

Symmetrieanalyse:  $\Gamma(\psi_0) \times \Gamma(\alpha_{ij}) \times \Gamma(\psi_1) \stackrel{!}{=} A$   
 (Raman-UIB)  $x^2, \dots, x_y, xz, \dots, (x^2-y^2)$

Zu CO<sub>2</sub>:  $\Gamma_{\text{vib}} = A_{1g} + A_{1u} + E_{1u}$  bzgl. Invarianz-  
 (D<sub>∞h</sub>) (Σ<sub>g</sub><sup>+</sup> + Σ<sub>u</sub><sup>+</sup> + Π<sub>u</sub>) zentrum: g/u

IR :	—	x	x	}	"Aktionverbot"
Raman :	(x)	—	—		

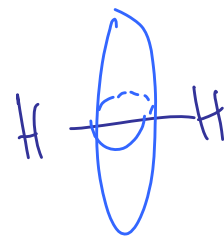
(Raman-Schwung: Parität = g)

Ethin: H-C≡C-H  
 (D<sub>∞h</sub>)  $\Gamma_{\text{vib}} = 2A_{1g} + A_{1u} + E_{1g} + E_{1u}$

IR	—	x	x	—
Raman	x	—	—	x

C. Raman - Rotation

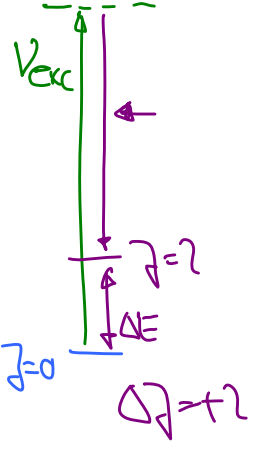
Voraussetzung: α anisotrop



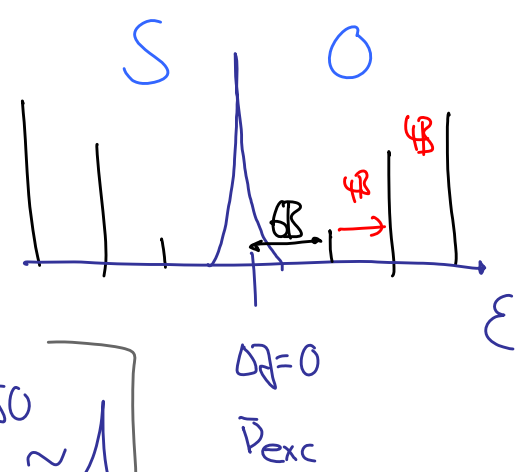
↳ α moduliert mit 2. Pot

↳ ΔJ = ±2

QM:  $\epsilon(J) = B J(J+1) - D J^2(J+1)^2$   
 → ΔJ = 0



$\Rightarrow \Delta J = +2 \rightarrow S\text{-Zweig}$   
 $\Delta J = -2 \rightarrow O\text{-Zweig}$



$$\Delta \epsilon = B(4J+6)$$

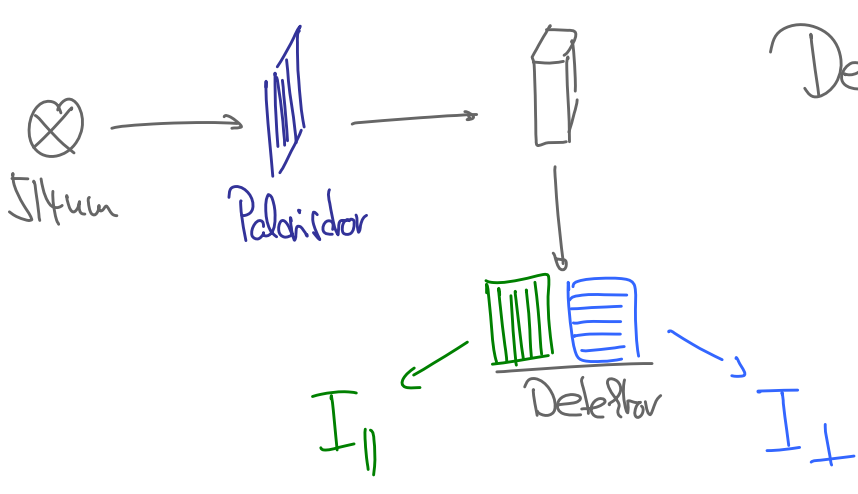
$$\left| \frac{N_1}{N_0} = e^{-4B/(kT/hc)} = e^{-1/50} \sim 1 \right|$$

$(1 \text{ cm}^{-1} \sim B, 300 \text{ K} \rightarrow kT \sim 200 \text{ cm}^{-1})$

→ Kerustabilisiert,  $N_2/H_2$

↳ Raman-Schwingungsrotationspektroskopie (Feinstruktur)

D. Polarisation von Ramanlinien



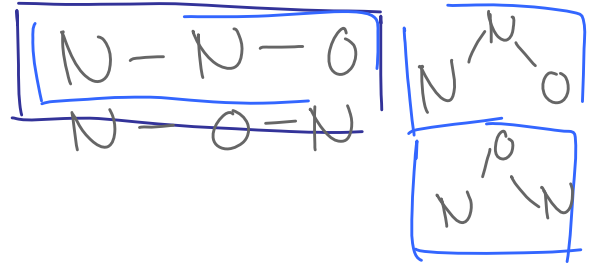
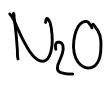
Depolarisationsgrad

$$\rho = I_{\perp} / I_{\parallel}$$

$I_{\perp} \rightarrow 0, \rho \rightarrow 0$   
 $\Rightarrow$  polarisierte Raman-Emission

↳ polarisierte → symm. Schwingungen  
 (depolarisiert → asymm. " )

⇒ Molekülstruktur?



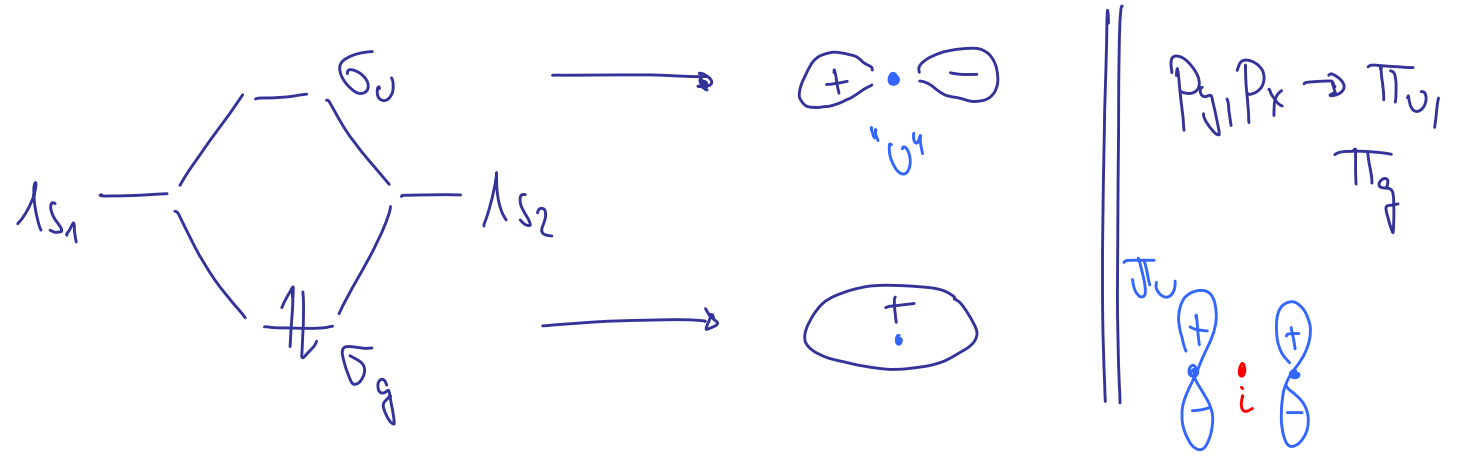
$\tilde{\nu}/\text{cm}^{-1}$	IR	Raman	
589	PQR	—	←
1285	PR	pol.	← Symm.
2224	PR	depol.	← asymm.

	IR	Raman
UIB	$\Delta v = \pm 1, \pm 2 \dots$ Kombination	Grundschwingung
Zweig/Polarisation	PR, PQR / —	SQO / pol / depolarisiert
Intensität	$\mu \uparrow \rightarrow \frac{\partial \mu}{\partial R} \uparrow$	$\frac{\partial \alpha}{\partial R} \uparrow$ (besonders bei $\mu \uparrow$ )

## 6. Molekülspektroskopie

Molekülorbitale ⇒ HMO

AO → MO :  $\psi_{MO_{\pm}} = N(\psi_A \pm \psi_B)$   
(LCAO)

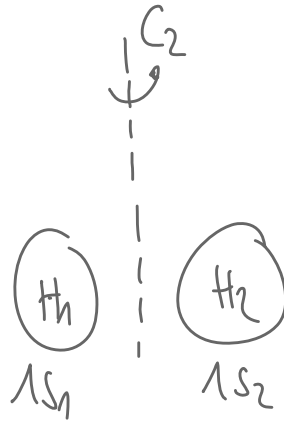
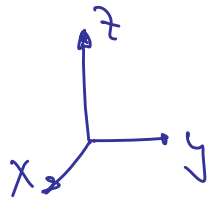


# Symmetrieorientierte MO's (SALC)

z.B.  $H_2O$  ( $C_{2v}$ )

→ Atomorbitale  $\underbrace{1s_1, 1s_2}_{2H}$ ,  $\underbrace{2s, 2p_x, 2p_y, 2p_z}_O$  |  $6AO$

(i) Wasserstoff



	E	$C_2$	$\sigma_{xz}$	$\sigma_{yz}$	
	2	0	0	2	
$\Leftrightarrow \Gamma_{(2H)} = A_1 + B_2$					

alternativ:

$1s_1 + 1s_2$

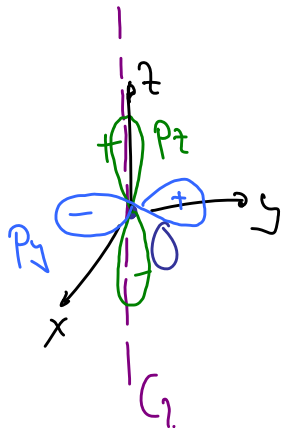


$1s_1 - 1s_2$

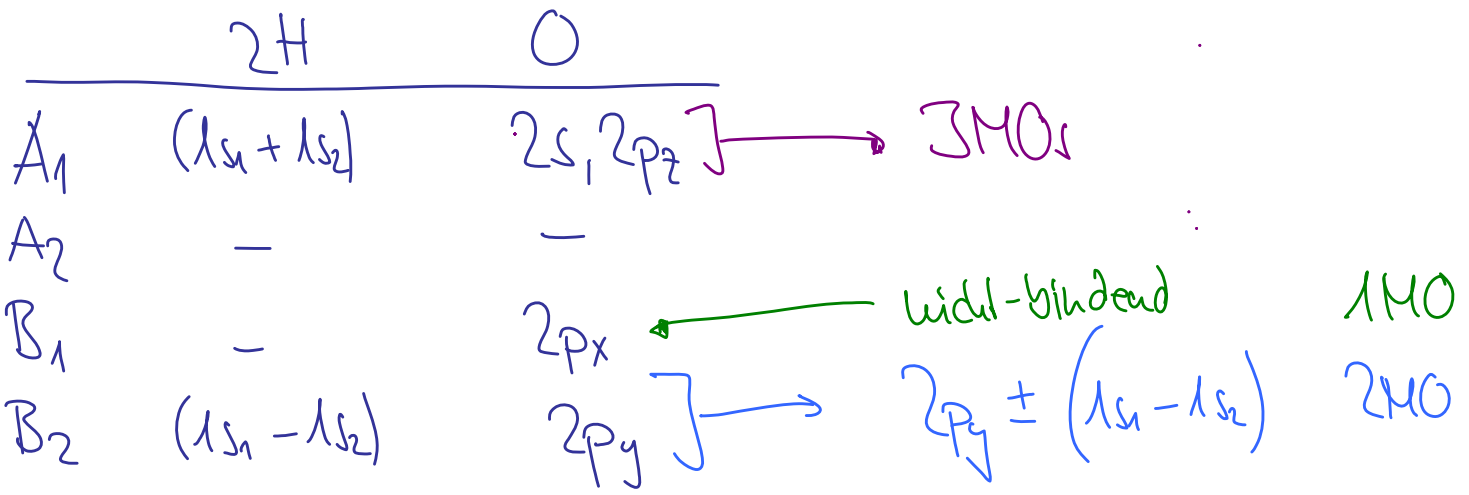


1	1	1	1	$A_1$
1	-1	-1	1	$B_2$

(ii) Sauerstoff



	E	$C_2$	$\sigma_{xz}$	$\sigma_{yz}$	
2s	1	1	1	1	$A_1$
2p_z	1	1	1	1	$A_1$
2p_y	1	-1	-1	1	$B_2$
2p_x	1	-1	1	-1	$B_1$



Elektronische Übergänge in H<sub>2</sub>O?

B<sub>1</sub> → A<sub>1</sub>?

$$\Gamma(2p_x) \times \Gamma(x_{1g1}) \times \Gamma(\psi_1) = A_1$$

B<sub>1</sub>
A<sub>1</sub>

A <sub>1</sub>	1	1	1	1
? B <sub>1</sub>	1	-1	1	-1
B <sub>1</sub>	1	-1	1	-1
A <sub>1</sub>	1	1	1	1

← B<sub>1</sub>  
↑  
Symmetrieerhalt, x

B<sub>1</sub> → B<sub>2</sub>?

B <sub>1</sub>	1	-1	1	-1
? B <sub>2</sub>	1	1	-1	-1
B <sub>2</sub>	1	-1	-1	1
A <sub>1</sub>	1	1	1	1

A<sub>2</sub>, aber keine (x,y,z)-Komponente in A<sub>2</sub>  
→ el. Übergang verboten