

Strukturaufklärung in der molekularen anorganischen Chemie

5. Mikrowellenspektroskopie

Mikrowellenstrahlung

	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 Å	5 Å	100 Å	2000 Å	400 nm	0.7 μm	2.5 μm	25 μm			1 mm	10 cm	→
			10 nm	200 nm	400 nm	700 nm	2500 nm						λ
	> 10 ⁹	2 × 10 ⁷	10 ⁶	5 × 10 ⁴	2.5 × 10 ⁴	1.4 × 10 ⁴	4000	400			10	0.1	ν̃ / 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

$$\nu = \sim 1 \text{ GHz} \text{ — } \sim 3 \text{ THz}$$

$$(\sim 0.03 \text{ cm}^{-1} \text{ — } \sim 100 \text{ cm}^{-1})$$

$$\tau = \sim 1 \text{ ns} \text{ — } \sim 0.3 \text{ ps.}$$

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

Klassische Vorstellung

Energie (1D):

$$E = \frac{1}{2} I_x \omega_x^2$$

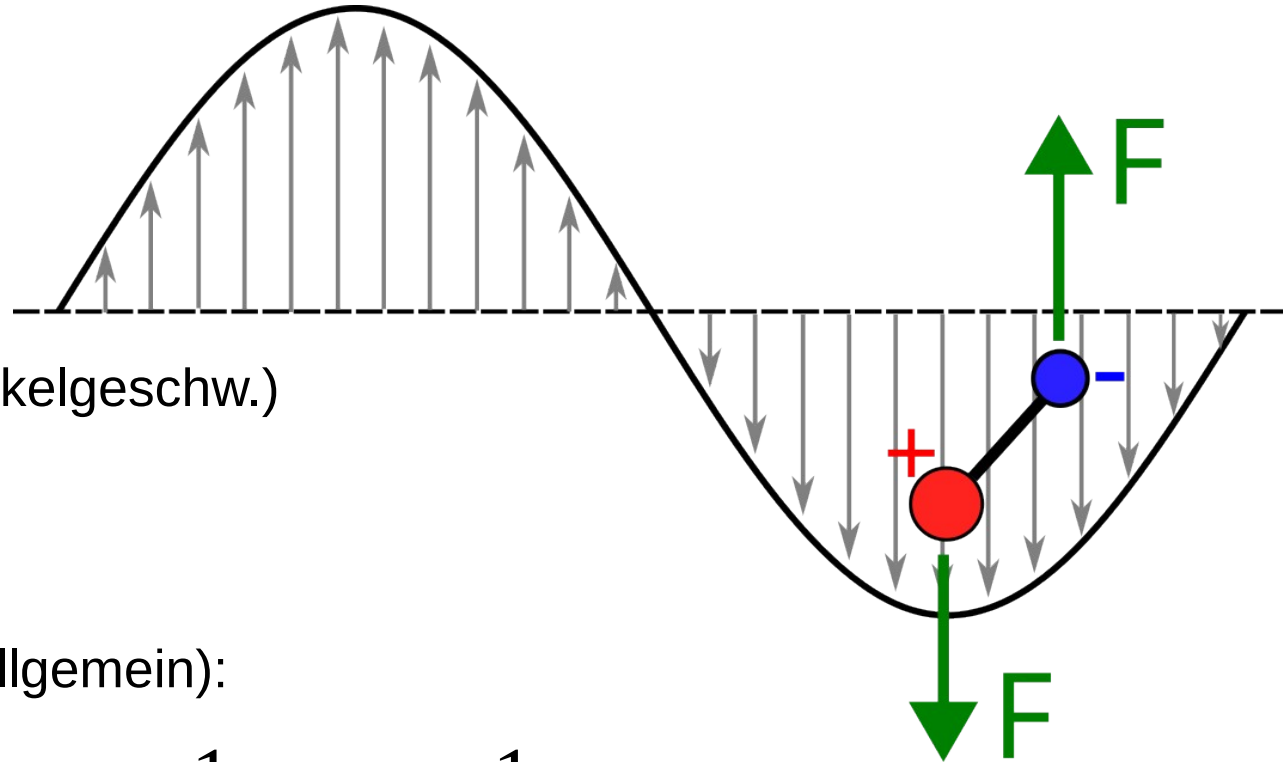
(I_x – Trägheitsmoment, ω_x – Winkelgeschw.)

Drehimpuls:

$$J_x = I_x \omega_x$$

Energie (Allgemein):

$$E = \frac{1}{2I_x} J_x^2 + \frac{1}{2I_y} J_y^2 + \frac{1}{2I_z} J_z^2$$



Zweiatomiges Molekül

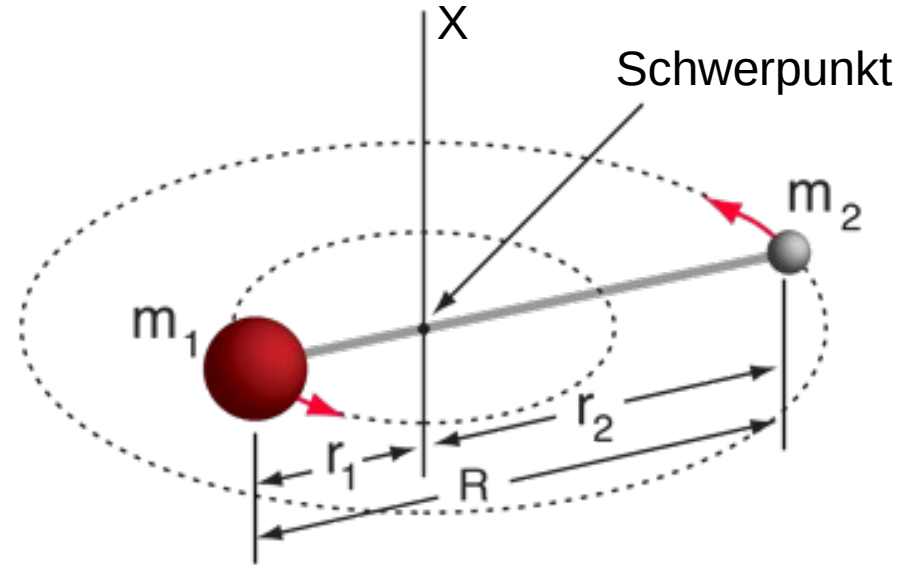
Trägheitsmoment:

$$I = \sum_i m_i r_i^2$$

Hier: $I = m_1 r_1^2 + m_2 r_2^2$

Schwerpunkt: $m_1 r_1 = m_2 r_2$

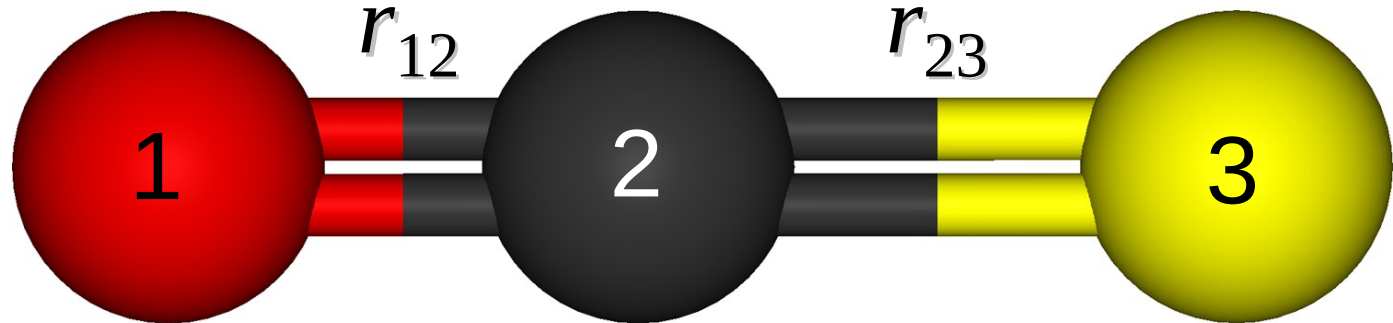
$$I = \frac{m_1 m_2 R^2}{m_1 + m_2} = \mu R^2$$



Reduzierte Masse: $\mu = \frac{m_1 m_2}{m_1 + m_2}$

Lineare Kreisel

z.B.: O=C=S



$$I_z = 0 \quad I_x = I_y = I$$

$$I = \frac{1}{M} \left[m_1 m_2 r_{12}^2 + m_2 m_3 r_{23}^2 + m_1 m_3 (r_{12} + r_{23})^2 \right]$$

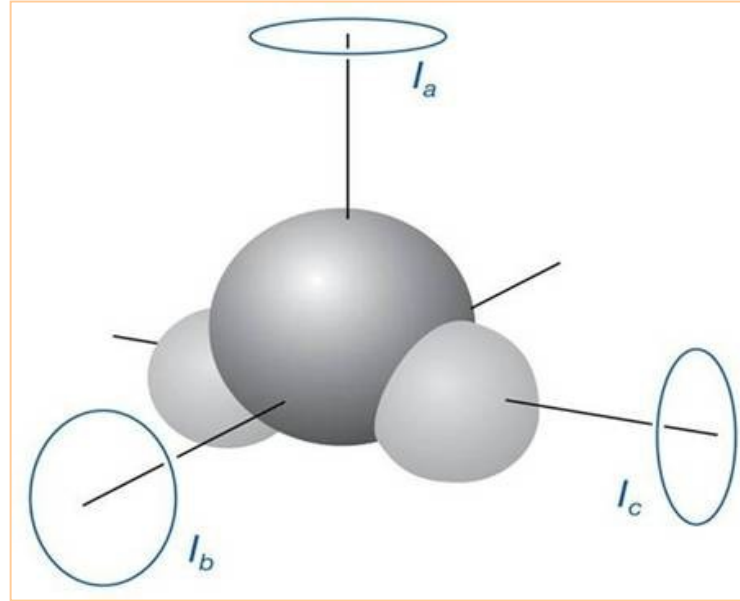
Gesamtmasse $M = m_1 + m_2 + m_3$

Kreisel

Konvention:

$$I_c \geq I_b \geq I_a$$

Trägheitstensor \mathbf{I}



$$I_x = \sum_i m_i r_{ix}^2$$

$$\mathbf{I} = \begin{bmatrix} I_{xx} & I_{xy} & I_{xz} \\ I_{yx} & I_{yy} & I_{yz} \\ I_{zx} & I_{zy} & I_{zz} \end{bmatrix}$$



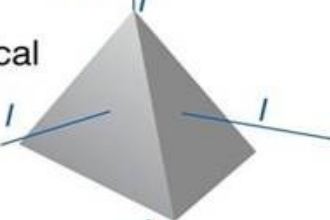
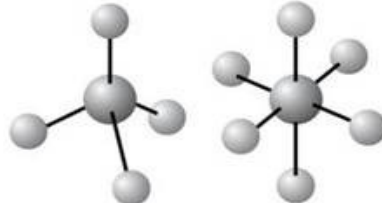
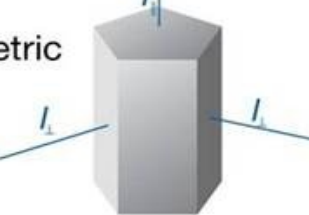
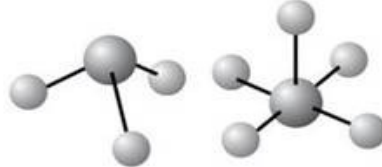
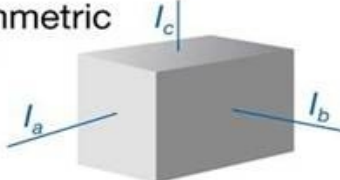
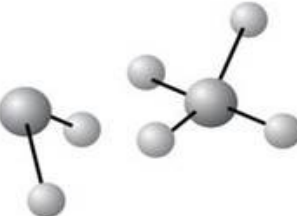
diagonalisieren



$$\mathbf{I} = \begin{bmatrix} I_x & 0 & 0 \\ 0 & I_y & 0 \\ 0 & 0 & I_z \end{bmatrix}$$

Haupt-
Trägheits-
System

Weitere Rotoren - Klassifizierung

				Beispiele
Linear			$I_a = 0, I_b = I_c$	CO CO ₂
Spherical rotor			$I_a = I_b = I_c$	CH ₄ SF ₆
Symmetric rotor			$I_a < I_b = I_c$ $I_a = I_b < I_c$	NH ₃ IF ₅
Asymmetric rotor			$I_a \neq I_b \neq I_c$	H ₂ O SF ₄

Konvention: $I_c \geq I_b \geq I_a$ daher $C \leq B \leq A$ (rot. Konstanten)

Quantenmechanische Rotation

$$\hat{H}_{rot} \Psi_{rot} = E_{rot} \Psi_{rot} \quad \hat{H}_{rot} = \frac{1}{2} \left(\frac{\hat{J}_x^2}{I_x} + \frac{\hat{J}_y^2}{I_y} + \frac{\hat{J}_z^2}{I_z} \right)$$

Drehimpulsoperator \hat{J}

$$\hat{J}^2 = \hat{J}_x^2 + \hat{J}_y^2 + \hat{J}_z^2 = \hat{J}_X^2 + \hat{J}_Y^2 + \hat{J}_Z^2$$

x,y,z Molekül-fixiertes Koordinatensystem

X,Y,Z Raum-fixiertes Koordinatensystem

Drehimpulsquantenzahlen J

Quantenzahlen

$$\hat{J}^2 = \hat{J}_x^2 + \hat{J}_y^2 + \hat{J}_z^2 = \hat{J}_X^2 + \hat{J}_Y^2 + \hat{J}_Z^2$$

x, y, z Molekül-fixiertes Koordinatensystem

X, Y, Z Raum-fixiertes Koordinatensystem

hier und im Weiteren
werden atomare
Einheiten benutzt

$$\langle J, K, M | \hat{J}^2 | J, K, M \rangle = J(J + 1)$$

$$\langle J, K, M | \hat{J}_z^2 | J, K, M \rangle = M^2$$

$$M = J, J-1 \dots -J$$

$$\langle J, K, M | \hat{J}_z^2 | J, K, M \rangle = K^2$$

$$K = J, J-1 \dots -J$$

Lineare Moleküle: R.-E.-Niveaus

$$\hat{H}_{\text{rot}} = \frac{1}{2I_x} \hat{J}_x^2 + \frac{1}{2I_y} \hat{J}_y^2 = \frac{1}{2I} \hat{J}^2$$

$$I_z = 0 \quad I_x = I_y = I$$

$$\hat{J}^2 = \hat{J}_x^2 + \hat{J}_y^2$$

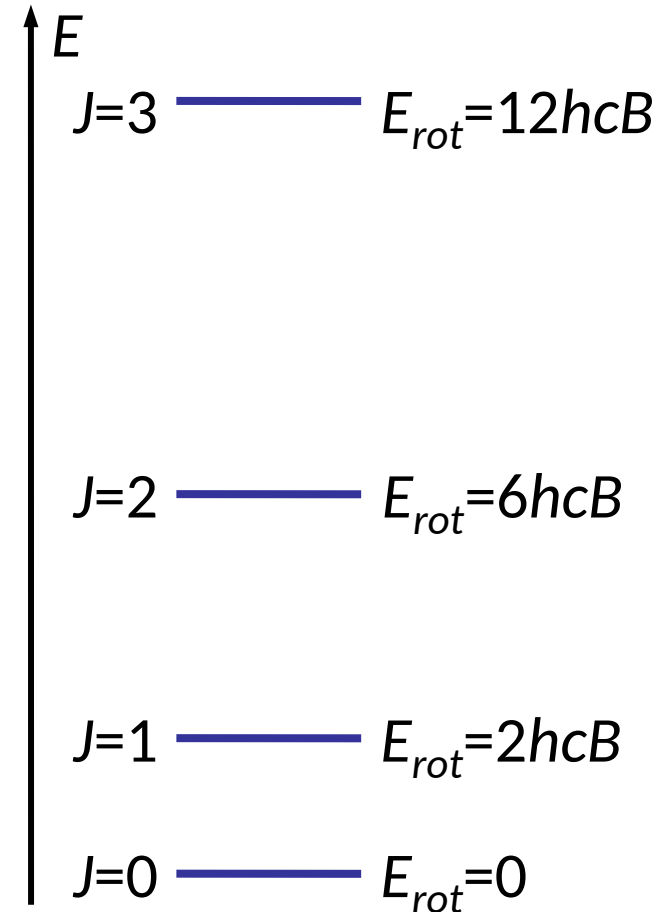


$$E_{\text{rot}} = hcBJ(J+1)$$

Drehimpuls-
quantenzahlen $J = 0, 1, 2, 3 \dots$

B :
Rotations-
Konstante
(in cm^{-1})

$$\frac{\hbar^2}{2I} = hcB$$



Lineare Moleküle

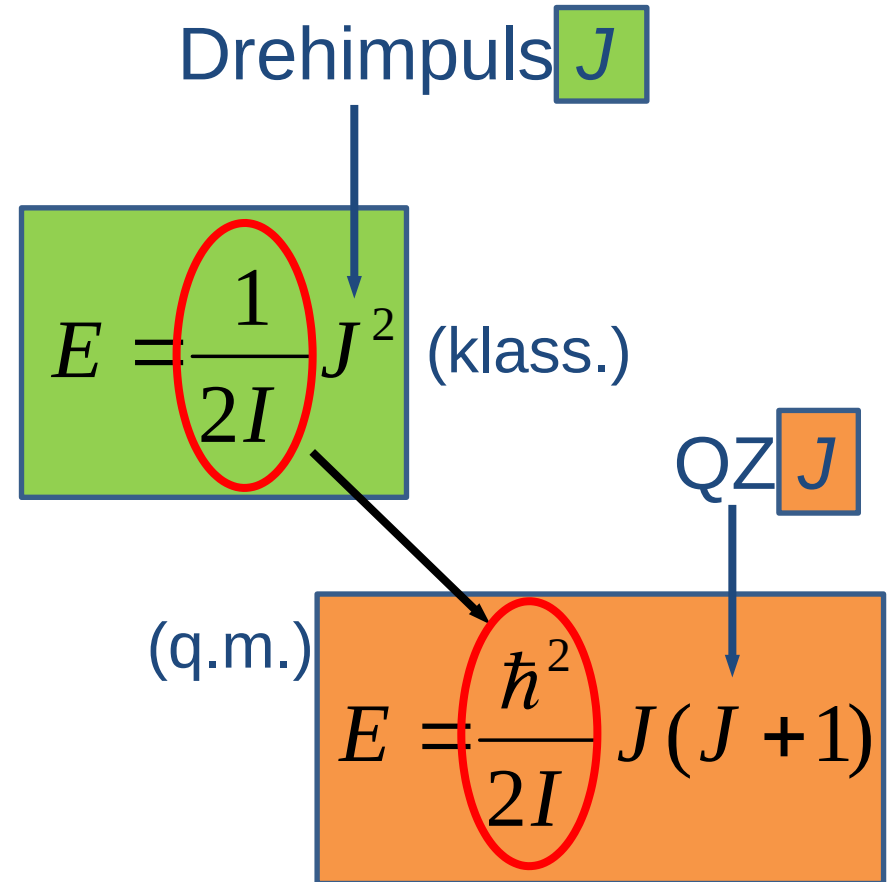
Nochmal klassisch: $E = \frac{1}{2} I_x \omega_x^2 \quad J_x = I_x \omega_x$

$$E = \frac{1}{2I_x} J_x^2 + \frac{1}{2I_y} J_y^2 + \frac{1}{2I_z} J_z^2 =$$

$$\frac{1}{2I} J_x^2 + J_y^2 = \frac{1}{2I} J^2$$

Klassisch \rightarrow quantenmechanisch
ersetzen von J^2 durch $J(J+1)\hbar^2$

$$B := \frac{\hbar}{4\pi c I} \quad \Rightarrow \quad \frac{\hbar^2}{2I} = hcB$$



Quellen für Verwirrung in der Literatur

$$E_{\text{rot}} = hcBJ(J + 1) \quad B := \frac{\hbar}{4\pi cI} \quad E \text{ in J (kJ)}$$

$$E_{\text{rot}} = hBJ(J + 1) \quad B := \frac{\hbar}{4\pi I} \quad E \text{ in Hz (MHz)}$$

$$E_{\text{rot}} = BJ(J + 1) \quad B := \frac{\hbar}{8\pi^2 I} \quad E \text{ in cm}^{-1}$$

Lineare Moleküle: Übergänge

$$E_{\text{rot}} = hcBJ(J + 1)$$

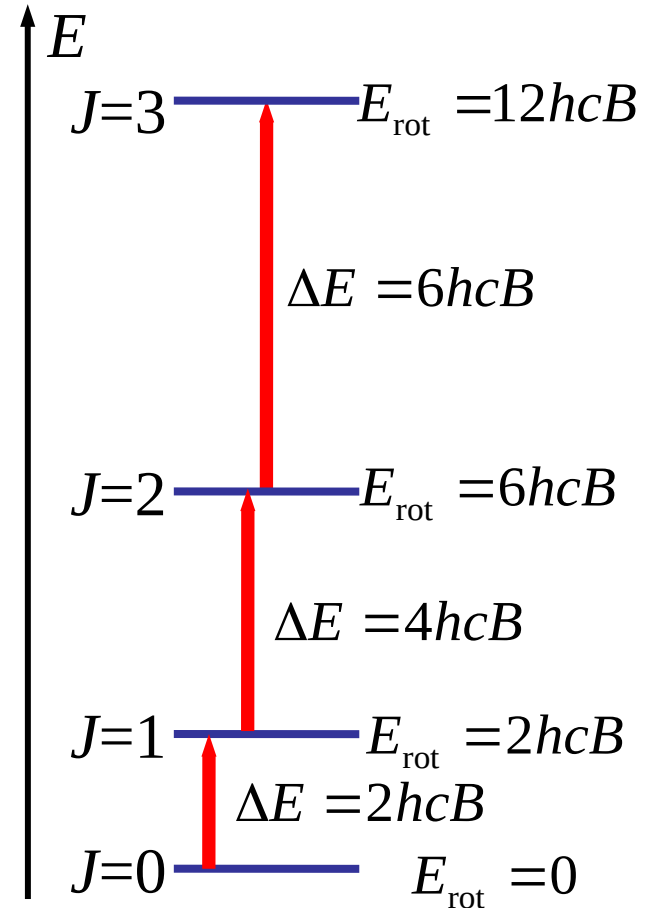
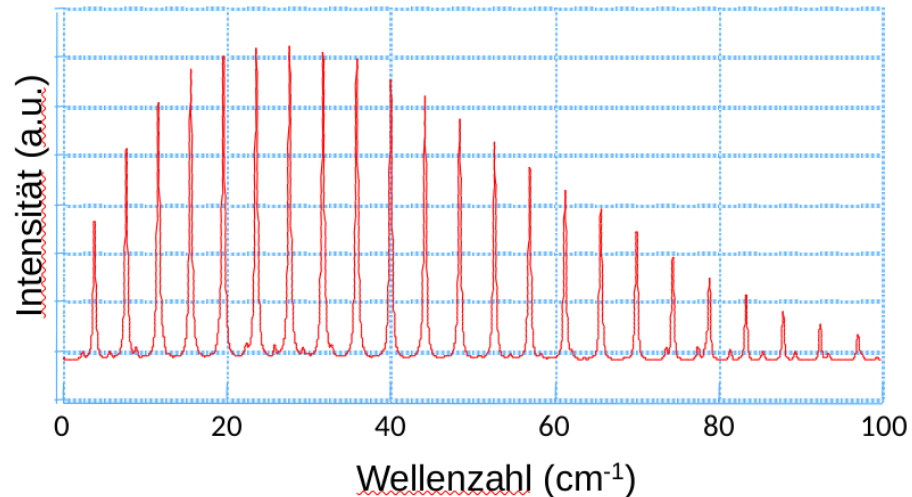
$$\Delta E(J + 1 \leftarrow J) =$$

$$= hcB[(J + 1)(J + 2) - J(J + 1)] =$$

$$= 2hcB(J + 1)$$

$$\Delta J = \pm 1$$

Auswahlregel



Lineare Moleküle: Übergänge

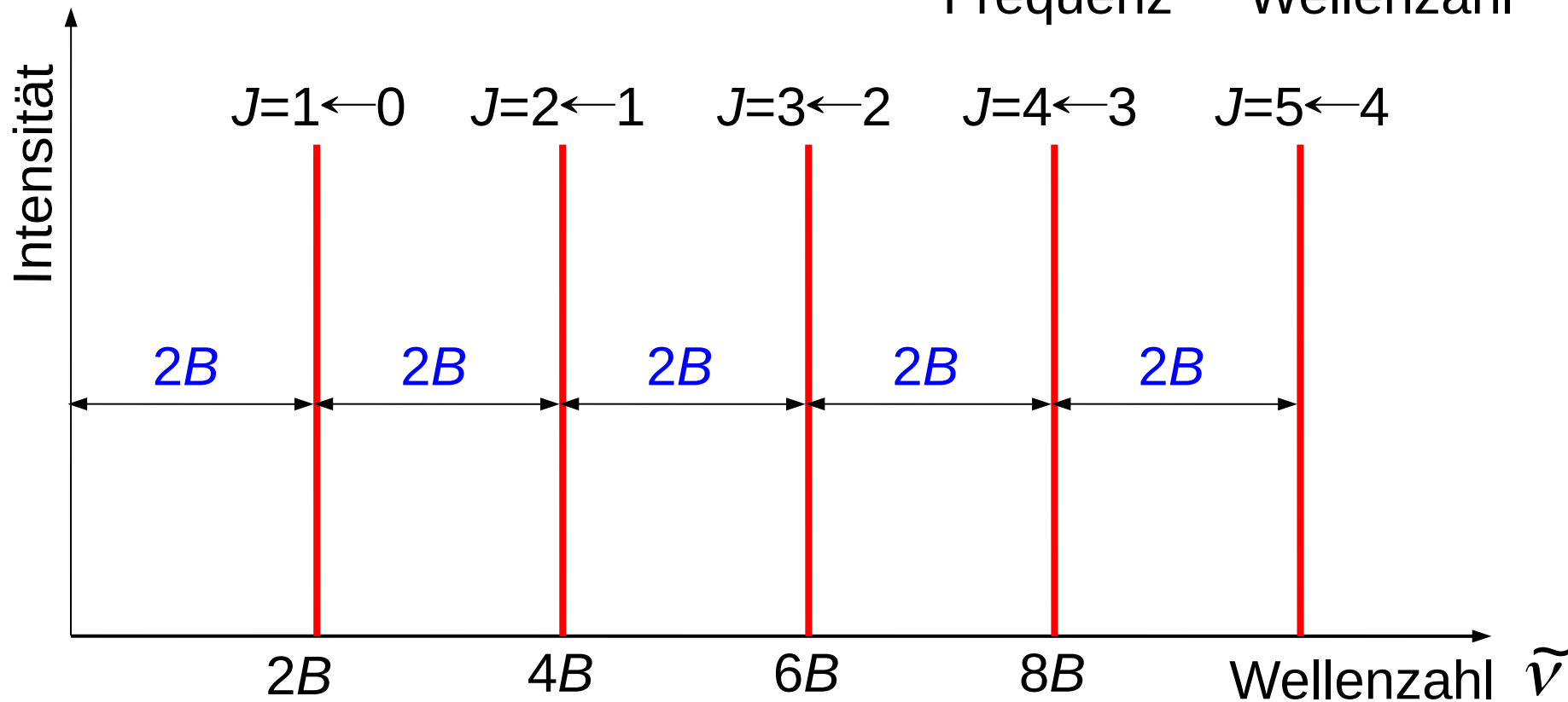
$$h\nu_{rot} = 2hcB(J + 1)$$

$$\tilde{\nu}_{rot} = 2B(J + 1)$$

$$E = h\nu_{rot} = hc\tilde{\nu}_{rot}$$

↑
Frequenz

↑
Wellenzahl



Linien-Intensitäten

(1) Entartung $g = 2J + 1$

(2) Boltzmann-Verteilung

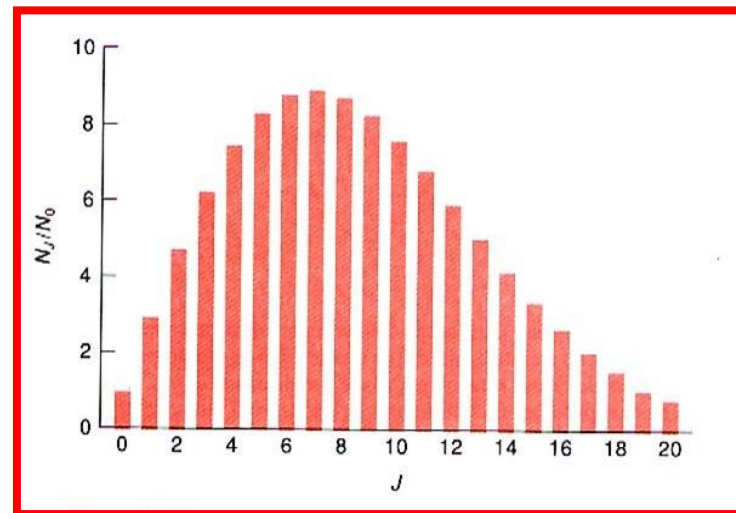
$$\frac{N_J}{N_0} = \frac{g_J}{g_0} e^{-\frac{\Delta E_{rot}}{kT}}$$



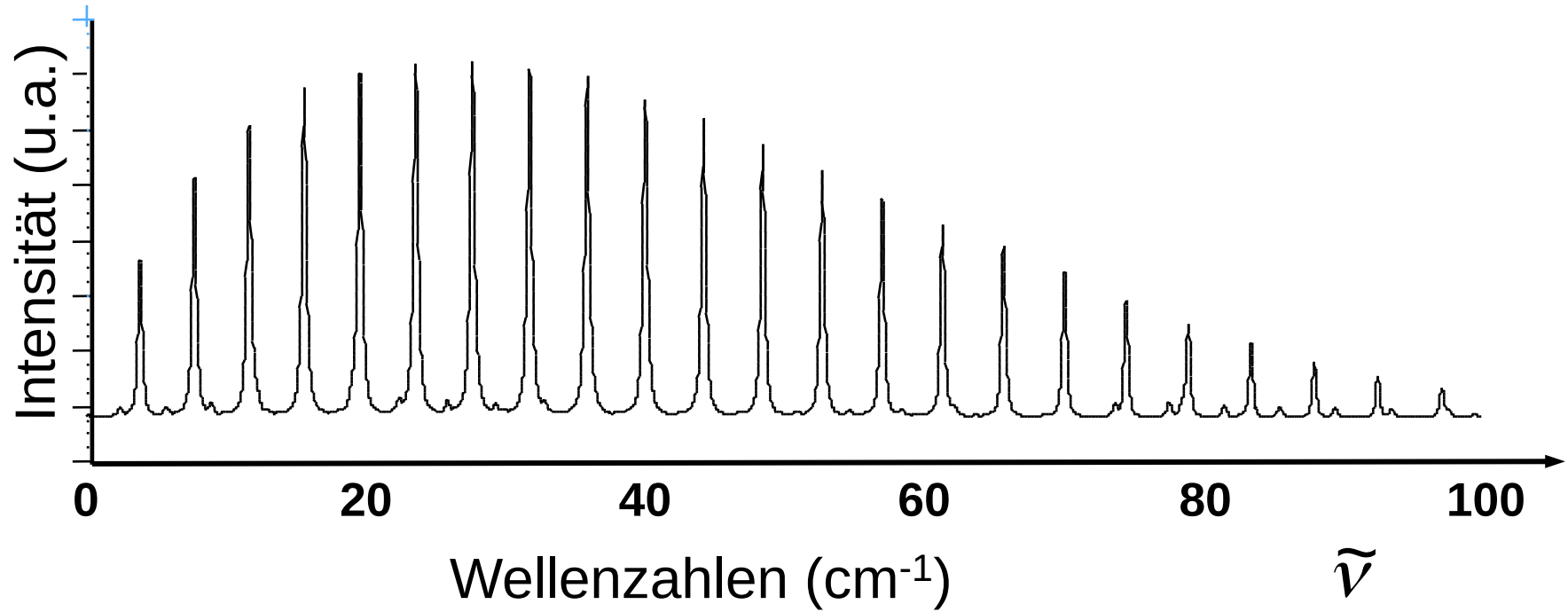
$$\frac{N_J}{N_0} = (2J + 1) e^{-\frac{\Delta E_{rot}}{kT}}$$

$$Int \propto \left(\frac{N_m}{g_m} - \frac{N_n}{g_n} \right) \left| \langle n | \mu | m \rangle \right|^2$$

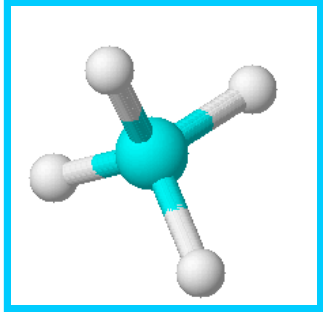
μ : Übergangsdipolmoment



MW-Rotationsspektrum von CO



Sphärische und symmetrische Kreisel



$\text{CH}_4, \text{SF}_6, \dots$

$$I_a = I_b = I_c = I$$

$$E_{\text{rot}} = hcB J(J+1)$$

Jedes Niveau:

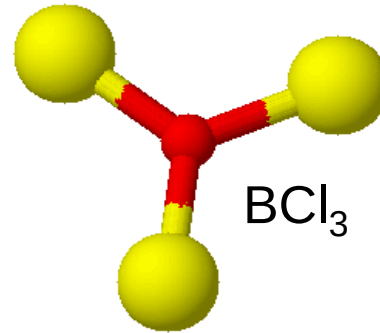
$(2J + 1)^2$ –fach entartet (K, M)

$\mu = 0$!!!

(z = Symmetrie-Achse)

$$I_x = I_y = I_{\perp}$$

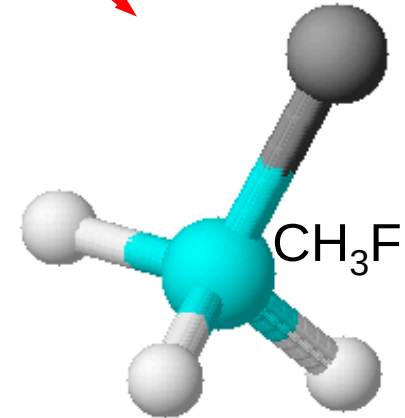
$$I_z = I_{\parallel}$$



BCl_3

abgeflacht
(oblate)

$$I_{\perp} < I_{\parallel}$$



CH_3F

gestreckt
(prolate)

$$I_{\perp} > I_{\parallel}$$

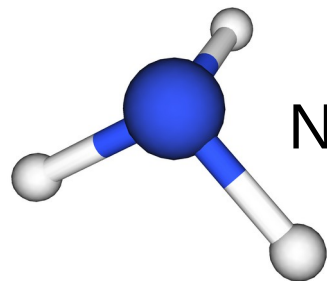
Symmetrische Kreisel

$$\frac{E_{rot}}{hc} = \frac{1}{2} \left[\frac{J(J+1)}{I_{\perp}} + \left(\frac{1}{I_{//}} - \frac{1}{I_{\perp}} \right) K^2 \right]$$

oblate

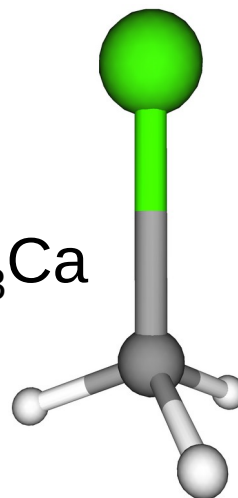
$$I_{\perp} < I_{//}$$

$$I_{//} = I_c$$



NH₃

CH₃Ca



prolate

$$I_{\perp} > I_{//}$$

$$I_{//} = I_a$$

Prolate: $E_{rot}/hc = BJ(J+1) + \overset{>0}{(A-B)}K^2$

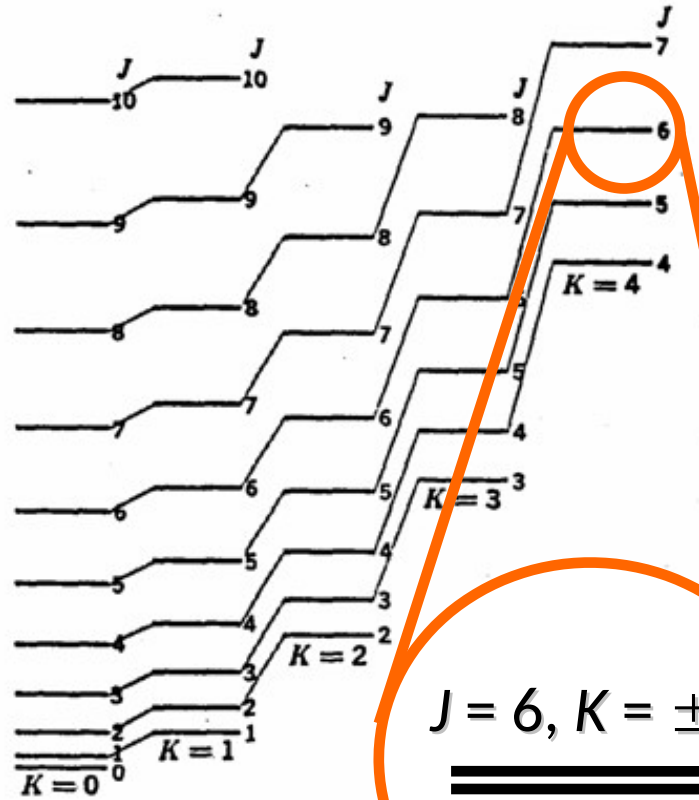
mit $A > B = C$

Oblate: $E_{rot}/hc = BJ(J+1) + \underset{<0}{(C-B)}K^2$

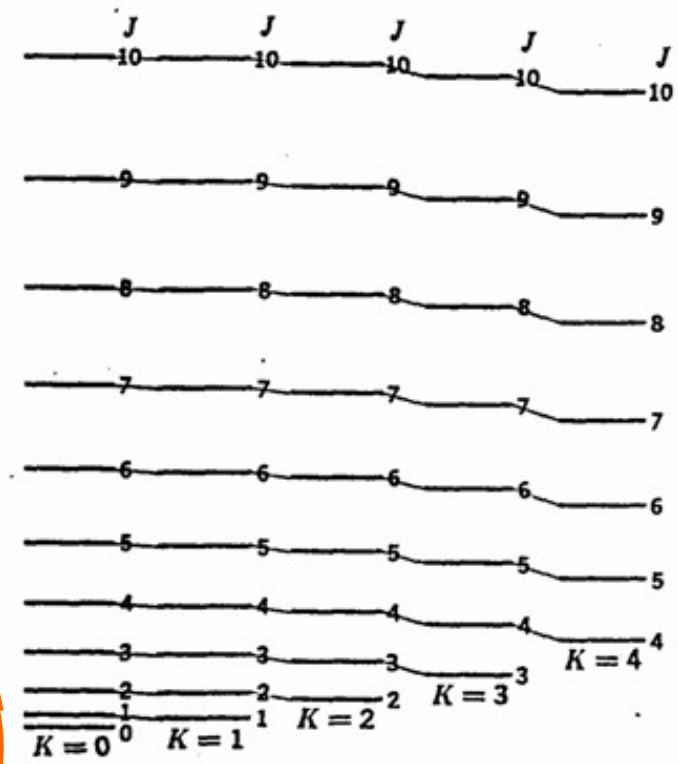
mit $A = B > C$

<0

Symmetrische Kreisel - Energieniveaus



$J = 6$ →



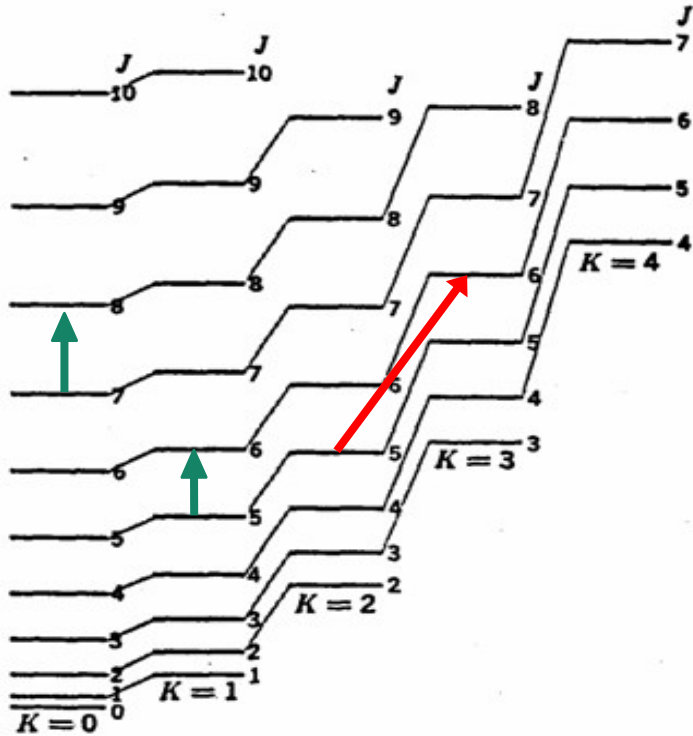
← $J = 6$

$J = 6, K = \pm 4$

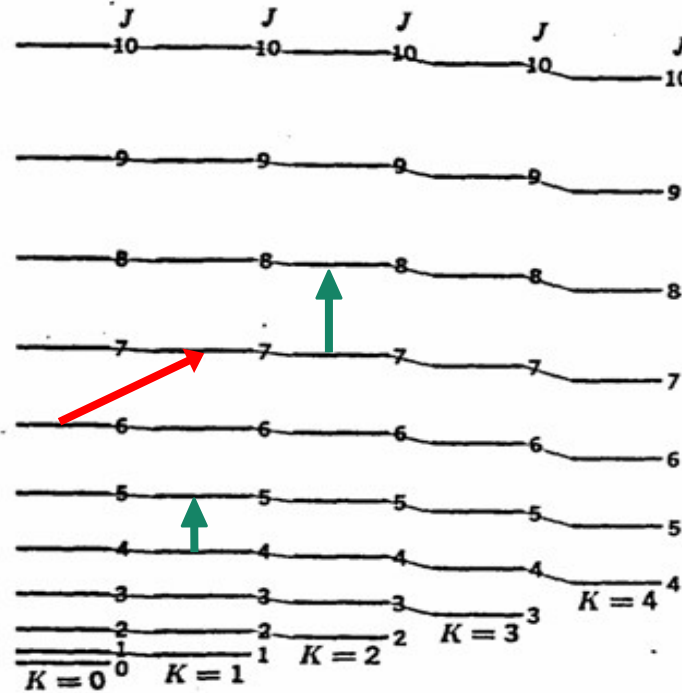
Prolate
 $A > B = C$

Oblate
 $A = B > C$

Symmetrische Kreisel – Auswahlregeln



Prolate
 $A > B = C$



Oblate
 $A = B > C$

Zusätzlich zu $\Delta J = \pm 1$:
 $\Delta K = 0$

Zentrifugale Verzerrung: lineare Moleküle

Störungstheorie

$$\hat{H}_{rot} = \hat{H}_{rot}^0 + \hat{H}'_{dist}$$

starrer
Rotor

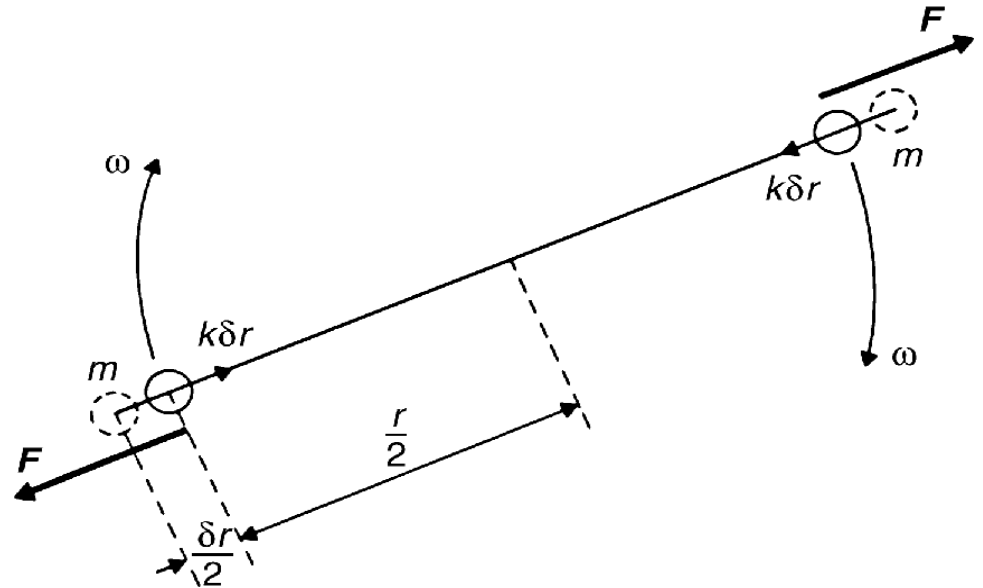
Störung (Distortion)

$$\hat{H}'_{dist} = -D_J \hat{J}^4$$

$$E'_{dist} = -hcD_J J^2 (J+1)^2$$

quartische Zentrifugal-
Verzerrungs-Konstante

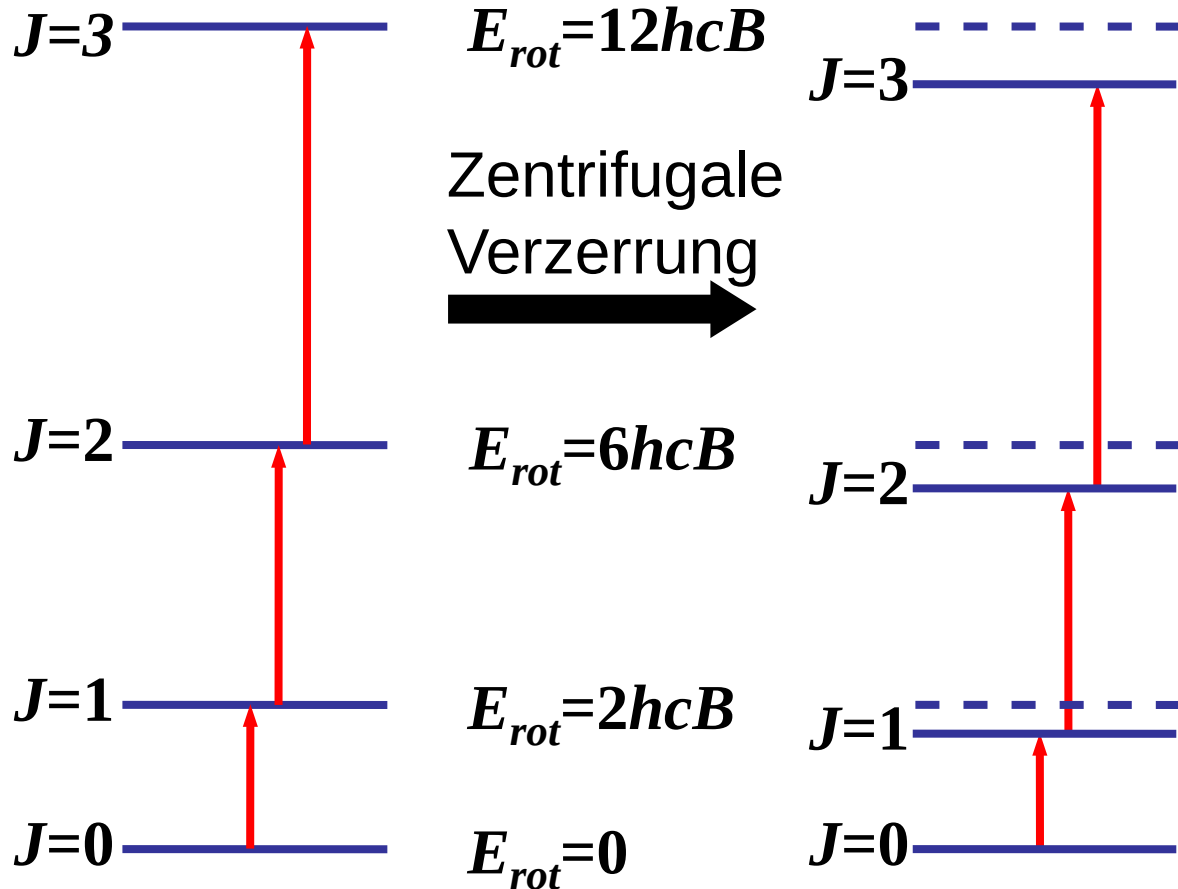
$$D_J = -\frac{\tau_{xxxx}}{4}$$



Zentrifugale Verzerrung: R.E.-Niveaus

$$\tilde{\nu}_{\text{rot}} = E_{\text{rot}} / hc = BJ(J+1) - D_J J^2(J+1)^2$$

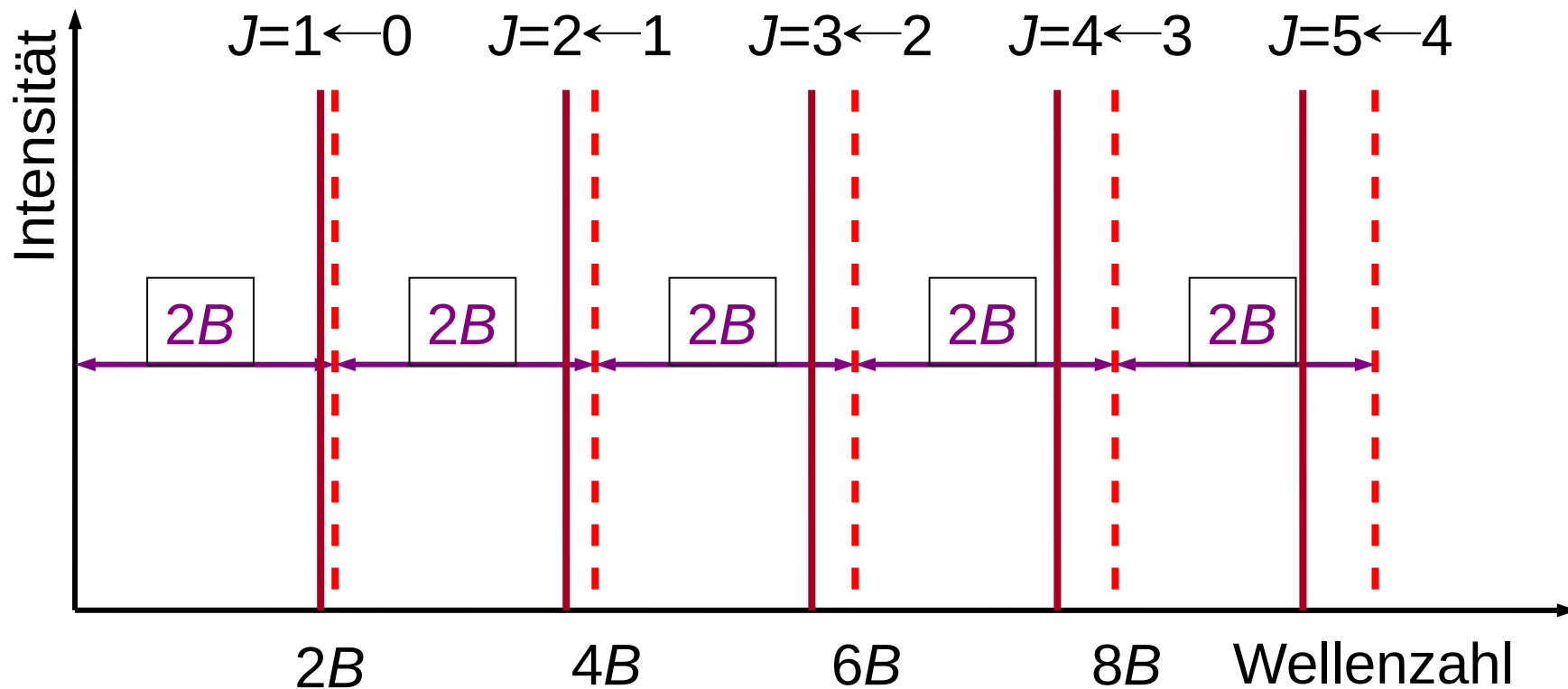
← E. von R.-Zustand!



für lineares
Molekül

Zentrifugale Verzerrung: Spektrum

$$\tilde{\nu}_{\text{rot}} = 2B(J+1) - 4D_J(J+1)^3 \quad \leftarrow \text{Übergangsenergie!}$$



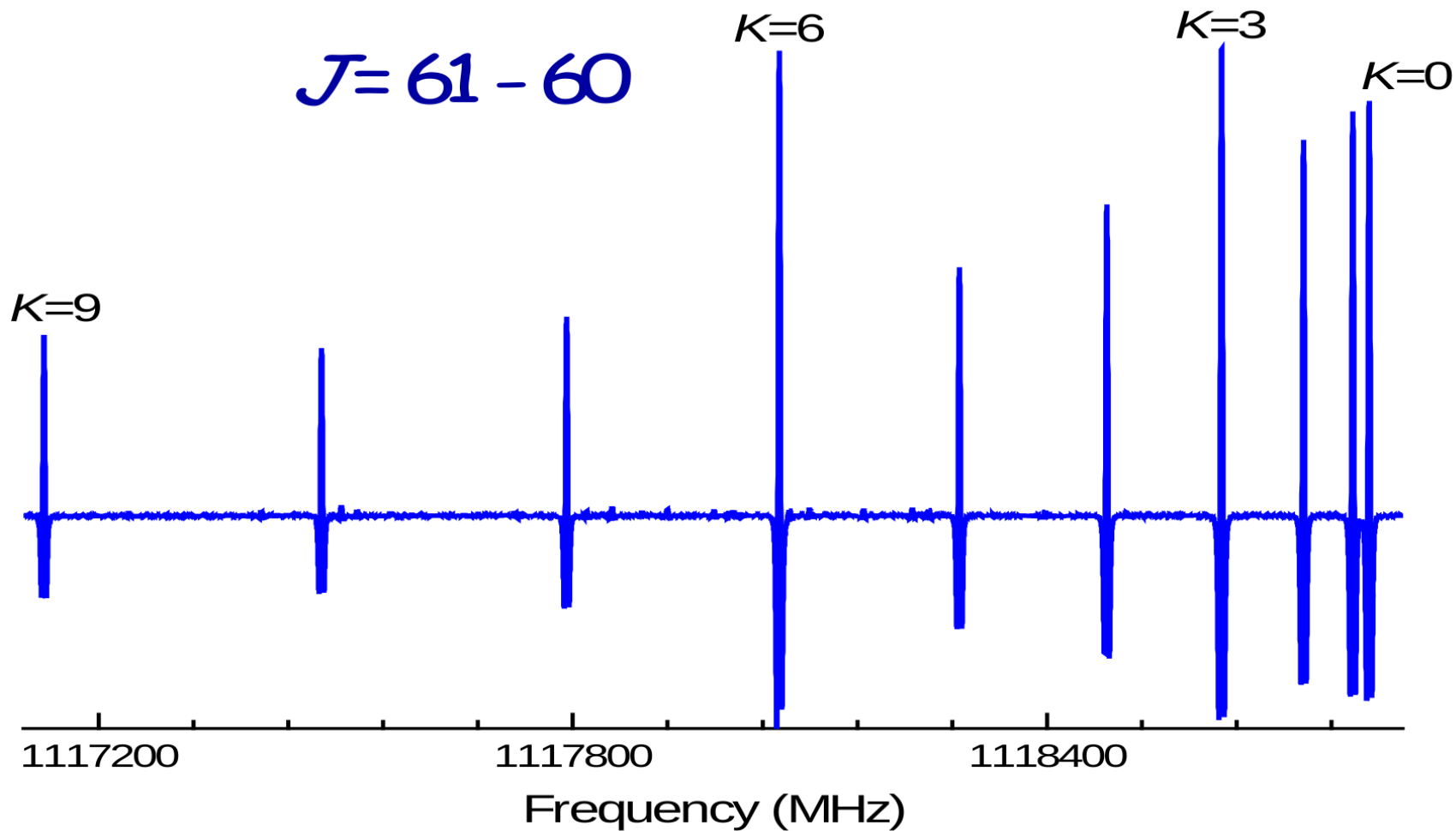
Zentrifugal-Verzerrung: symmetrische Kreisel

Zusätzliche Zentrifugal-Verzerrungs-Konstanten sind nötig, um Verzerrung zu beschreiben, die nicht nur von Rotation um Hauptachse herrührt;
(Korrekturen aus QM-Rechnungen)

$$\tilde{\nu}_{\text{rot}} = B(J+1) + (a-B)K^2 - D_J J^2 (J+1)^2 - D_{JK} J(J+1)K - D_K K^4$$

Dabei ist a entweder A oder C , je nachdem welches von B verschieden ist

Rotationsspektrum von CH_3CN : Ausschnitt



Asymmetrische Kreisel

$$\hat{H}_{\text{rot}} = \frac{1}{2} \left(\frac{\hat{J}_x^2}{I_x} + \frac{\hat{J}_y^2}{I_y} + \frac{\hat{J}_z^2}{I_z} \right)$$

Es ist nicht möglich, den Hamiltonian so zu schreiben, dass er ausschließlich aus $\hat{\mathbf{J}}$ und einer $\hat{\mathbf{J}}^2$ Komponente besteht.



Es ist nicht möglich, die Rotationsbewegung, als eine bestimmte Bewegung um eine Molekül-Achse zu beschreiben.



Diagonalisierung

Zur Vereinfachung:

Beziehung zum symmetrischen Kreisel

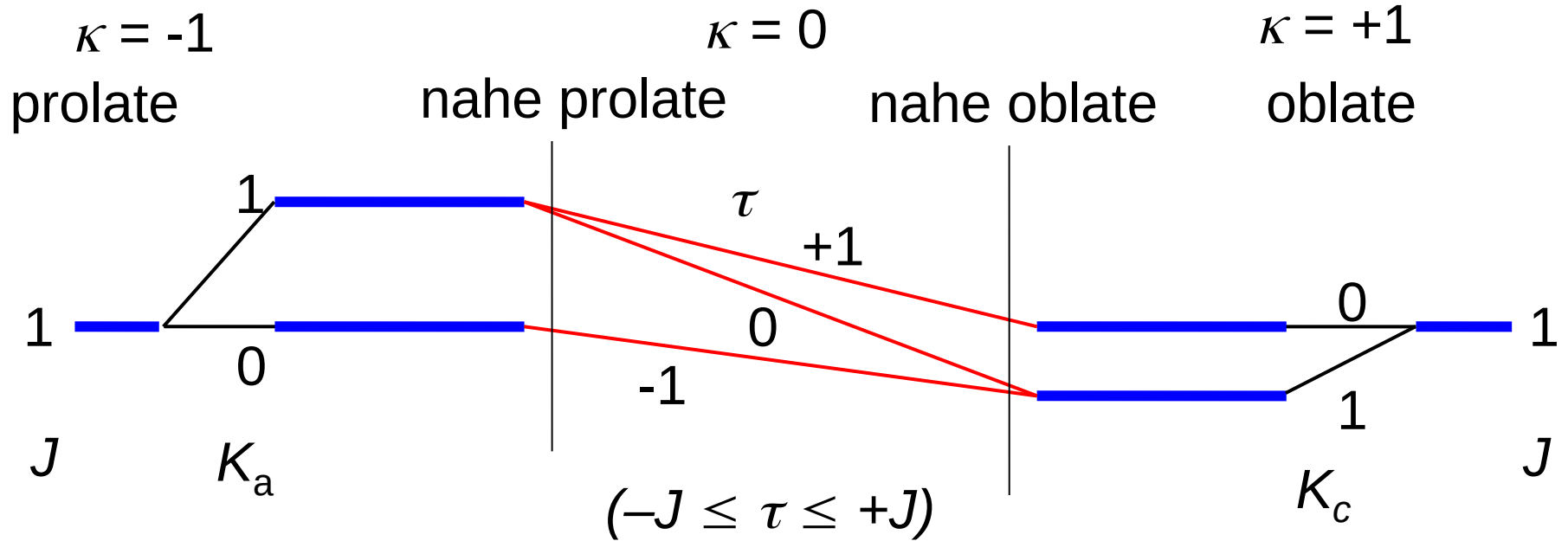
Pseudo Quanten-Zahlen K :

$K_a \rightarrow$ begrenzt den prolaten symmetrischen Kreisel

$K_c \rightarrow$ begrenzt den oblaten symmetrischen Kreisel

Asymmetrische Kreisel: R.-E.-Niveaus

2 Notationsschemata: J_{K_a, K_c} oder J_τ

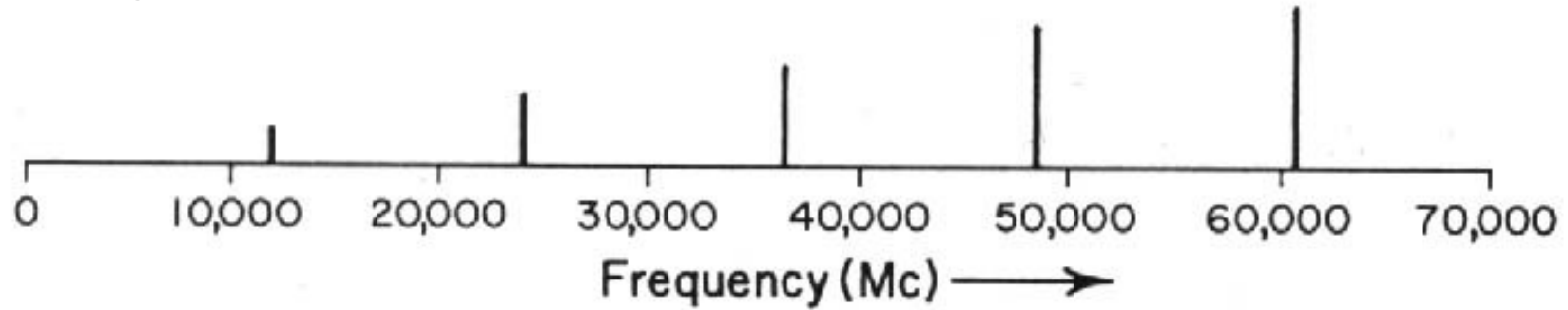


Asymmetrieparameter κ

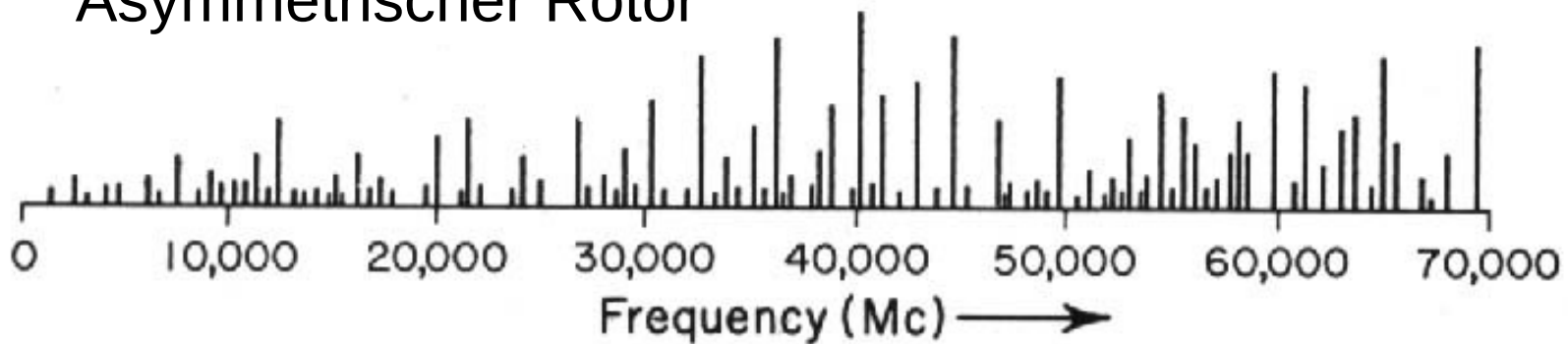
$$\kappa = \frac{2B - A - C}{A - C}$$

Asymmetrische Kreisel: Spektrum

Symmetrischer Rotor



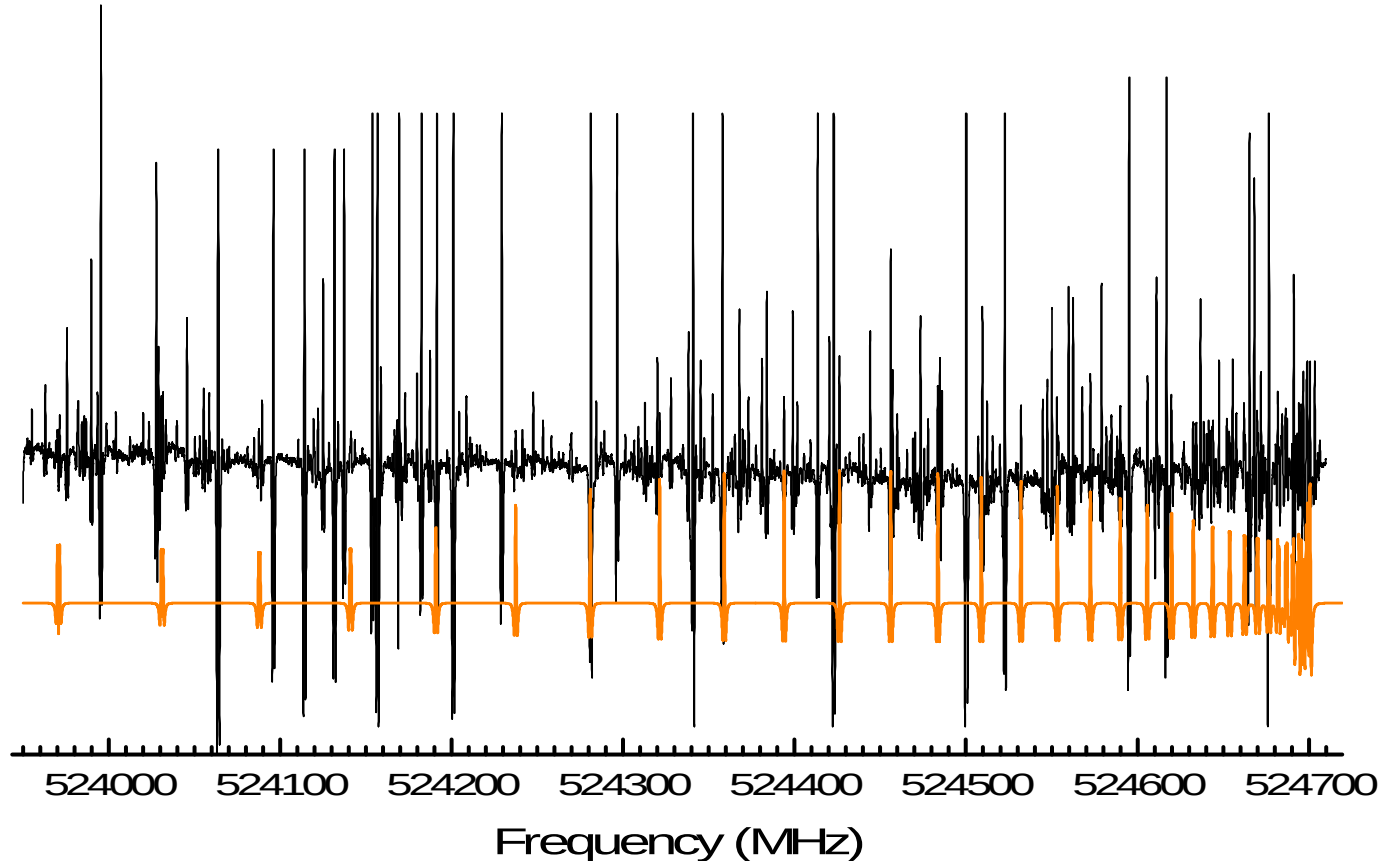
Asymmetrischer Rotor



Asymmetrische Kreisel: Spektrum

kleiner Ausschnitt aus dem Spektrum

trans-CH³⁵Cl=CHF



Zusammenfassung

Lineare M.:

$$E_{\text{rot}} = hcBJ(J + 1)$$

$$\Delta E(J + 1 \leftarrow J) = 2hcB(J + 1)$$

$$I = \sum_i m_i r_i^2$$

Auswahlregel:

$$\Delta J = \pm 1$$

$$B = \frac{\hbar}{4\pi c I}$$

Intensitäten:

$$\frac{N_J}{N_0} = (2J + 1) e^{-\frac{\Delta E_{\text{rot}}}{kT}}$$

Symm. Kreisel:

$$E_{\text{rot}} / hc = B(J + 1) + (a - B)K^2$$

$$a = (A \text{ oder } C) \neq B$$

$$\Delta K = 0$$

Mit Zentrifugalverzerrung:

$$E_{\text{rot}} / hc = B(J + 1) + (a - B)K^2 - D_J J^2 (J + 1)^2 - D_{JK} J(J + 1)K - D_K K^4$$

Hyperfein-Struktur

Rotations-Hamiltonian

$$\hat{H}_{\text{rot}} = \hat{H}_J + \hat{H}_Q + \hat{H}_{\text{SR}} + \hat{H}_{\text{SS}}$$

(Direkte) Spin-Spin-
Wechselwirkung

$$AJ_A^2 + BJ_B^2 + CJ_C^2$$

Rotationskonstanten

$$\sum_{K>L} I_K D_{KL} I_L$$

Spin-Rotations-
Wechsel-
wirkung

$$\sum_K I_K C_K J$$

Kopplung: $I + J = F$

Auswahlregel: $\Delta F = 0; \pm 1$

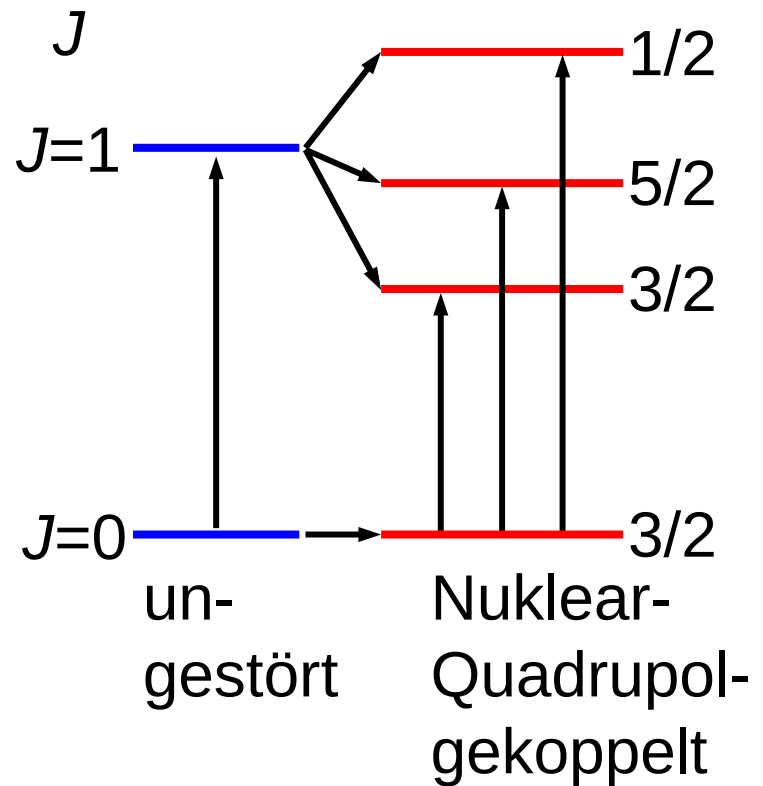
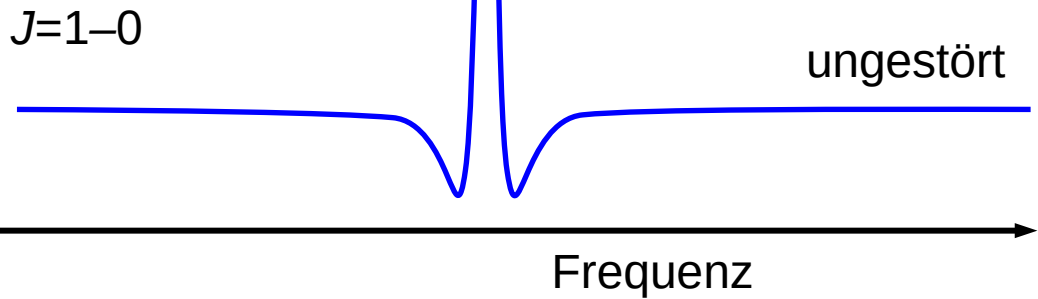
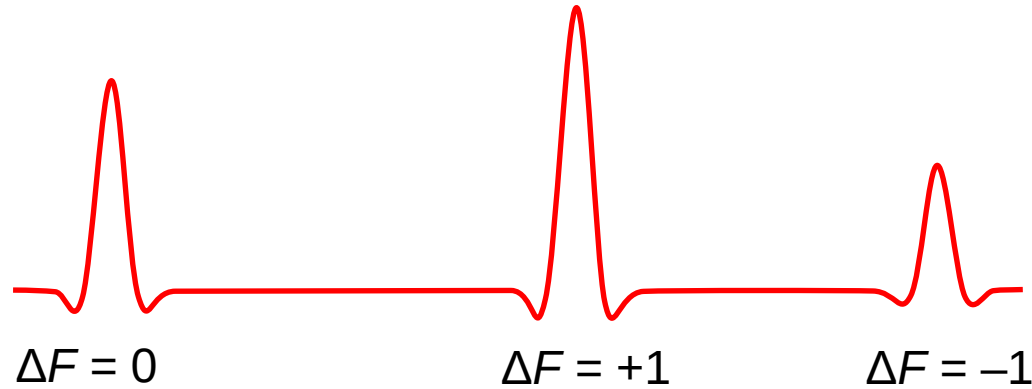
Kern-Quadrupol-Kopplung

$$\frac{1}{2} \sum_K \frac{-eQ_K q_J^K}{2I_K (2I_K - 1) J (2J - 1)} [3(I \cdot J)^2 + \frac{3}{2}(I \cdot J) - I^2 J^2]$$

Kern-Quadrupol-Kopplung

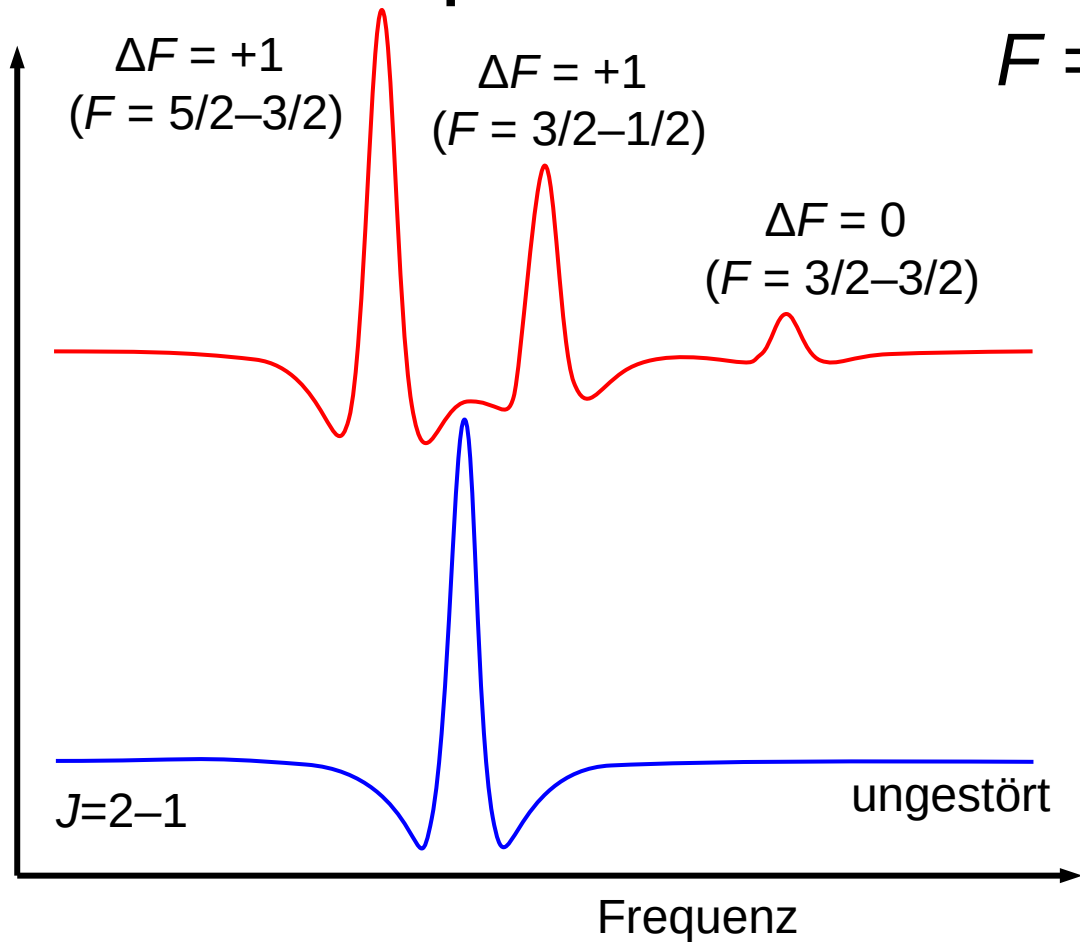
$$F = J+I, J+I-1, \dots, |J-I|$$

E \longrightarrow $F =$



$[I_K \geq 1] \quad I_K = 3/2; eQq < 0$

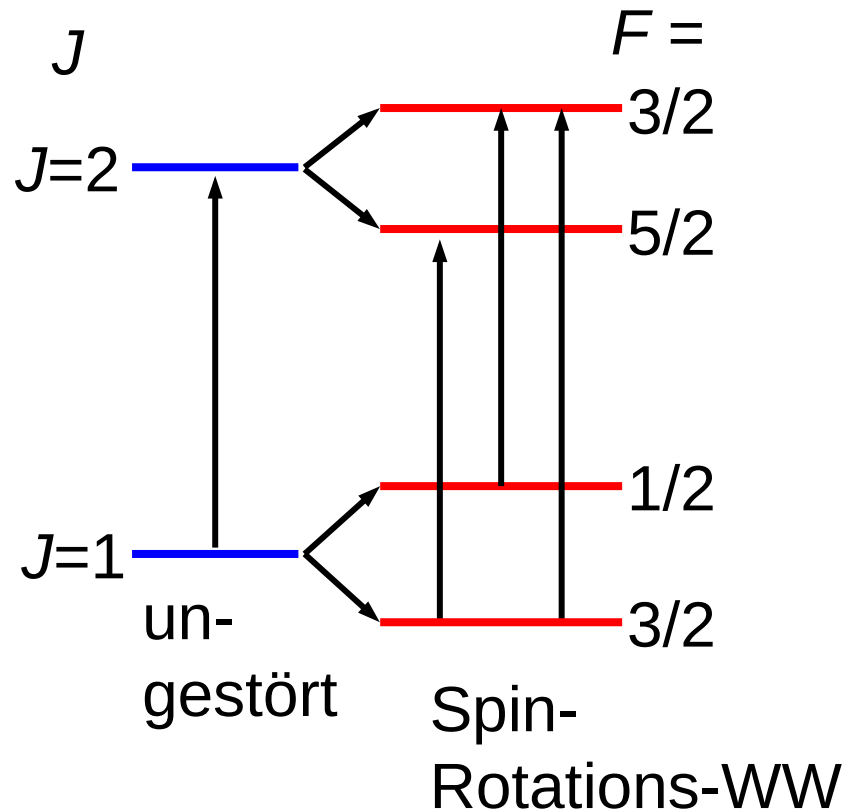
Spin-Rotations-Wechselwirkung



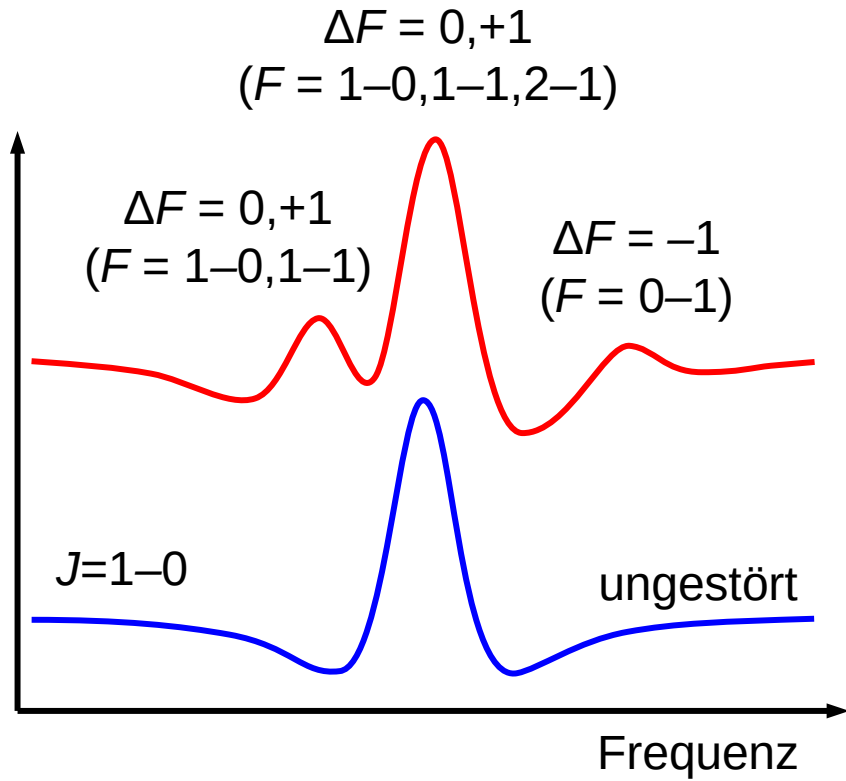
$[I_K \geq 1/2] \quad I_K = 1/2; C < 0$

$$F = J+I, J+I-1, \dots, |J-I|$$

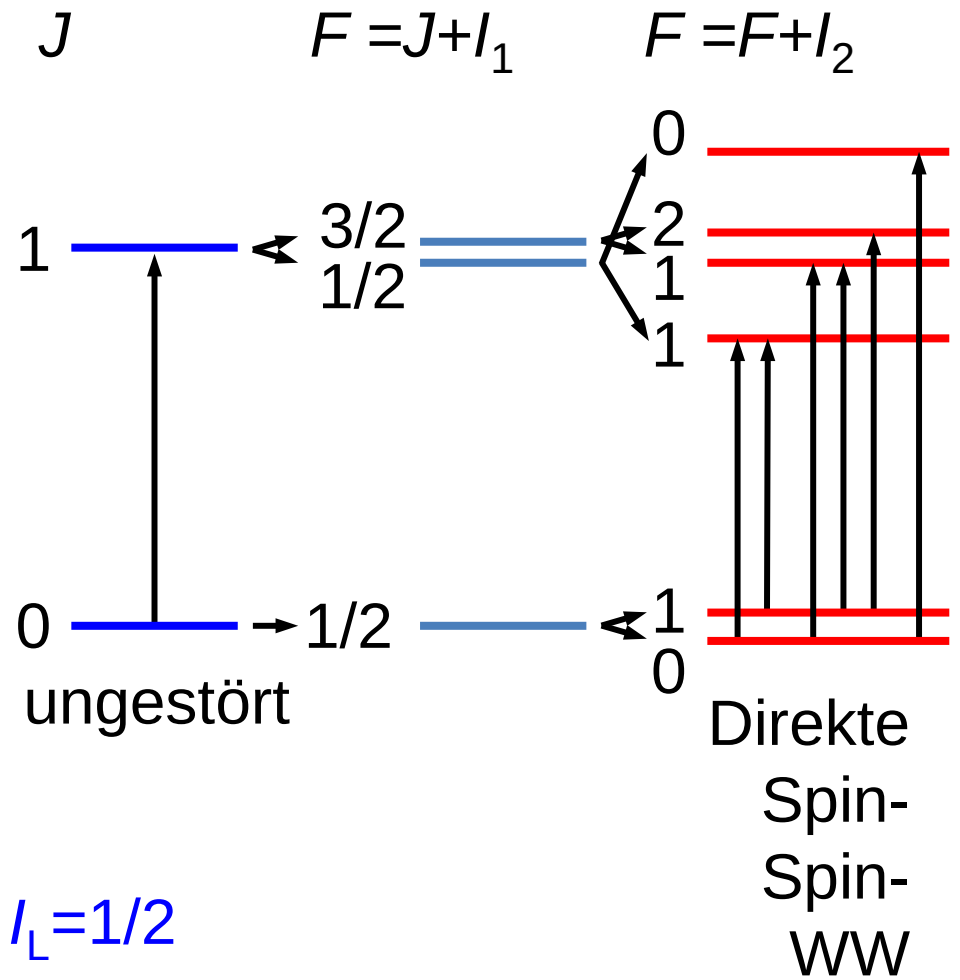
\xrightarrow{E}



Direkte Spin-Spin-Wechselwirkung



$I_K = 1/2$ und $I_L = 1/2$

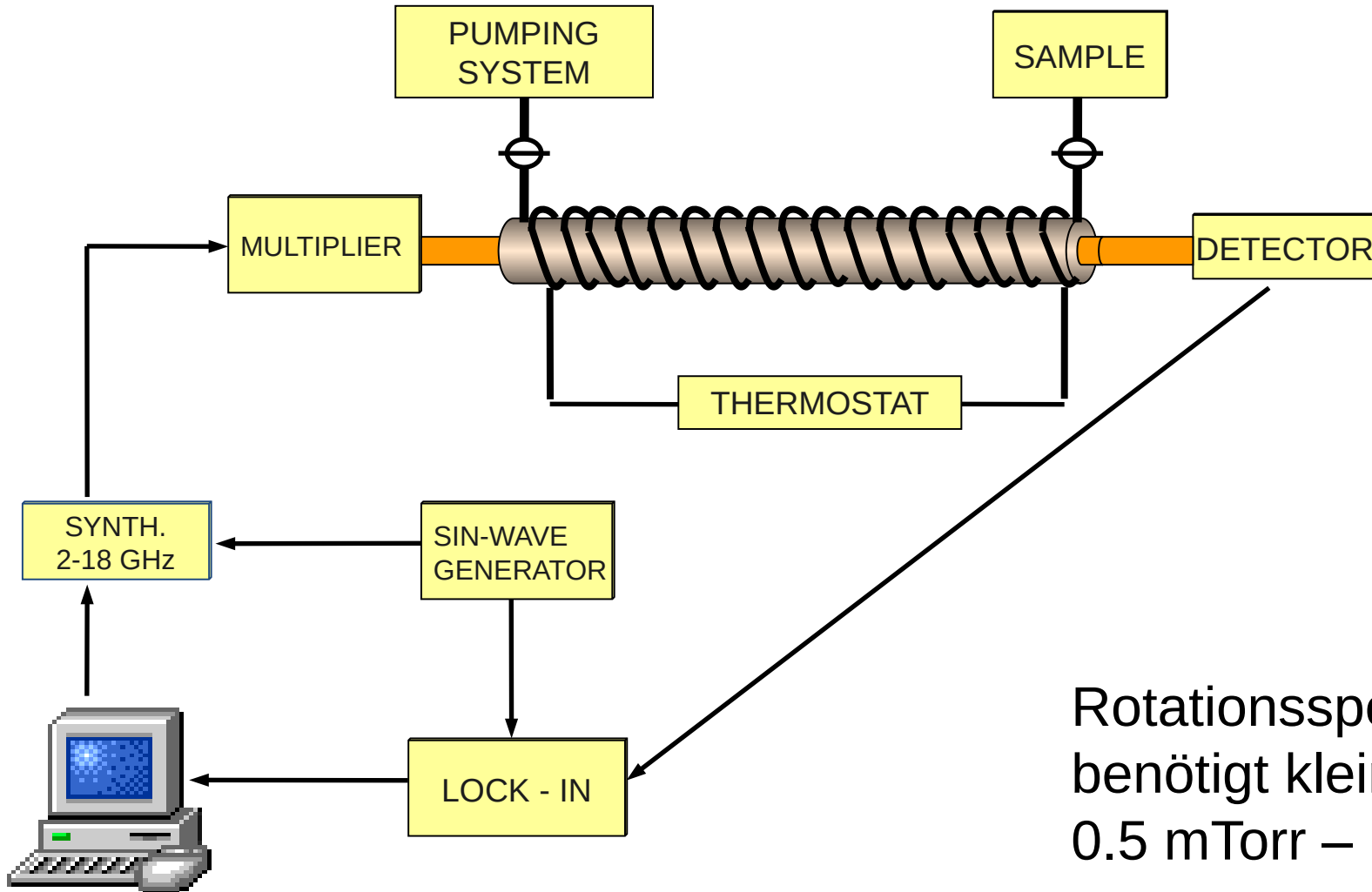


Spektrometer - Typen

- Fourier-Transform (FT) -Spektrometer
(bis ca. 140 GHz)
- Continuous-wave (CW) -Spektrometer
(alle Frequenzen):



Block-Diagramm (8–120 GHz Spektrometer)



Rotationsspektroskopie
benötigt kleine Drucke p :
0.5 mTorr – 1 Torr

CP-FTMW-Spektrometer

COMPACT spectrometer:

Jack B. Graneek

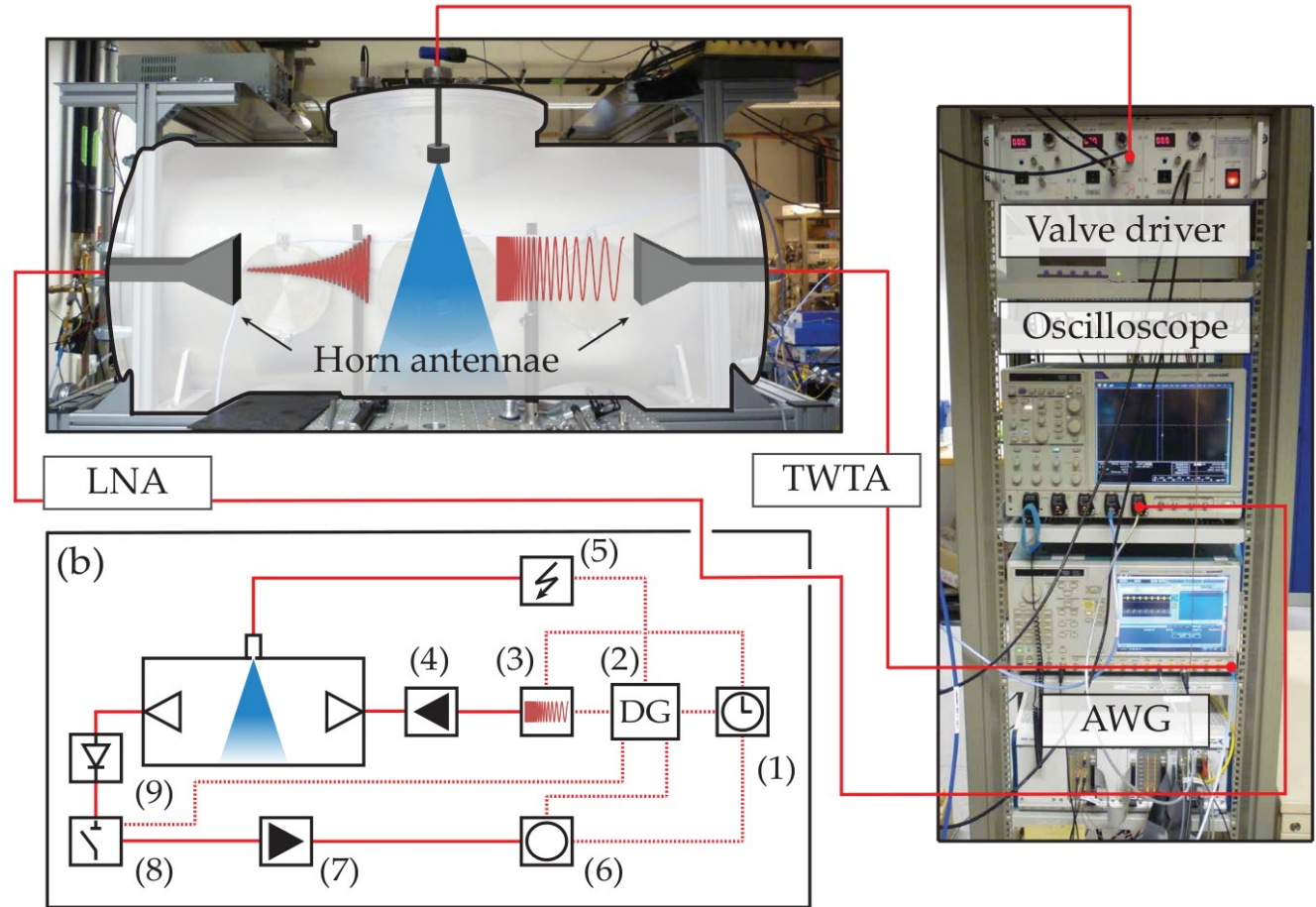
Dissertation @

Max-Planck-Institut für
Struktur und Dynamik der
Materie

und

Deutsches Elektronen-
Synchrotron,

Hamburg










Molekül(e) des Tages

Volume 19 | Number 22 | 14 June 2017 | Pages 14189–14862

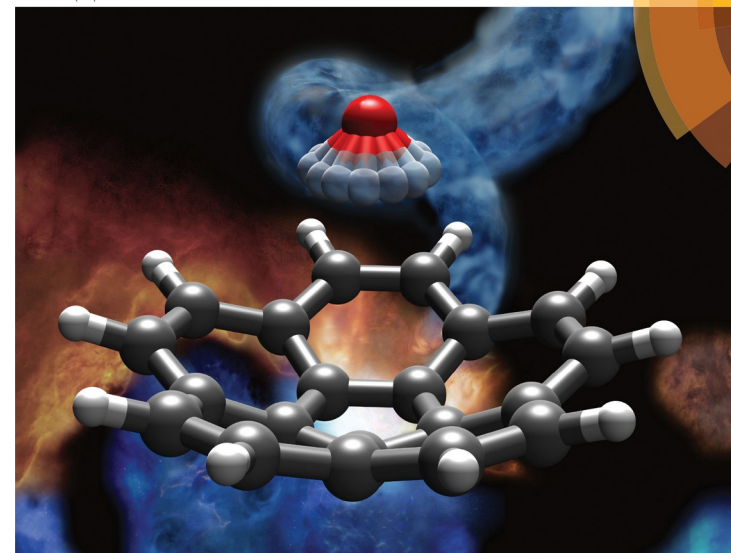
Corannulene and its complex with water: a tiny cup of water†

Cite this: *Phys. Chem. Chem. Phys.*,
2017, 19, 14214

Cristóbal Pérez, ^{abc} Amanda L. Steber, ^{abc} Anouk M. Rijs, ^d
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Zbigniew Kisiel ^{*g} and Melanie Schnell ^{*abc}

PCCP

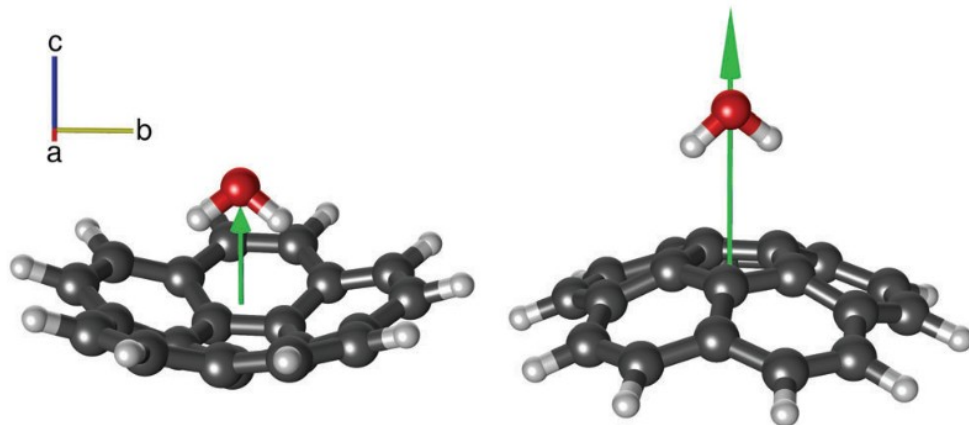
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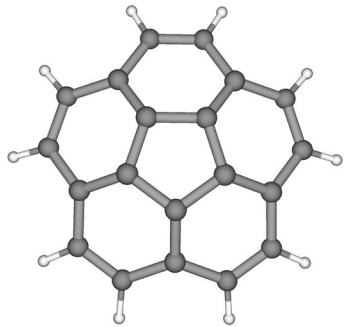


PAPER
Zbigniew Kisiel, Melanie Schnell et al.
Corannulene and its complex with water: a tiny cup of water



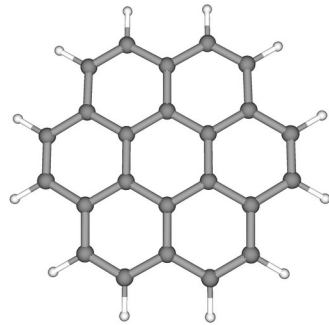
Circulene

[5]circulen
Corannulen (C_{5v})



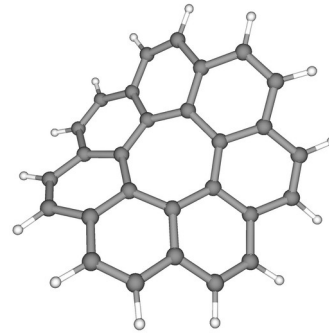
gebogen

[6]circulen
Coronen (D_{6h})



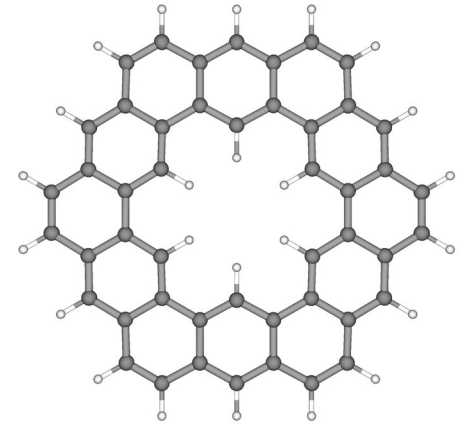
flach

[7]circulen (C_s)

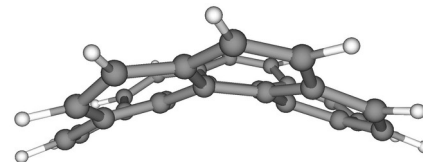
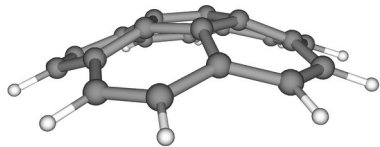


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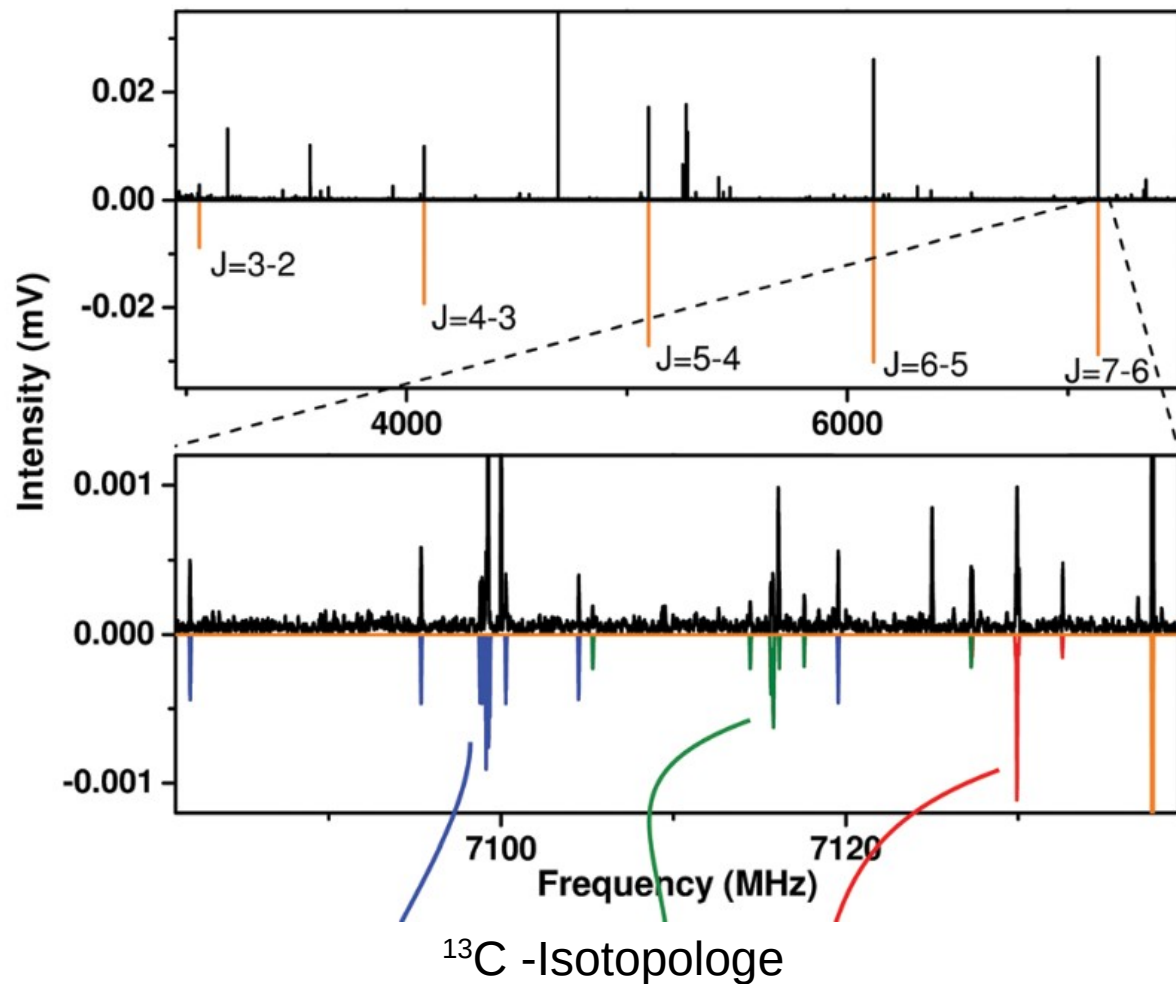
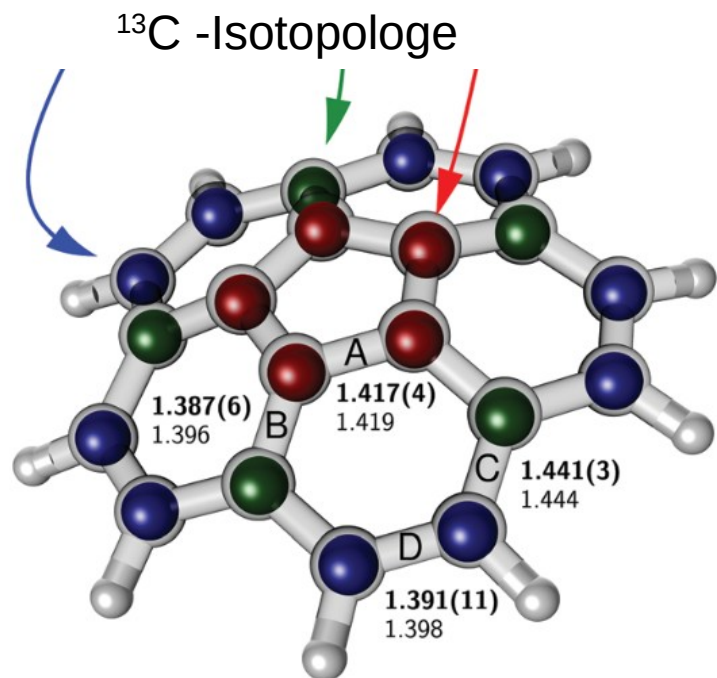
[12]circulen
Kekulen (D_{6h})



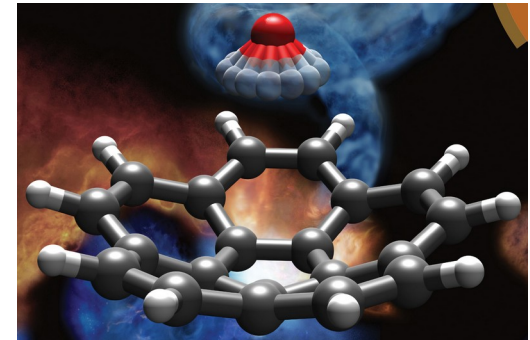
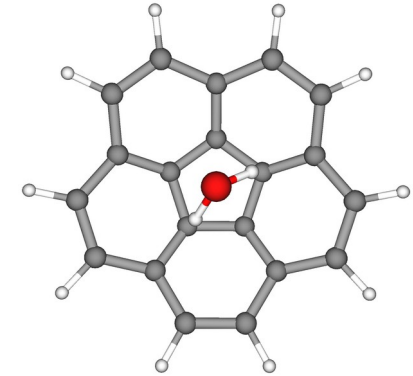
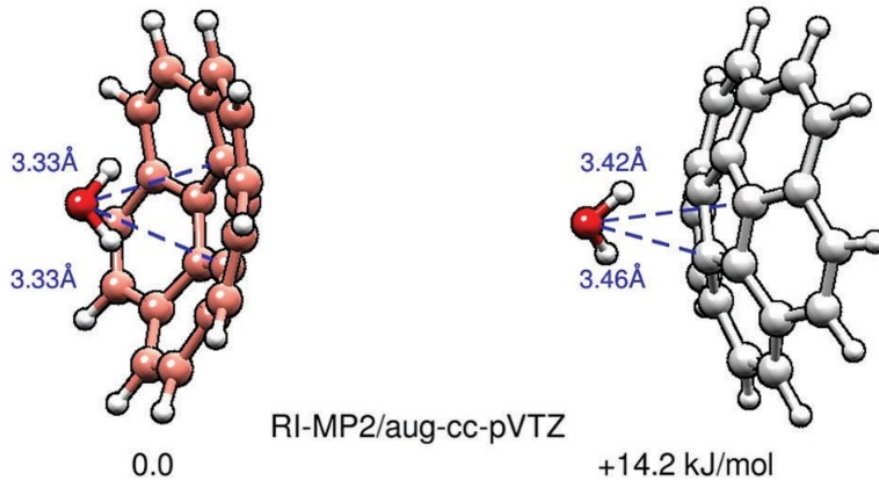
flach



Molekül(e) des Tages



Molekül(e) des Tages



Aber: Spektrum eines symmetrischen Kreisels!
Charakteristische Zeiten!

$$B = 455 \text{ MHz} \rightarrow t = 1 \text{ ns } (10^{-9} \text{ s})$$
$$\nu(\text{tors}) = 100 \text{ cm}^{-1} = 3 \times 10^6 \text{ MHz} \rightarrow t = 0.3 \text{ ps } (0.3 \times 10^{-12} \text{ s})$$

(s. Animation für MD @ $T = 10 \text{ K}$)

Quellen/Literatur

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- W. Caminati, J.-U. Grabow, “*Chapter 15 - Microwave Spectroscopy: Molecular Systems*”. In: J. Laane, editor. *Frontiers of Molecular Spectroscopy*. Elsevier, Amsterdam, 2009. Pp. 455–552.