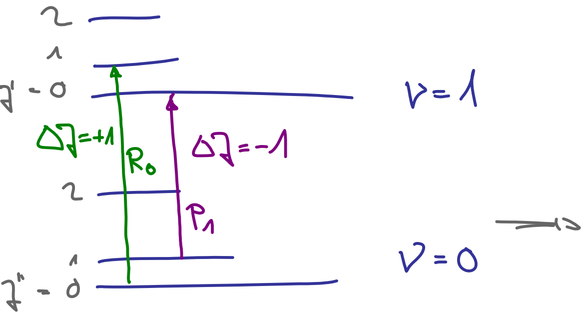
Note Title

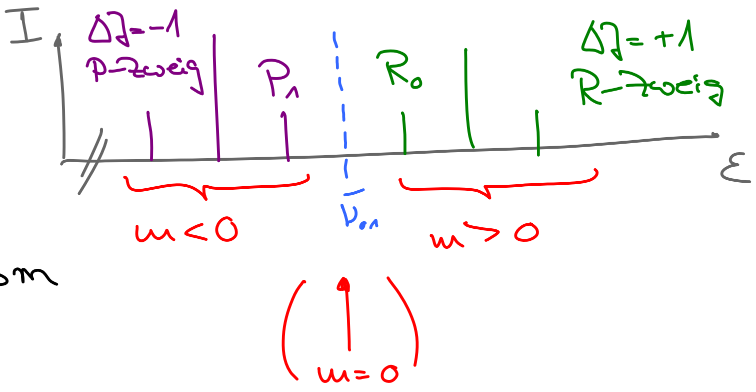
V9

RotVib



Δν = ±1, ±2 ...

ΔJ = ±1 (2-atomig)



$$\hookrightarrow \bar{\nu}_{spect} = \bar{\nu}_{01} + 2Bm$$

$$m = \pm 1, \pm 2 \ldots$$

– Zentrifugaldehnung: $\bar{\nu}_{spect} = \bar{\nu}_{01} + 2B\underline{m} - 4D\underline{m}^3$

– Kopplung Rot/Vib: $B(\nu) = B_e - \alpha \cdot (\nu + \frac{1}{2})$

$$\hookrightarrow \bar{\nu}_{spect} = \bar{\nu}_{01} + \underline{(B_1 + B_0)}\, m + \underline{(B_1 - B_0)}\, m^2 \rightarrow r_0, r_1\,(r_e), \alpha ..$$

Rotationseffekte

(i) mehratomig, linear

- ⊥-Schwingungen: ΔJ = 0 erlaubt, Q-Zweig

  $$\downarrow$$

  $$\bar{\nu}_{spect} = \bar{\nu}_{01} + J(J+1)(B_1 - B_0)$$

  $$\Uparrow$$

  1. Oberton durch Q-Zweig etc.

- ∥-Schwingungen: PR-Zweig
- Kernstatistik

Kernstatistik für Fermionen

$I = 1/2$ $\quad$ ${}^1H - C \equiv C - {}^1H$ $\quad$ $I = 1/2$

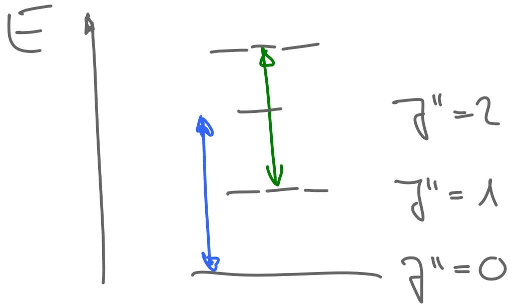
parallel ↑ ↑ $\quad S_{ges} = 1 \longrightarrow$ 3fach gepaart ↑ ↓ $S_{ges} = 0$ → 1-fach

PAULI: $\boxed{\Psi_{ges}}$ für Fermionen muß VZ wechseln beim Austausch

$$\hookrightarrow = \Psi_{el} \cdot \Psi_{vib} \cdot \boxed{\Psi_{rot}} \cdot \boxed{\Psi_{nucl}}$$

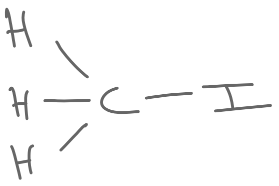
(1) paralleler Spin $(+\uparrow\uparrow+) \Longrightarrow J = 1, 3, 5 \ldots \; (-)$ "ortho-Ethin"

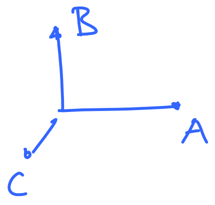
(2) gepaarter Spin $(+\uparrow\downarrow-) \Longrightarrow J = 0, 2, 4 \ldots \; (+)$ "para-Ethin"



→ "alternierende" Intensität beobachtbarer Linien: $\dfrac{g_a}{g_b} = \dfrac{I}{I+1}$

(ii) symmetrische Kreisel





$I_A < I_{B,C}$

$$\varepsilon(J, v, K) = \bar{\nu}_{0n} + BJ(J+1) + (A-B)K^2$$

Parallelbanden:

$\Delta v = \pm 1, \pm 2 ..$

$\Delta J = 0, \pm 1$ → PQR

$\Delta K = 0$

Intensität der Q-Zweiges: $\sim I_A / I_B$ (für $I_A \to 0$ ⇒ "linear")

Senkrechtbanden:

$\Delta v = \pm 1, \pm 2$

$\Delta J = 0, \pm 1$

$\Delta K = 0, \pm 1$

P-Zweig: $\Delta J = -1, \; \Delta K = \pm 1$

(R-Zweig) $\Delta E = \bar{\nu}_{0n} \mp 2B(J+1) + (A-B)(1 \pm 2K)$

Q-Spektrum: $\Delta J = 0,\ \Delta K = \pm 1$

$\hookrightarrow \Delta E = \bar{\nu}_0 + \underline{(A-B)(1 \pm 2K)}$

↳ Linienspektrum mit Abstand = $2(A-B)$

5. Raman-Spektroskopie

Lichtstreuung: – elastisch ≡ RAYLEIGH ($\lambda \gg d_{\text{Teilchen}}$)

$\sim \frac{1}{\lambda^4}$

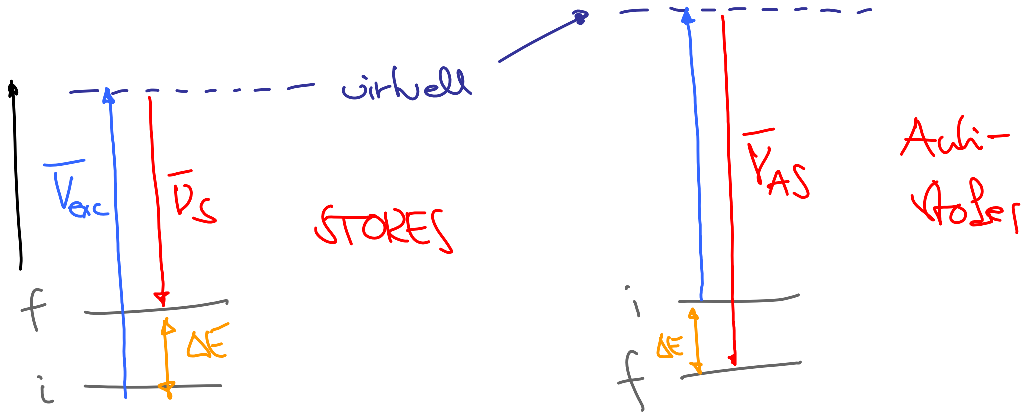
– inelastisch, RAMAN (1923 Smekal, 1928 Raman)

Ramaneffekt

λ_{exc}

(final)

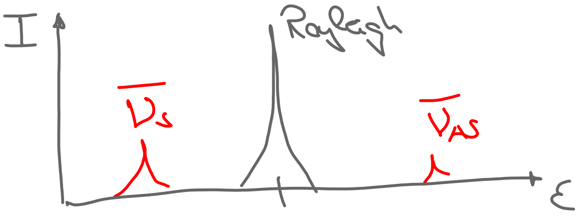
(initial)



$$\bar{\nu}_S = \bar{\nu}_{exc} - \Delta E \qquad \bar{\nu}_{AS} = \bar{\nu}_{exc} + \Delta E$$

$$\boxed{hc\bar{\nu}_{exc} \gg \Delta E}$$

↳



Zur Intensität:

$$\sim N_f / N_i = e^{-\Delta E / kT}$$

$\underline{\bar{\nu}_{exc}\,?}$

– schmalbandiges == monochromatisches Licht

– hohe Anregungsintensitäten

↳ Nd-YAG, 532nm (Linienbreite ∼ $0.1\,\text{cm}^{-1}$), HeNe 632.8nm

⇒ Raman-Spektroskopie:

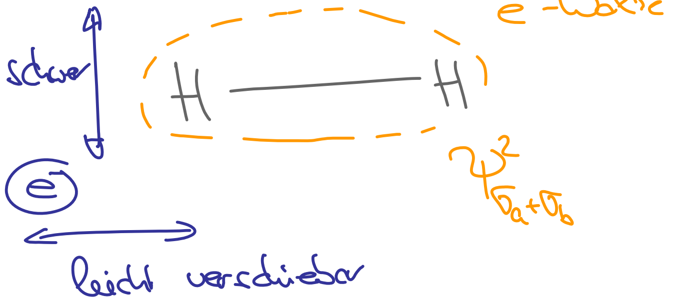
– H_2, N_2 ⇒ Raman-Rotationsspektrum

– IR-inaktive Schwingungen können Raman-aktiv sein

A. Klass. Betrachtung

$\vec{E} \longrightarrow \mu_{ind} = \boxed{\alpha} \cdot |\vec{E}|$

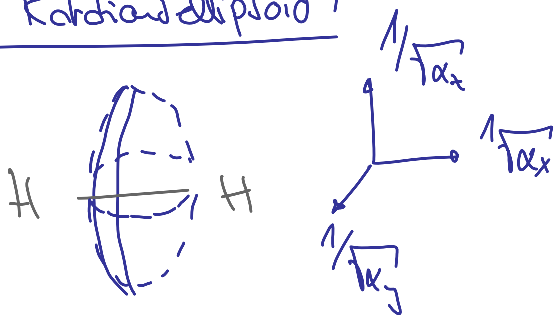
Polarisierbarkeit



$\Downarrow$

$\vec{\mu}_{ind} = \alpha \cdot \vec{E}$, $\alpha = \begin{pmatrix} \alpha_{xx} & \alpha_{xy} & \dots \\ \vdots & \alpha_{yy} & \\ & & \alpha_{zz} \end{pmatrix}$

Polarisationsellipsoid



Ausgangslicht (532nm)

Osz. $\vec{E}$-Feld: $|\vec{E}| = E_0 \cdot \sin \omega_{exc} t$

$\hookrightarrow \mu_{ind} = \alpha \cdot E_0 \cdot \sin \omega_{exc} t$ ⟸ Rayleigh!

α = const

Und bei Resonanz?

H—H $\xrightarrow{\Delta E}$ H———H

$\hookrightarrow$ α verändert sich

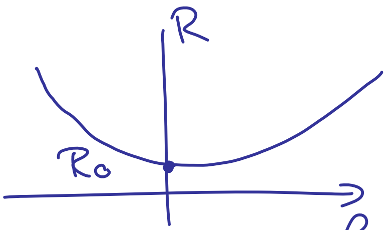
$$\alpha = \alpha_0 + \beta \cdot \sin \omega_{mol} \cdot t$$

$$\sin A \cdot \sin B = \frac{1}{2}\left(\cos(A-B) - \cos(A+B)\right)$$

$$\hookrightarrow \mu_{ind} = \left(\alpha_0 + \beta \sin \omega_{mol} t\right) \cdot E_0 \sin \omega_{exc} t$$

$$= \underbrace{\alpha_0 E_0 \sin \omega_{exc} t}_{\text{Rayleigh}} + \frac{1}{2} E_0 \beta \left(\underbrace{\cos(\omega_{exc} - \overset{\hat{=}\Delta E}{\omega_{mol}})t}_{\text{STOKES}} - \underbrace{\cos(\omega_{exc} + \overset{\hat{=}\Delta E}{\omega_{mol}})t}_{\text{ANTI-STOKES}} \right)$$

B. Raman-Vib



β = Auslenkung

$$R = R_0 + \beta \cdot \sin \omega_{vib} t$$

$$\alpha(R) = \alpha(R_0) + \frac{\partial \alpha}{\partial R}(R - R_0)$$

(Taylor)

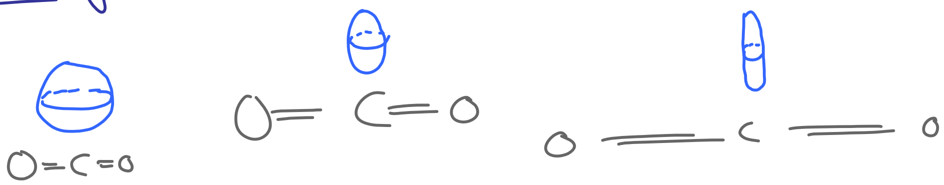
$$\mu_{ind} = \alpha|\vec{E}| = \underbrace{\alpha(R_0) \cdot E_0 \sin \omega_{exc} t}_{\text{Rayleigh}} + \frac{1}{2} E_0 \beta \cdot \frac{\partial \alpha}{\partial R} \left(\underbrace{\cos(\omega_{exc} - \omega_{vib})t}_{\text{Stokes}} - \cos(\omega_{exc} + \omega_{vib})t \right)$$

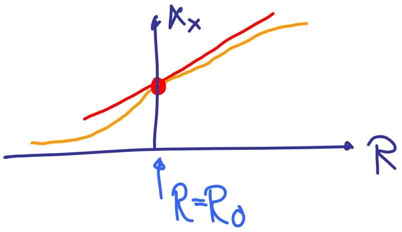
Anti-Stokes

⟹ AUSWAHLREGEL RAMAN-VIB. $\frac{\partial \alpha}{\partial R} \neq 0$

⟹ H_2, N_2 : $\frac{\partial \alpha}{\partial R} \neq 0$, Raman-aktiv

Symm. Valenzschwingung von CO_2 :





$\frac{\partial \alpha}{\partial R}(R_0) \neq 0$

⟹ Symmetrieanalyse?