Schwingungsspektro

08.06.18

5.~~4~~ Theoretische Verfahren

5.1 Interne Koordinaten

z.B. Δr, $\Delta\alpha$, etc.: direkteres Bezug zu Moleküleigenschaften

allg: Anzahl interner Koordinaten $\geq 3N-6$ $(3N-5)$

Bsp.: NH_3 – Normalschwingungen $3N-6=6$

interne Koordinaten: $\Delta r_1, \Delta r_2, \Delta r_3, \Delta\alpha_{12}, \Delta\alpha_{13}, \Delta\alpha_{23}$

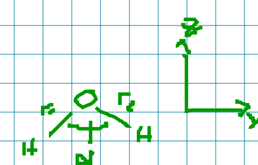
↳ Symmetrie der Schwingungen?

	C_{3v}	E	$2C_3$	$3\sigma_v$
reduzible Darstellung →	Γ^{ic}	6	0	2

Red → $\Gamma^{ic} = 2\Gamma_{A_1} \oplus 2\Gamma_E$ (→ vgl. ÜB 7)

Bsp. H_2O

interne Koord.: $\Delta r_1, \Delta r_2, \Delta\alpha$



C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v'(yz)$
Γ^{ic}	3	1	1	3

Red → $\Gamma^{ic} = 2\Gamma_{A_1} \oplus \Gamma_{B_2}$

5.2 Symmetriekoordinaten

Vorteil: $\hat{H}_{vib}$ = invariant → $\psi_{vib} \sim \Gamma^{ic}$

Bsp.: H_2O – woher Symmetriekoord.

↳ Projektionsoperatoren

Schwingungsspektro 08.06.18

5. Theoretische Verfahren

5.1 Interne Koordinaten

z.B. Δr, $\Delta\alpha$, etc.: direkteren Bezug zu Moleküleigenschaften

__allg:__ Anzahl interner Koordinaten $\geq 3N-6$ $(3N-5)$

__Bsp.:__ NH_3 – Normalschwingungen $3N-6 = 6$

interne Koordinaten: $\Delta r_1, \Delta r_2, \Delta r_3, \Delta\alpha_{12}, \Delta\alpha_{13}, \Delta\alpha_{23}$

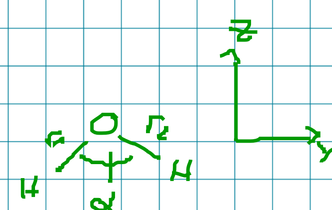
↳ Symmetrie der Schwingungen?

C_{3v}	E	$2C_3$	$3\sigma_v$
reduzible Darstellung → Γ^{ic}	6	0	2

Red → $\Gamma^{ic} = 2\Gamma_{A_1} \oplus 2\Gamma_E$ (→ vgl. ÜB 7)

__Bsp.:__ H_2O

interne Koord.: $\Delta r_1, \Delta r_2, \Delta\alpha$



C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v'(yz)$
Γ^{ic}	3	1	1	3

Red → $\Gamma^{ic} = 2\Gamma_{A_1} \oplus \Gamma_{B_2}$

5.2 Symmetriekoordinaten

Vorteil: $\hat{H}_{vib}$ = invariant ⇝ $\psi_{vib} \sim \Gamma^{ic}$

__Bsp.:__ H_2O – woher Symmetriekoord.

↳ Projektionsoperatoren

$$\hat{P}^{\Gamma_i} = \sum_R \chi(R)(R)$$

angewand auf Koord., Vektor, etc.

$$\hat{P}^{A_1}(\Delta r_1) = \Delta r_1 + \Delta r_2 + \Delta r_2 + \Delta r_1 = 2(\Delta r_1 + \Delta r_2)$$

symm. Streckschw.

$$\hat{P}^{B_2}(\Delta r_1) = \Delta r_1 - \Delta r_2 - \Delta r_2 + \Delta r_1 = \cancel{2\Delta r_1} \quad 2(\Delta r_1 - \Delta r_2)$$

$\hookrightarrow$ $S_1 = \frac{\Delta r_1 + \Delta r_2}{\sqrt{2}}$ $\underline{A_1}$

$S_2 = r\,\Delta\alpha$ $\underline{A_1}$ $\underline{r = \sqrt{r_1 r_2}}$

$S_3 = \frac{\Delta r_1 - \Delta r_2}{\sqrt{2}}$ $\underline{B_2}$

$\longrightarrow$ ÜB 8

=> bei $2C_3$ -> 2x Drehen!

5.3 Normalmodenanalyse (GF-Matrix-Methode)

T -> Massen, Geometrie

V -> Ww (Kraftkonstanten)

Bsp.: H_2O - interne Koordinaten

$$V = \frac{1}{2} f_{11}(\Delta r_1)^2 + \frac{1}{2} f_{22}(\Delta r_2)^2 + \frac{1}{2} f_{33}(r\Delta\alpha)^2$$
$$+ f_{12}(\Delta r_1)\cancel{(r\Delta\alpha)}(\Delta r_2) + f_{13}(\Delta r_1)(r\Delta\alpha) + f_{23}(\Delta r_2)(r\Delta\alpha)$$

Symmetriekoordinaten:

$$\Delta r_1 = \frac{S_1 + S_3}{\sqrt{2}} \;;\; r\Delta\alpha = S_2 \;;\; \Delta r_2 = \frac{S_1 - S_3}{\sqrt{2}}$$

$$V(S_1, S_2, S_3) = \underbrace{\frac{(f_{11} + f_{12})S_1^2}{2}}_{\text{symm. Streckschw.}} + \underbrace{\frac{(f_{11} - f_{12})S_3^2}{2}}_{\text{asymm. Streckschw.}}$$

$$+ \underbrace{\frac{f_{33} S_2^2}{2}}_{\text{Biegeschw.}} \qquad + \underbrace{\sqrt{2}\, f_{13} S_1 S_2}_{\text{Ww. Streck-Biege}}$$

$- S_1 S_3$? ~ nicht invariant, weil nicht totalsymm.
↳ darf nicht vorkommen

Transformation in Symmetriekoord.

$$\begin{pmatrix} S_1 \\ S_2 \\ S_3 \end{pmatrix} = \begin{pmatrix} \frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} & 0 \\ 0 & 0 & 1 \\ \frac{1}{\sqrt{2}} & -\frac{1}{\sqrt{2}} & 0 \end{pmatrix} \begin{pmatrix} \Delta r_1 \\ \Delta r_2 \\ \Delta r_3 \end{pmatrix}$$

$$\vec{S} = U \cdot \vec{r} \quad \leftrightarrow \quad \vec{r} = U^{-1} \cdot \vec{S} = U^{+} \cdot \vec{S}$$

$$\begin{pmatrix} \Delta r_1 \\ \Delta r_2 \\ \Delta r_3 \end{pmatrix} = \begin{pmatrix} \frac{1}{\sqrt{2}} & 0 & \frac{1}{\sqrt{2}} \\ \frac{1}{\sqrt{2}} & 0 & -\frac{1}{\sqrt{2}} \\ 0 & 1 & 0 \end{pmatrix} \begin{pmatrix} S_1 \\ S_2 \\ S_3 \end{pmatrix}$$

V in Matrixschreibweise

$$V(\Delta r_1, \Delta r_2, r\Delta\alpha) = \frac{1}{2} (\Delta r_1, \Delta r_2, r\Delta\alpha) \begin{pmatrix} f_{11} & f_{12} & f_{13} \\ f_{12} & f_{22} & f_{13} \\ f_{13} & f_{13} & f_{33} \end{pmatrix} \begin{pmatrix} \Delta r_1 \\ \Delta r_2 \\ r\Delta\alpha \end{pmatrix}$$

$$\frac{1}{2} \cdot r^{+} \cdot F_r \cdot r$$

V in Symmetriekoordinaten

A_1

$$V(S_1, S_2, S_3) = \frac{1}{2} (S_1, S_2, S_3) \begin{pmatrix} f_{11}+f_{12} & \sqrt{2} f_3 & 0 \\ \sqrt{2} f_3 & f_{33} & 0 \\ 0 & 0 & f_{11}-f_{12} \end{pmatrix} \begin{pmatrix} S_1 \\ S_2 \\ S_3 \end{pmatrix} \qquad f_3 = f_{13}$$

$$\frac{1}{2} \cdot S^{+} \quad F_S \quad S$$

B_2

$$V(\Delta r_1, \Delta r_2, r\Delta\alpha) = V(S_1, S_2, S_3)$$

$$V = \frac{1}{2} r^t F_r \cdot r = \frac{1}{2} (U^t S)^t F_r U^t S$$
$$= \frac{1}{2} U S^t F_r U^t S$$
$$= \frac{1}{2} S^t \underbrace{U F_r U^t}_{F_S} S = \frac{1}{2} S^t F_S S$$

$$V = \frac{1}{2} (S_1, S_2, S_3) \begin{pmatrix} F_{11} & F_{12} & 0 \\ F_{12} & F_{22} & 0 \\ 0 & 0 & F_{33} \end{pmatrix} \begin{pmatrix} S_1 \\ S_2 \\ S_3 \end{pmatrix}$$

$$F_{11} = f_{11} + f_{12} \ldots$$

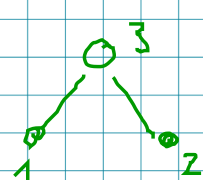
ursprünglich $3 \times 3 \rightarrow 2 \times 2$ & 1×1

A_1 B_2

$$V \rightarrow \frac{1}{2} S^t F_S S$$
$$T \rightarrow \frac{1}{2} \dot{S}^t G^{-1} \dot{S}$$

$\downarrow$

Inverse der G-Matrix $G_S = S m^{-1} S^t$



$$m^{-1} = \begin{pmatrix} \mu_1 & 0 & 0 \\ 0 & \mu_1 & 0 \\ 0 & 0 & \mu_3 \end{pmatrix}$$

$\mu_1 = \frac{1}{m_1}$

$\mu_3 = \frac{1}{m_3}$

Normalschwingungen?

$$H = T + V$$

Lagrange Bewegungsgleichung

$$\rightarrow \frac{d}{dt}\left(\frac{\partial T}{\partial \dot{S}_j}\right) + \frac{\partial V}{\partial S_j} = 0 \quad ; \quad S_j = A_j \cos(\sqrt{\lambda_j}\, t + \delta_j)$$

$$\Rightarrow \sum_j \left(-\lambda G^{-1}_{ij} + F_{ij}\right) A_j = 0$$

<u>Matrixform</u>

$$(-\lambda G^{-1} + F) A = 0 \quad | \cdot G$$

$$(-\lambda E + GF) A = 0$$

$$(GF - \lambda E) A = 0$$

$$|\underbrace{GF}_{\text{GF-Matrix}} - \lambda E| = 0 \quad \longrightarrow \text{nicht triviale Lösung}$$

<u>Bsp.:</u> H_2O – A_1 – Spezies

$$|GF - \lambda E| = \begin{vmatrix} G_{11}F_{11} + G_{12}F_{21} - \lambda & \\ & \end{vmatrix} = 0$$

$\mu_1 = \mu_H = 0{,}99206$
$\mu_3 = \mu_O = 0{,}06252$
$r = 0{,}96\,\text{Å}$; $\alpha = 105°$

} G – Matrix

$f_{11} = 8{,}4280$; $f_{12} = -0{,}1050$; $f_{13} = 0{,}2625$

$f_{33} = 0{,}7680$

$\Rightarrow$ F – Matrix

$\hookrightarrow$ $\lambda_1 = 8{,}61475$; $\lambda_2 = 1{,}60914$

$\hookrightarrow$ $\tilde{\nu}_1 = 3824\ cm^{-1}$; $\tilde{\nu}_2 = 1633\ cm^{-1}$ $\rightarrow$ <u>A_1</u>

Exp (3657) (1595)

$\hookrightarrow$ analog B_2 : $\lambda_3 = 9{,}13681 \rightarrow \tilde{\nu}_3 = 3938\ cm^{-1}$
(3756)