

Strukturaufklärung in der molekularen anorganischen Chemie

3. Infrarotspektroskopie

Klassifizierung

Wechselwirkung mit Strahlung:

- (Optische/Radio) Spektroskopie
- Streuung/Diffraktion
- Resonanzmethode
- Elektrische Methode
- Ionisation

Probe Beeinflussung:

- Destruktiv
- Nicht destruktiv

Anwendung:

- Identifizierung/Sauberkeit
- Elementaranalyse
- Chemische Gruppen
- Chemische Konnektivität
- Konformations-Eigenschaften
- Symmetrie
- Geometrie (Längen, Winkel)
- Schwingungen
- Elektronische Struktur (/Dichte)
- (Elektrische) Dipolmomente

Charakteristische Zeit:

- Langsame Methode
- Mittelschnelle Methode
- Schnelle Methode

Aggregatzustand der Probe:

- Gas
- Flüssigkeit
- Feststoff

IR Bereiche

γ -ray	Hard X-ray	Soft X-ray	Vacuum UV	Near UV	Visible blue red	Near IR	Mid IR	Far IR	Sub-mmwave	mm-wave	Micro-wave	Radio-wave
$< 0.1 \text{ \AA}$	5 \AA	100 \AA	2000 \AA		0.7 \mu m	2.5 \mu m	25 \mu m			1 mm		10 cm
$> 10^9$	2×10^7	10^6	5×10^4	2.5×10^4	1.4×10^4	4000	400			10		0.1
1.2×10^7	2.4×10^5	1200	600	300	170	48	4.8			0.12		1.2×10^{-3}
$120\,000$	2400	120	6	3	1.7	0.5	0.05			0.001		0.00001
3×10^{19}	6×10^{17}	3×10^{16}	1.5×10^{15}	7.5×10^{14}	4×10^{14}	1.2×10^{14}	1.2×10^{13}			3×10^{11}		3×10^9

Nahinfrarot Spektroskopie (NIR): ca. $13000 - 4000 \text{ cm}^{-1}$ ($770 - 2500 \text{ nm}$)

Mittlere Infrarot Spektroskopie (MIR): ca. $4000 - 400 \text{ cm}^{-1}$

Ferninfrarot-Spektroskopie (FIR, Terahertz-): ca. $400 - 10 \text{ cm}^{-1}$ ($1.2 \times 10^7 - 3.0 \times 10^5 \text{ MHz}$)

Charakteristische Zeit



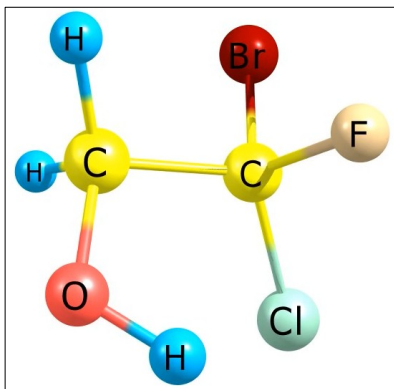
Charakteristische Zeit: IR

$$\tilde{\nu} = \frac{\nu}{c} = \frac{1}{\lambda}$$

$10 \text{ cm}^{-1} \rightarrow 3 \times 10^{11} \text{ Hz} \rightarrow 3.3 \times 10^{-12} \text{ Sek.} = 3.3 \text{ ps}$ (Pikosekunden, [Pico- im Englischen])

$4000 \text{ cm}^{-1} \rightarrow 1.2 \times 10^{14} \text{ Hz} \rightarrow 8.3 \times 10^{-15} \text{ Sek.} = 8.3 \text{ fs}$ (Femtosekunden)

s. Animation:



MD (GFN2-xTB, NVT, $T = 600 \text{ K}$),
 $t = 1 \text{ ps}$, $\Delta t = 1 \text{ fs}$.

Theorie (ganz schematisch)

$$\hat{H}\Psi = E\Psi$$

1) $\hat{T}_n = 0$
 2) Adiabatische N. } BO-Näherung

$$\hat{H}_e \Psi_e = E_e \Psi_e$$

$$(\hat{T}_n + E_e) \Psi_n = E_n \Psi_n$$

$$\Psi = \Psi_e \cdot \Psi_n, E = E_e + E_n$$

Korrespondenzprinzip
 (quant. \rightarrow klassisch)

$$E_n = E_{\text{trans}} + E_{\text{rot}} + E_{\text{vib}}$$

$3N$	3	$3(2)$	$3N-6$
Freiheitsgrade			$(3N-5)$

Basis q

Lagrange-Formalismus
 Hamiltonsche Prinzip

GF-Methode

$$T = \frac{1}{2} \sum_{ij} t_{ij} \dot{q}_i \dot{q}_j$$

$$V = \frac{1}{2} \sum_{ij} d_{ij} q_i q_j$$

Taylorreihe
 $\frac{\partial^2 E_e}{\partial q_i \partial q_j}$

$$\left\{ \sum_{j=1}^n (d_{ij} - \lambda t_{ij}) l_j = 0 \right.$$

$$\boxed{GFL = L\Lambda}$$

$$\lambda_k = 4\pi^2 \nu_k^2 (!)$$

$$\bar{Q} = L \cdot \bar{q} (!)$$

s. weiter

$\bar{Q}, \bar{\lambda}$ Q_k sind orthogonal!

$$T = \frac{1}{2} \sum_k \dot{Q}_k^2 ; V = \frac{1}{2} \sum_k \lambda_k Q_k^2$$

Korrespondenzprinzip
(klassisch \rightarrow quanten-)

$$\hat{H}_{\text{vib}} = \sum_k^{3N-6} \hat{H}_k \implies \Psi_{\text{vib}} = \prod_k \Psi_k(Q_k) ; E_{\text{vib}} = \sum_k E_k(\nu_k)$$

$$\hat{H}_k = -\frac{1}{2} \hbar^2 \left(\frac{\partial^2}{\partial Q_k^2} \right) + \frac{1}{2} \lambda_k Q_k^2$$

↓ Lösung

$$\Psi_{k,i} = N_{\text{vib}} \cdot H_{(i)}(Q_k^0) \cdot e^{-\frac{1}{2\hbar} \sqrt{\lambda_k} \cdot Q_k^2}$$

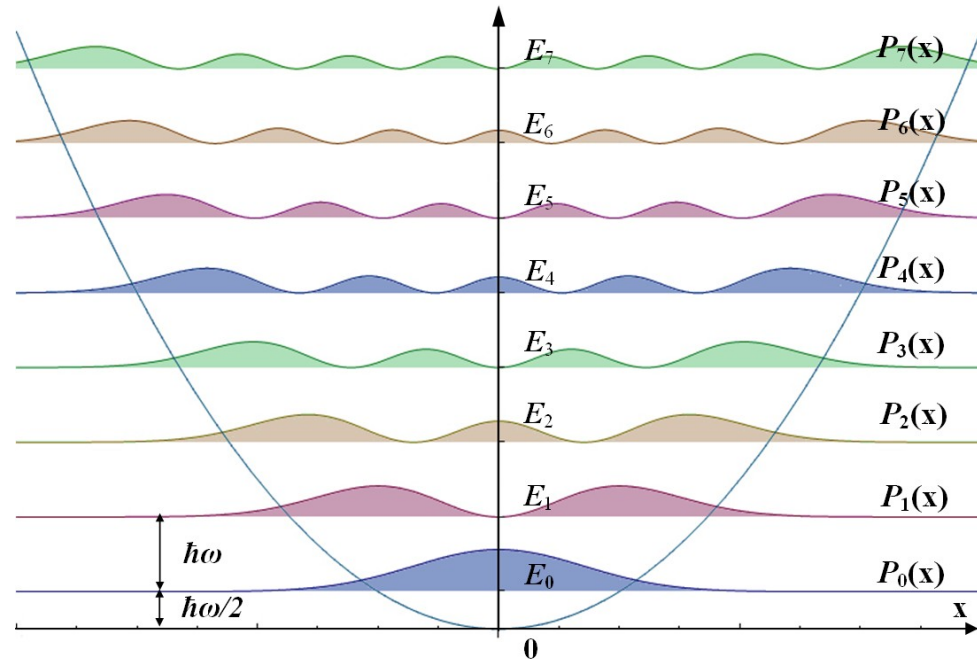
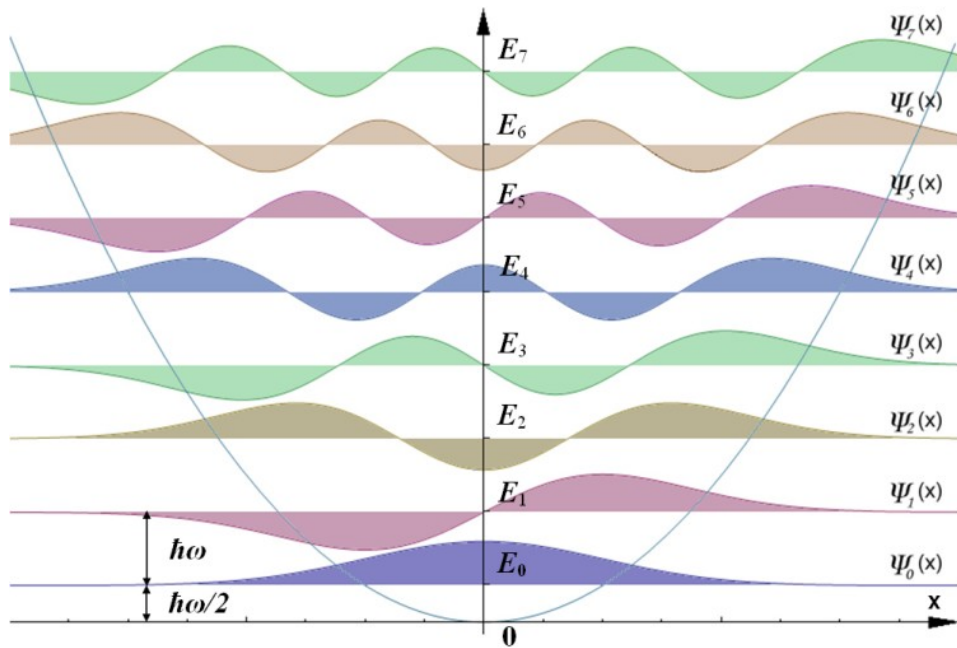
$(Q_k^0 = Q_k \sqrt{\lambda_k^{1/2} / \hbar})$

Harmonisch!

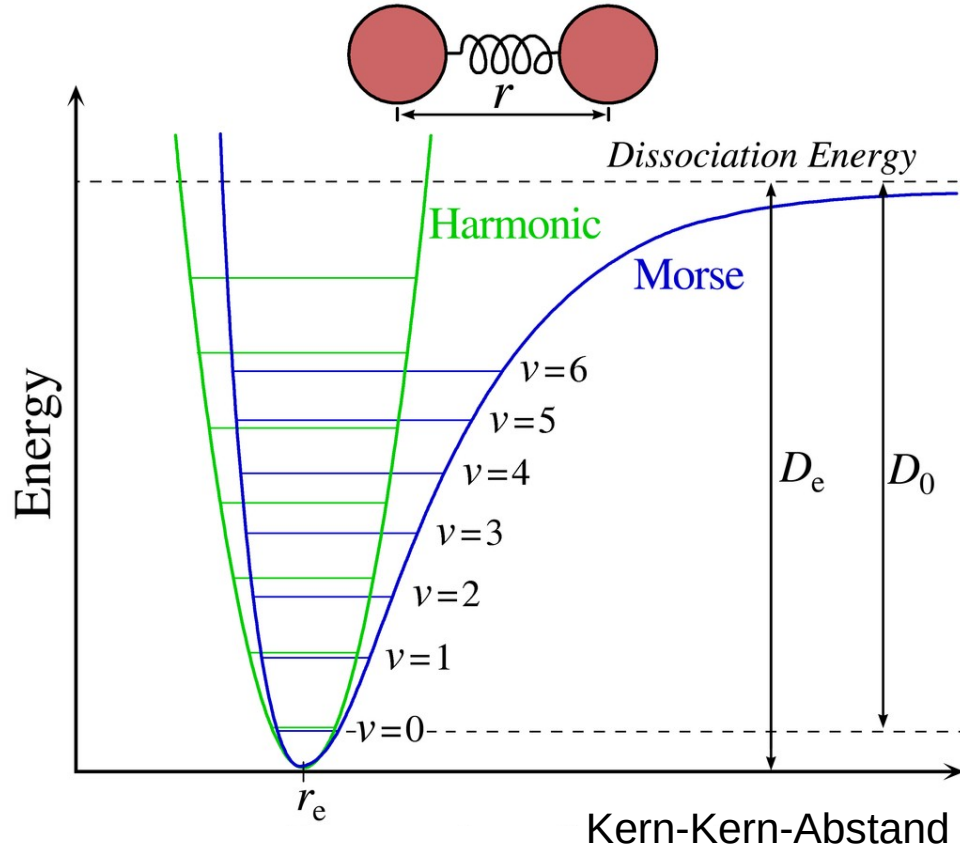
$$E_k(\nu_k) = \hbar \nu_k \left(\nu_k + \frac{1}{2} \right)$$

$\nu_k = 0, 1, 2, \dots$

Der harmonische Oszillator (1D)



Harmonisch vs. Anharmonisch



Morse Potential:

$$V(r) = D_e (1 - e^{-a(r-r_e)})^2$$

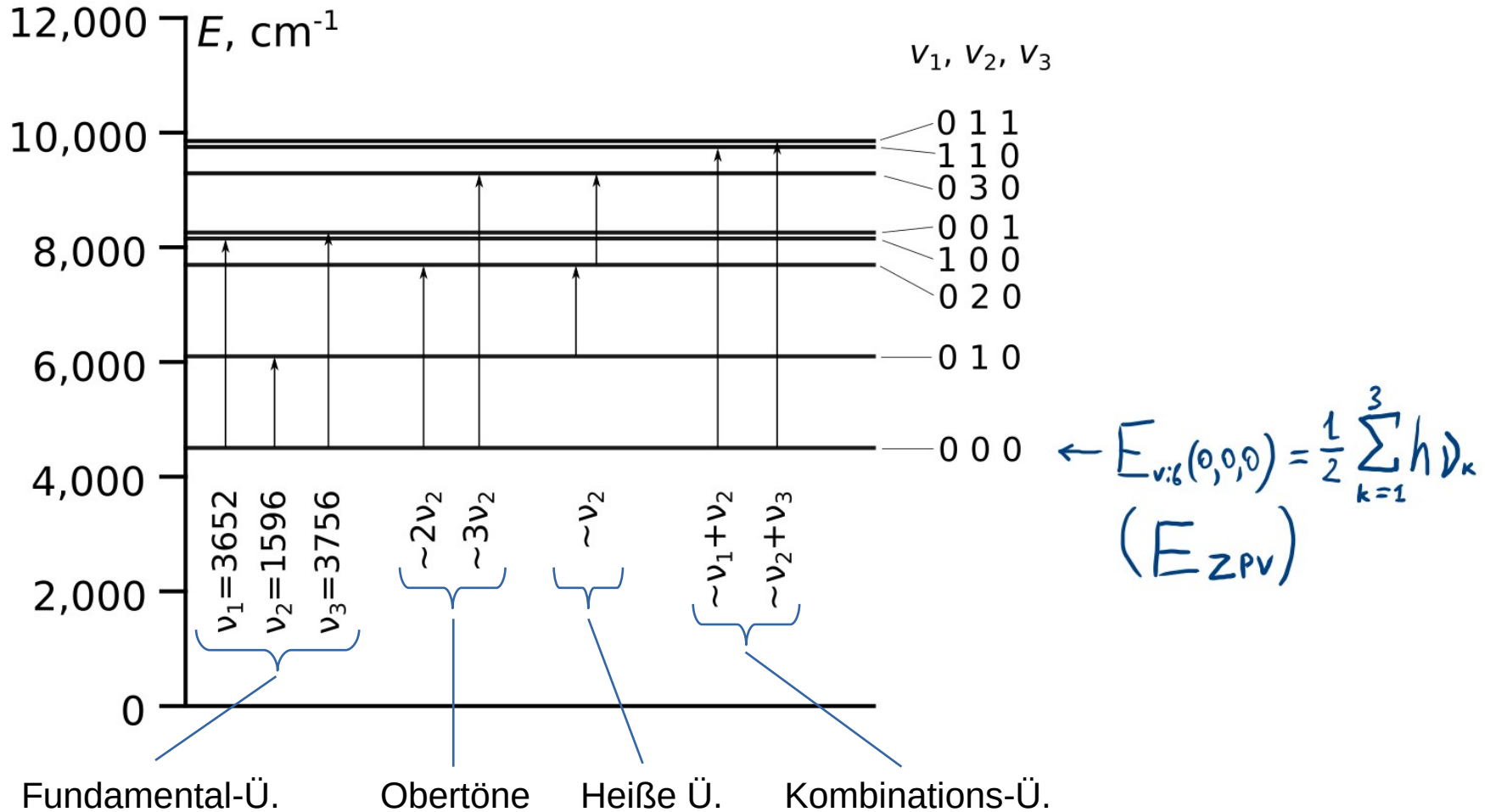
D_e (spektroskopische) Dissoziationsenergie

r_e Gleichgewichtsabstand im Potentialminimum

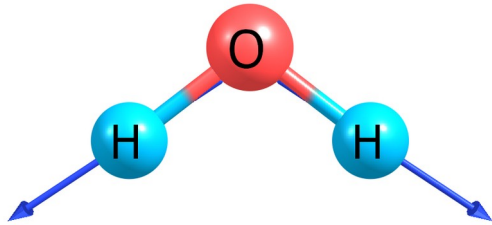
a Konstante, die die Steifigkeit des Potentials beschreibt

$$E_v = h\nu_e \left(v + \frac{1}{2} \right) - h\chi_e \nu_e \left(v + \frac{1}{2} \right)^2 .$$

H₂O Schwingungsniveaus

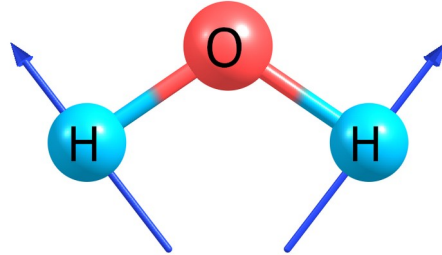


H₂O Schwingungsformen



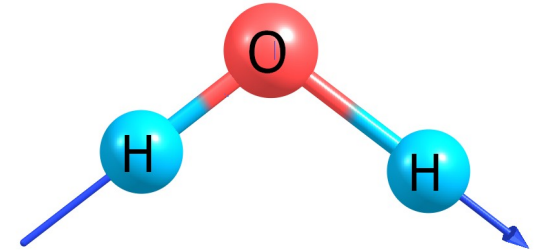
$$\nu_1 = 3652 \text{ cm}^{-1}$$

A₁



$$\nu_2 = 1596 \text{ cm}^{-1}$$

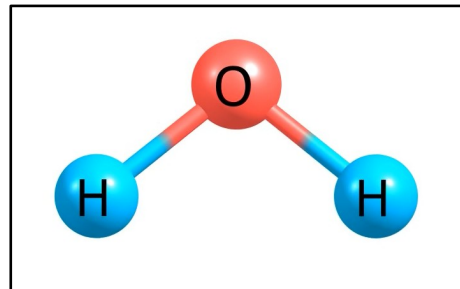
A₁



$$\nu_3 = 3756 \text{ cm}^{-1}$$

B₂

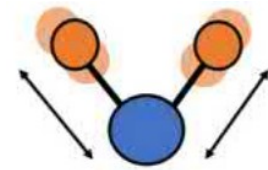
s. Animation:



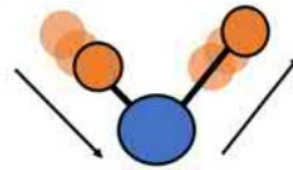
Schwingungsformen

(s. Animation)

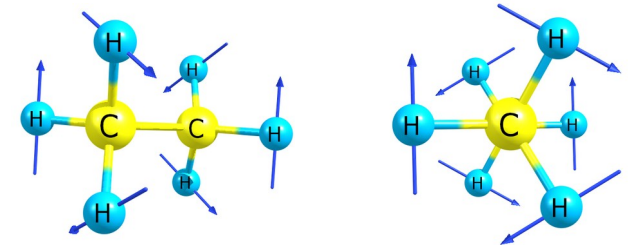
Valenzschwingungen
(Streckschwingungen)



symmetrische

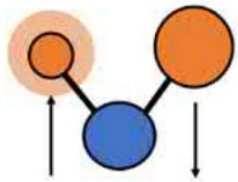


antisymmetrische

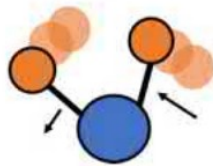


Torsionsschwingungen

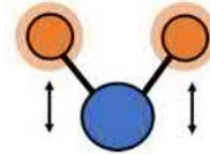
Deformationsschwingungen



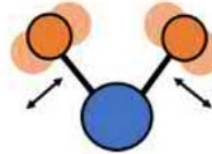
Drehschwingung
(engl. twisting)



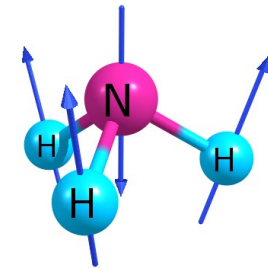
Wippschwingung
(engl. wagging)



Schaukelschwingung
(engl. rocking)



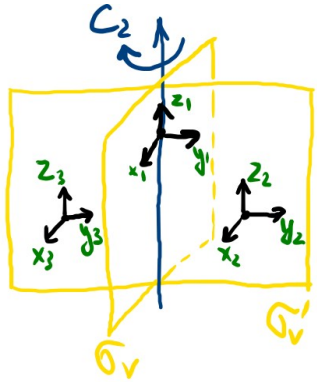
Biegeschwingung
(engl. scissoring oder bending)



Inversionsschwingungen

Symmetrie

Beispiel: H₂O



Basis: $\{\Delta x_i, \Delta y_i, \Delta z_i\}$ (3N!)

$$\longrightarrow \Gamma_{\text{total}}^{(\text{red})} = (9 \quad -1 \quad 1 \quad 3)$$

$$\Gamma = k_1 \underline{A_1} + k_2 \underline{A_2} + k_3 \underline{B_1} + k_4 \underline{B_2}$$

$$k_i = \frac{1}{h} \sum_{\hat{R}} n \cdot \chi^R \cdot \chi_i^R$$

Reduktionsformel ↗

Reduktion:

$$k_{A_1} = \frac{1}{4} (1 \cdot 9 + 1 \cdot (-1) + 1 \cdot 1 + 1 \cdot 3) = 3$$

$$k_{A_2} = \frac{1}{4} (1 \cdot 9 + 1 \cdot (-1) - 1 \cdot 1 - 1 \cdot 3) = 1$$

$$k_{B_1} = \frac{1}{4} (1 \cdot 9 - 1 \cdot (-1) + 1 \cdot 1 - 1 \cdot 3) = 2$$

$$k_{B_2} = \frac{1}{4} (1 \cdot 9 - 1 \cdot (-1) - 1 \cdot 1 + 1 \cdot 3) = 3$$

$$\left. \begin{aligned} \Gamma_{\text{total}} &= (3 \quad 1 \quad 2 \quad 3) = \Gamma_{\text{trans}} + \Gamma_{\text{rot}} + \Gamma_{\text{vib}} \\ \Gamma_{\text{trans}} &= A_1 + B_1 + B_2; \quad \Gamma_{\text{rot}} = A_2 + B_1 + B_2 \end{aligned} \right\} \Rightarrow \Gamma_{\text{vib}} = 2A_1 + B_2$$

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma'_v(yz)$	
A_1	1	1	1	1	z
A_2	1	1	-1	-1	R_z
B_1	1	-1	1	-1	x, R_y
B_2	1	-1	-1	1	y, R_x

Auswahlregeln

$$E_k(v_k) = h\nu_k \left(v_k + \frac{1}{2} \right) \quad \Delta v_k = \pm 1 \quad (\text{harmonische N.})$$

$$I_{IR} \propto |M_v|^2 \quad (M_v - \text{Übergangsdipolmoment}) \quad \text{H}_2\text{O}: \Gamma_{vib} = 2A_2 + B_2$$

$$|M_v|^2 = |M_x|^2 + |M_y|^2 + |M_z|^2$$

$$M_x = \langle \varphi_i^* | M_x | \varphi_j \rangle$$

$$M_y = \langle \varphi_i^* | M_y | \varphi_j \rangle$$

$$M_z = \langle \varphi_i^* | M_z | \varphi_j \rangle$$

$$M_q \approx M_q^0 + \left(\frac{\partial M_q}{\partial Q_k} \right)_0 \cdot Q_k$$

$$M_q = M_q^0 \cdot \underbrace{\langle \varphi_i | \varphi_j \rangle}_{\emptyset} + \left(\frac{\partial M_q}{\partial Q_k} \right)_0 \cdot \underbrace{\langle \varphi_i^* | Q_k | \varphi_j \rangle}_{\Delta v_k = \pm 1}$$

(!)

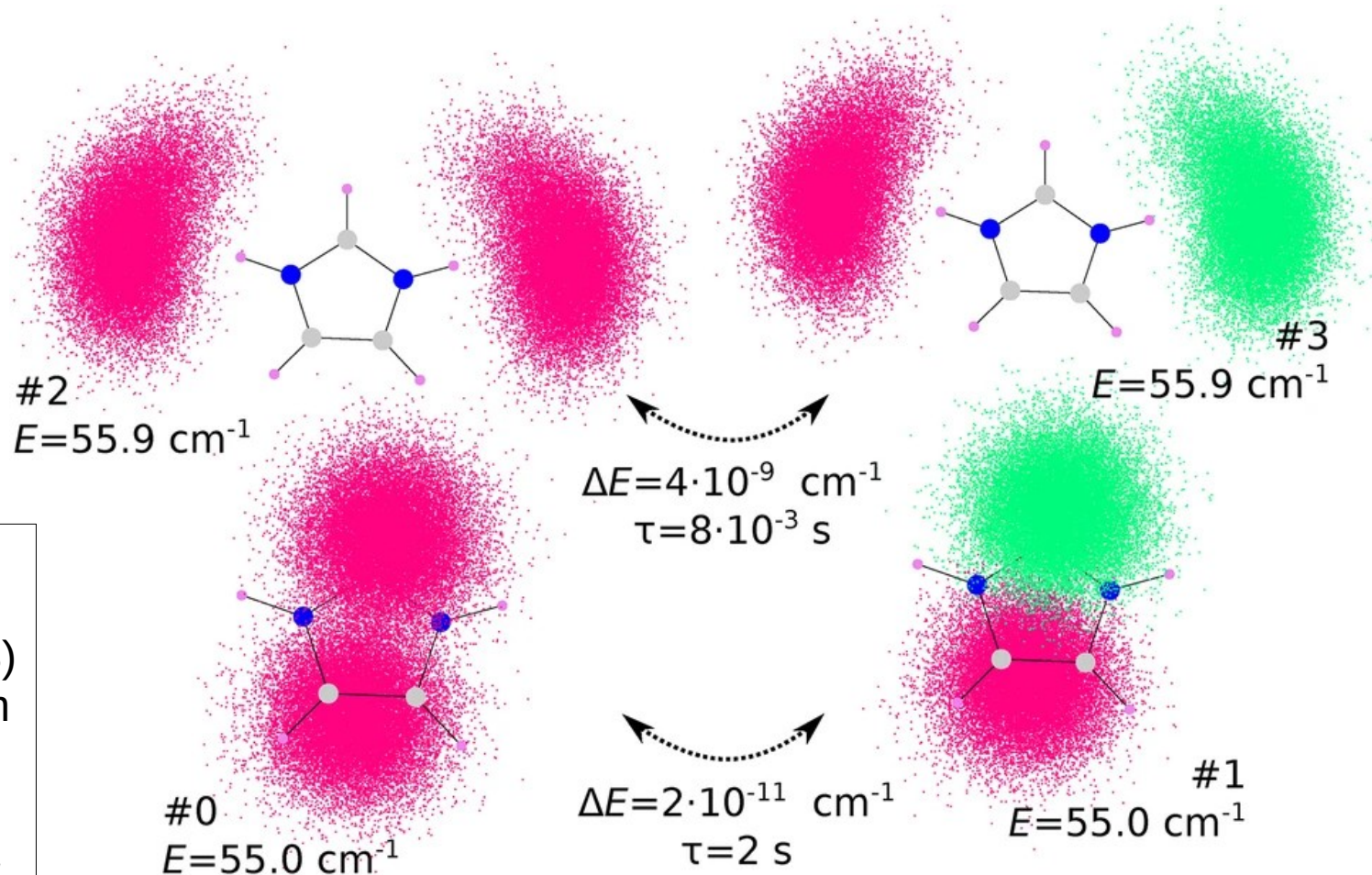
C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma'_v(yz)$	
A_1	1	1	1	1	z
A_2	1	1	-1	-1	R_z
B_1	1	-1	1	-1	x, R_y
B_2	1	-1	-1	1	y, R_x

A_1 (und analogisch B_2) sind IR-aktiv! A_2 wäre nicht a.!

(Aufgabe: gibt es C_{2v} -symmetrische Moleküle mit A_2 Fundamentalschwingung(en)?)

Ein komplizierter Fall

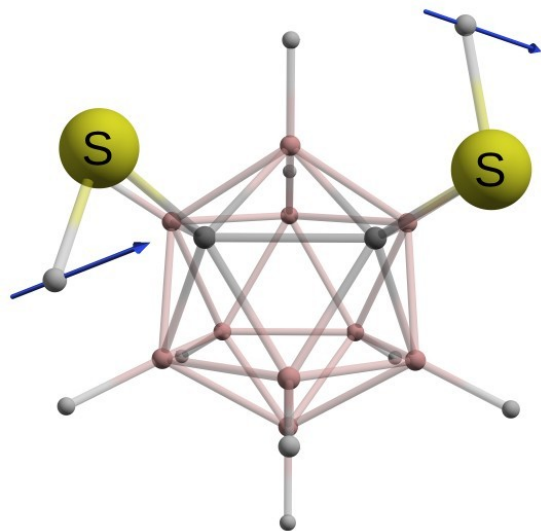
Wellenfunktionen der niedrigsten Schwingungszustände der He-Bewegung um (Imidazol)H⁺.



D. S. Tikhonov et al., „Structures of the (Imidazole)_nH⁺...Ar ($n=1,2,3$) complexes determined from IR spectroscopy and quantum chemical calculations“, *Struct. Chem.* 34 (2023) 203.

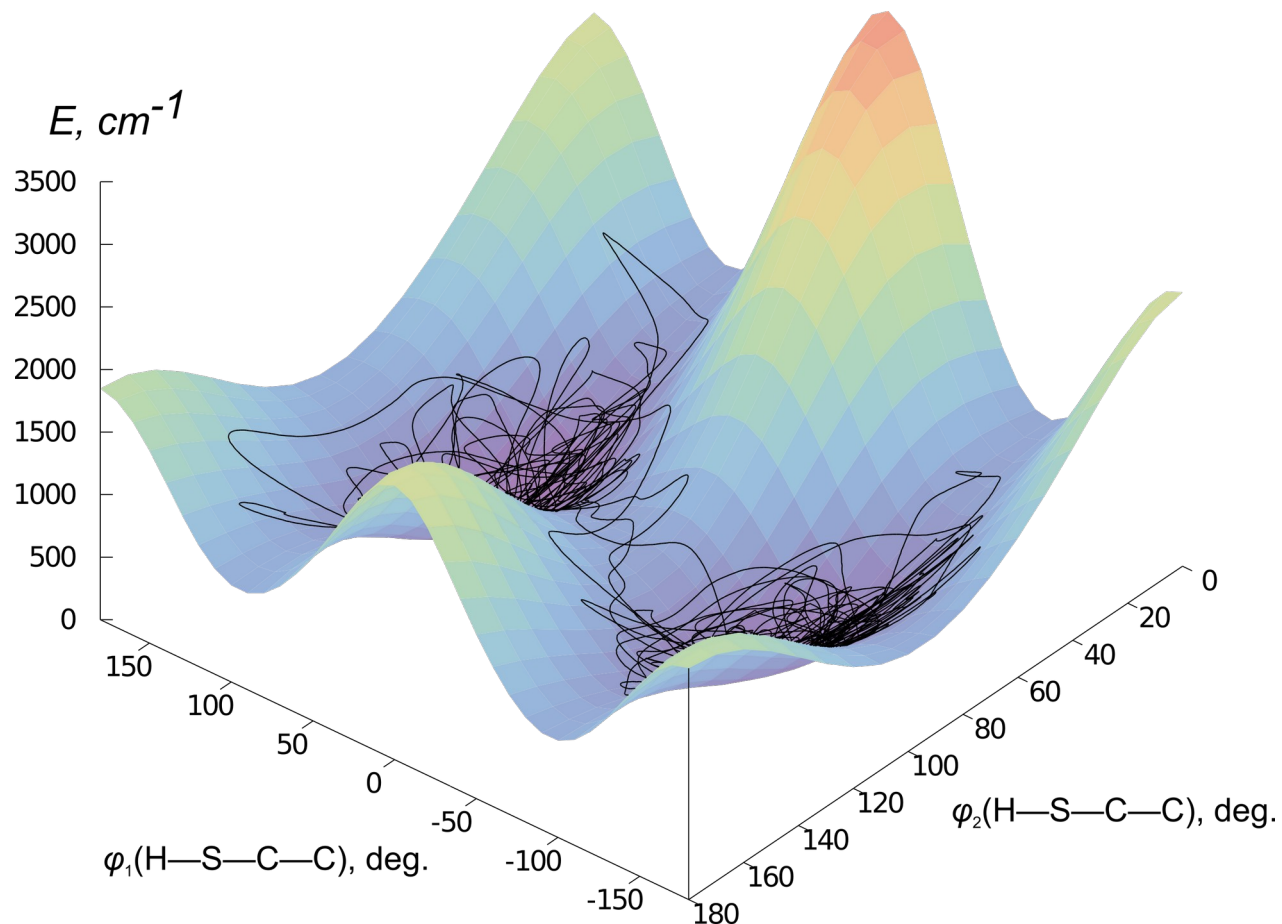
Normalmoden \neq reale Schwingungen

1,2-(SH)₂-*closo*-1,2-C₂B₁₀H₁₀



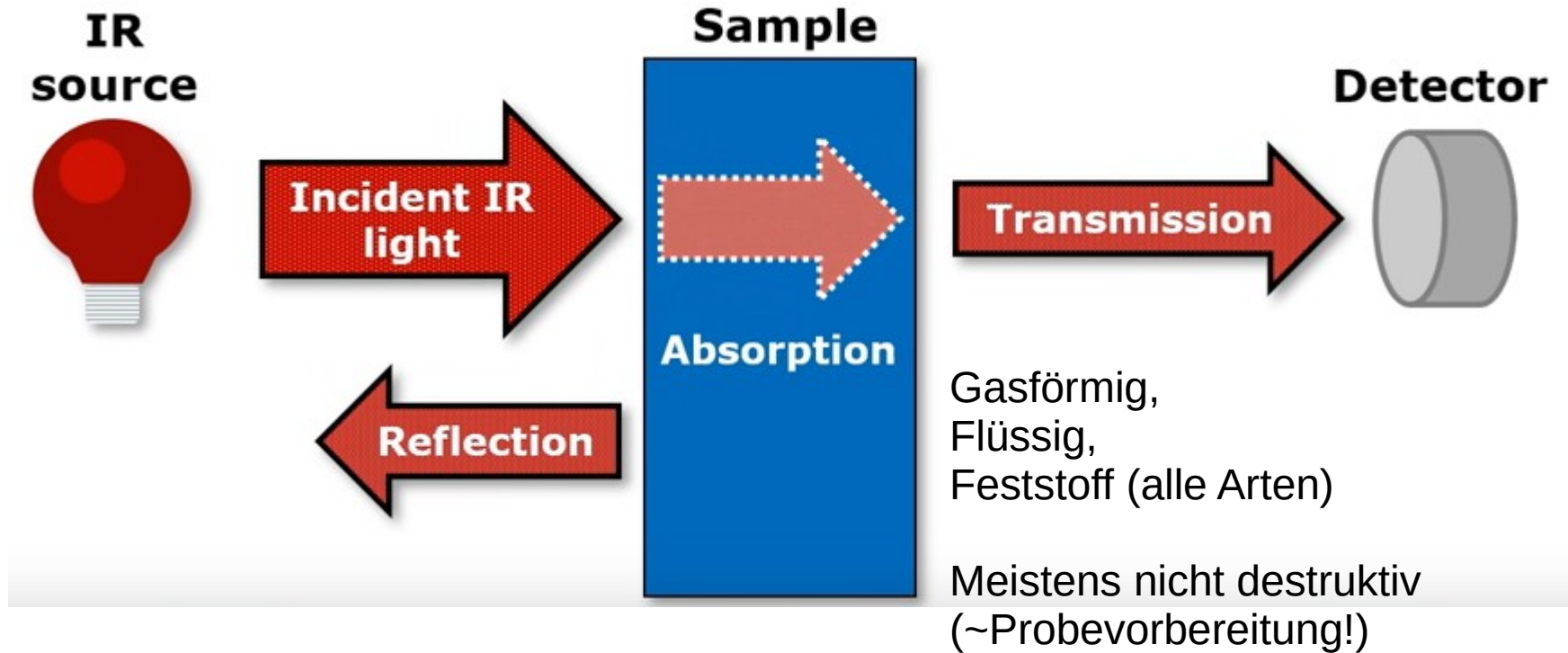
$\nu_4 = 220 \text{ cm}^{-1}$ (B)

(s. Animation)



Technik (ganz schematisch)

Transmission/Absorption/Reflexion



Lichtquelle/Detektor

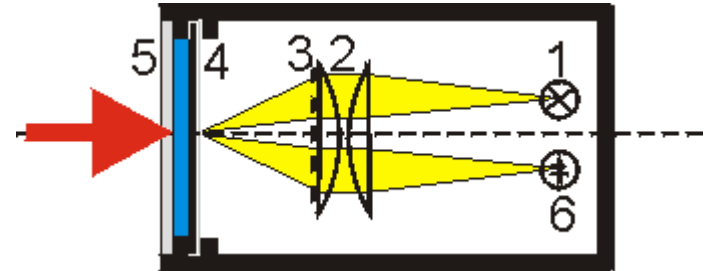
Schwarzer Strahler



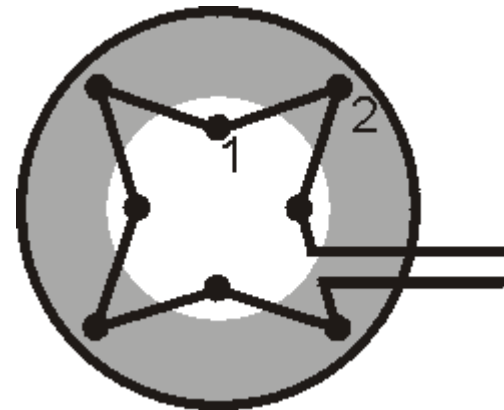
Globar (Siliziumcarbid)

Metallwiderstand

Golay-Zelle

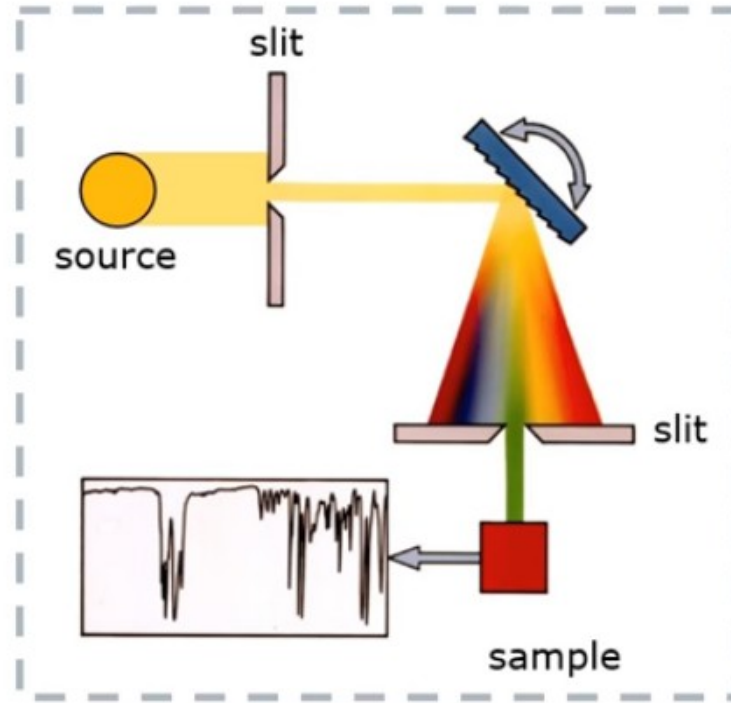


Thermosäule



(Das beste: Quantendetektoren) 20

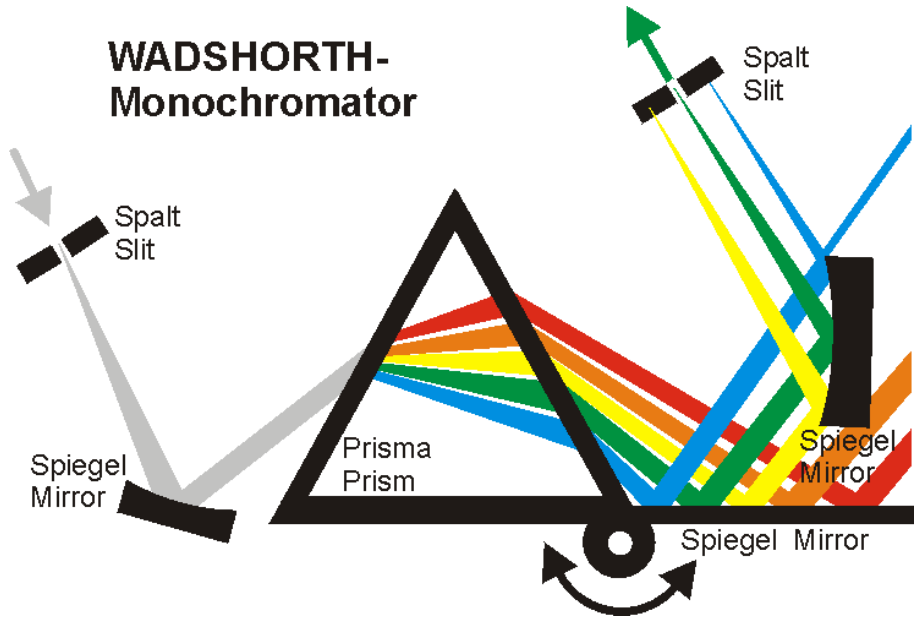
Dispersive Geräte



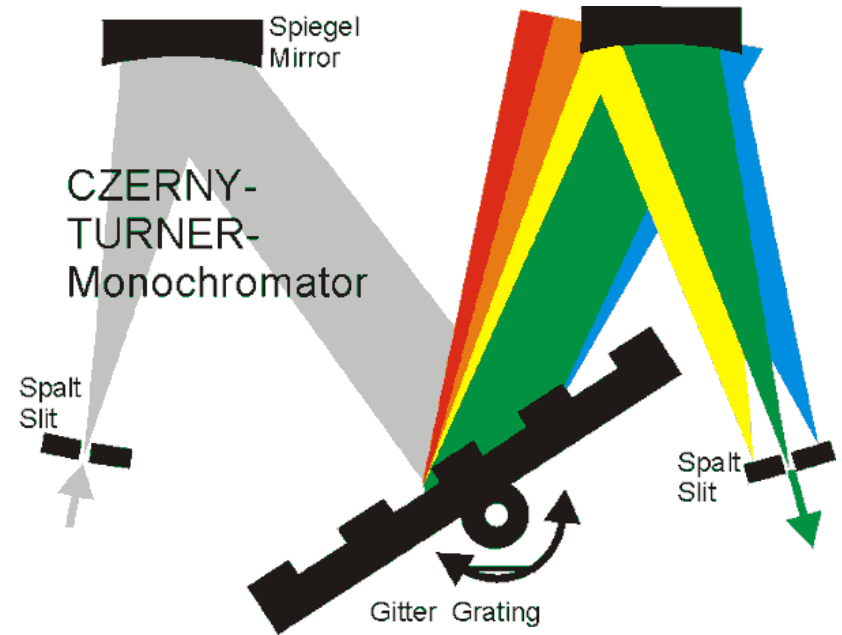
Traditional dispersive
infrared spectrometer

Monochromator

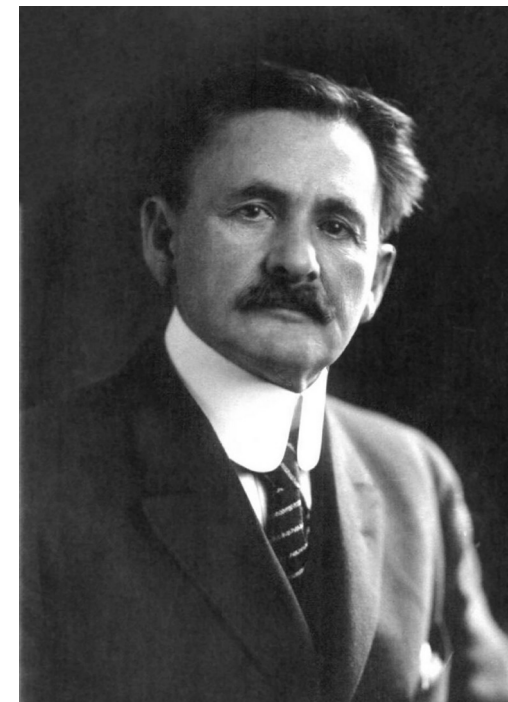
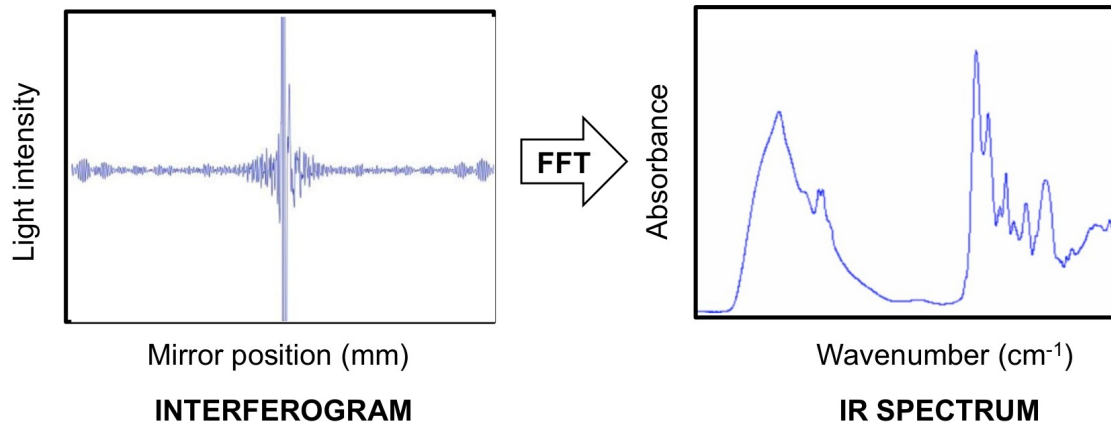
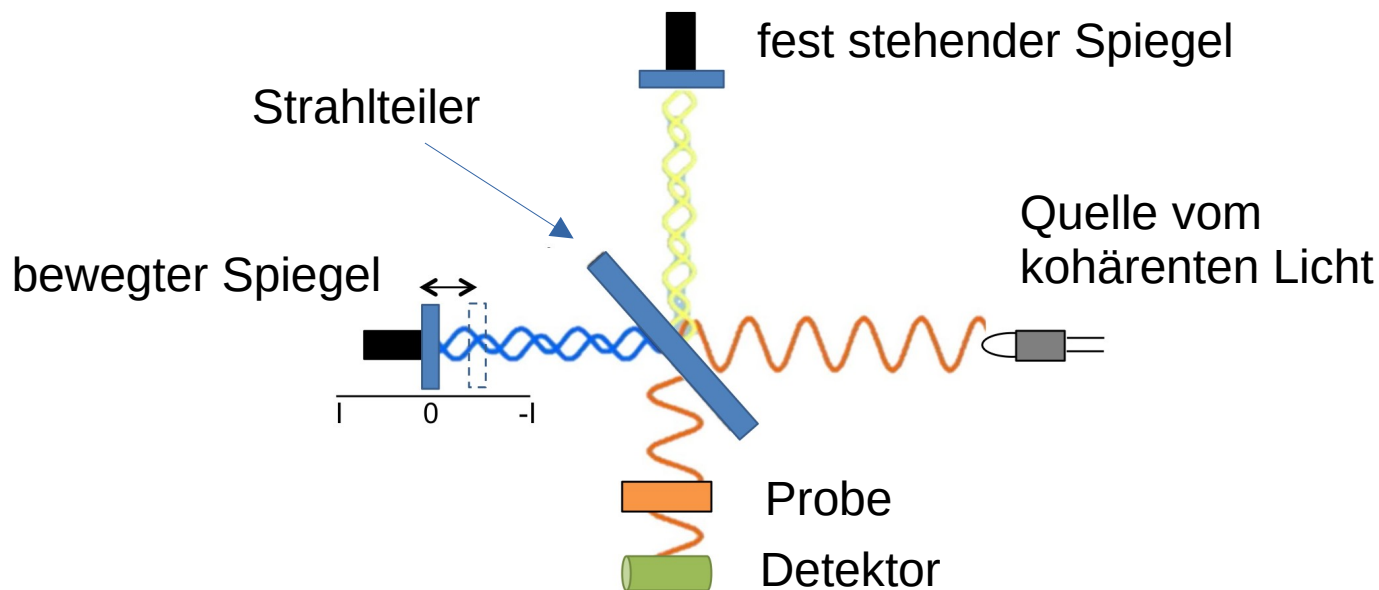
WADSHORTH-Monochromator



CZERNY-TURNER-Monochromator



FT-IR: Michelson Interferometer



Albert A. Michelson
1852 – 1931
1907 Nobelpreis f. Physik

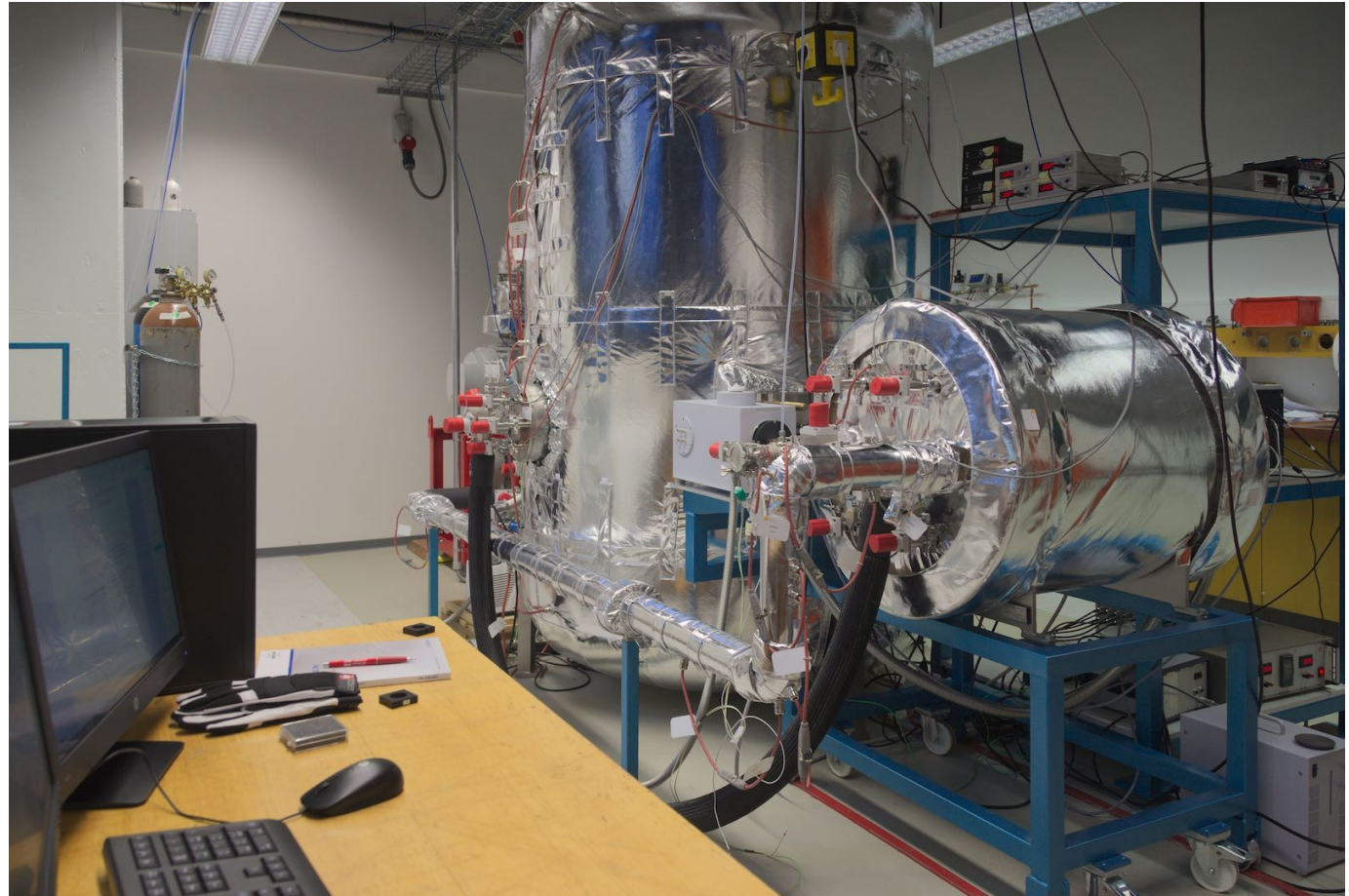
Ein reales Gerät: FT-IR f. Gasphase

The Gratin-jet

Gas-recycling atom-economic infrared spectroscopy

Key specs

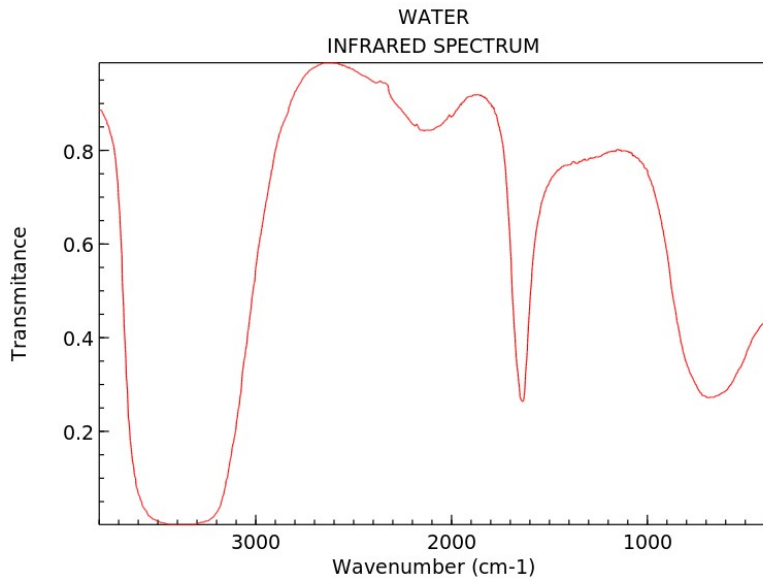
Nozzle	700 × 0.2mm ² (typical)
Detector	7 mm ² InGaAs, 3 mm ² InSb, 4 mm ² HgCdTe,
Spectral range	8000–800 cm ⁻¹
Spectral resolution	2 cm ⁻¹ (typical)



Beispiele und Anwendungen

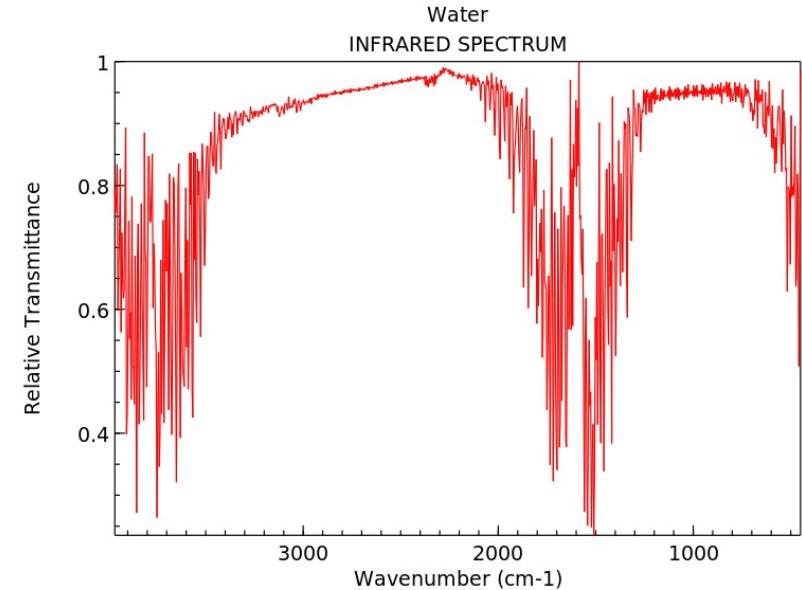
H₂O: Reale IR Spektren

Flüssigkeit



NIST Chemistry WebBook (<https://webbook.nist.gov/chemistry>)

Gas



NIST Chemistry WebBook (<https://webbook.nist.gov/chemistry>)

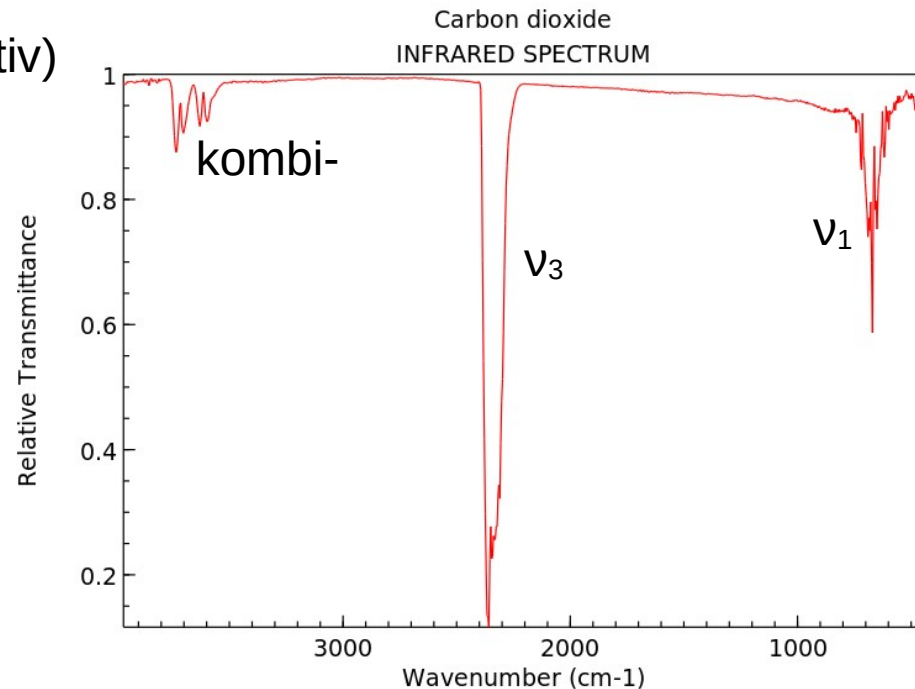
Symmetrie von CO₂

C_{2v} : $n=3N-6=3$, $\Gamma_{\text{vib}} = 2A_1 + B_2$ (alle IR-aktiv)

$D_{\infty h}$: $n=3N-5=4$, $\Gamma_{\text{vib}} = \Pi_u + \Sigma_g^+ + \Sigma_u^+$ (nur 2 IR-aktiv)

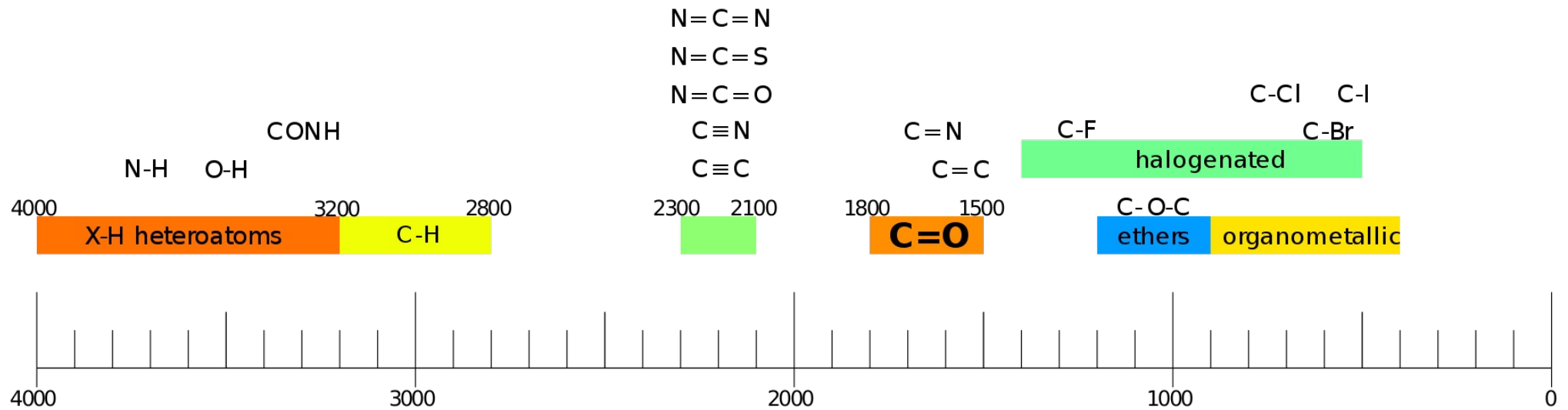
$D_{\infty h}$	E	$2C_{\infty}^{\Phi}$...	$\infty\sigma_v$	i	$2S_{\infty}^{\Phi}$...	∞C_2		
Σ_g^+	1	1	...	1	1	1	...	1		x^2, y^2, z^2
Σ_g^-	1	1	...	-1	1	1	...	-1	R_z	
Π_g	2	$2c\Phi$...	0	2	$-2c\Phi$...	0	(R_x, R_y)	(xz, yz)
Δ_g	2	$2c2\Phi$...	0	2	$2c2\Phi$...	0		(x^2-y^2, xy)
...		
Σ_u^+	1	1	...	1	-1	-1	...	-1	z	
Σ_u^-	1	1	...	-1	-1	-1	...	1		
Π_u	2	$2c\Phi$...	0	-2	$2c\Phi$...	0	(x, y)	
Δ_u	2	$2c2\Phi$...	0	-2	$-2c2\Phi$...	0		
...		

^a c stands for cos.



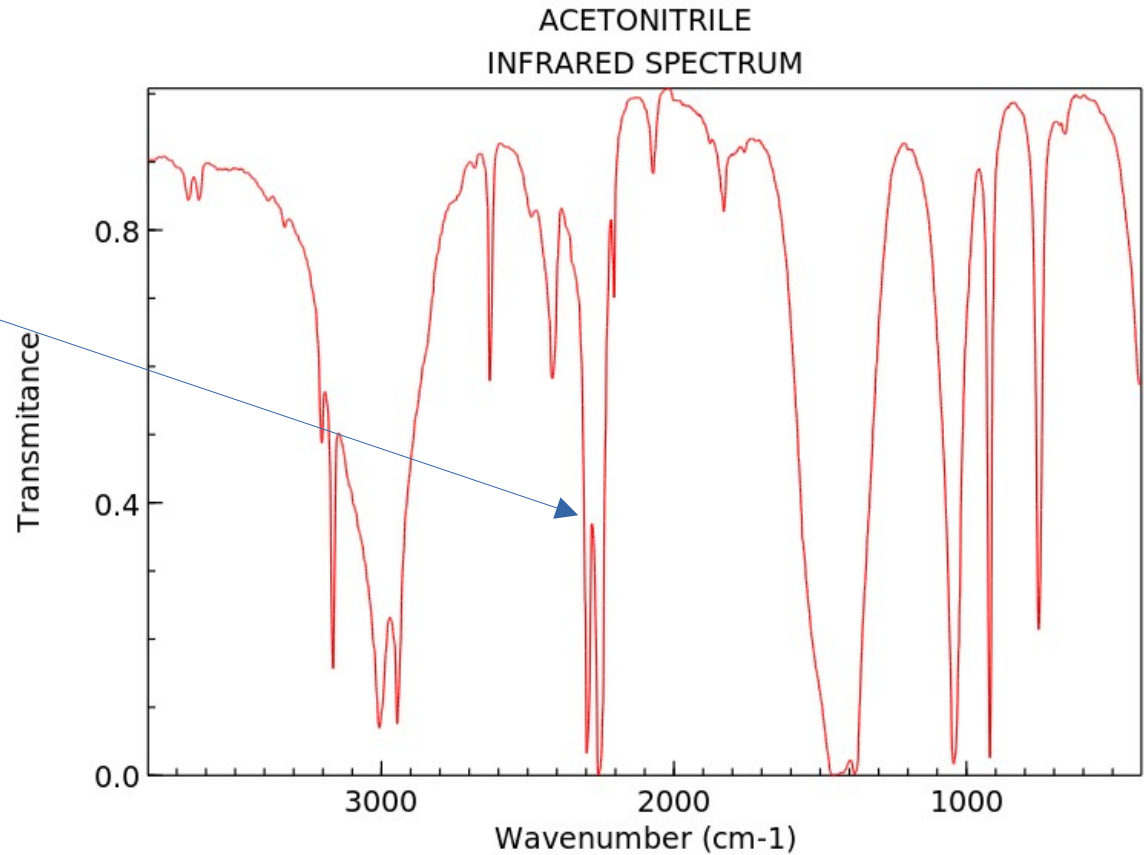
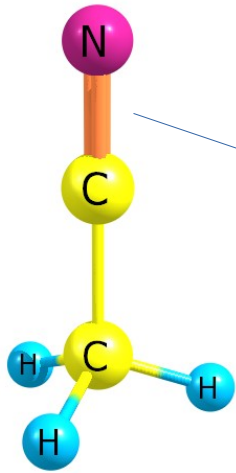
NIST Chemistry WebBook (<https://webbook.nist.gov/chemistry>)

Charakteristische Banden



Siehe mehr in D. W. H. Rankin, N. W. Mitzel, C. A. Morrison, Structural Methods in Molecular Inorganic Chemistry, John Wiley & Sons, Chichester, 2013

Charakteristische Banden

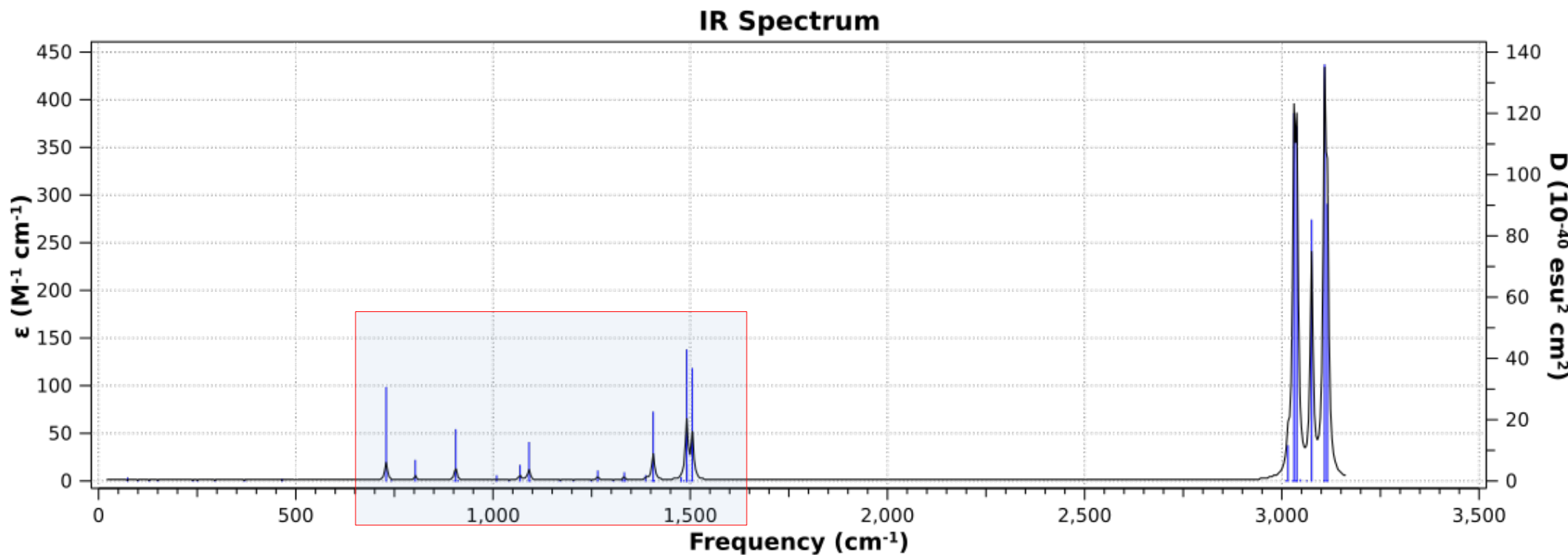


(Aufgabe: welche noch charakteristische Banden kann man hier erkennen?)

NIST Chemistry WebBook (<https://webbook.nist.gov/chemistry>)

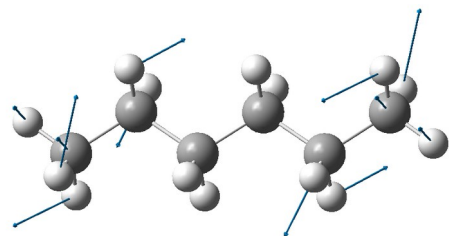
NICHTcharakteristische Banden

Beispiel: *n*-Hexan

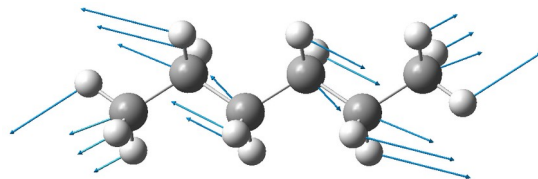


NICHTcharakteristische Moden

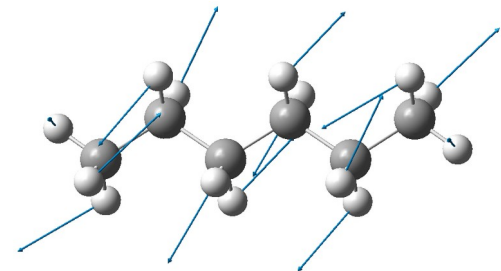
n-Hexan, exemplarisch (s. Animation)



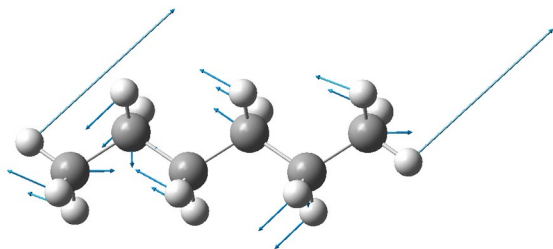
$$\nu_1 = 74$$



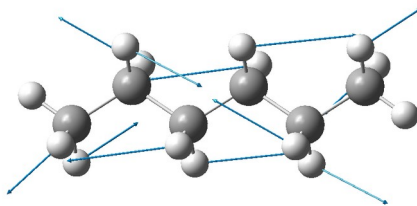
$$\nu_8 = 370$$



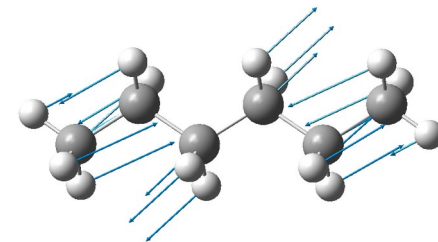
$$\nu_{12} = 802 \text{ cm}^{-1}$$



$$\nu_{14} = 905$$

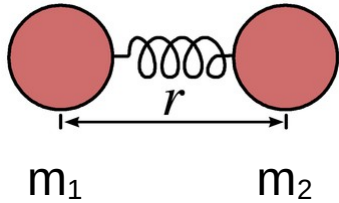


$$\nu_{16} = 1009$$



$$\nu_{17} = 1040 \text{ cm}^{-1}$$

Isotopeneffekt



$$F = -kx = -\frac{dV(x)}{dx} \Rightarrow V(r) = \frac{1}{2}k(r-r_0)^2 \leftarrow \text{harmonisch}$$

$$E_v = h\nu\left(v + \frac{1}{2}\right) \quad \nu = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}} \leftarrow \begin{array}{l} \text{Kraftkonstante} \\ \text{Reduzierte Masse} \end{array}$$

Z.B.: X-H vs. X-D

$$\frac{1}{\mu} = \frac{1}{m_1} + \frac{1}{m_2}; \mu = \frac{m_1 \cdot m_2}{m_1 + m_2}$$

dann $k_1 \approx k_2$

wenn $m_X \gg m_H$, dann

$$\frac{\nu_1}{\nu_2} \approx \sqrt{\frac{\mu_2}{\mu_1}}$$

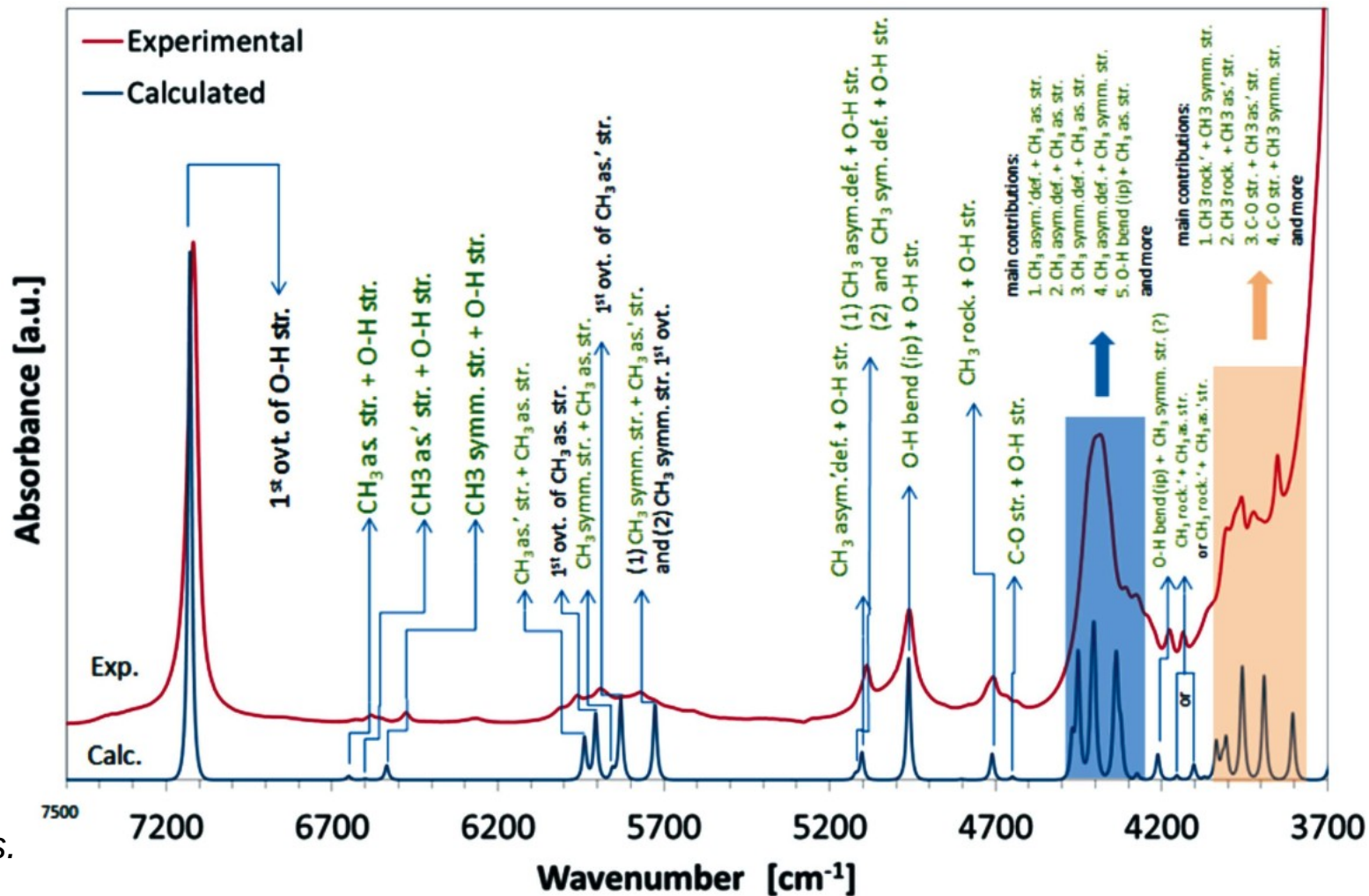
$$\Rightarrow \sqrt{\frac{\mu_2}{\mu_1}} \approx \sqrt{2}$$

$$\boxed{\nu_{X-D} \approx \frac{\nu_{X-H}}{\sqrt{2}}}$$

Reale Beispiele: H₂O vs. D₂O

$\nu_s(O-H)$:	gemessen	3657	2671 cm ⁻¹
	gerechnet		2586 cm ⁻¹

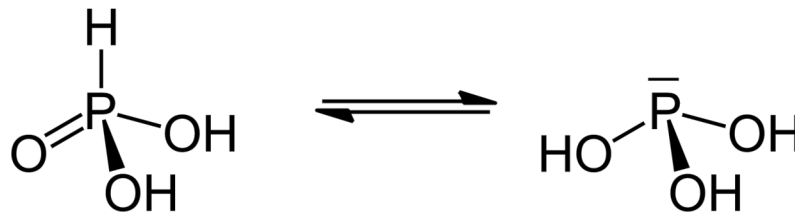
Beispiel NIR: CH₃OH



K. B. Beć, Y. Futami,
M. J. Wójcik, Y. Ozaki,
Phys. Chem. Chem. Phys.
2016, 18, 13666–13682.

Molekül(e) des Tages

Phosphonsäure

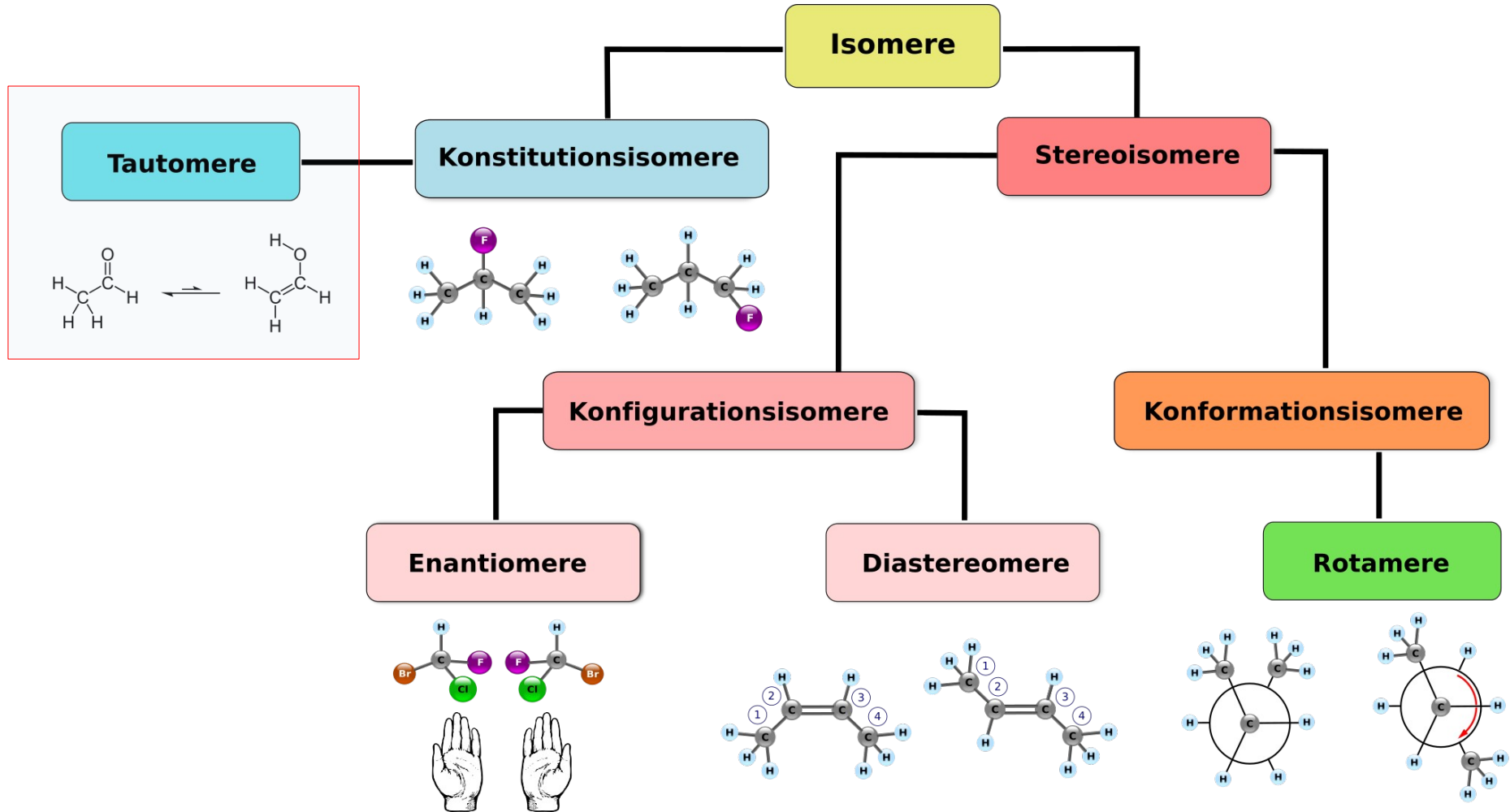


$E = 0$

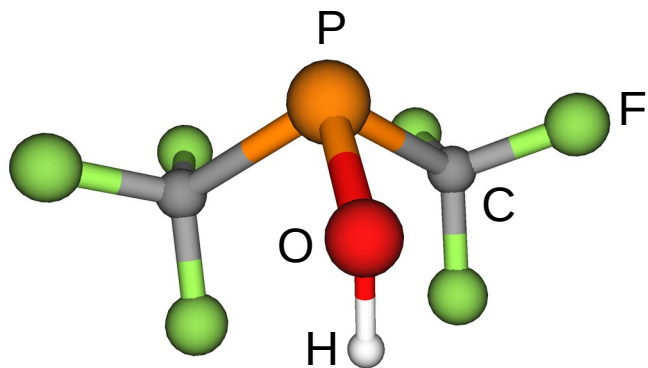
+11 kcal/mol @ PBE0-D3BJ/def2-QZVPP
(0% @ RT, 1% @ 1100 K hypothetisch!)

R_2POH vs. $\text{R}_2\text{P}(\text{O})\text{H}$???

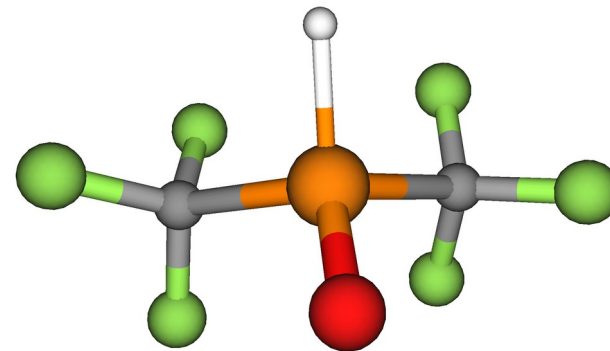
Tautomerie



$(\text{CF}_3)_2\text{POH}$ oder $(\text{CF}_3)_2\text{P}(\text{O})\text{H}$?



$E = 0$

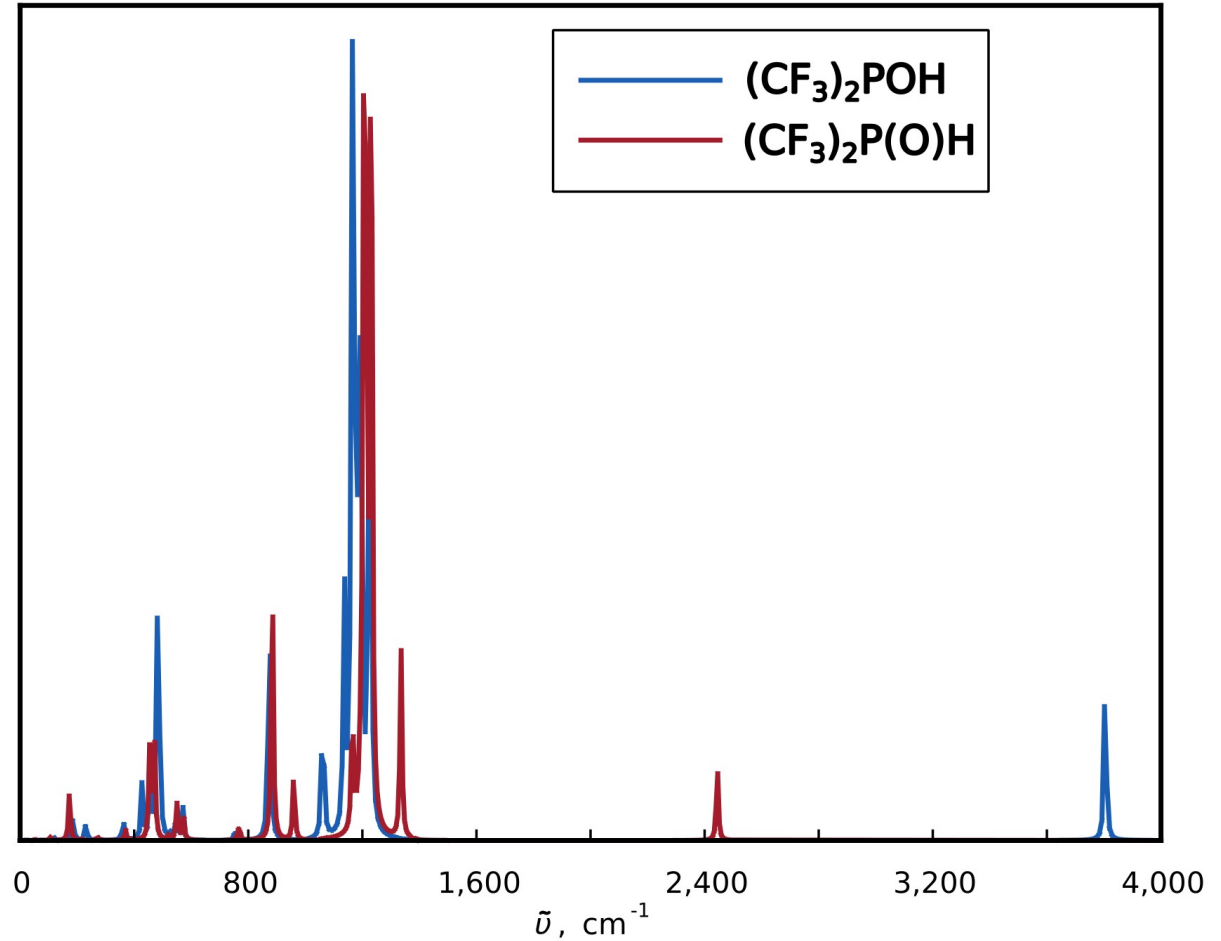
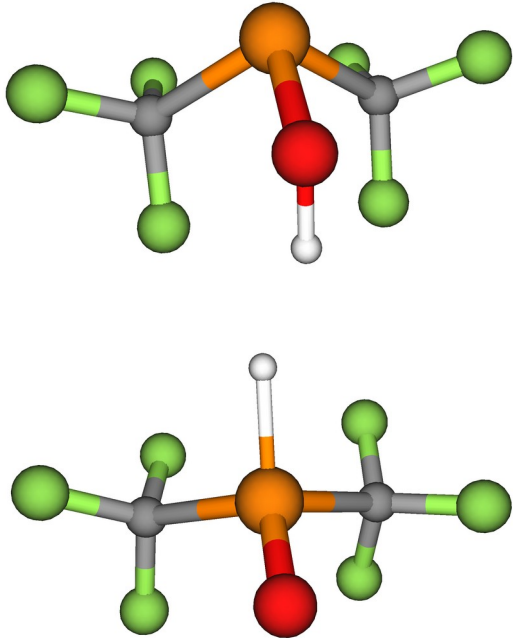


+5 kcal/mol @ PBE0-D3BJ/def2-QZVPP
(0% @ RT, 1% @ 550 K hypothetisch!)

Experiment?

$(\text{CF}_3)_2\text{POH}$ oder $(\text{CF}_3)_2\text{P}(\text{O})\text{H}$?

Harmonische IR Spektren,
Gerechnet @ PBE0-D3BJ/def2-QZVPP



(CF₃)₂POH: IR-Spektren

Gemessen:

$$\nu(\text{O-H}) = 3620 \text{ cm}^{-1}$$

$$\nu(\text{O-D}) = 2640 \text{ cm}^{-1}$$

Gerechnet:

Grob:

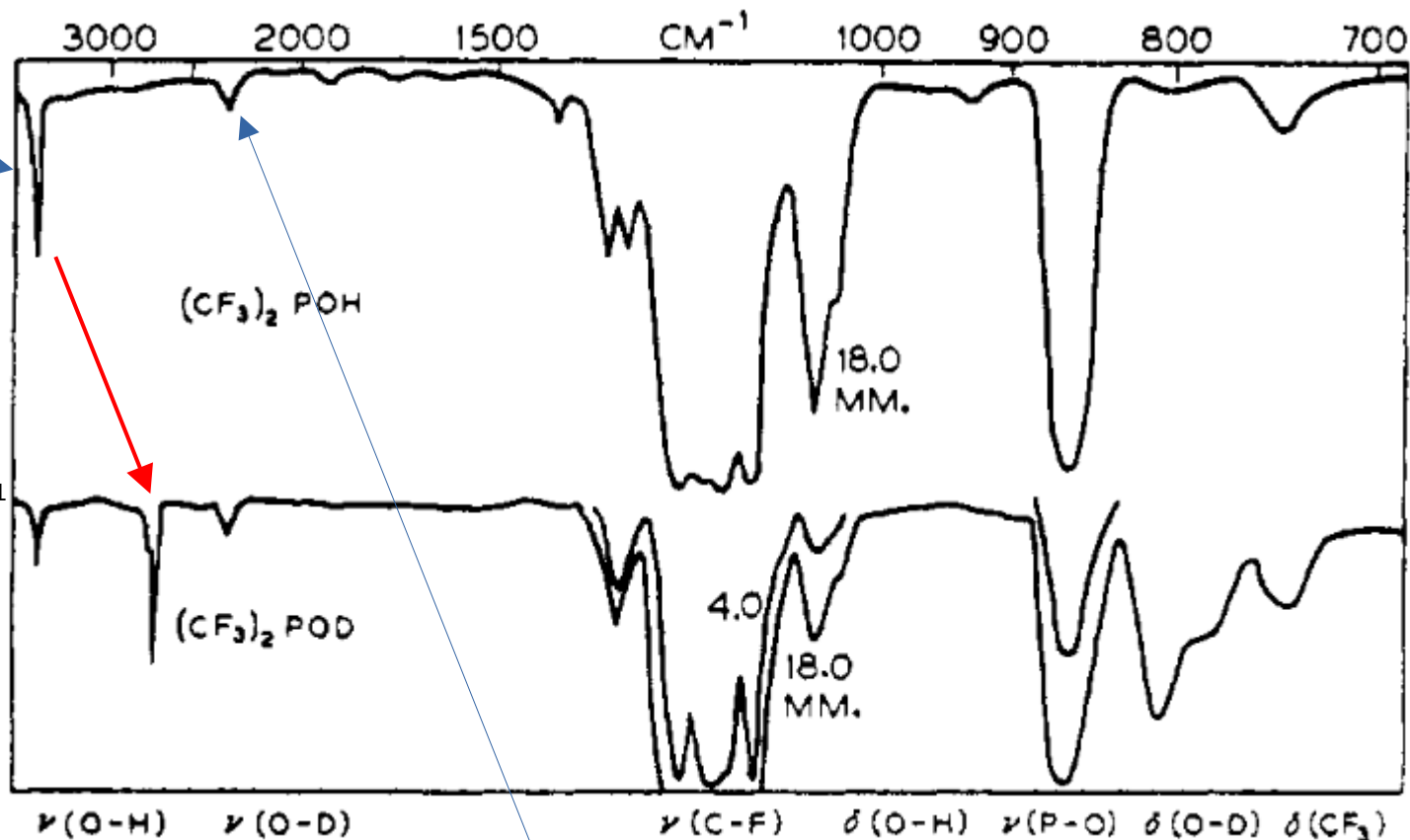
$$\nu(\text{O-D}) \approx 1/\sqrt{2} \nu(\text{O-H}) \approx 2560 \text{ cm}^{-1}$$

Genauer:

$$\mu_1(\text{O-H}) = 16/17$$

$$\mu_2(\text{O-D}) = 32/18$$

$$\nu(\text{O-D}) \approx \sqrt{(\mu_1/\mu_2)} \nu(\text{O-H}) \approx 2634$$



(Aufgabe: ist das $\nu(\text{P-H})$ wegen Spuren von (CF₃)₂P(O)H ?)

Quellen/Literatur

- D. W. H. Rankin, N. W. Mitzel, C. A. Morrison, Structural Methods in Molecular Inorganic Chemistry, John Wiley & Sons, Chichester, 2013.
- B. Campanella, V. Palleschi, S. Legnaioli, Introduction to vibrational spectroscopies, *ChemTexts*, 2021, 7, 5.
- <http://www.ir-spektroskopie.de>