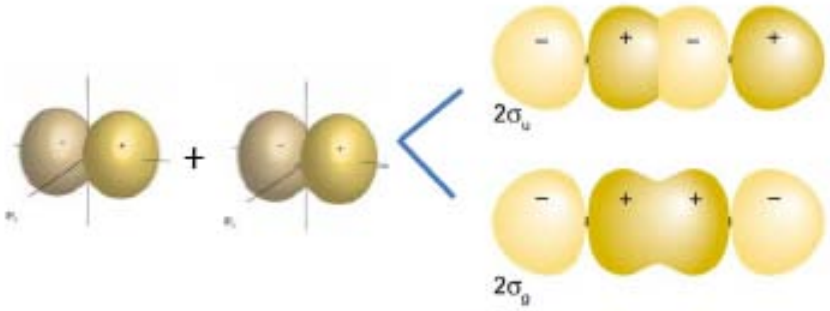
Classify according to angular momentum around the internuclear axis, λ.

λ is similar to m_l in atoms, so for a *p* orbital: λ=0, ±1

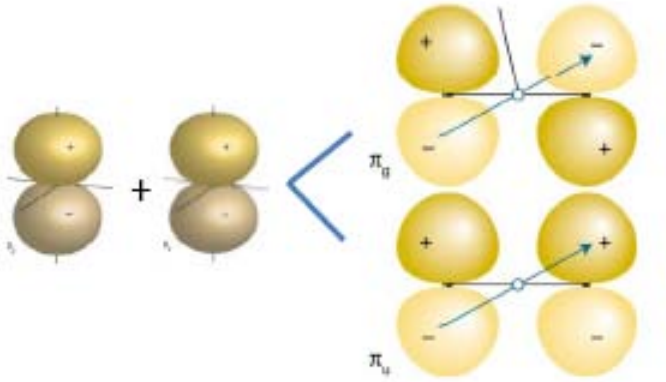


Two p orbitals : sigma(σ) and pi(π) molecular orbitals

p_z (m_l=0) so (λ =0): σ , σ* *MOs*

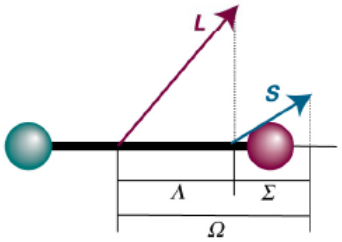


$p_{x,y}$ (m_l= ±1) so (λ =±1): π, π* MOs



$$\Lambda = \sum_i \lambda_i = \lambda_1 + \lambda_2 + \lambda_3 + \ldots$$

Overall angular momentum on the internuclear axis



Spin-orbit levels : $\Omega = |\Lambda + \Sigma|$,

Σ is the projection of S on internuclear axis

spin multiplicity =(2s+1)

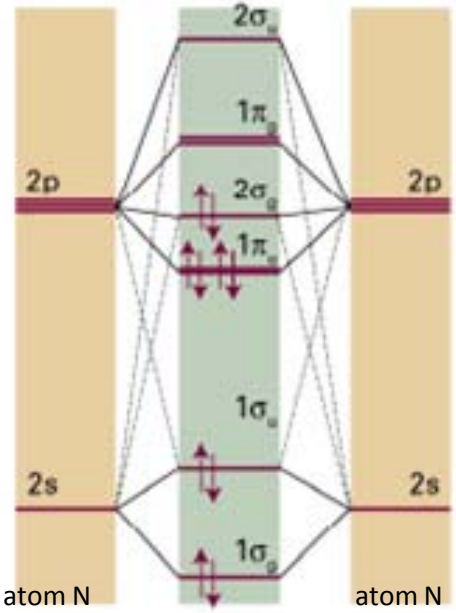
Singlet, doublet and triplet states

$^2\Pi_{3/2}$

Λ values , according to:

Σ for Λ=0, Π for $\Lambda = \pm 1$

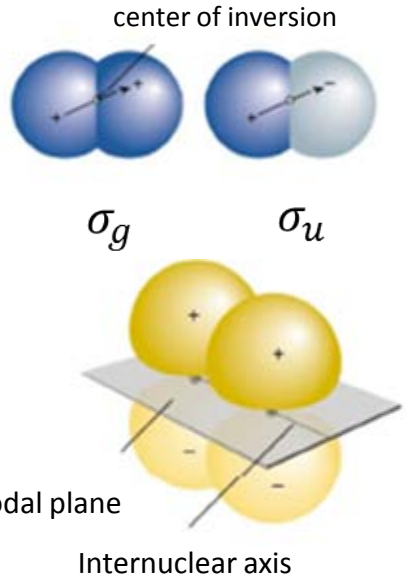
Δ for $\Lambda = \pm 2$, Φ for $\Lambda = \pm 3$,… .



N_2-ground state

$^1\Sigma_g^+$

$(2s\sigma_g)^2(2s\sigma_u)^2(2p\pi_u)^4(2p\sigma_g)^2$



g⊗g=g

u⊗g=u

u⊗u=g

$\hat{\imath}\Psi_e = \mp\Psi_e$

$\hat{\sigma_v}\ \Psi_e = \mp\Psi_e$

For ***sigma terms***,the symmetry is shown as (+/-) considering the reflection in a plane contains the internuclear axis.

Selection rules

1. $\Delta\Lambda = 0, \pm 1,$

example: transitions Σ-Σ, Π-Σ, Δ-Π and so on are allowed but Δ- Σ or Π-Φ are forbidden .

2. $\Delta S = 0,$

(true for light atoms, however does not hold for very heavy atoms, for example in I_2).

3. $\Delta\Omega$=0,±1,

for transitions between multiple components.

4.Further subdivision for Σ states: only Σ^+-Σ^+ or Σ^--Σ^- transitions are allowed.

notice:$\Sigma^+ - \Pi$, $\Sigma^- - \Pi$ are both allowed.

5. g↔u,

g to g or u to u transitions are forbidden.

From: P.F.Bernath, chap.16-electronic spectroscopy of Diatomic molecules

Transition dipole moment integral

(Time dependent hamiltonian , how are the selection rules obtained)

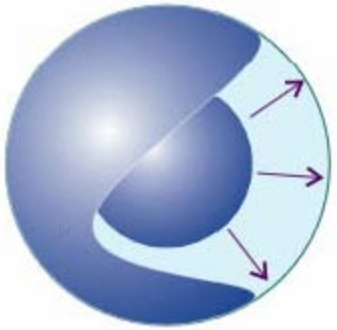
$$\hat{H} = \hat{H^0} + \hat{H^1}\,(t) \qquad \hat{H^1}\,(t) = -\mu_z \cos\omega t$$

$$R_{21} = \int \psi *_2 \hat{\mu}\psi_1 d\tau = \langle \psi_2 | \mu | \psi_1 \rangle \qquad \mu_x = ex, \mu_y = ey, \mu_z = ez$$

2: final state, 1: initial state

Übergangsdipolmomentintegral

Born-Oppenheimer Näherung: $\psi_{tot}=\psi_e(r).\psi_{vib}(R)$



1s---> 2s

verboten

$$R_{21} = \langle \psi'_{el}\psi'_{vib} \left| \hat{\mu} \right| \psi''_{el}\psi''_{vib} \rangle = -e \iint \psi'^{*}_{el}(r)\psi'^{*}_{vib}(R)\, r\, \psi''_{el}(r)\psi''_{vib}(R)\,dr\,dR$$

$$R_{21} = -e \int \psi'^{*}_{el}(r)\, r\, \psi''_{el}(r)\,dr \int \psi'^{*}_{vib}(R)\psi''_{vib}(R)\,dR$$

Electronic transition moment — Vibrational overlap

S(v,v') ***Überlappungsintegral***

1s---> 2p

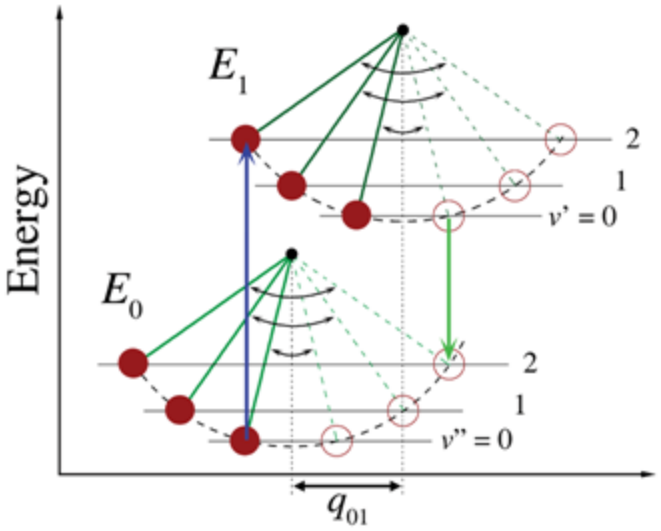
✓ Erlaubt

Transition intensity $\propto R_{21}^2 \propto \left(\int \psi'^{*}_{el}(r)\, r\, \psi''_{el}(r)\,dr\right)^2 \left(\int \psi'^{*}_{vib}(R)\psi''_{vib}(R)\,dR\right)^2$

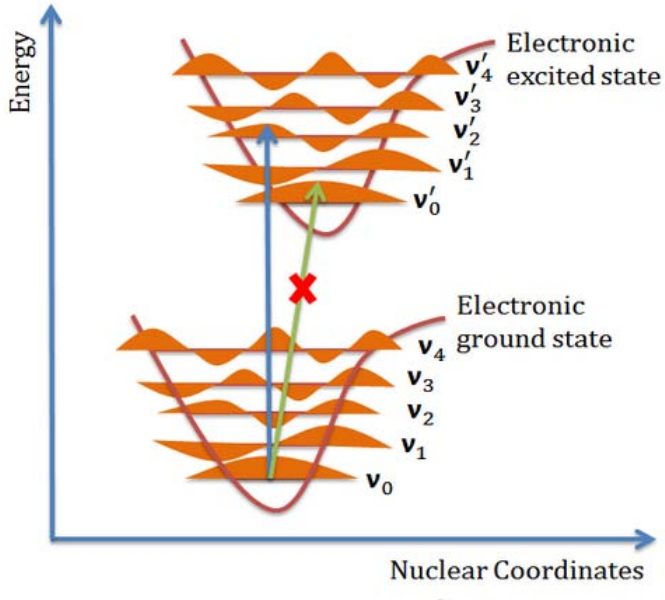
Franck-Condon factor
(square of the vibrational overlap integral)

$\Delta\Lambda = 0, \pm 1$
$\Delta S = 0$ and $\Delta\Sigma = 0$
$g \leftrightarrow u$ (where g, u exist)
$+ \leftrightarrow +$; $- \leftrightarrow -$ (for Σ–Σ transitions)

Franck-condon principle

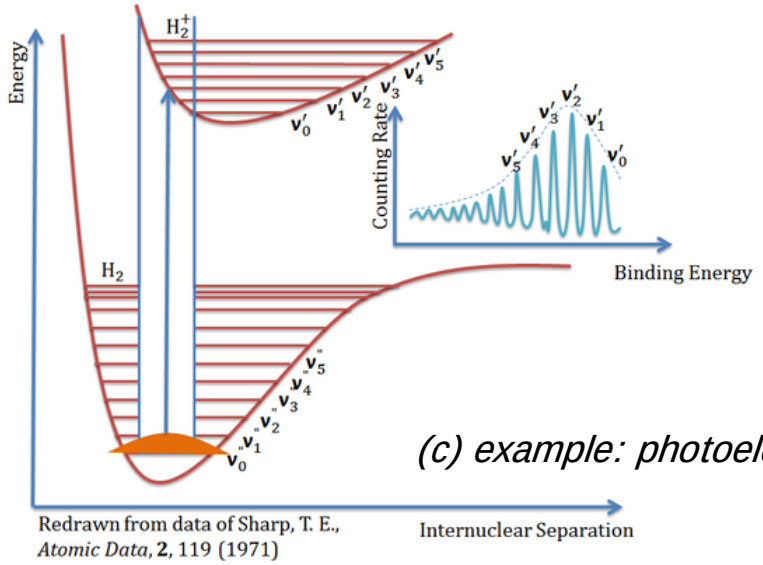


(a) How does the internuclear distance change?



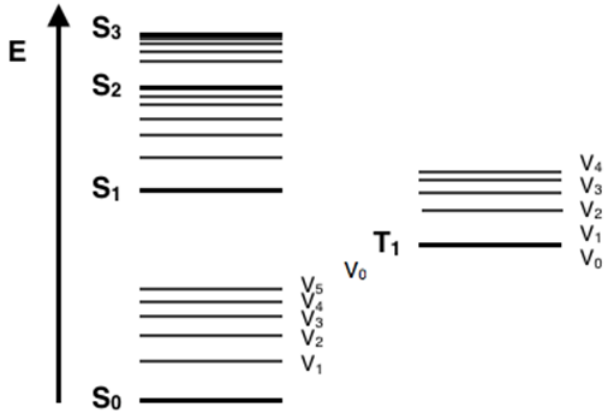
(b) Franck-condon energy diagram

(Vertical transitions)

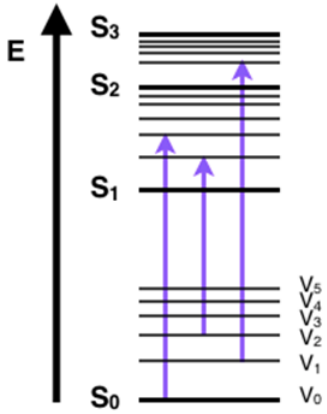


(c) example: photoelectron spectrum of the ionization H_2

Fate of molecule? Jablonski diagram

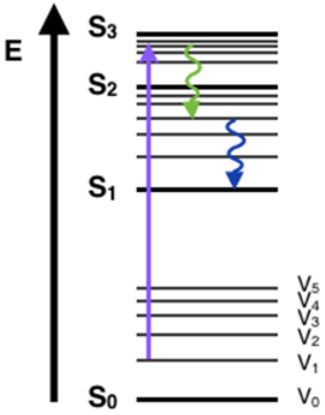


- *schematic energy diagram ,*
- *specific multiplicities,*
- *electronic states (bold),*
- *vibronic energy states/rotations,*
- *continuous energy band,*
- *straight/curved lines.*

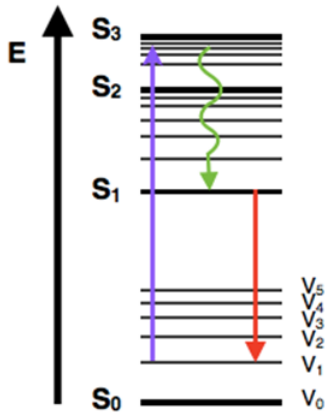


The foundation of a typical Jablonski diagram

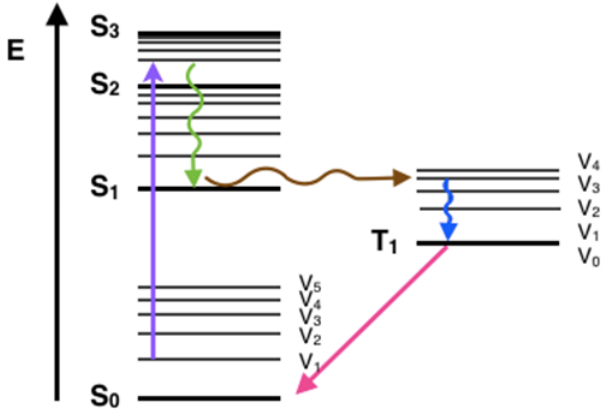
Possible absorptions (10^{-15}s)



Absorbance, internal conversion and vibratoinal relaxation (10^{-14}-10^{-11}s)



Fluorescence (10^{-9}-10^{-7}s)



Intersystem crossing (10^{-8}-10^{-3}s), phosphorescence (10^{-4}-10^{-1}s)