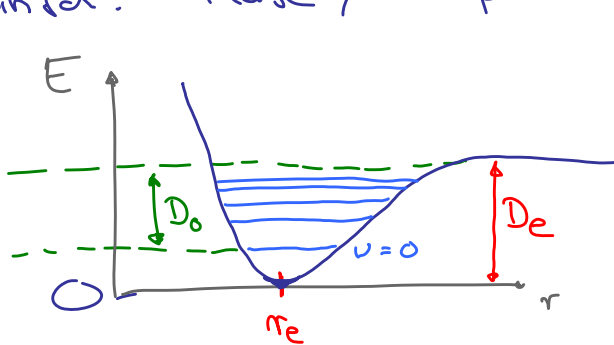


B. Anharmon. Oszillat.

Beobachtung: Dissociation, Übergänge $0 \rightarrow 2$, $0 \rightarrow 3$, abnehmende Schwingungsfrequenz

empirisch: Morse, $E_{\text{pot}}(r) = D_e \left(1 - e^{-\alpha(r-r_e)}\right)^2$



$$\alpha = \sqrt{\frac{\mu}{2D_e}} \cdot \omega_e^2$$

$$x_e = \frac{h\nu_e}{4D_e}$$

QM: $E(v) = (v + \frac{1}{2})h\nu_e - (v + \frac{1}{2})^2 \cdot x_e \cdot h\nu_e$

Auswahlregel: $\Delta v = \pm 1, \pm 2, \pm 3, \dots$ ($\mu_{0 \rightarrow 1} \gg \mu_{0 \rightarrow 2} \dots$)

Vergleich

$$E(v) = (v + \frac{1}{2}) \cdot \bar{D}_{0, \text{harm}}$$

$$\Delta E = \bar{D}_{0, \text{harm}}$$

$$E(v) = \bar{D}_e (v + \frac{1}{2}) \cdot [1 - x_e (v + \frac{1}{2})]$$

$$\Delta E = \bar{D}_e [1 - 2x_e (v + 1)]$$

($v \rightarrow v+1$)

$$\tilde{D}_v = \bar{D}_e [1 - x_e (v + \frac{1}{2})]$$

$\rightarrow \tilde{D}_v$ nimmt ab mit $v \uparrow$

$$\rightarrow \tilde{D}_0 = \bar{D}_e \cdot (1 - \frac{1}{2}x_e) \quad (\neq \bar{D}_{0, \text{harm}}?)$$

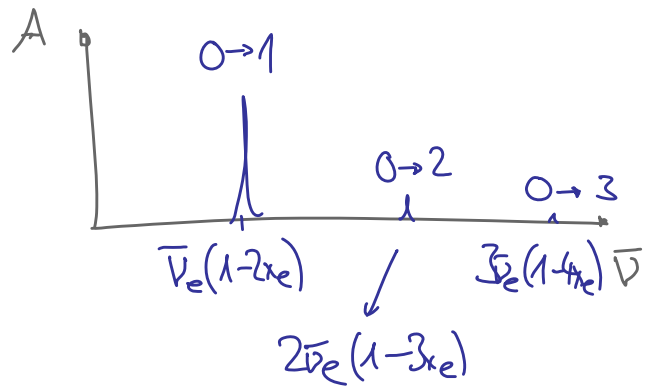
für "E=0" ($v = -\frac{1}{2}$): " $\tilde{D}_{-\frac{1}{2}}$ " = \bar{D}_e

$\hookrightarrow r_e, \bar{D}_e$ sind reine Reduzierungsgrößen der anharmon. Osz.

ANWENDUNGEN

(i) Bestimmung von x_e, \bar{v}_e

$$\Delta E(0 \rightarrow \nu) = \nu \bar{v}_e (1 - x_e (\nu + 1))$$



HCE: $\bar{v}_{0 \rightarrow 1} = 2886 \text{ cm}^{-1}$,

$\bar{v}_{0 \rightarrow 2} = 5668 \text{ cm}^{-1}$, $\bar{v}_{0 \rightarrow 3} = 8347 \text{ cm}^{-1}$

$\Rightarrow \bar{v}_e = 2990 \text{ cm}^{-1}$, $x_e = 0.0174$, $D_e = \frac{h\nu_e}{4x_e} = 5.3 \text{ eV}$

(ii) höchstes Schwingungsniveau?

$$E_{\text{pot}}(\nu_{\text{max}}) = D_e \cdot h c \bar{v}_e \left(\left(\nu_{\text{max}} + \frac{1}{2} \right) - \left(\nu_{\text{max}} + \frac{1}{2} \right)^2 \cdot x_e \right)$$

$\hookrightarrow \nu_{\text{max}}(\text{HCl}) = 22$ (harmonisch: " $\nu_{\text{max}} = 14$ ")

(iii) Dissociationsenergie vs. R_{vib} : $D_e = \frac{h}{4x_e} \cdot \sqrt{\frac{R_{\text{vib}}}{\mu}}$

C. Isotopeneffekt

$\hookrightarrow R_{\text{vib}}$ sinkt bei Isotopenaustausch

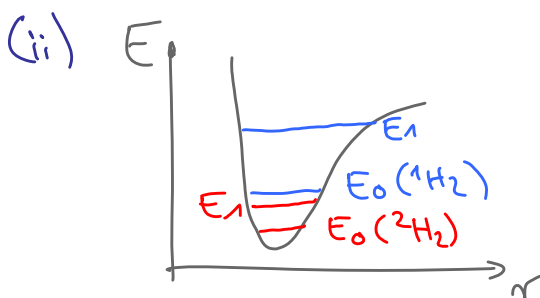
$$D_0 = D_e - \frac{1}{2} h \nu$$

$\nu = \sqrt{\frac{R_{\text{vib}}}{\mu}}$

(i) Nullpunktenergie-Nachweis

$D_0(^2\text{H}_2) = 4.55 \text{ eV}$, $D_0(^1\text{H}_2) = 4.47 \text{ eV}$

$\Delta D_0 = \Delta E_0 = \Delta \frac{1}{2} h \nu$ \downarrow 0.08 eV, 621 cm^{-1}

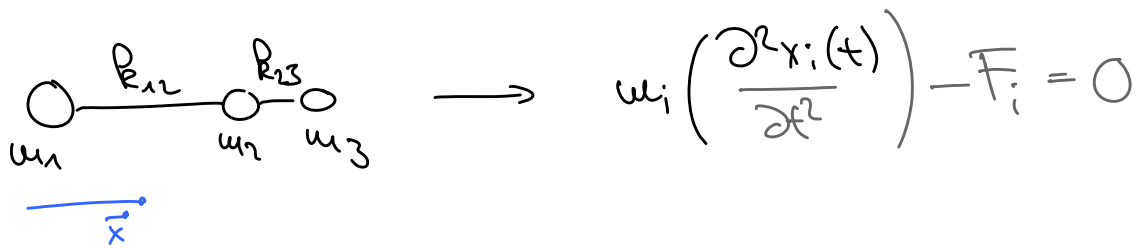


$\Rightarrow \bar{v}_{0 \rightarrow 1} (^2\text{H}_2) = 2990 \text{ cm}^{-1}$
 $\bar{v}_{0 \rightarrow 1} (^1\text{H}_2) = 4160 \text{ cm}^{-1}$ } $\Delta E = 1170 \text{ cm}^{-1}$

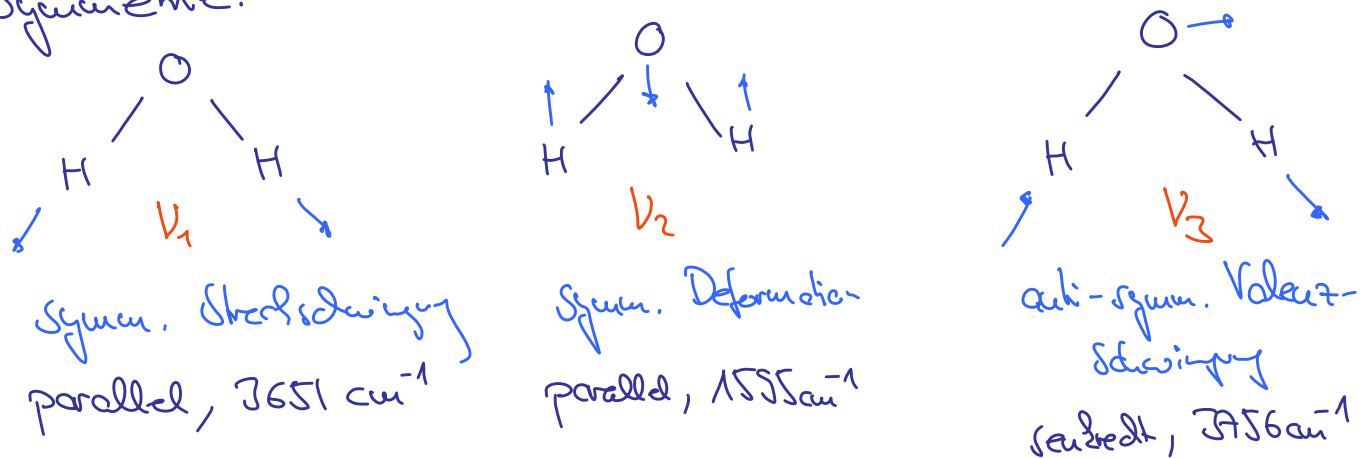
$\hookrightarrow \frac{\bar{v}_{0 \rightarrow 1} (^2\text{H}_2)}{\bar{v}_{0 \rightarrow 1} (^1\text{H}_2)} = \sqrt{\frac{\mu(^1\text{H}_2)}{\mu(^2\text{H}_2)}} = 0.719$
 $(\rightarrow R \sim \text{const})$

D. Schwingung mehratomiger Moleküle

(i) Klass. Mechanik:



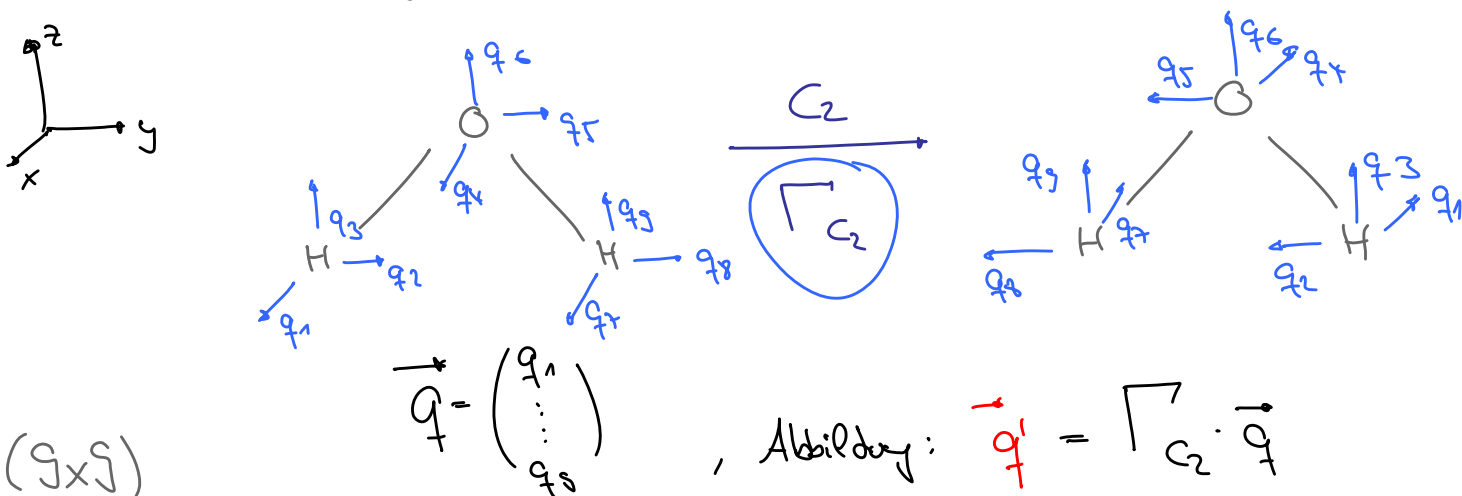
(ii) Symmetrie:



(iii) GRUPPENTHEORIE

① Punktgruppe bestimmen: C_{2v} , 4 Symmetrieelemente

② Verschiebungsvektoren



(9×9)

$$\Gamma_{C_2} = \begin{pmatrix} 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & -1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 \end{pmatrix}$$

Diagonalelemente: "Charakter" von H_2O bzgl. C_2 -Drehung

$$\chi_{C_2}(H_2O) = \sum_{i=1}^3 (\Gamma_{C_2})_{ii} = -1$$

$$\hookrightarrow \chi_E = 3, \chi_{\sigma_{xz}} = +1, \chi_{\sigma_{yz}} = +3$$

	E	C_2	σ_{xz}	σ_{yz}
$\chi(H_2O)$	3	-1	1	3

Charaktere der Symmetrieoperationen für H_2O

③ "Ausreduzieren" $\rightarrow \Gamma_{ges} = C_1 \cdot A_1 + C_2 \cdot A_2 + C_3 \cdot B_1 + C_4 \cdot B_2$

$$\hookrightarrow C_1(A_1) = \frac{1}{h} \cdot \sum_{j=1}^4 \left(\underbrace{n(R_j)} \cdot \underbrace{\chi(R_j, A_1)} \cdot \underbrace{\chi(R_j, H_2O)} \right)$$

Gruppenordnung
 $h=4$
 H_2O, C_{2v}

für alle $j=1 \dots 4$
Symmetrieklassen R_j

Multiplizität
von R_j

Charakter von
 R_j in A_1 (für C_1 ?)

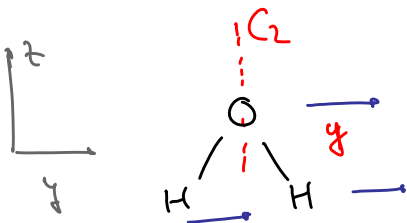
$$\Rightarrow C_1 = \frac{1}{4} \cdot (1 \cdot 1 \cdot 3 + 1 \cdot 1 \cdot (-1) + 1 \cdot 1 \cdot 1 + 1 \cdot 1 \cdot 3) = 3$$

$$\Gamma_{ges} = 3A_1 + A_2 + 2B_1 + 3B_2$$

reduzierte Darstellung
aller FG von H_2O

(mit $\Gamma_{ges} = \Gamma_{trans} + \Gamma_{rot} + \Gamma_{vib}$)

* Translations-FG



$$\Rightarrow \begin{array}{c|cccc} & E & C_2 & \sigma_{xz} & \sigma_{yz} \\ \hline & 1 & -1 & -1 & 1 \end{array} B_2$$

andere Betrachtung der Translation in z, x liefert:

$$\Gamma_{\text{trans}} = A_1 + B_1 + B_2$$

(z) (x) (y)

* Rotations-FG:

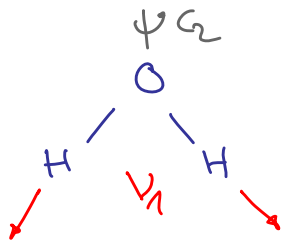
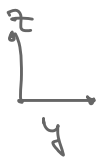
(ablesen aus G_{2v})

$$\Gamma_{\text{rot}} = A_2 + B_1 + B_2$$

(R_z) (R_y) (R_x)

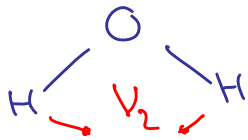
* Schwingungs-FG:

$$\Gamma_{\text{vib}} = 2A_1 + B_2$$

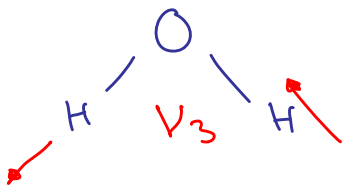


$$\chi(\nu_1) \quad | \quad 1 \quad 1 \quad 1 \quad 1$$

A_1



A_1



$$\chi(\nu_3) \quad | \quad 1 \quad -1 \quad -1 \quad 1$$

B_2

ANMERKUNG: $\chi_{C_3} = 0$ (← Symmetrieanalyse von NH_3)