V13

Note Title

WDH

$(2S+1)$ +/−

abgeschlossene Schalen: $^1\Sigma_g^+$

zu O_2: $2p_x\pi_g^{(-)*}$ ↑ ↑ $2p_y\pi_g^{(+)*}$ $^3\Sigma_g^-$

↑↓ — $^1\Delta_g$

↯ ↑ ↑ $^1\Sigma_g^+$

(↑ ↑)

allg.: $\Gamma(\Psi_e) = \prod_i \Gamma(\varphi_{i,MO})$

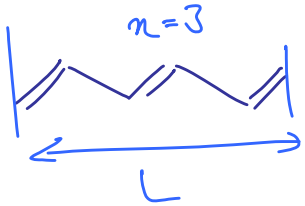
"$\pi_g \times \pi_g$" = $^3\Sigma_g^- + {}^1\Sigma_g^+ + {}^1\Delta_g$

Auswahlregeln: $\Delta S = 0$ g ⟷ u

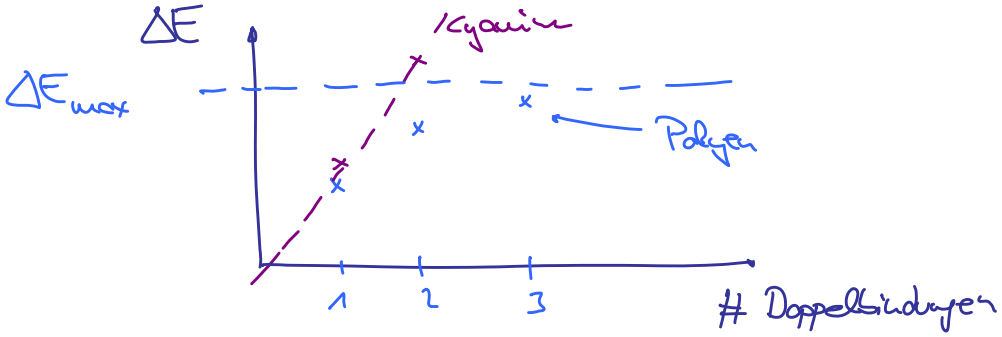
$\Delta\Lambda = 0, \pm 1$ + ⟷ + / − ⟷ −

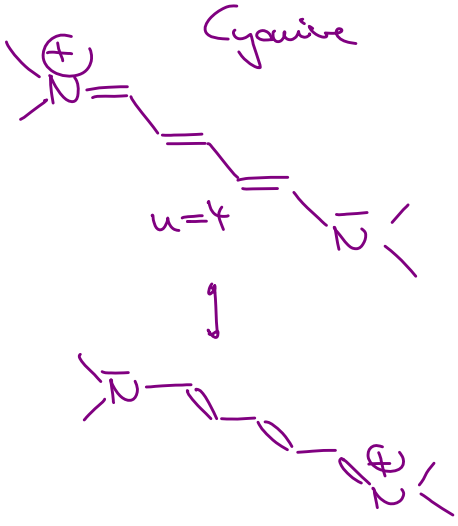
Polyen: ΔE (HOMO → LUMO)

(Rdm)



$E \sim \frac{1}{L^2}$





7. Experimentelle Molekülspektroskopie

Born-Oppenheimer: $E_{ges} = E_{el} + E_{vib} + E_{rot}$

$\Rightarrow$ (Spektroskopie)

$\Delta E_{ges} = \Delta E_{el} + \Delta E_{vib} + \Delta E_{rot}$

$\sim 10^5\,cm^{-1}$	$\sim 1000\,cm^{-1}$	$\sim 1\,cm^{-1}$
$\sim 10^{-15}\,s$	$\sim 10^{-12}\,s$	$\sim 10^{-3}\,s$
1 fs	1 ps	1 µs

Schwingungsfeinstruktur ("grob"),
Feinstruktur (i.d.R. Gasphase)

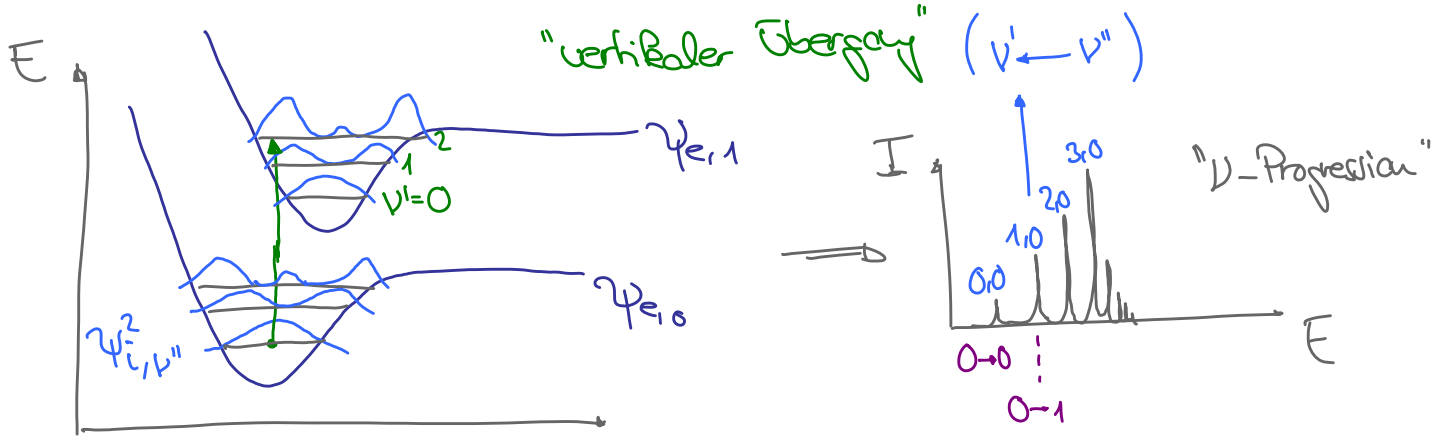
A. Schwingungsstruktur

$$\bar{\nu}_{spekt} = \left(\varepsilon_{el,angeregt} - \varepsilon_{el,GZ}\right) + \left[\left(\nu' + \tfrac{1}{2}\right)\bar{\nu}_e' - x_e'\left(\nu' + \tfrac{1}{2}\right)^2 \bar{\nu}_e'\right] - \left[\left(\nu'' + \tfrac{1}{2}\right)\bar{\nu}_e'' - x_e''\left(\nu'' + \tfrac{1}{2}\right)^2 \bar{\nu}_e''\right]$$

$\psi_{el,GZ}|\nu'' \longrightarrow \psi_{el,angeregt}|\nu'$

$\bar{\nu}_e'' > \bar{\nu}_e'$

Franck-Condon (Intensität von $\bar{\nu}_{spekt}$)



Erinnerung: $f_{i\to f} = const. \cdot |\vec{\mu}_{i\to f}|^2$ | Oszillatorstärke

$$|\vec{\mu}_{i\to f}| = \int \psi_f^* \cdot \hat{\mu} \cdot \psi_i \, d\tau$$

$$= q \int \left(\psi_{e,f}^* \cdot \psi_{vib,f}^*\right) \hat{r} \left(\psi_{e,i} \cdot \psi_{vib,i}\right)$$

$\hat{\mu} = q \cdot \hat{r}$

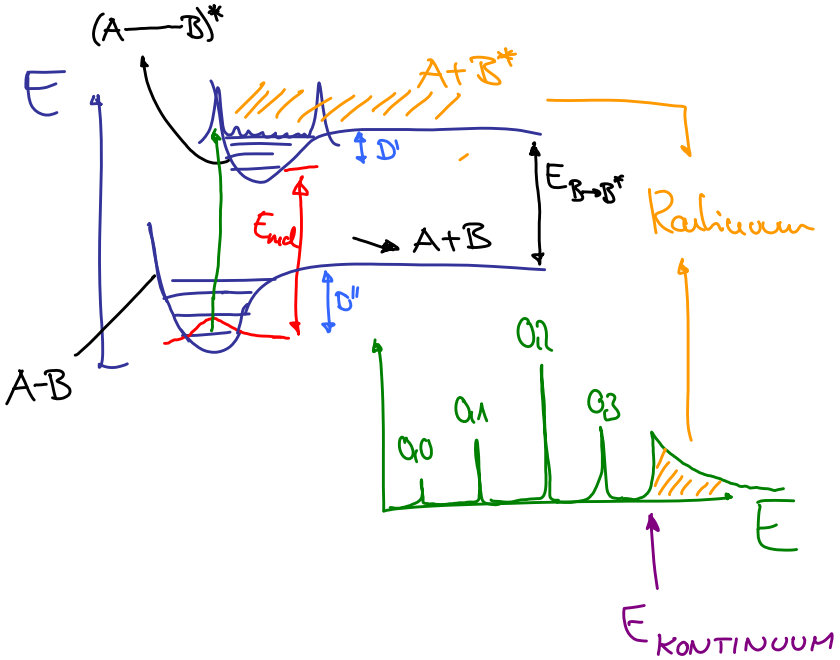
$\psi = (\psi_e \cdot \psi_{vib})$

$$= q \int \underbrace{\left(\varphi_{e,f}^{*} \cdot \hat{r} \cdot \varphi_{e,i}\right)}_{\neq 0} \cdot \underbrace{\left(\varphi_{vib,f}^{*} \cdot \varphi_{vib,i}\right)}_{\text{Überlappintegral, } S = \langle \varphi_{vib,f} | \varphi_{vib,i} \rangle} d\tau$$

$$\Longrightarrow \text{FC-Faktor: } \boxed{f_{FC} \sim S\left(\varphi_{vib,f}, \varphi_{vib,i}\right)^2}$$

Dissoziation

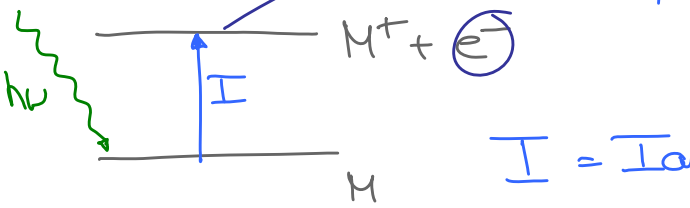
mit elektron. Anregung: (NUR!)



$$E_{KONTINUUM} = E_{vib} + D' - E_{B\to B^*} + D''$$

Photoelektronenspektroskopie (PES)

äußere Photoeffekt



I = Ionisierungsenergie

Koopman: $I \triangleq -\varepsilon_{HO}$

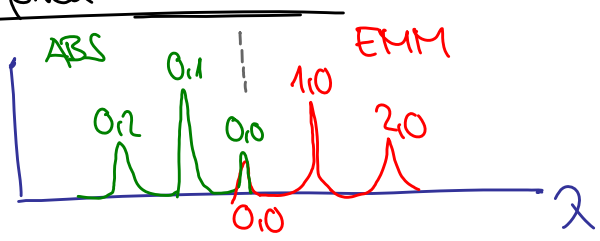
He (I) - Strahlung

$He(1s^1 2p^1) \longrightarrow He(1s^2) + h\nu$

21eV / 58nm

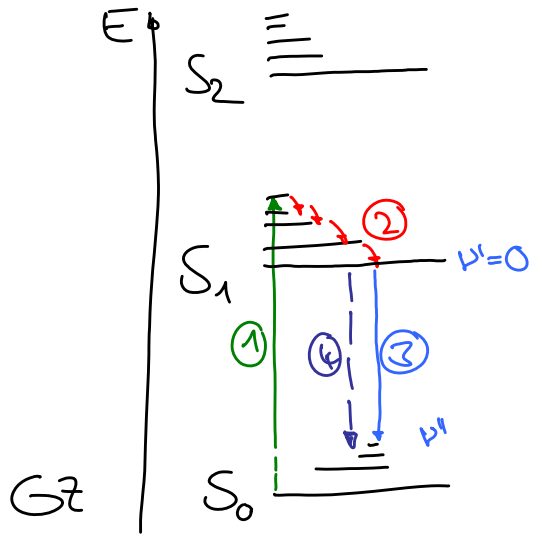
8. "Schicksal" elektronisch angeregter Zustände

A. Absorption + Fluoreszenz



⟹ "mirror image rule"

JABLONSKI

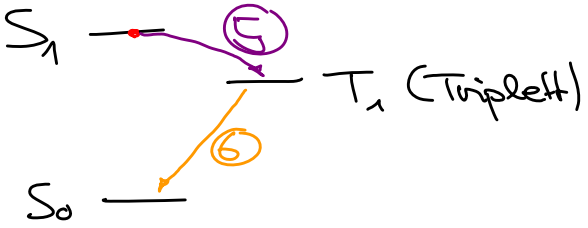


① Absorption, ~ 1 fs

② "interne Konversion"
$\sim 10^{-10} - 10^{-12}$ s

③ Fluoreszenz
$\sim 10^{-9}$ s (1 ns)

④ strahlungslose Deaktivierung



⑤ = Inter-System Crossing (ISC)
~ 1 µs

⑥ Phosphoreszenz, 1 ms – s

KASHA's Regel: Fluoreszenz i.d.R. aus S_1 ($\nu'=0$)

zur Fluoreszenz:

Quantenausbeute: $\Phi_F = \frac{\text{emittierte Photonen}}{\text{absorbierte Photonen}} = 0 \ldots 1$

$\longrightarrow \Phi_F = \frac{k_F}{k_F + \sum_i k_i}$

Depopulation von S_1

k_{ISC}, k_{nr} "non-radiative"

Lebensdauer: $\boxed{\tau_F = \frac{1}{k_F + \sum_i k_i}}$