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

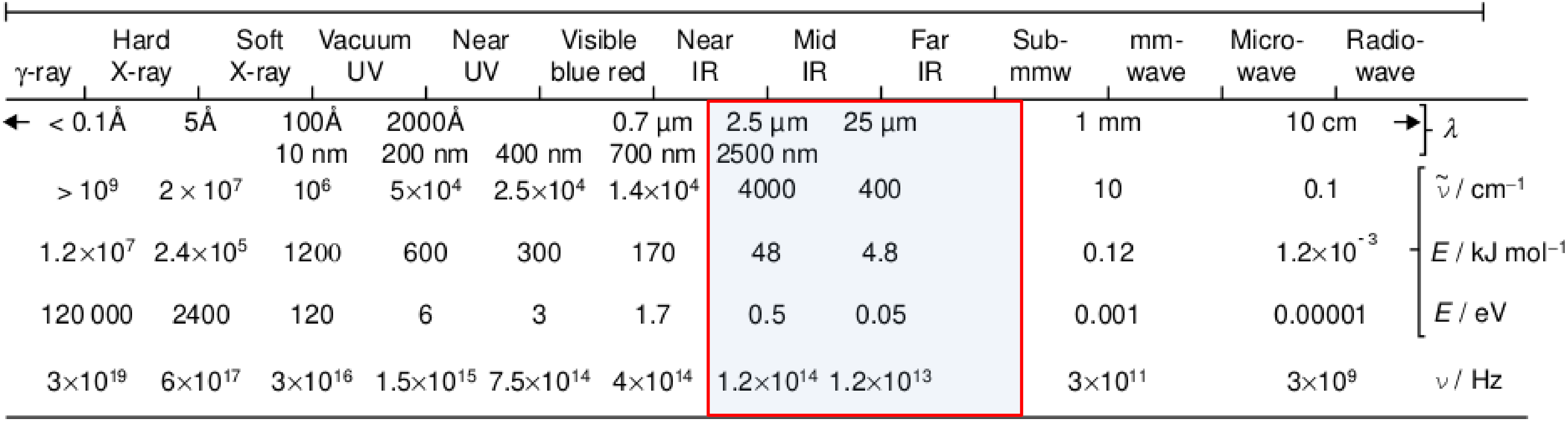
Charakteristische Zeit:

- Langsame Methode
- Mittelschnelle Methode
- Schnelle Methode

Aggregatzustand der Probe:

- Gas
- Flüssigkeit
- Feststoff

IR Bereiche



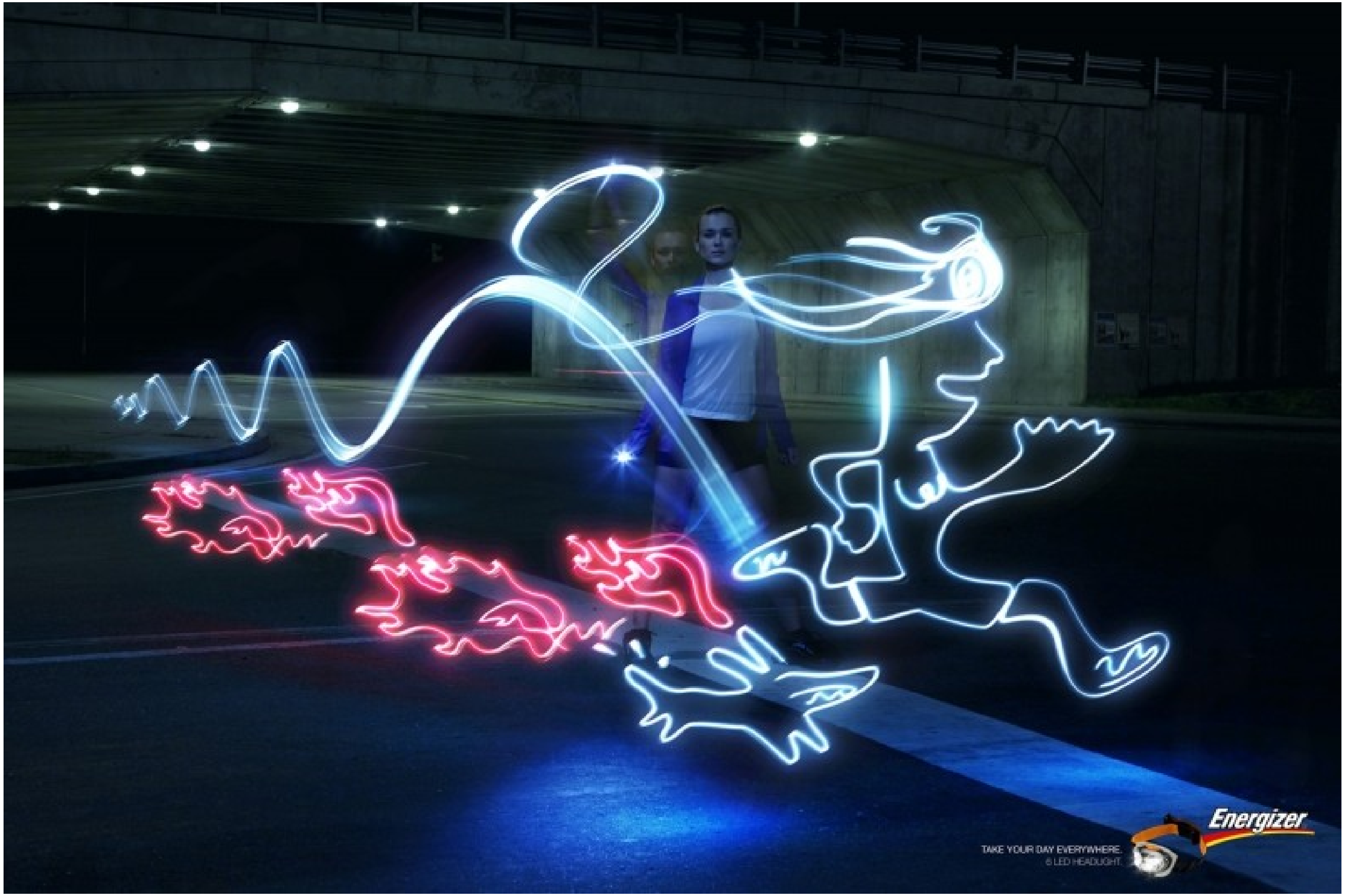
γ-ray	Hard X-ray	Soft X-ray	Vacuum UV	Near UV	Visible blue red	Near IR	Mid IR	Far IR	Sub-mmw	mm-wave	Micro-wave	Radio-wave	
← < 0.1Å	5Å	100Å 10 nm	2000Å 200 nm	400 nm	0.7 µm 700 nm	2.5 µm 2500 nm	25 µm		1 mm		10 cm →		λ
$> 10^9$	2×10^7	10^6	5×10^4	2.5×10^4	1.4×10^4	4000	400		10		0.1		$\tilde{\nu}$ / cm^{-1}
1.2×10^7	2.4×10^5	1200	600	300	170	48	4.8		0.12		1.2×10^{-3}		E / kJ mol^{-1}
120 000	2400	120	6	3	1.7	0.5	0.05		0.001		0.00001		E / eV
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		ν / Hz

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

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

Ferninfrarot-Spektroskopie (FIR, Terahertz-): ca. 400 – 10 cm^{-1} (1.2x10^7 – 3.0x10^5 MHz)

Charakteristische Zeit



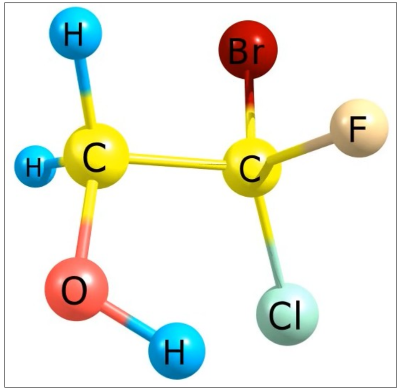
Charakteristische Zeit: IR

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

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

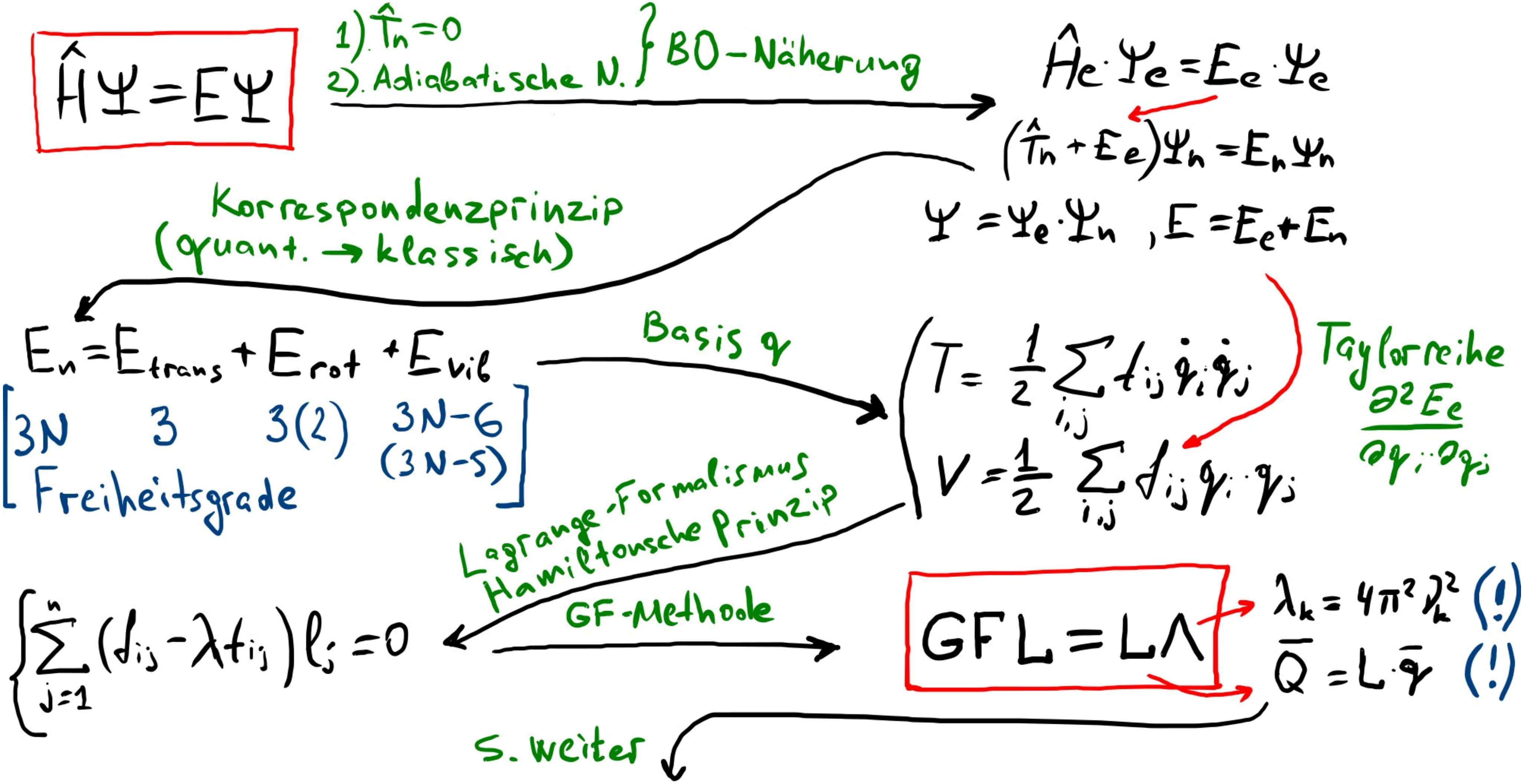
4000 cm^{-1} → $1.2\text{x}10^{14}$ Hz → $8.3\text{x}10^{-15}$ Sek. = 8.3 fs (Femtosekunden)

s. Movie:



MD (GFN2-xTB, NVT, T = 600 K),
t = 1 ps, Δt = 1 fs.

Theorie
(ganz schematisch)



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

1) $\hat{T}_n = 0$

2) Adiabatische N.

} BO-Näherung

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

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

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

Korrespondenzprinzip (quant. → klassisch)

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

$$\left[\begin{matrix} 3N & 3 & 3(2) & 3N-6 \\ & & & (3N-5) \end{matrix}\right]$$

Freiheitsgrade

Basis q

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

$$V = \frac{1}{2}\sum_{i,j} d_{ij}\,q_i \cdot q_j$$

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

Lagrange-Formalismus

Hamiltonsche Prinzip

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

GF-Methode

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

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

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

s. weiter

$$\bar{Q}, \bar{\lambda} \xrightarrow{Q_k \text{ sind orthogonal!}} T = \frac{1}{2} \sum_k \dot{Q}_k^2 \; ; \; V = \frac{1}{2} \sum_k \lambda_k Q_k^2$$

Korrespondenzprinzip
(klassisch- → quanten-)

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

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

↓ Lösung

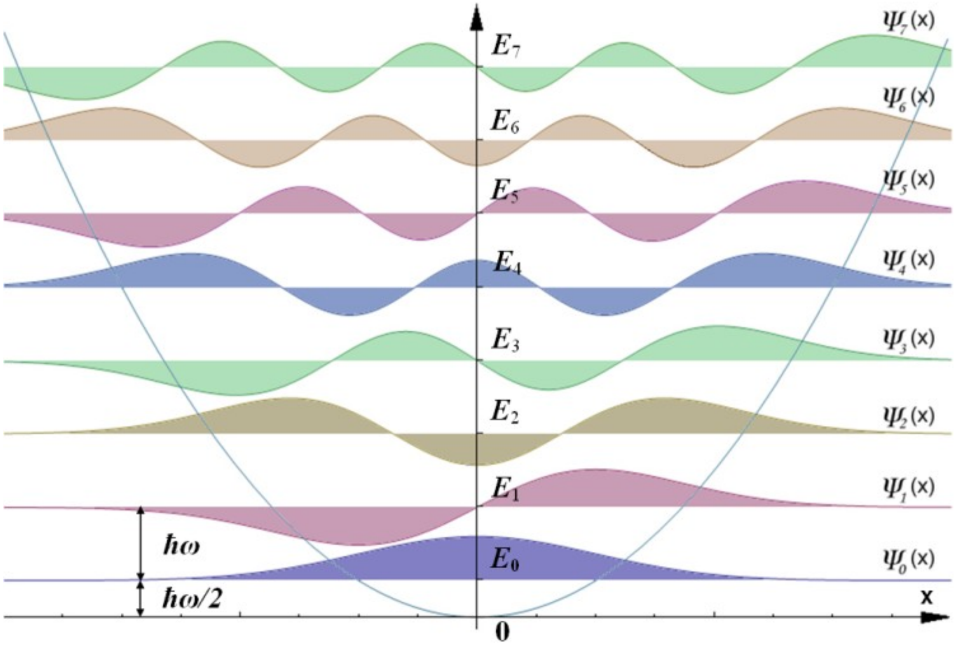
$$\Psi_{k,i} = N_{vib} \cdot H_{(i)}(Q_k^0) \cdot e^{-\frac{1}{2\hbar} \cdot \sqrt{\lambda_k} \cdot Q_k^2}$$

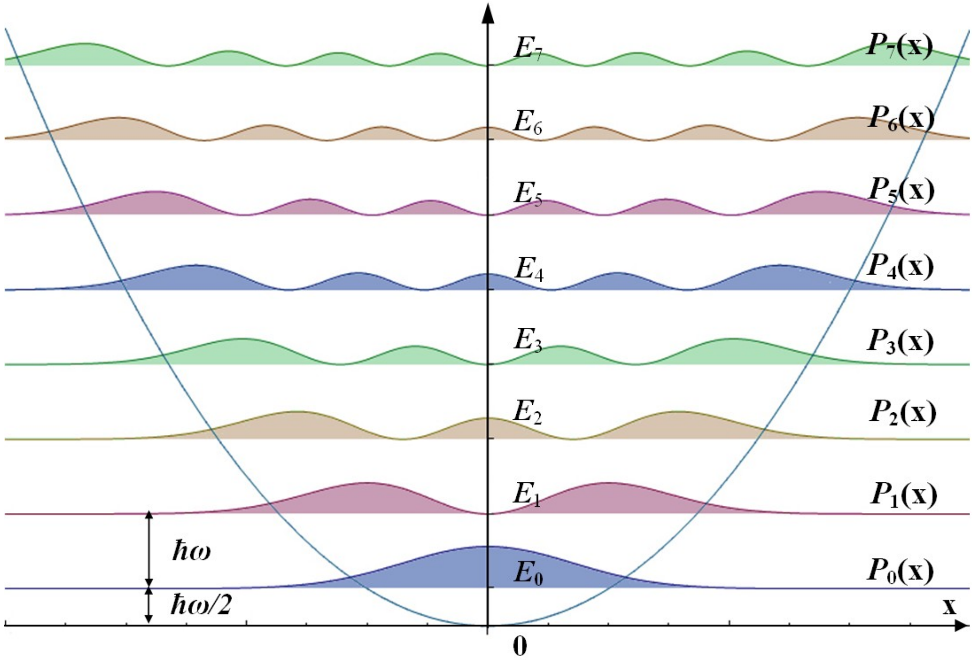
$$\left(Q_k^0 = Q_k \cdot \sqrt{\lambda_k^{1/2} / \hbar} \right)$$

Harmonisch!

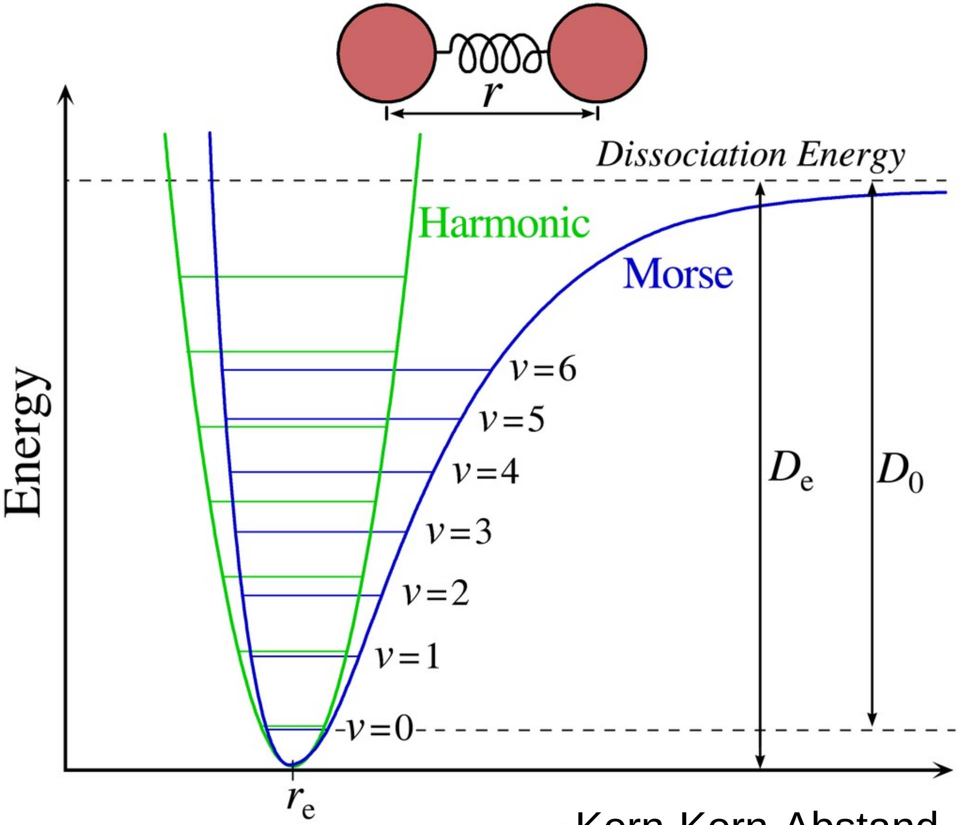
$$\boxed{\begin{array}{c} E_k(v_k) = h\nu_k \left(v_k + \frac{1}{2} \right) \\ v_k = 0, 1, 2, \dots \end{array}}$$

Der harmonische Oszillator (1D)





Harmonisch vs. Anharmonisch



Kern-Kern-Abstand

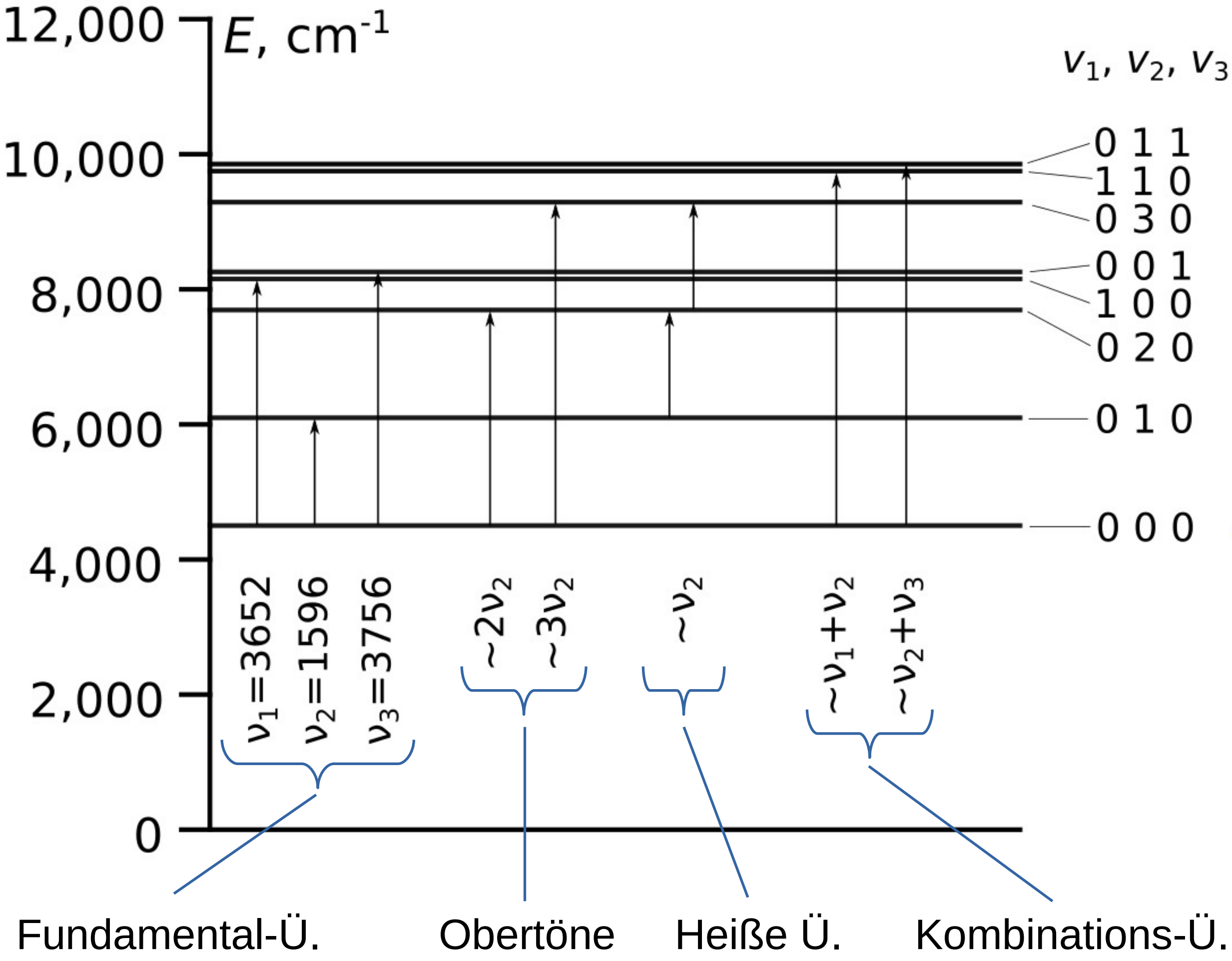
Morse Potential:

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

D_e	(spektroskopische) Disssoziationsenergie
r_e	Gleichgewichtsabstand im Potentialminimum
a	Konstante, die die Steifigkeit des Potentials beschreibt

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

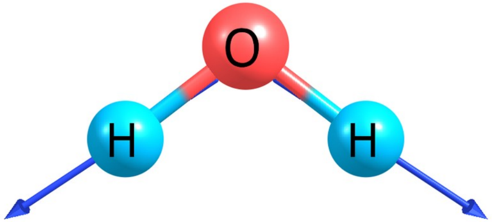
H_2O Schwingungsniveaus



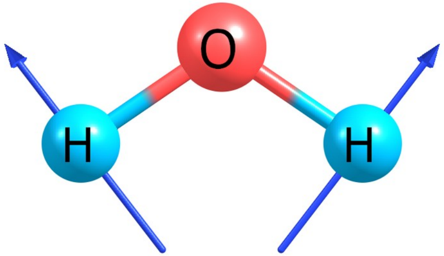
$$\leftarrow E_{vib}(0,0,0) = \frac{1}{2}\sum_{k=1}^{3} h\nu_k$$

$$(E_{ZPV})$$

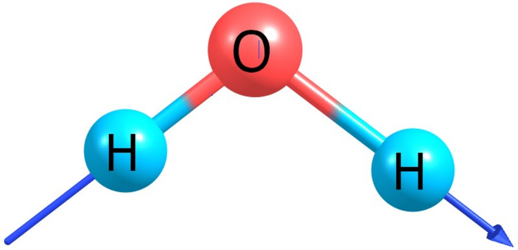
H_2O Schwingungsformen



$\nu_1 = 3652\ \mathrm{cm}^{-1}$
A_1

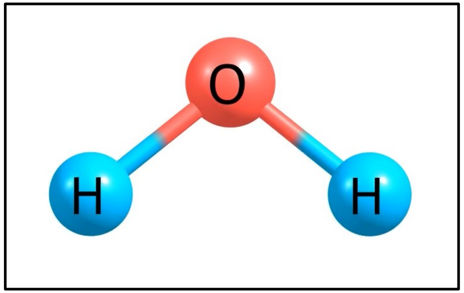


$\nu_2 = 1596\ \mathrm{cm}^{-1}$
A_1



$\nu_3 = 3756\ \mathrm{cm}^{-1}$
B_2

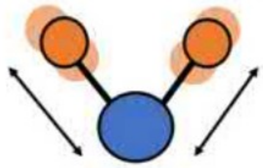
s. Movies:



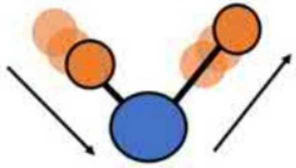
Schwingungsformen

(s. Movies!)

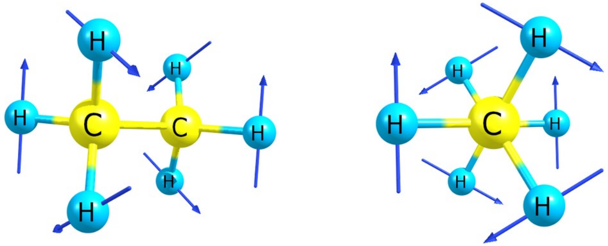
Valenzschwingungen
(Streckschwingungen)



symmetrische

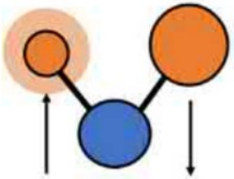


antisymmetrische

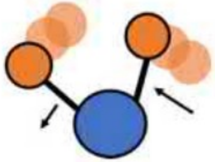


Torsionsschwingungen

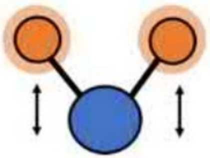
Deformationsschwingungen



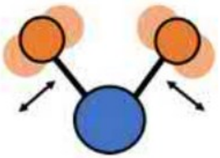
Drehschwingung
(engl. twisting)



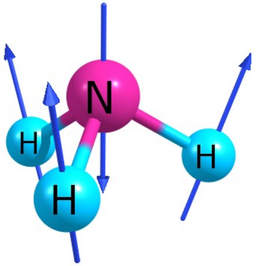
Schaukelschwingung
(engl. rocking)



Wippschwingung
(engl. wagging)



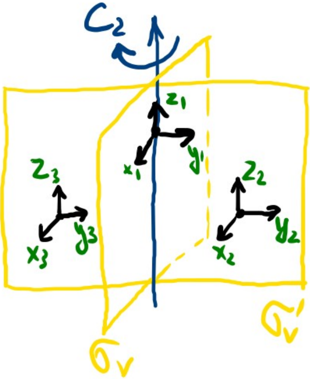
Biegeschwingung
(engl. scissoring oder bending)



Inversionsschwingungen

Symmetrie

Beispiel: H_2O



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

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

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

Reduktionsformel ↲

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

Reduktion:

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

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

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

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

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

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

Auswahlregeln

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

$I_{IR} \propto |M_v|^2$ (M_v - Übergangsdipolmoment) H_2O: $\underline{\Gamma_{vib} = 2A_1 + \underline{B_2}}$

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

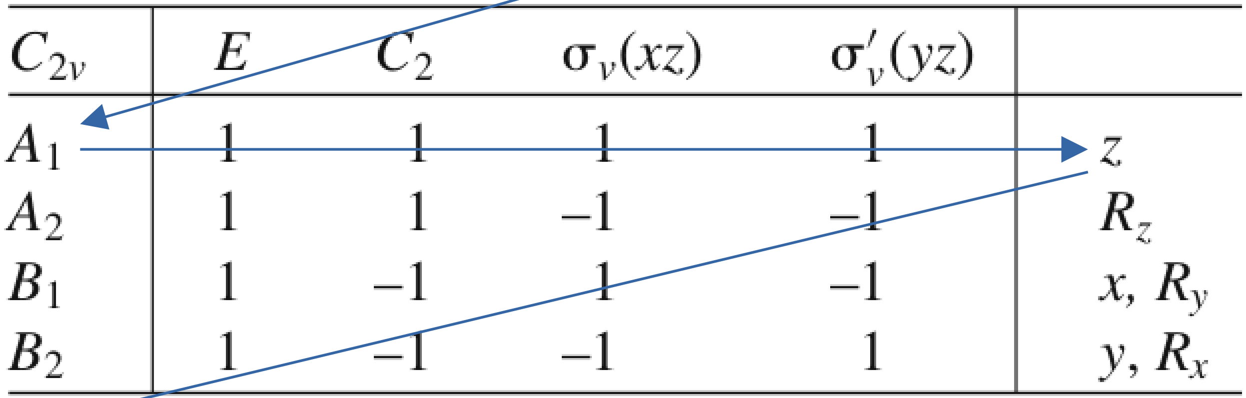
$M_x = \langle \varphi_i^* | \mu_x | \varphi_j \rangle$

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

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

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

$$\mu_q = \mu_q^0 \cdot \underbrace{\langle \varphi_i | \varphi_j \rangle}_{\varnothing} + \underset{(!)}{\left(\frac{\partial \mu_q}{\partial Q_k}\right)_0} \cdot \underbrace{\langle \varphi_i^* | Q_k | \varphi_j \rangle}_{\downarrow \; \Delta v_k = \pm 1}$$



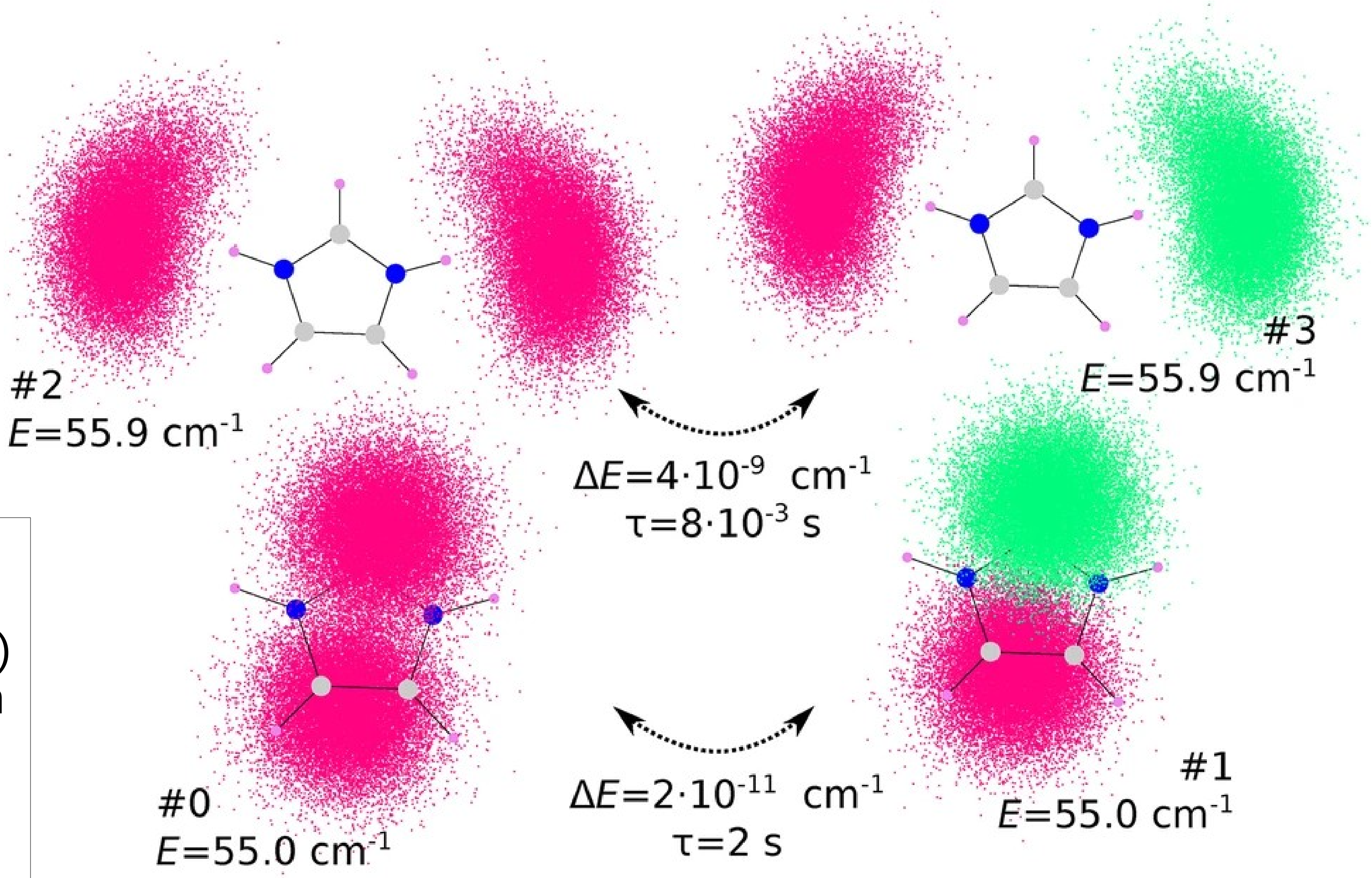
C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v'(yz)$	
A_1	1	1	1	1	z
A_2	1	1	–1	–1	R_z
B_1	1	–1	1	–1	x, R_y
B_2	1	–1	–1	1	y, R_x

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

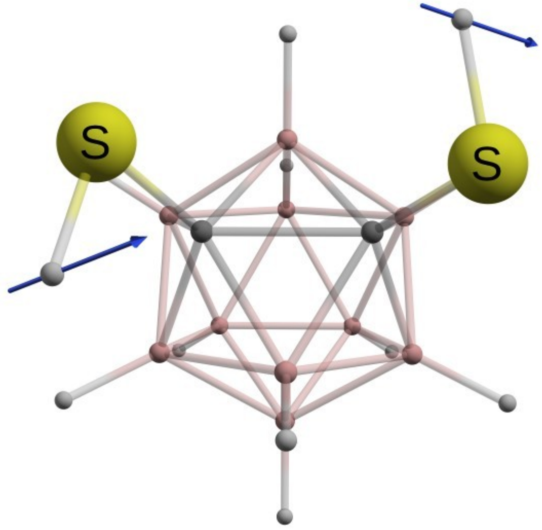
Wellenfunktionen der niedrigsten Schwingungszustände der He-Bewegung um (Imidazol)H^+.



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

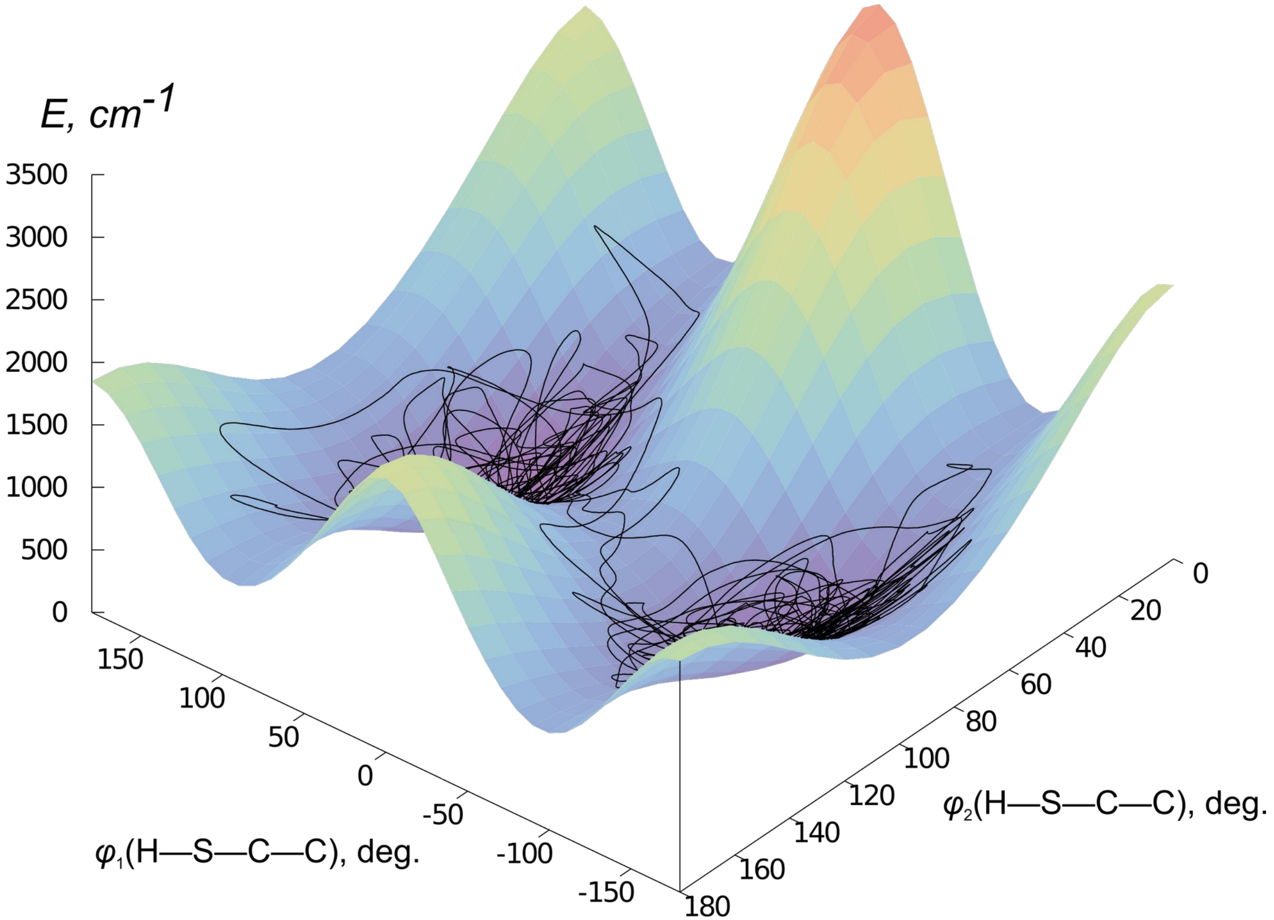
Normalmoden ≠ reale Schwingungen

1,2-$(SH)_2$-*closo*-1,2-$C_2B_{10}H_{10}$



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

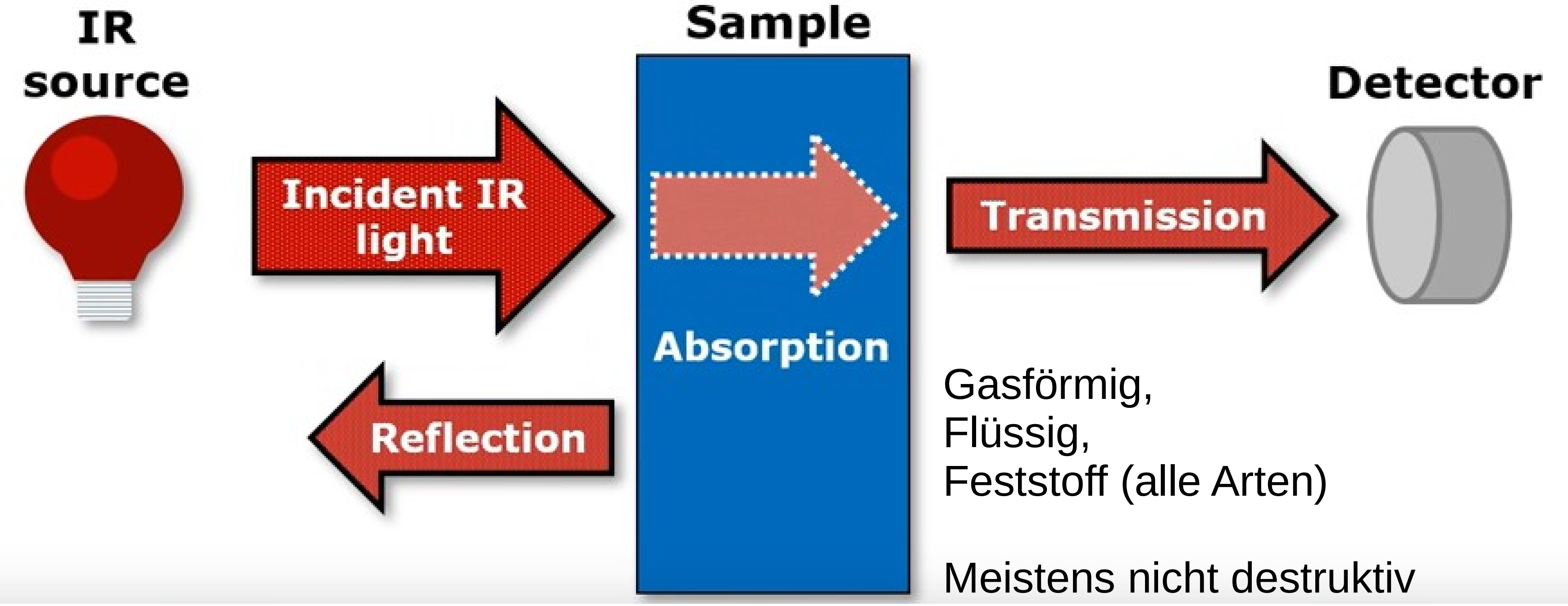
s. Movies!



Chem. Eur. J. 25 (2019) 2313.

Technik
(ganz schematisch)

Transmission/Absorption/Reflexion



Gasförmig,
Flüssig,
Feststoff (alle Arten)

Meistens nicht destruktiv
(~Probevorbereitung!)

Quelle: Bruker, https://www.youtube.com/watch?v=KRoWMB3AR3s

Lichtquelle/Detektor

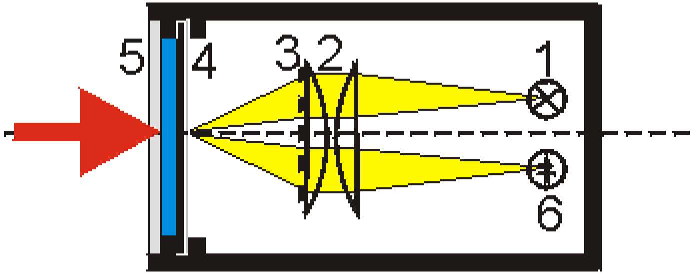
Schwarzer Strahler

Globar (Siliziumcarbid)

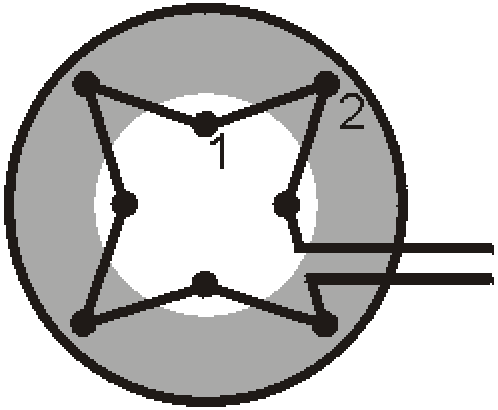
Metallwiderstand

Quelle: http://www.ir-spektroskopie.de

Golay-Zelle

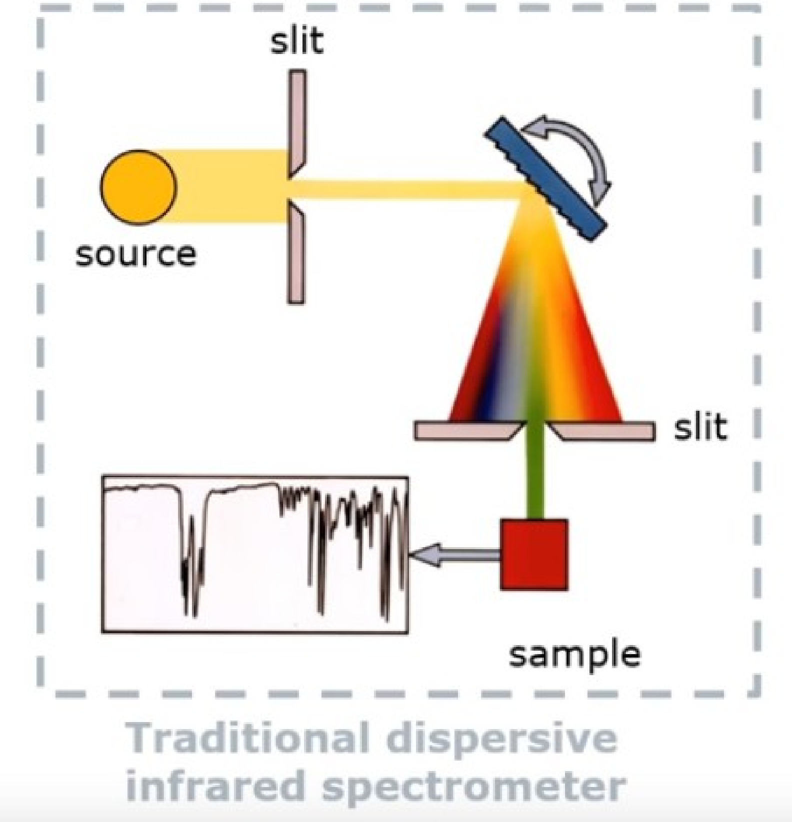


Thermosäule



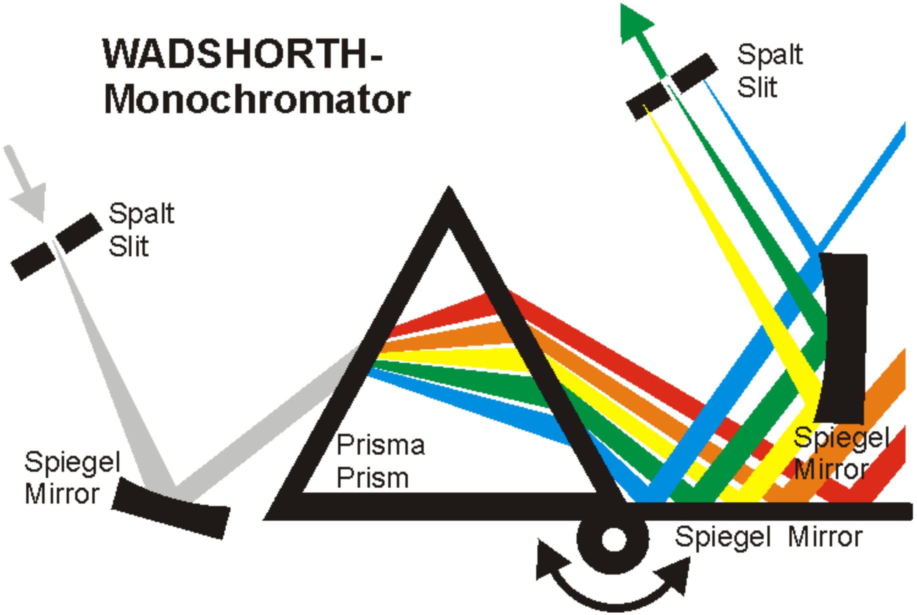
(Das beste: Quantendetektoren)

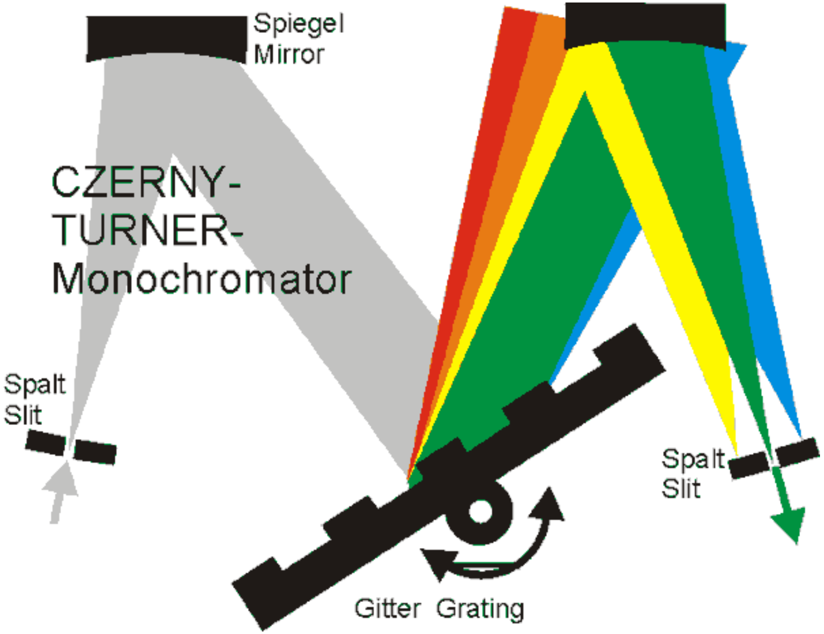
Dispersive Geräte



Quelle: Bruker, https://www.youtube.com/watch?v=KRoWMB3AR3s

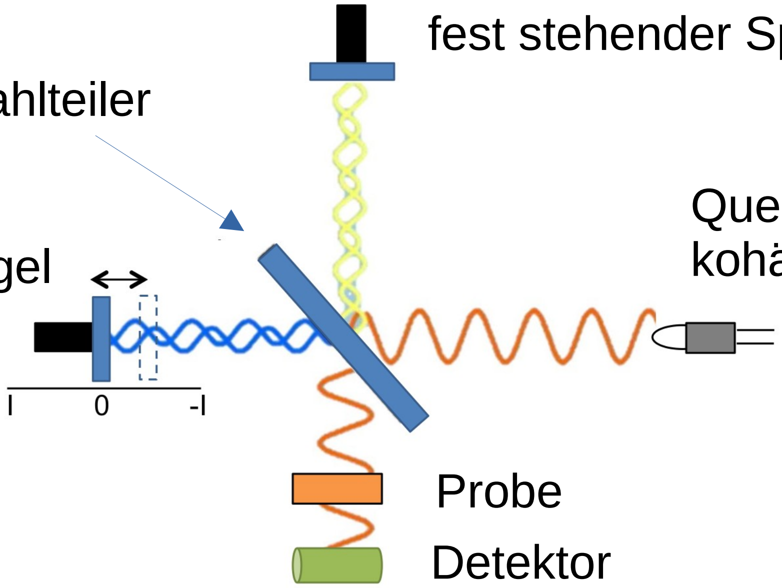
Monochromator





Quelle: http://www.ir-spektroskopie.de

FT-IR: Michelson Interferometer



fest stehender Spiegel

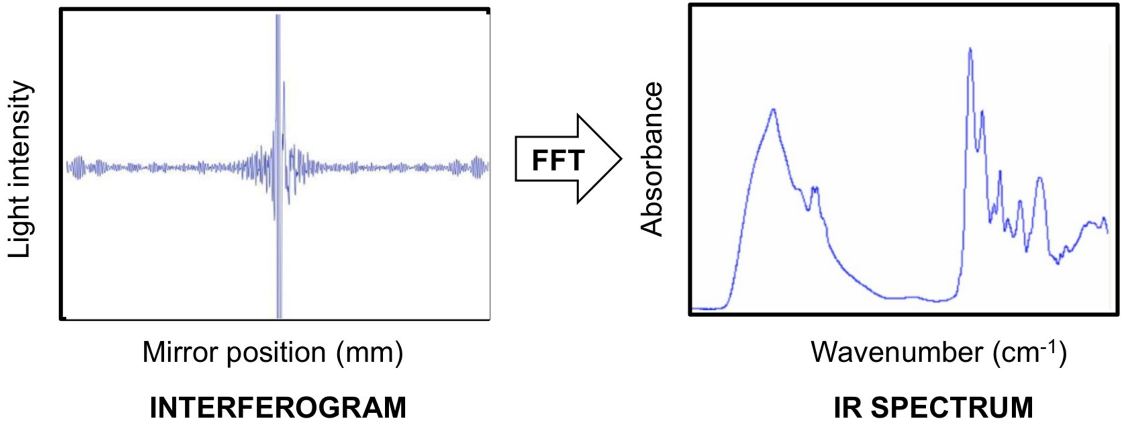
Strahlteiler

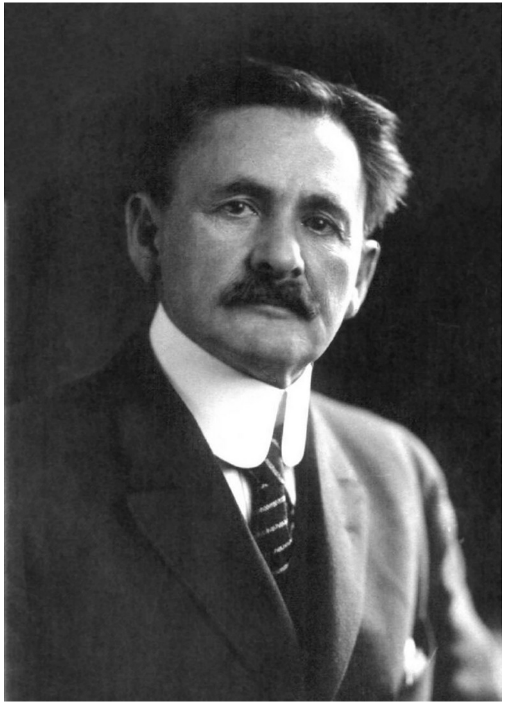
Quelle vom kohärenten Licht

bewegter Spiegel

Probe

Detektor





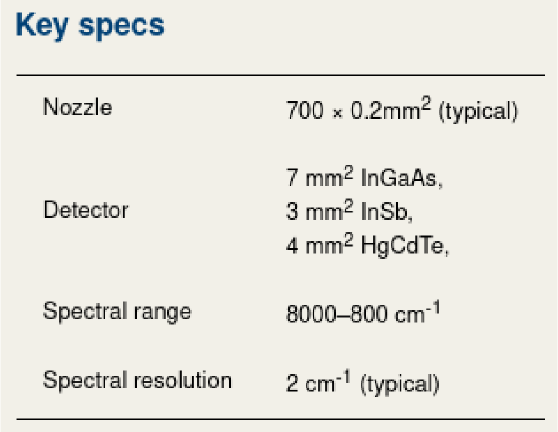
Albert A. Michelson
1852 – 1931
1907 Nobelpreis f. Physik

B. Campanella,
V. Palleschi,
S. Legnaioli,
ChemTexts
2021, 7, 5.

Ein reales Gerät: FT-IR f. Gasphase

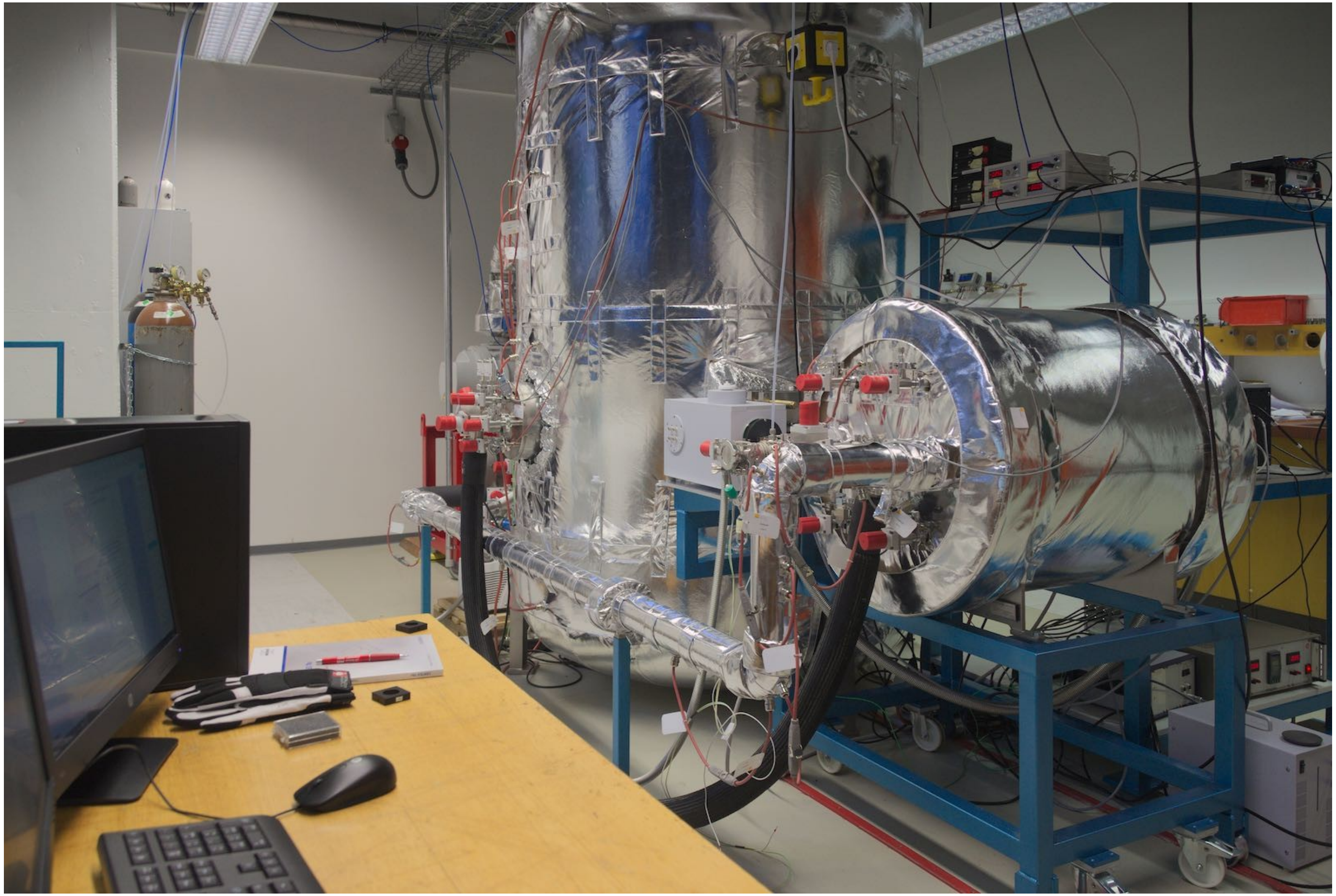
The Gratin-jet

Gas-recycling atom-economic infrared spectroscopy



Key specs

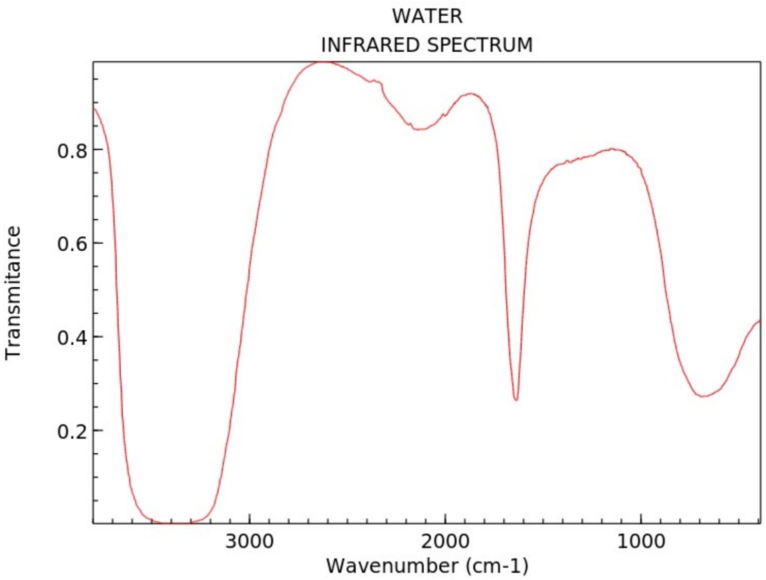
Nozzle	700 × 0.2mm^2 (typical)
Detector	7 mm^2 InGaAs, 3 mm^2 InSb, 4 mm^2 HgCdTe,
Spectral range	8000–800 cm^{-1}
Spectral resolution	2 cm^{-1} (typical)



Beispiele und Anwendungen

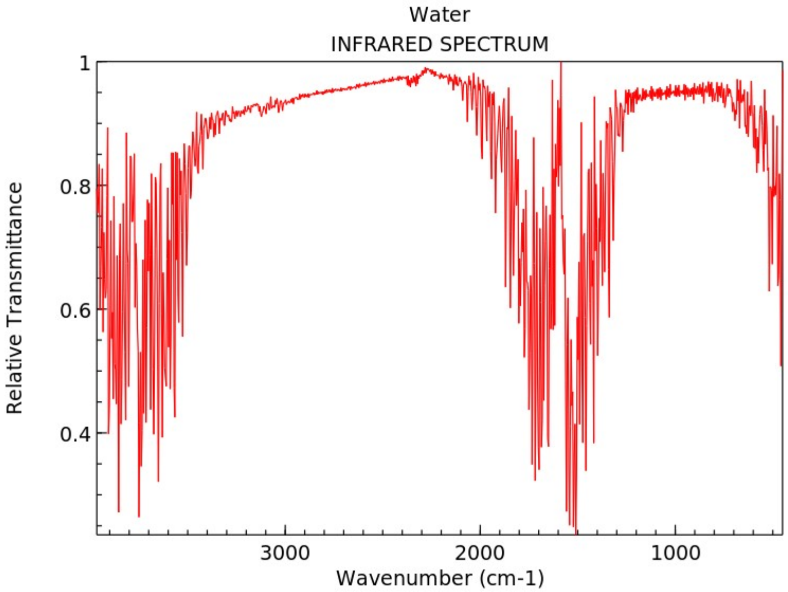
H_2O: Reale IR Spektren

Flüssigkeit



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

Gas



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

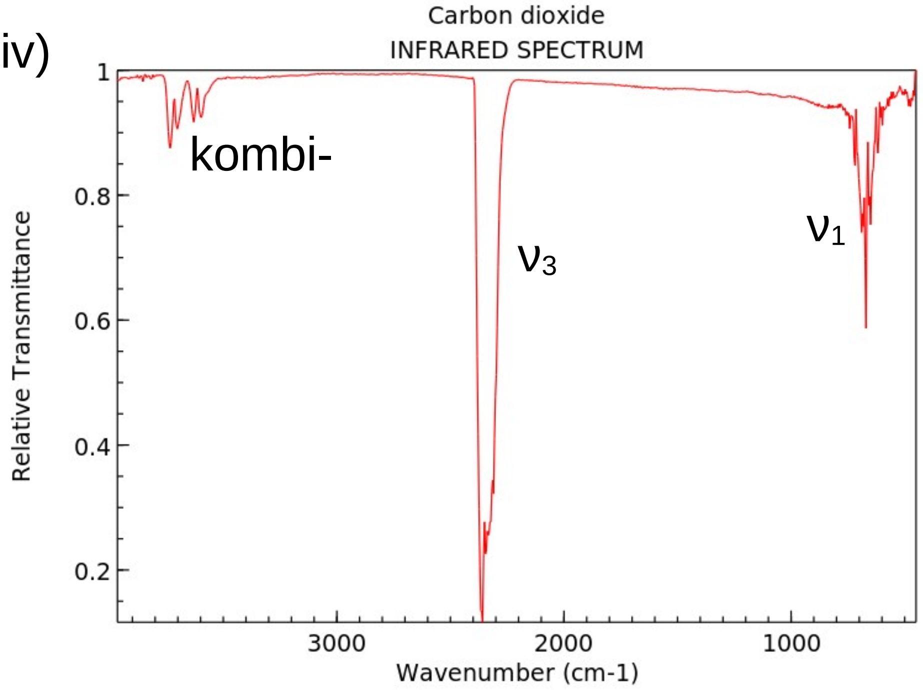
Symmetrie von CO_2

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

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

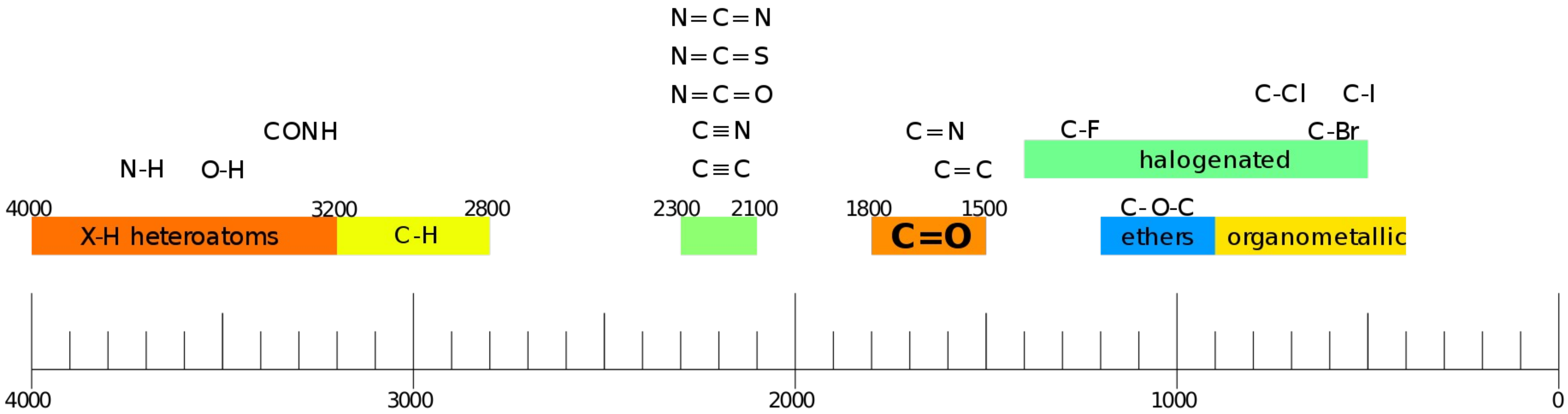
$D_{\infty h}$	E	$2C_\infty^\Phi$	...	$\infty\sigma_v$	i	$2S_\infty^\Phi$	...	∞C_2		
Σ_g^+	1	1	...	1	1	1	...	1		x^2, y^2, z^2
Σ_g^-	1	1	...	–1	1	1	...	–1	R_z	
Π_g	2	2cΦ	...	0	2	–2cΦ	...	0	(R_x, R_y)	(xz, yz)
Δ_g	2	2c2Φ	...	0	2	2c2Φ	...	0		$(x^2\text{-}y^2, xy)$
...	..	...	...	..	..	...	...	..		
Σ_u^+	1	1	...	1	–1	–1	...	–1	z	
Σ_u^-	1	1	...	–1	–1	–1	...	1		
Π_u	2	2cΦ	...	0	–2	2cΦ	...	0	(x, y)	
Δ_u	2	2c2Φ	...	0	–2	–2c2Φ	...	0		
...	..	...	...	..	..	...	...	..		

[a] c stands for cos.



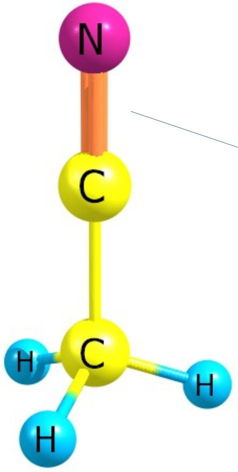
NIST Chemistry WebBook (https://webbook.nist.gov/chemistry)

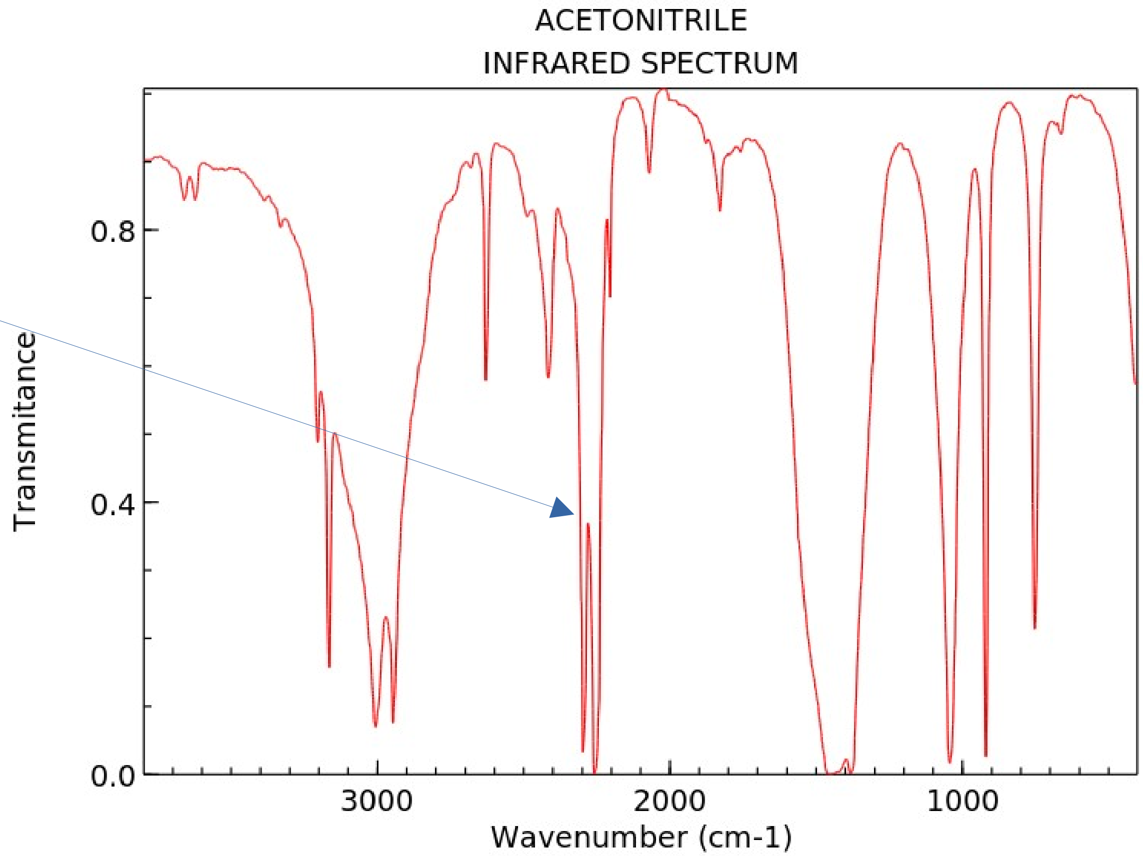
Charakteristische Banden



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



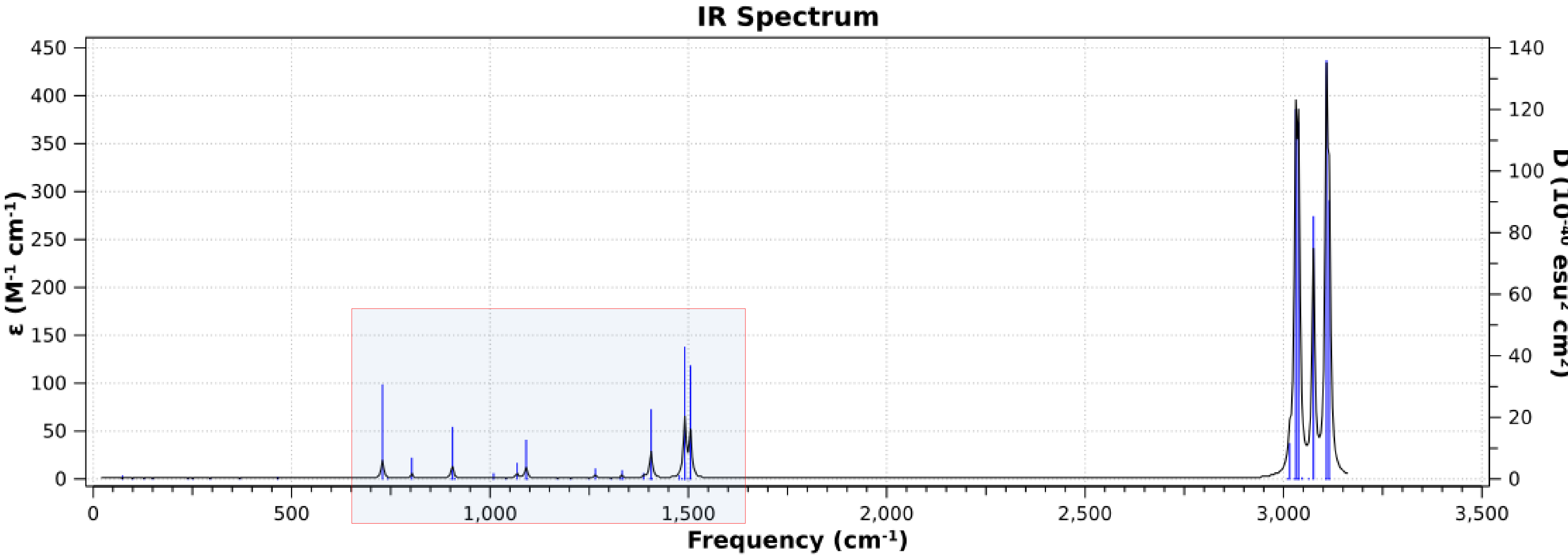


NIST Chemistry WebBook (https://webbook.nist.gov/chemistry)

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

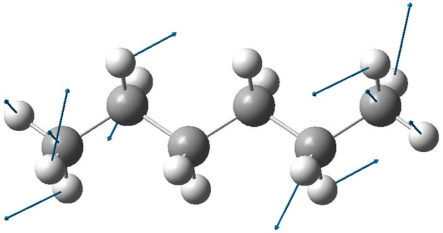
NICHTcharakteristische Banden

Beispiel: *n*-Hexan

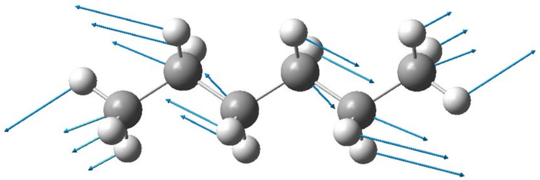


NICHTcharakteristische Moden

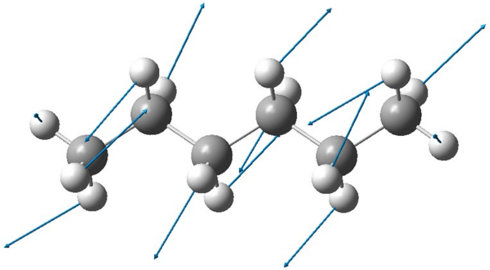
n-Hexan, exemplarisch (s. Movies!)



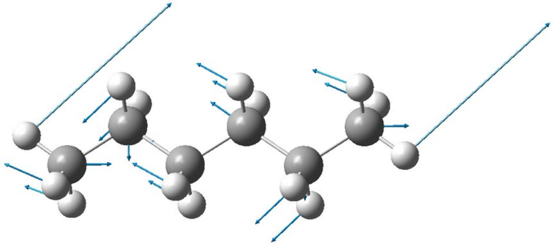
ν_1 = 74



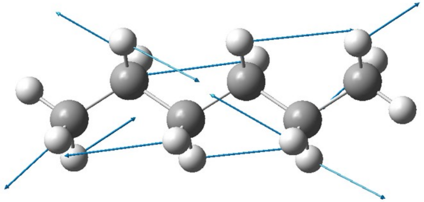
ν_8 = 370



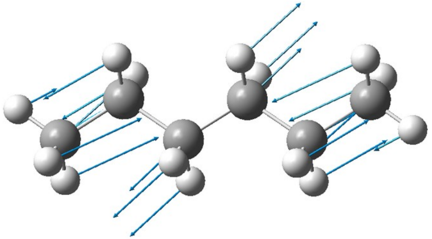
ν_{12} = 802 $\mathrm{cm^{-1}}$



ν_{14} = 905

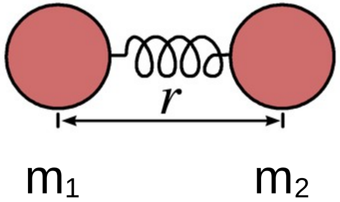


ν_{16} = 1009



ν_{17} = 1040 $\mathrm{cm^{-1}}$

Isotopeneffekt



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

$$E_v = h\nu\left(v+\frac{1}{2}\right) \qquad \nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$$

← Kraftkonstante

← Reduzierte Masse

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

z.B.: X−H vs. X−D

$$k_1 \approx k_2$$

dann

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

wenn $m_X >> m_H$, dann

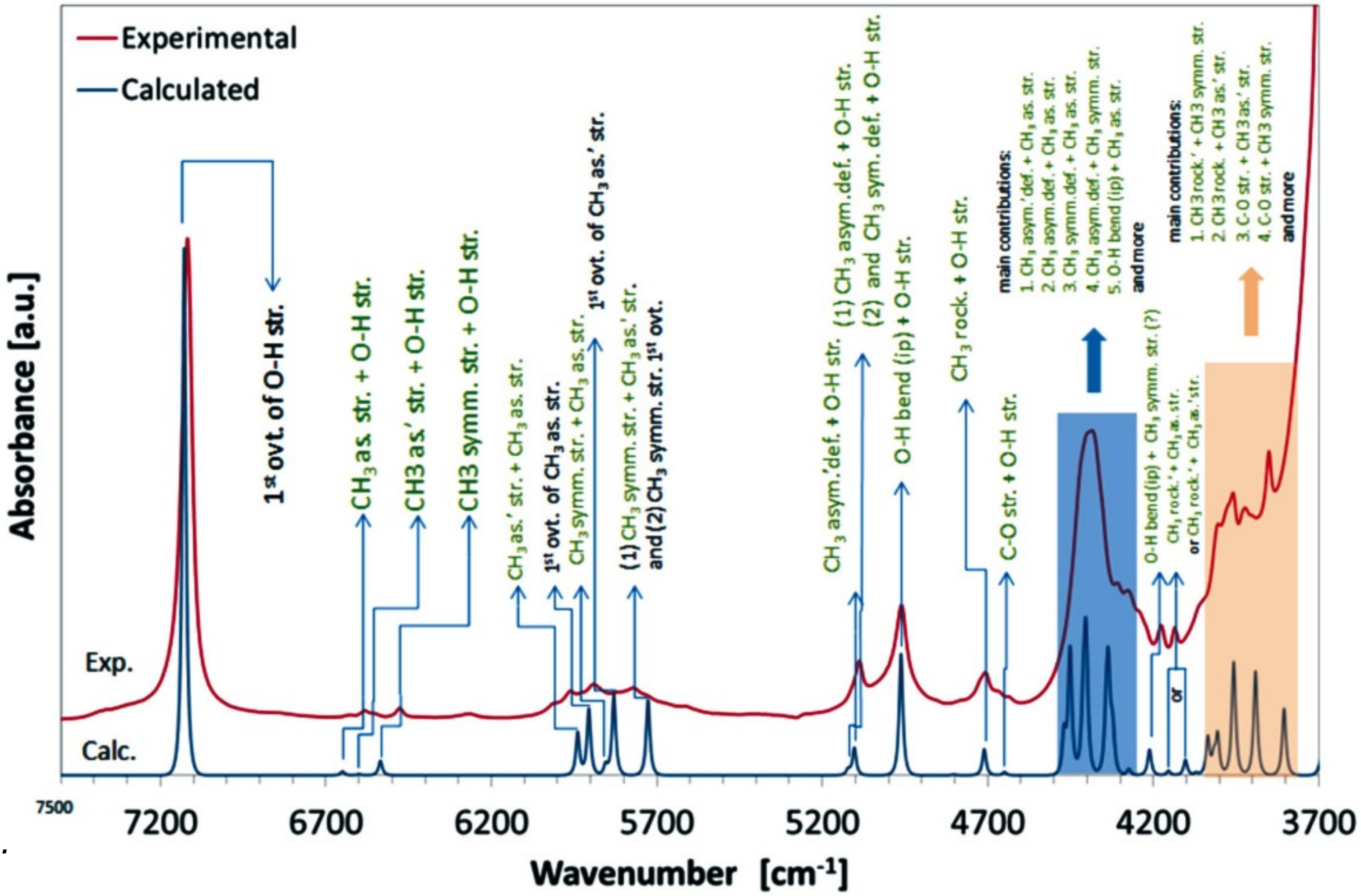
$$\sqrt{\frac{\mu_2}{\mu_1}} \approx \sqrt{2}$$

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

Reale Beispiele: H_2O vs. D_2O

$\nu_s(O-H)$:	H_2O	D_2O
gemessen	3657	2671 cm^{-1}
gerechnet		2586 cm^{-1}

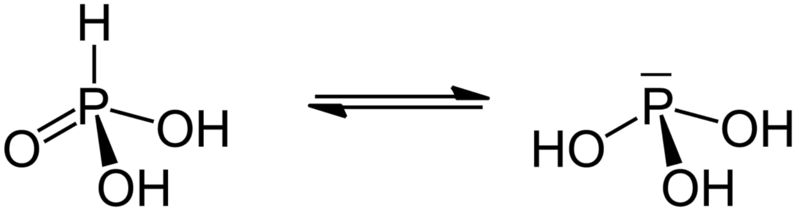
Beispiel NIR: CH_3OH



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

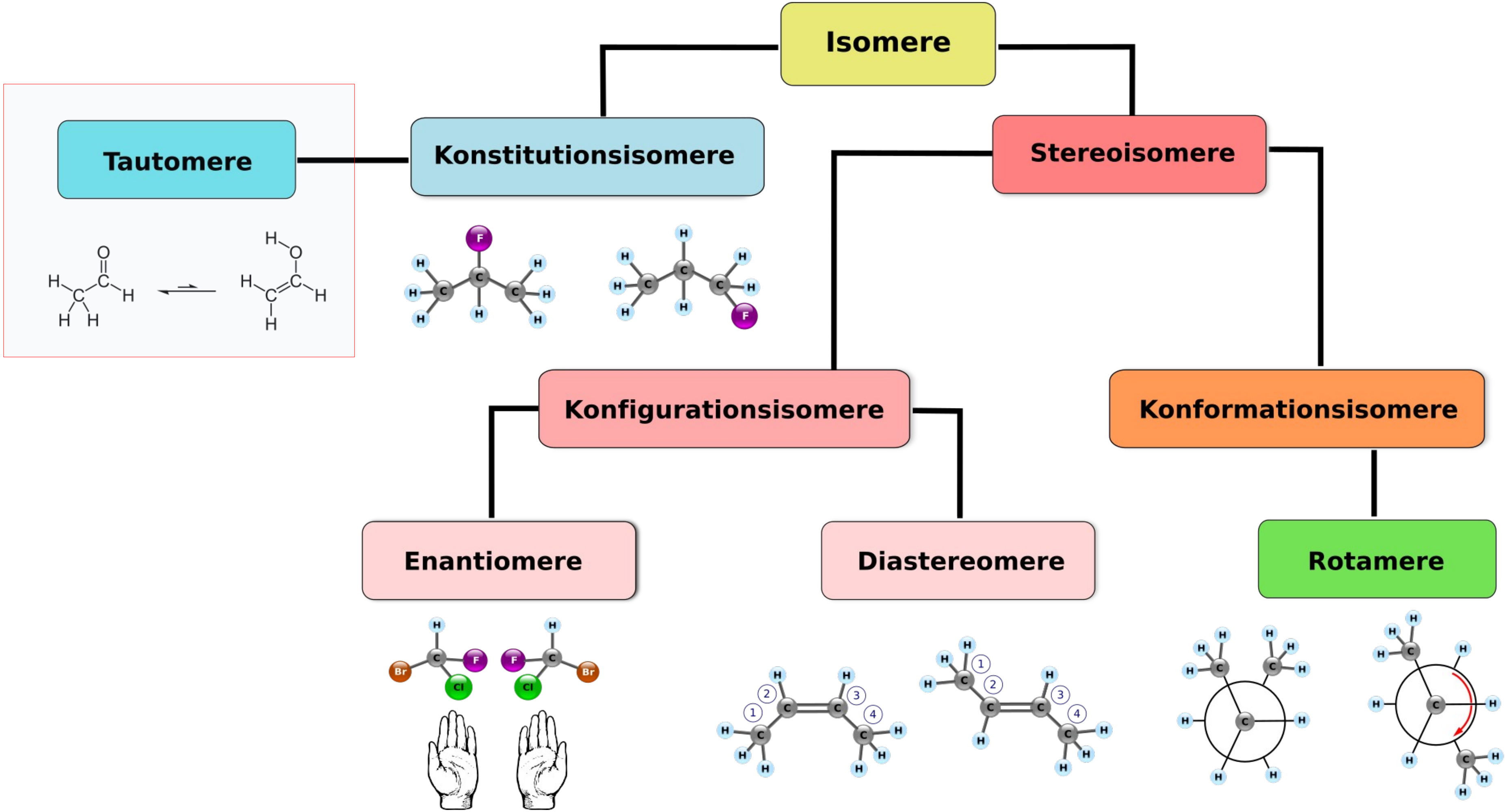
+11 kcal/mol @ PBE0-D3BJ/def2-QZVPP

(0% @ RT, 1% @ 1100 K hypothetisch!)

R_2POH vs. $R_2P(O)H$???

B. Hoge, S. Neufeind, S. Hettel, W. Wiebe, C. Thösen, *J. Organomet. Chem.* 2005, 690, 2382–2387.

Tautomerie



Isomere

Tautomere

Konstitutionsisomere

Stereoisomere

Konfigurationsisomere

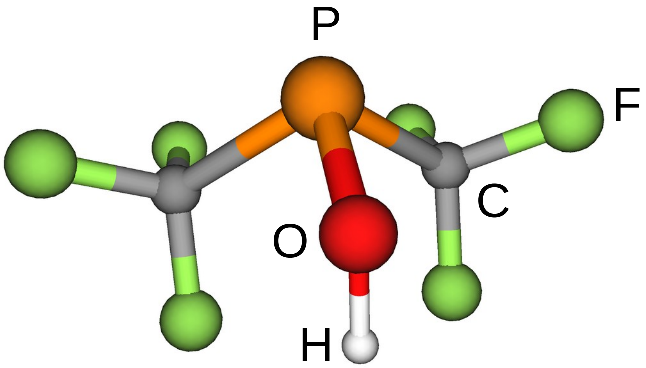
Konformationsisomere

Enantiomere

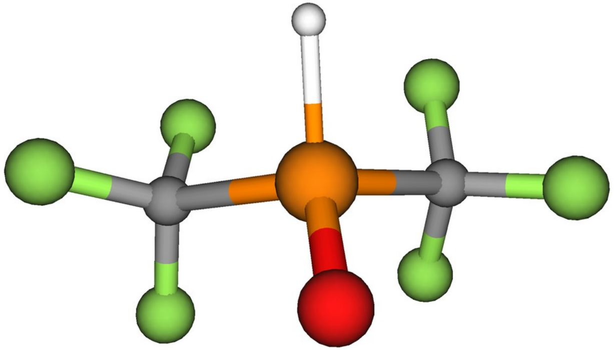
Diastereomere

Rotamere

$(CF_3)_2POH$ oder $(CF_3)_2P(O)H$?



E = 0



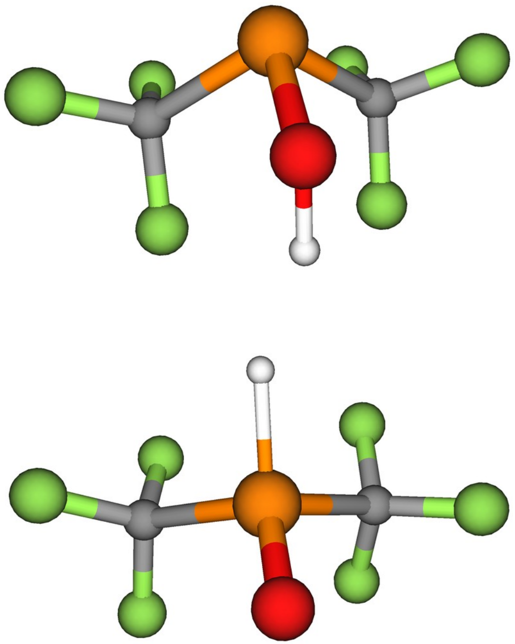
+5 kcal/mol @ PBE0-D3BJ/def2-QZVPP

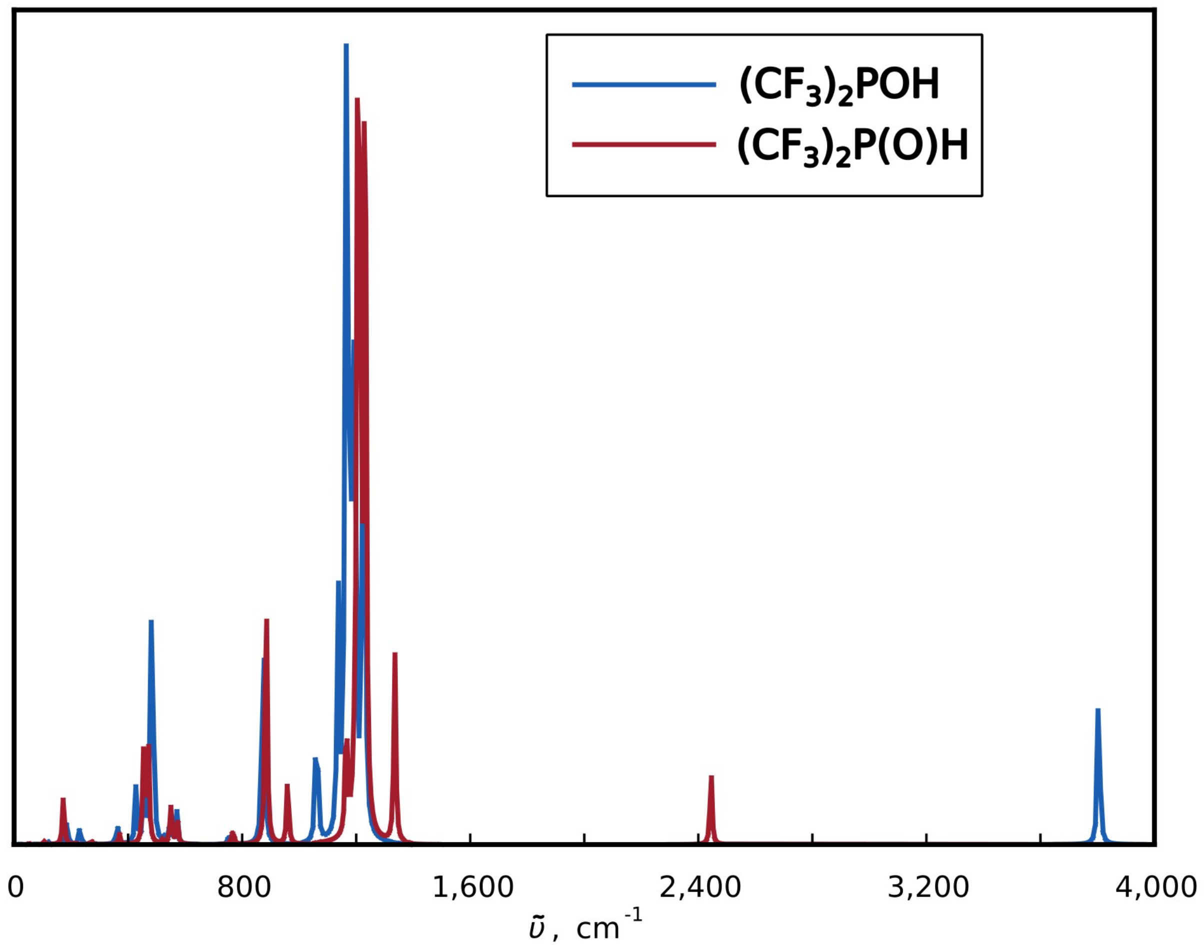
(0% @ RT, 1% @ 550 K hypothetisch!)

Experiment?

$(CF_3)_2POH$ oder $(CF_3)_2P(O)H$?

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



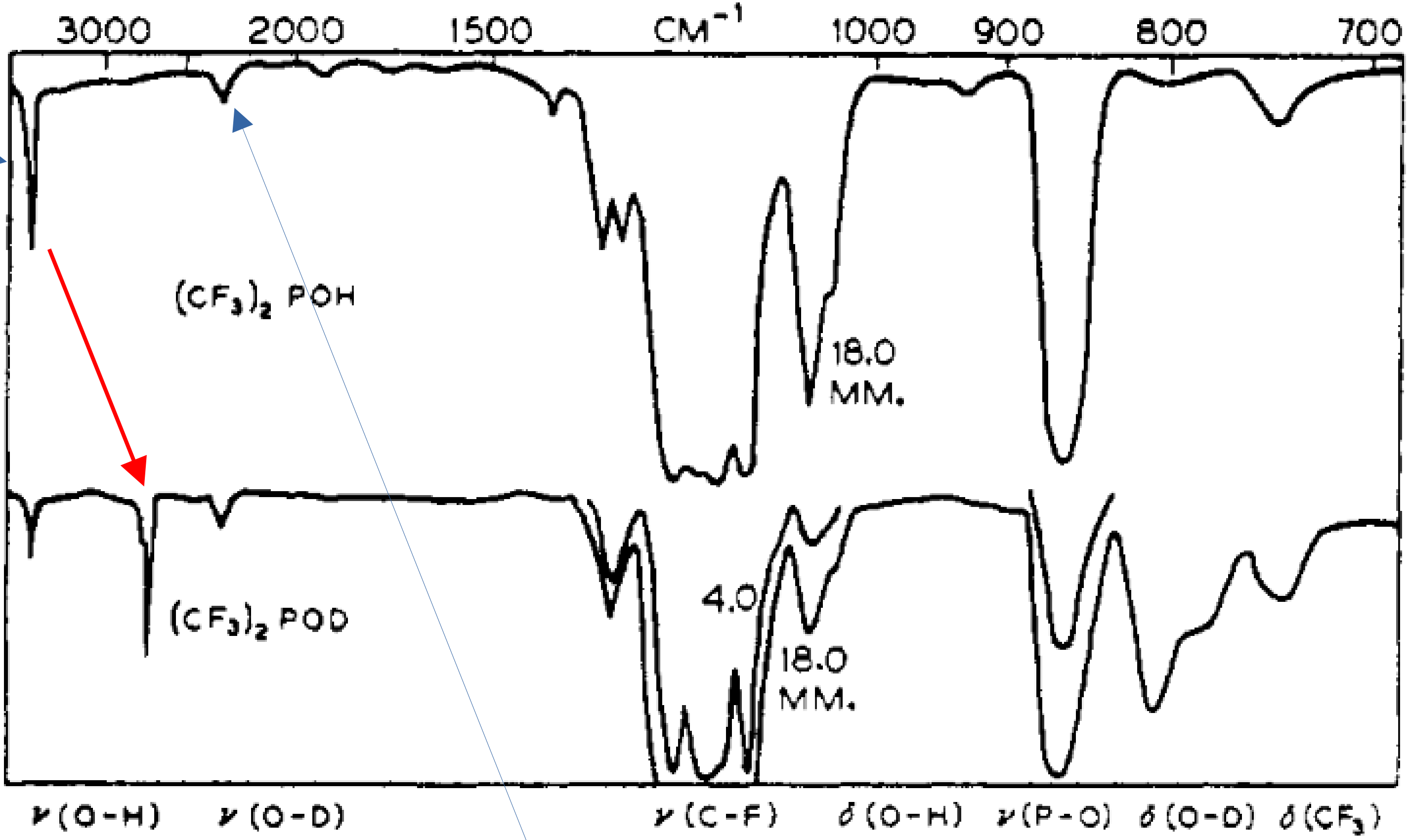


$(CF_3)_2POH$: IR-Spektren

Gemessen:

ν(O-H) = 3620 cm^{-1}

ν(O-D) = 2640 cm^{-1}



Gerechnet:

Grob:
ν(O-D) ≈ $1/\sqrt{2}$ ν(O-H) ≈ 2560 cm^{-1}

Genauer:
μ_1(O-H) = 16/17
μ_2(O-D) = 32/18
ν(O-D) ≈ $\sqrt{(\mu_1/\mu_2)}$ ν(O-H) ≈ 2634

(Aufgabe: ist das ν(P-H) wegen Spuren von $(CF_3)_2P(O)H$?)

J. E. Griffiths, A. B. Burg,
J. Am. Chem. Soc. 1962, 84, 3442–3450.

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