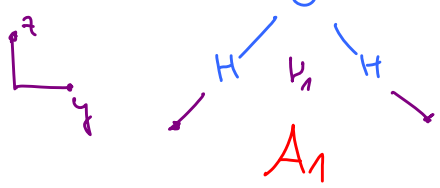
V7

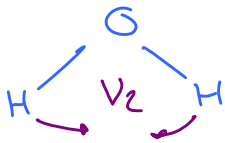
Note Title

(WDH)

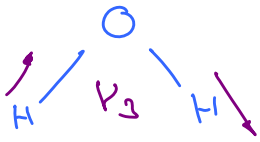


A_1

	E	C_2	σ_{xz}	σ_{yz}
	1	1	1	1



A_1



	1	−1	−1	+1

B_2

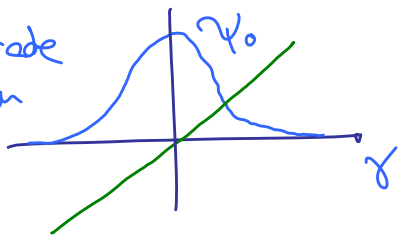
Auswahlregel: "allg." (IR) $\partial\mu/\partial t \neq 0$

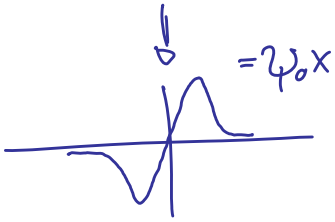
$$\hookrightarrow \mu_{0\to 1}^{(x)} = \langle \psi_1 | \hat{\mu}_x | \psi_0 \rangle \neq 0$$

$$= q \cdot \langle \psi_1 | \hat{x} | \psi_0 \rangle$$

$$= q \cdot \int \psi_1^* \cdot x \cdot \psi_0 \, d\tau$$

$$\int x \psi_0 \, d\tau = \begin{cases} \psi_0 = N \cdot \underbrace{1}_{H_0(\gamma)} \cdot e^{-\gamma^2/2} & \leftarrow \text{gerade Funktion} \\ x & \leftarrow \text{ungerade Funktion} \end{cases}$$





$\Rightarrow$ ψ_1 muß ungerade in x-Richtung sein, damit $\mu_{0\to 1} \neq 0$!

"Übersetzung" in Gruppentheorie:

$$\boxed{\Gamma(\psi_0) \times \Gamma(x) \times \Gamma(\psi_1) = A} \quad (A_1 \text{ in } C_{2v})$$

↳ für IR-aktive Schwingung $\psi_0 \xrightarrow{\mu_x} \psi_1$

äquivalente Aussage zu ?

$\langle \psi_1 | \mu_x | \psi_0 \rangle \neq 0$.

H_2O, ν_1 (A_1)

für μ_x (mit $\Gamma(x) = B_1$):

↳ $\mu_{0\to 1}^{(x)} = 0$

$\Gamma(\psi_0)$	↑	↑	↑	↑
$\Gamma(x)$	↑	↓	↑	↓
$\Gamma(\psi_1)$	↑	↑	↑	↑
	↑	↓	↑	↓ ⇐ B_1 ↯

für $\mu_{0\to 1}^{(z)}$:

$\Gamma(\psi_0)$	↑	↑	↑	↑
$\Gamma(z)$	↑	↑	↑	↑
$\Gamma(\psi_1)$	↑	↑	↑	↑
	↑	↑	↑	↑ ⇐ A_1 ✓

$\mu_{0\to 1}^{(z)} \neq 0$ IR-erlaubt !

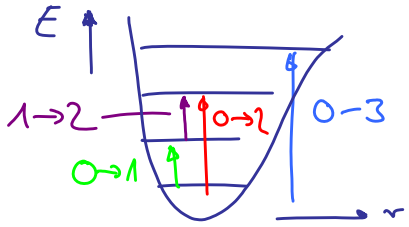
H_2O, ν_3 (B_2)

$\mu_{0\to 1}^{(y)}(\nu_3) \neq 0$

$\Gamma(\psi_0)$	↑	↑	↑	↑
$\Gamma(y)$	↑	↓	↓	↑ ← B_2
$\Gamma(\psi_1)$	↑	↓	↓	↑
	↑	↑	↑	↑ ⇐ A_1 ✓

(ii) Obertöne

$\Delta E = 2\cdot\bar{\nu}_i,\ 3\cdot\bar{\nu}_i$



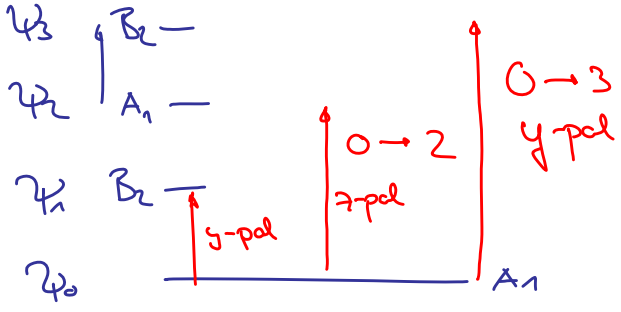
$1 \to 2$: heiße Bande
$0 \to 1$: Fundamentale
$0 \to 2$: 1. Oberton

Symmetriebetrachtung:

(am Bsp. $\nu_3(H_2O)$, B_2)

↳ $0 \to \nu$: $(B_2)^\nu$

$\Gamma(\psi_0) = A_1$
$\Gamma(\psi_1) = B_2$
$\Gamma(\psi_2) = B_2 \times B_2 = A_1$
$\Gamma(\psi_3) = B_2 \times B_2 \times B_2 = B_2$



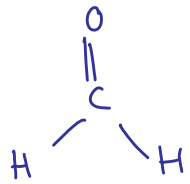
(iii) Kombinationsschwingungen

$\Delta\varepsilon = \nu_1 \pm \nu_2$, $\nu_1 \pm 2\nu_2$ etc.

Bsp.: ν_1 und ν_3 von H_2O : $\Gamma((\nu_1+\nu_3)) = A_1 \times B_2 = B_2$
(A_1) (B_2)

↪ $(\nu_1+\nu_3)$ ist IR-erlaubt, y-polarisiert (B_2)

Bsp.:



$\Gamma_{vib} = 3A_1 + B_1 + 2B_2$

Kombination: $(\nu_{B_1} + \nu_{B_2})$ erlaubt?

↪ $B_1 \times B_2$: | 1 1 −1 −1 | A_2 nicht IR-erlaubt

Hinweis: CH_2F_2 , Γ_{vib} enthält A_2-Darstellung

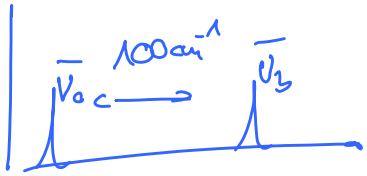
(iv) Fermi-Resonanz

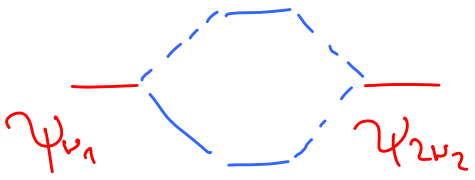
Bsp:

$\tilde{\nu}_1 = 1330\,cm^{-1}$
$2\tilde{\nu}_2 = 1334\,cm^{-1}$

Fermi-Resonanz

Beobachtung:





Intensitätsverhältnis: $\delta = \frac{I(\nu_a)}{I(\nu_b)}$, $\nu_{1/2} = \left(\frac{\nu_a \pm \nu_b}{2}\right) \pm \left(\frac{\nu_a - \nu_b}{2}\right)\left(\frac{\delta-1}{\delta+1}\right)$

(>=c=O)