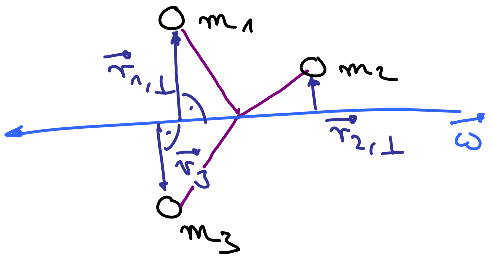
Note Title V3

2. Rotationsspektroskopie

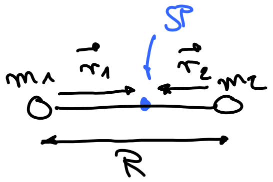
A. Rotation, Trägheitsmoment



$\longrightarrow \; I_\omega = \sum_i m_i |\vec{r}_{i,\perp}|^2$

↑ Rotation um ω

2-atomige Moleküle:



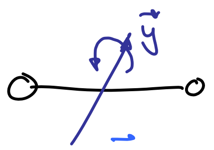
$$m_1 \cdot |\vec{r}_1| + m_2 |\vec{r}_2| = 0$$

$$m_1 r_1 - m_2 \underbrace{r_2}_{} = 0$$

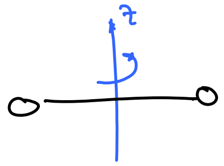
$$r_1 = \frac{m_2}{m_1+m_2} \cdot R = \frac{\mu}{m_1} \cdot R \Longleftarrow \quad m_1 r_1 - m_2 (R - r_1) = 0$$

$$\left(r_2 = \mu / m_2 \cdot R \right)$$

$I_x \approx 0$ (da $r_{i,\perp}$ sehr klein)



$$I_y = m_1 r_1^2 + m_2 r_2^2 = \mu R^2$$

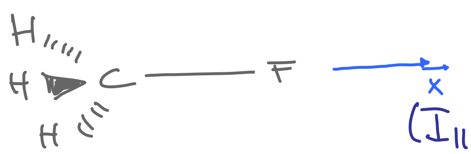


$$I_z = \mu R^2 \qquad \vec{L} = I \vec{\omega}$$

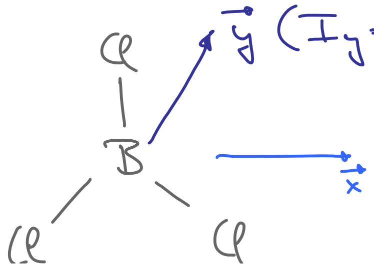
Rotationsenergie: $E_{rot} = \frac{1}{2} I \cdot |\vec{\omega}|^2 = \frac{1}{2} \vec{L} \cdot \vec{\omega} = \boxed{\frac{\vec{L}^2}{2I}}$

↳ keine Rotation um x-Achse (wg $E_{rot} \to \infty$; kein oszillierender Dipol)

Symmetrische Kreisel



$(I_{\|} = I_x)$



$\vec{y}$ $(I_y = I_{\|})$

(prolater Kreisel) $I_y = I_z\,,\quad I_x \neq 0$

(oblate Kreisel) $2I_x = 2I_z = I_y$

Sphärischer Kreisel (CH_4): $I_x = I_y = I_z$

für CH_4: $I_x = \frac{8}{3}\pi\, m_H \cdot R^2_{CH}$

B. QM der Rotation (2-atomig, starr)

$$\hat{H} = -\frac{\hbar^2}{2m}\cdot\nabla^2 + \underbrace{V(\vec{r})}_{=0}$$

mit $\delta r = 0$:
$$-\frac{\hbar^2}{2m}\cdot\frac{1}{r^2}\cdot\Lambda^2\,\psi(\theta,\varphi) = E\,\psi(\theta,\varphi)$$

Lösungen: (1) $E = \ell(\ell+1)\,\hbar^2/2I\,, \quad \ell = 0, 1, \ldots$

$$\Longrightarrow L = \sqrt{\ell(\ell+1)}\,\hbar$$

in der MW-Spektroskopie: $E = J(J+1)\frac{\hbar^2}{2I}$

$$= J(J+1)\,hc\cdot B$$

$$B = \frac{h}{8\pi^2 c I} \Longleftarrow$$ Rotationskonstante, $[B] = cm^{-1}$

(2) Richtungsquantelung von ℓ

$\Rightarrow$ Rotationsniveaus $(2J+1)$-fach entartet, M_J

$\xrightarrow[\text{(stat TD)}]{}$ $\sim (2J+1)\cdot e^{-BhcJ(J+1)/kT}$

$B \sim$ "einige cm^{-1}"

C. Auswahlregeln

$M_{J\to J+1}$ immer sehr ähnlich

$$\mu_{0\to1} = \int Y_{1,0}\cdot q\hat{r}\cdot Y_0$$

$$\mu_{J\to J+2,\; J\to J+3} = 0$$

↳ spezielle Auswahlregel: $\Delta J = \pm 1$ (und $\Delta M_J = 0, \pm 1$)

D. MW-Spektren

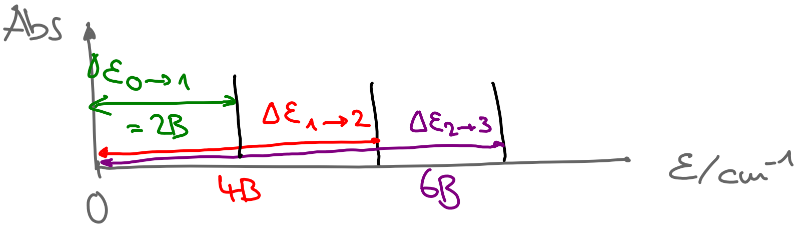
2-atomig, $I_{\parallel} = 0$, $I_{\perp} = \mu R^2$

$$E = hcB\, J(J+1)$$

$$\Delta E_{0\to 1} = E_{J=1} - E_{J=0} = 2B \cdot hc$$

$$\Delta \varepsilon_{0\to 1} = \tilde{\nu}_{0\to 1} = \frac{\Delta E_{0\to 1}}{hc} = 2B$$

$$\tilde{\nu}_{J\to J+1} = 2B(J+1)(J+2) - 2BJ(J+1) = 2B(J^2+3J+2-J^2-J)$$
$$= 2B(J+1)$$



⟸ Rotationslinien sind äquidistant, 2B

Bsp.: CO, $B = 3.843\,\mathrm{cm}^{-1}$

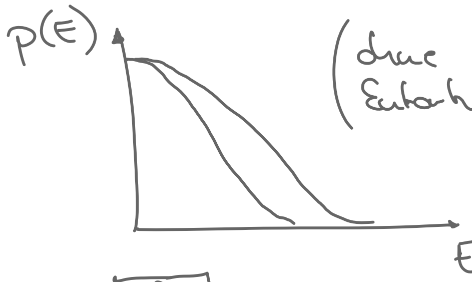
↳ $I_{CO,\parallel} = \frac{h}{8\pi^2 cB} = 14.6 \cdot 10^{-47}\,\mathrm{kg}/\mathrm{m}^2 = \mu R^2_{C-O}$

↳ $R_{C-O} = 113\,\mathrm{pm}$

E. Intensität der Rotationslinien

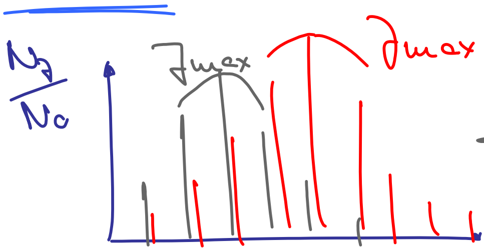
⟶ $\Delta J = \pm 1$ ähnlich wahrscheinlich

⟶ $N_J/N_0 \sim g_J, E_{rot}$



(ohne Entartung)

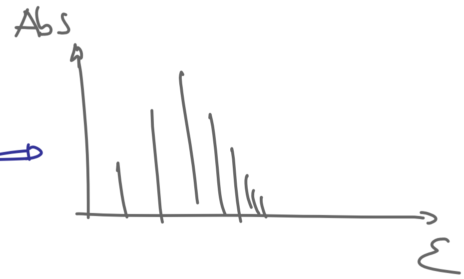
durch $(2J+1)$:



⟶ $J_{max}(B,T) = \sqrt{\frac{kT}{2hcB}} - \frac{1}{2}$

D. Nicht-starrer, 2-atomiger Rotator

Hintergrund: $B \sim \frac{1}{r^2} \leftarrow I = \sum_i m_i r_i^2 \Rightarrow$



$$E_{rot} = \frac{L^2}{2 m r_{eq}^2} - \frac{1}{2} k_{vib} (r - r_{eq})^2$$

$\uparrow$ Gleichgewichtsabstand

$\Downarrow$

SGL liefert: $E(J) = hcBJ(J+1) - hcDJ^2(J+1)^2$

Zentrifugaldehnungskonstante

$$D = \frac{\hbar^3}{4\pi k_{vib} I^2 r^2 c}, \quad [D] = cm^{-1}$$

$\hookrightarrow \boxed{\varepsilon_{J \to J+1} = ?}$

$\hookrightarrow \boxed{k_{vib,CO} = ?}$