PC III 16.4.13

Quantenmechanische Formulierung: Franck-Condon-Prinzip

Born-Oppenheimer-Näherung: Separation von Elektronen- und Schwingungsbewegung (analog Rotation)

$$E_{ges} = E_{el} + E_{vib} \ (+ E_{rot})$$

$$\Psi_{ges} = \Psi_{el} \cdot \Psi_{vib} \ (\cdot \Psi_{rot})$$

Übergangsmoment R (Int $\propto |R|^2$)

$$R = e \int \Psi_{el}'^{*} \Psi_{vib}'^{*} \sum_i z_i \vec{r}_i \Psi_{el}'' \Psi_{vib}'' \, d\tau_{el} \, d\tau_{vib}$$

$$\vec{\mu} = e \sum_i z_i \vec{r}_i = \vec{\mu}_{el} + \vec{\mu}_{kern}$$

Elektronen- und Kernbeitrag zu $\vec{\mu}$

$$R = \int \Psi_{el}'^{*} \Psi_{vib}'^{*} \vec{\mu}_{el} \Psi_{el}'' \Psi_{vib}'' \, d\tau_{el} \, d\tau_{vib} + \int \Psi_{el}'^{*} \Psi_{vib}'^{*} \vec{\mu}_{kern} \cdot \Psi_{el}'' \Psi_{vib}'' \, d\tau_{el} \, d\tau_{vib}$$

$$\rightarrow \underbrace{\int \Psi_{el}'^{*} \Psi_{el}'' \, d\tau_{el}}_{=0} \int \Psi_{vib}'^{*} \vec{\mu}_{kern} \Psi_{vib}'' \, d\tau_{vib}$$

elektronische Wellenfunktionen orthogonal

$$R = \int \Psi_{el}'^{*} \vec{\mu}_{el} \Psi_{el}'' \, d\tau_{el} \underbrace{\int \Psi_{vib}'^{*} \Psi_{vib}'' \, d\tau_{vib}}_{\text{Überlappungsintegral}}$$

Franck-Condon-Faktoren: Quadrat des Überlappungsintegrals bestimmt Intensitätsverteilung

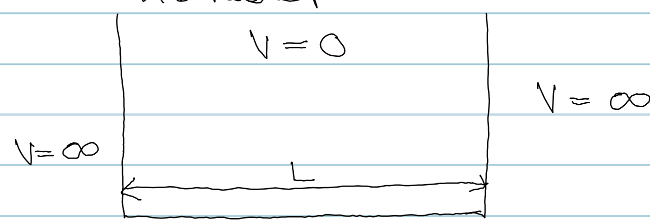
Polyene: Teilchen im Kasten
Beschreibung π - Elektronen

Polyen

C=C−C=C−C=C

$\longleftarrow L \longrightarrow$

1D Kastenpotenzial

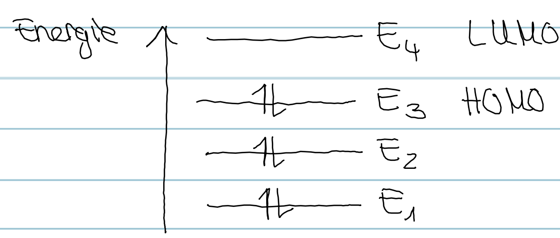


$L = N \cdot \overline{R}_{CC}$

$\overline{R} = 144\ pm$

z. B. Hexatrien

1) Bestimme den langwelligsten elektronischen Übergang!



$L = N \cdot \overline{R}_{CC} = 5 \cdot 144\ pm = 720\ pm$

Hexatrien: $6\ \pi\ e^-$

$n_{HOMO} = 3$

$n_{LUMO} = 4$

$$E_n = \frac{n^2 h^2}{8 m L^2}$$

$$\Delta E = E_4 - E_3 = 7 \frac{h^2}{8 m L^2} = 8{,}14 \cdot 10^{-19}\ J$$

$$\Delta E = h \cdot \nu = h \frac{c}{\lambda}$$

$$\lambda = \frac{hc}{\Delta E} = 2{,}44 \cdot 10^{-7}\ m = 244\ nm \quad \text{(farblos)}$$

2) Bestimme die Normierungskonstante N, wenn
$\psi(x) = N \sin\left(\frac{n\pi x}{L}\right)$

$\sin(\alpha) \sin(\beta) = \frac{1}{2} \cos(\alpha - \beta) - \frac{1}{2} \cos(\alpha + \beta)$ für $\alpha = \beta$
$\alpha \neq \beta$

$$N^2 \int_0^L \psi^*(x)\,\psi(x)\,dx = 1$$

$$N^2 \int_0^L \sin\left(\frac{n\pi x}{L}\right) \sin\left(\frac{n\pi x}{L}\right) dx = N^2\,\frac{1}{2}\int_0^L \cos(0)\,dx - N^2\,\frac{1}{2}\int_0^L \cos\left(\frac{2n\pi x}{L}\right)dx$$

$$= N^2\,\frac{1}{2}\,\left[x\right]_0^L - N^2\,\frac{1}{2}\,\frac{L}{2n\pi}\,\underbrace{\left[\sin\left(\frac{2n\pi x}{L}\right)\right]_0^L}_{0}$$

$$\frac{N^2}{2}L = 1 \longrightarrow N = \sqrt{\frac{2}{L}}$$

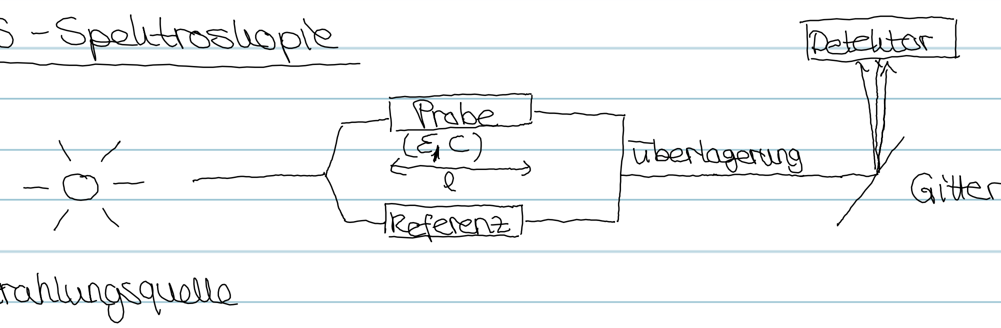
$$\psi(x) = \sqrt{\frac{2}{L}}\,\sin\left(\frac{n\pi x}{L}\right)$$

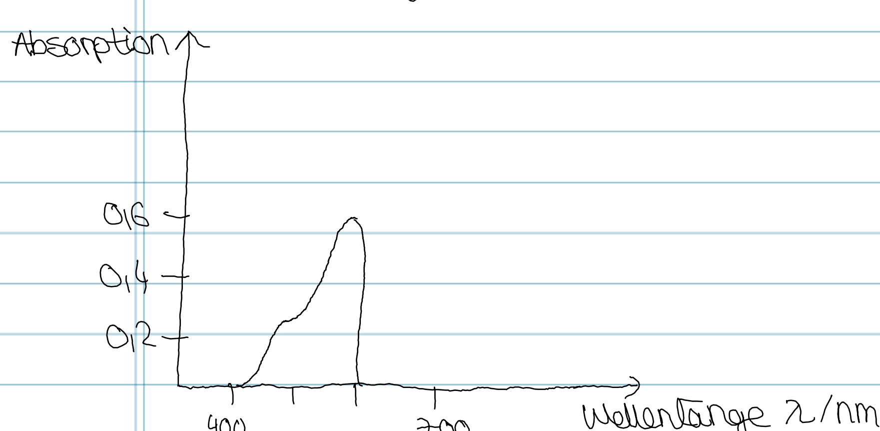
$$\left.\begin{aligned}\psi_1(x) &= \sqrt{\frac{2}{L}}\,\sin\left(\frac{\pi x}{L}\right)\\ \psi_2(x) &= \sqrt{\frac{2}{L}}\,\sin\left(\frac{2\pi x}{L}\right)\end{aligned}\right] \rightarrow \text{orthogonal ?}$$

$$\int_0^L \psi_1^*(x)\,\psi_2(x)\,dx = \frac{2}{L}\int_0^L \sin\left(\frac{\pi x}{L}\right)\sin\left(\frac{2\pi x}{L}\right) dx = 0$$

UV-VIS-Spektroskopie

Exp.:





Intensitäten

Transmission $T = \frac{I}{I_0}$

molarer Extinktionskoeff.
Absorptions

Lambert-Beersches-Gesetz : $\boxed{I = I_0\, 10^{-\varepsilon c l}}$

Absorption : $A = -\log \frac{I}{I_0} = \varepsilon c l$

$\boxed{A = \varepsilon c l}$