

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 10 nm	2000 Å 200 nm	400 nm	0.7 μm 700 nm	2.5 μm 2500 nm	25 μm			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	λ
	1.2 × 10 ⁷	2.4 × 10 ⁵	1200	600	300	170	48	4.8			0.12	1.2 × 10 ⁻³	ν̃ / cm ⁻¹
	120 000	2400	120	6	3	1.7	0.5	0.05			0.001	0.00001	E / kJ mol ⁻¹
	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	E / eV
													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):

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

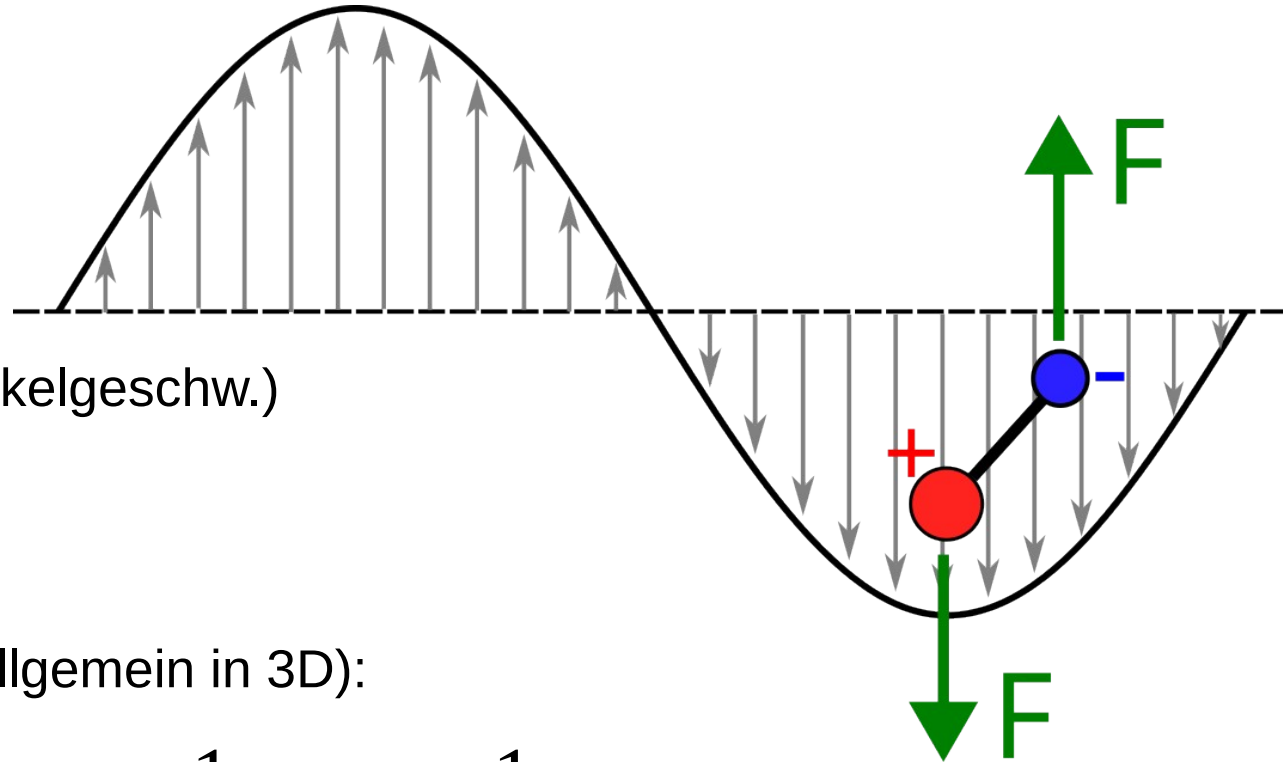
(I_x – Trägheitsmoment, ω_x – Winkelgeschw.)

Drehimpuls:

$$J_x = I_x \omega_x$$

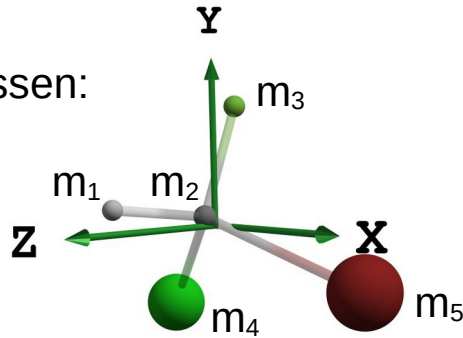
Energie (Allgemein in 3D):

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



Trägheitstensor

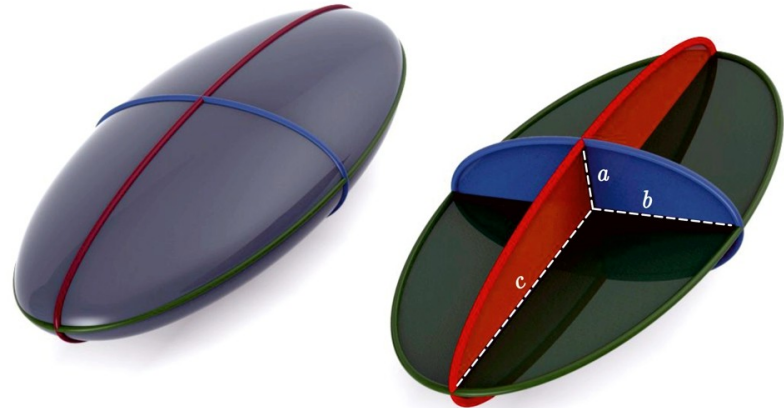
Punktmassen:



$$\mathbf{I} = \begin{bmatrix} I_{11} & I_{12} & I_{13} \\ I_{21} & I_{22} & I_{23} \\ I_{31} & I_{32} & I_{33} \end{bmatrix} = \begin{bmatrix} I_{xx} & I_{xy} & I_{xz} \\ I_{yx} & I_{yy} & I_{yz} \\ I_{zx} & I_{zy} & I_{zz} \end{bmatrix} = \begin{bmatrix} \sum_{k=1}^N m_k (y_k^2 + z_k^2) & -\sum_{k=1}^N m_k x_k y_k & -\sum_{k=1}^N m_k x_k z_k \\ -\sum_{k=1}^N m_k x_k y_k & \sum_{k=1}^N m_k (x_k^2 + z_k^2) & -\sum_{k=1}^N m_k y_k z_k \\ -\sum_{k=1}^N m_k x_k z_k & -\sum_{k=1}^N m_k y_k z_k & \sum_{k=1}^N m_k (x_k^2 + y_k^2) \end{bmatrix}$$

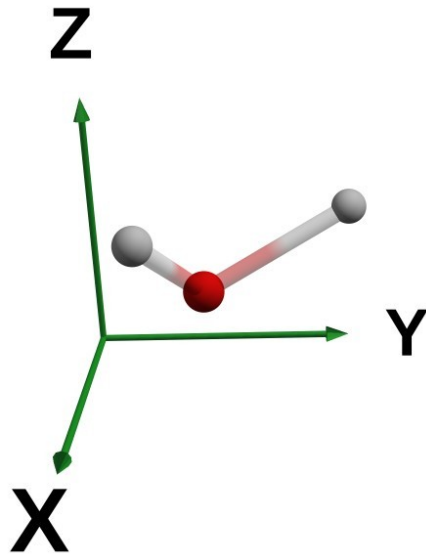
Ein Trägheitstensor entspricht einem Ellipsoid:

$$\left(\frac{x}{1/\sqrt{I_1}} \right)^2 + \left(\frac{y}{1/\sqrt{I_2}} \right)^2 + \left(\frac{z}{1/\sqrt{I_3}} \right)^2 = 1$$



Kreisel im Hauptträgheits-System

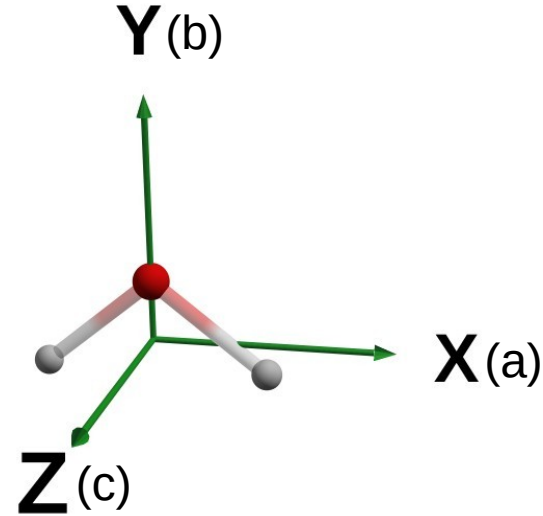
H₂O



X,Y,Z-System

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

diagonalisieren



Hauptträgheits-System

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

Konvention:

$$I_x \stackrel{\text{def}}{=} I_a$$

$$I_y \stackrel{\text{def}}{=} I_b$$

$$I_z \stackrel{\text{def}}{=} I_c$$

$$I_c \geq I_b \geq I_a$$

Zweiatomiges Molekül

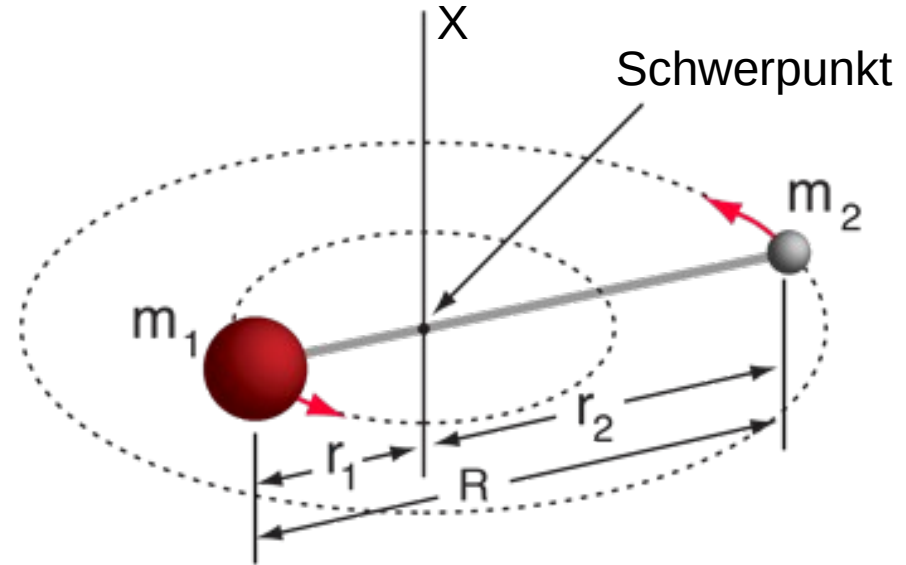
Trägheitsmoment
für lineare Moleküle:

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

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

Schwerpunkt: $m_1 r_1 = m_2 r_2$

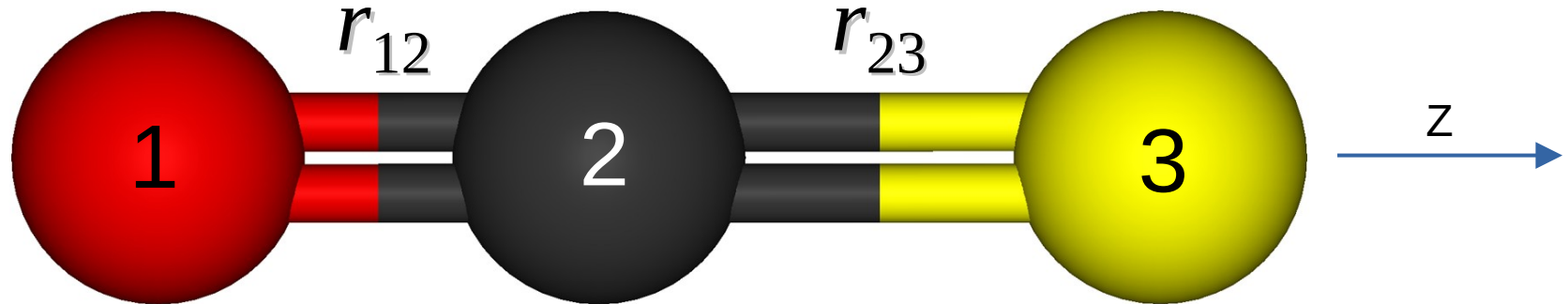
$$I = \frac{m_1 m_2 R^2}{m_1 + m_2} = \mu R^2$$



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

Lineare Kreisel

z.B.: O=C=S



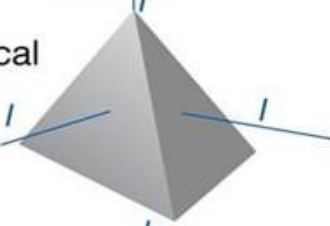
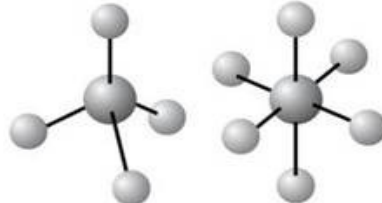
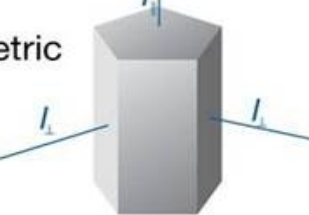
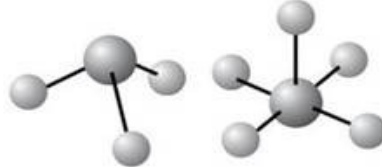
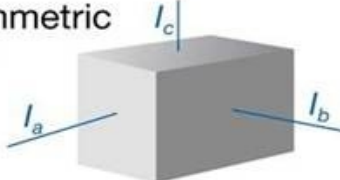
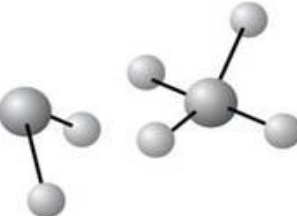


$$I_z = 0 \quad I_x = I_y = I$$

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

Gesamtmasse: $M = m_1 + m_2 + m_3$

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: $I_c \geq I_b \geq I_a$

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 J, K, M

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

x, y, z Molekül-fixiertes Koordinatensystem
 X, Y, Z Raum-fixiertes Koordinatensystem

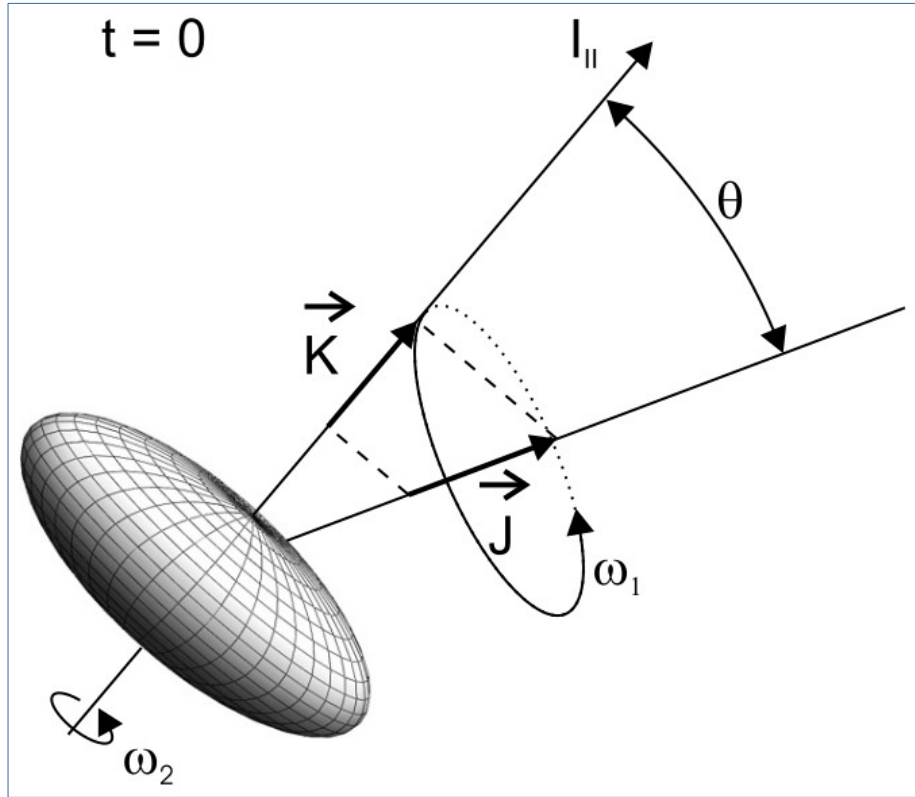
hier und im Weiteren
werden atomare
Einheiten benutzt

$$\left\langle J, K, M \left| \hat{J}^2 \right| J, K, M \right\rangle = J(J + 1) \quad \boxed{J = 0, 1, 2 \dots}$$

$$\left\langle J, K, M \left| \hat{J}_z^2 \right| J, K, M \right\rangle = K^2 \quad \boxed{K = -J, -J+1 \dots J}$$

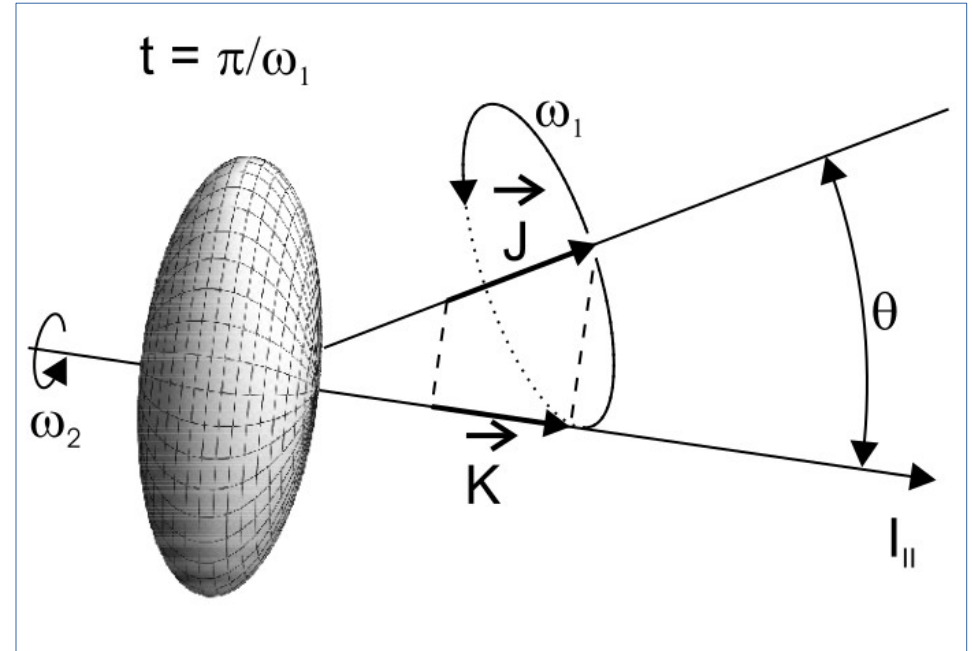
$$\left\langle J, K, M \left| \hat{J}_Z^2 \right| J, K, M \right\rangle = M^2 \quad \boxed{M = -J, -J+1 \dots J}$$

Quantenzahlen J, K



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

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



Lineare Moleküle: R.-E.-Niveaus

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

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

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

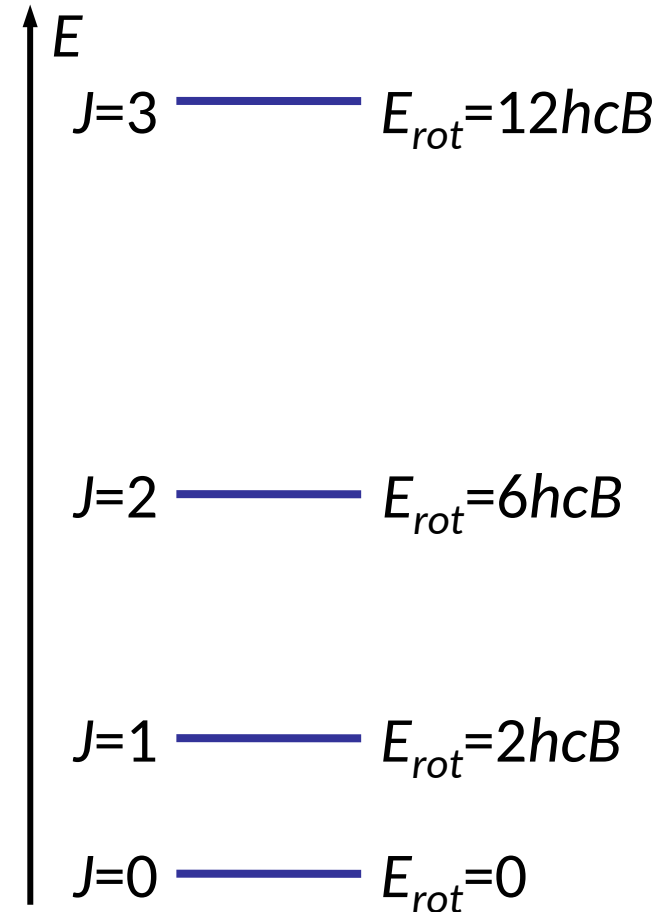


$$E_{\text{rot}} = hcBJ(J + 1)$$

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

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

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



Korrespondenzprinzip

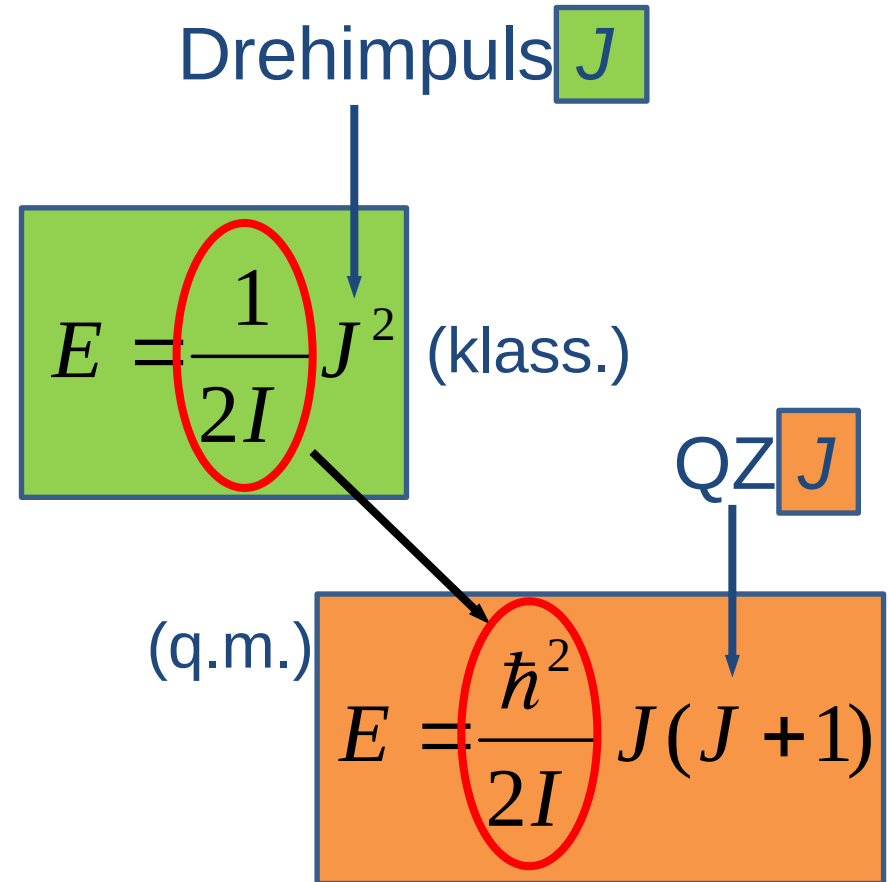
Nochmal klassisch: $E = \frac{1}{2} I_x \omega_x^2 \quad J_x = I_x \omega_x$

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

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

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

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



Lineare Moleküle: Übergänge

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

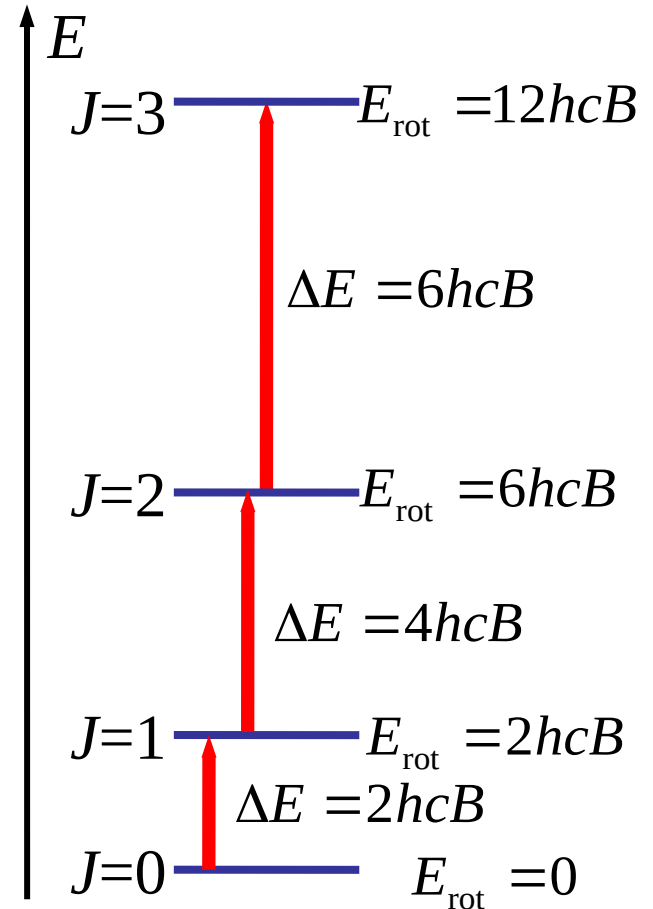
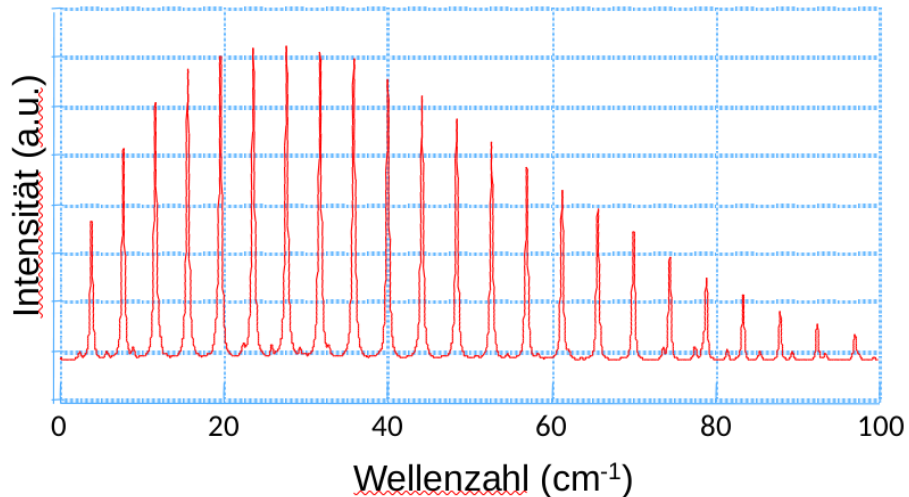
$$\Delta E(J + 1 \leftarrow J) =$$

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

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

$$\Delta J = \pm 1$$

Auswahlregel



Lineare Moleküle: Übergänge

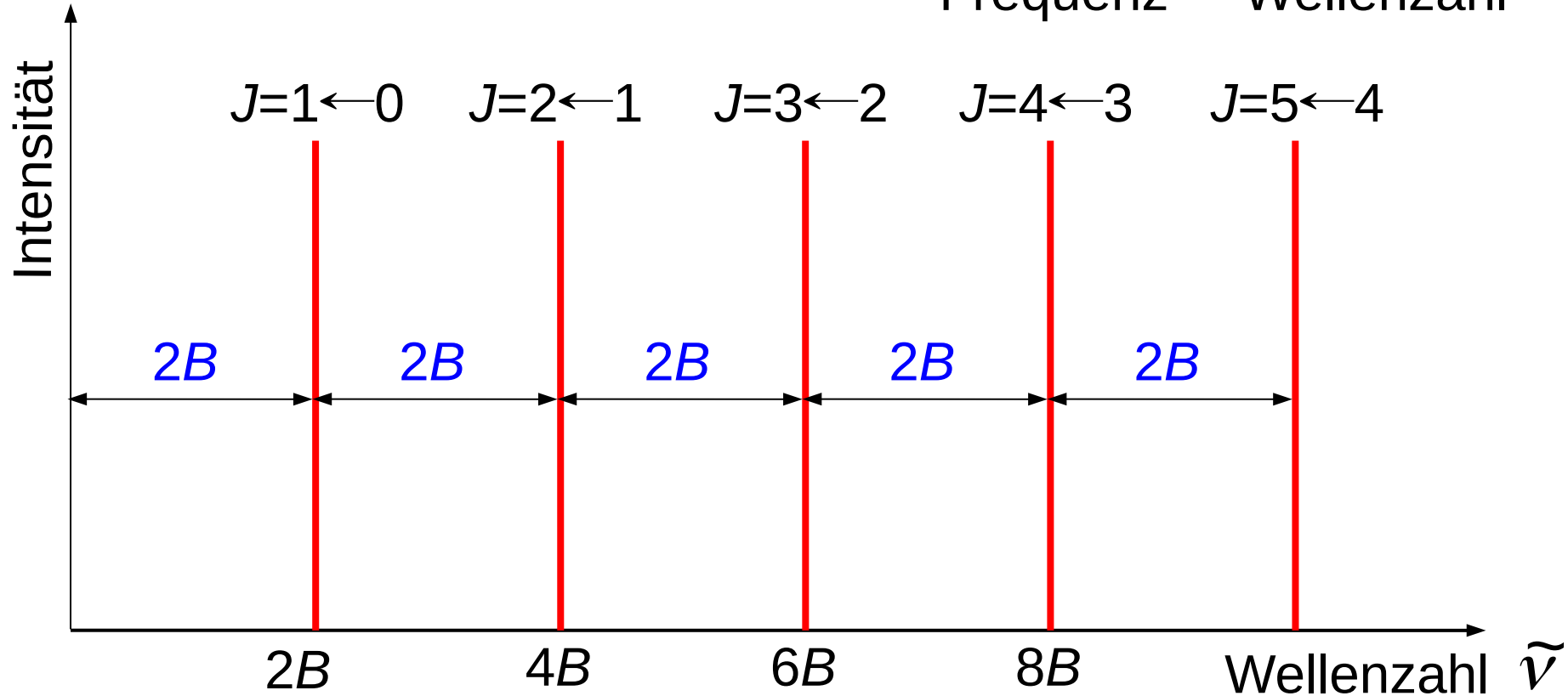
$$h\nu_{rot} = 2hcB(J+1)$$

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

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

↑
Frequenz

↑
Wellenzahl



Linien-Intensitäten

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

(2) Boltzmann-Verteilung

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

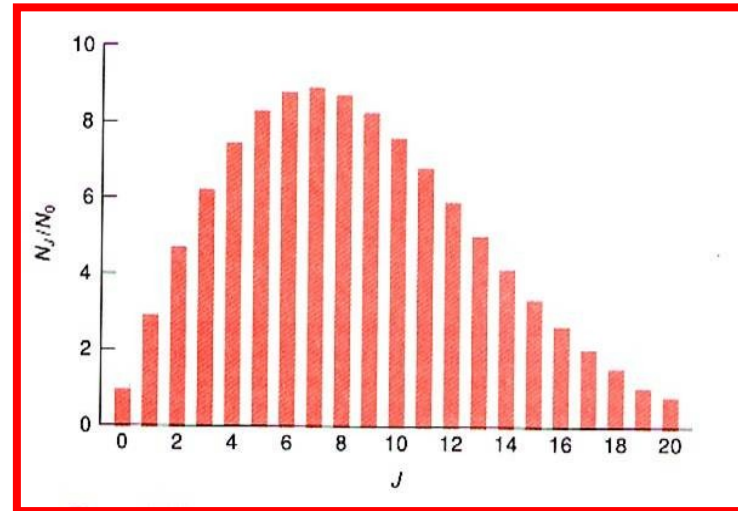


$$\frac{N_J}{N_0} = (2J + 1) e^{-\frac{\Delta E_{rot}}{kT}}$$

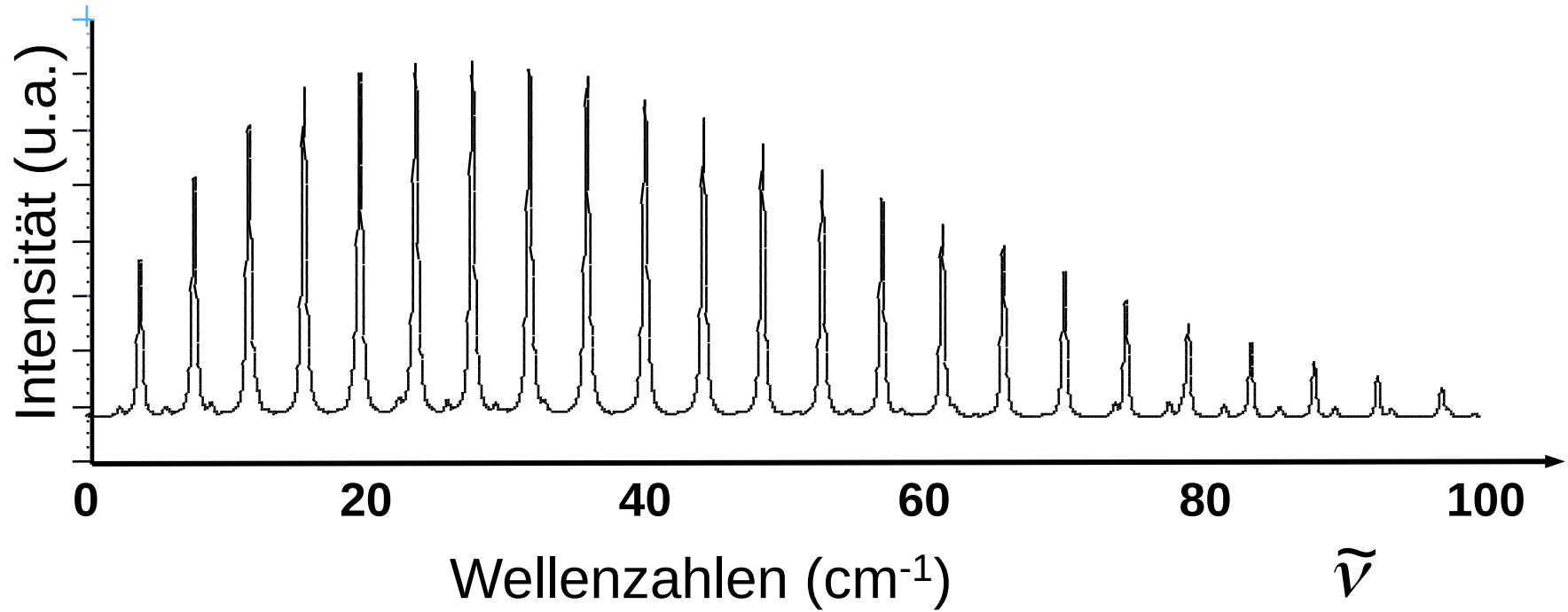
$$Int \propto \left(\frac{N_m}{g_m} - \frac{N_n}{g_n} \right) \left| \langle n | \mu | m \rangle \right|^2$$

μ : Übergangsdipolmoment

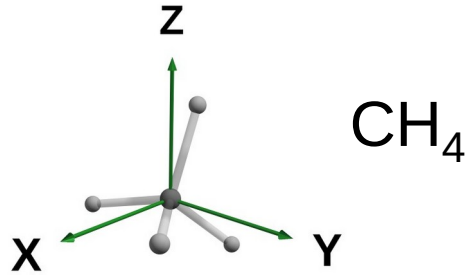
(d. h. mindestens μ_a , μ_b oder μ_c muss $\neq 0$!)



MW-Rotationsspektrum von CO



Sphärische und symmetrische Kreisel



$$I_a = I_b = I_c = I$$

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

Jedes Niveau:

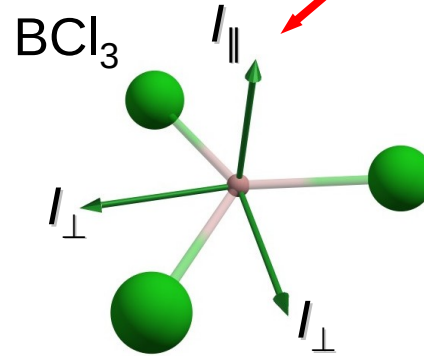
$(2J + 1)^2$ –fach entartet (K, M)

$\mu_a = \mu_b = \mu_c = 0 \rightarrow$ Keine Spektren

(z = Symmetrie-Achse)

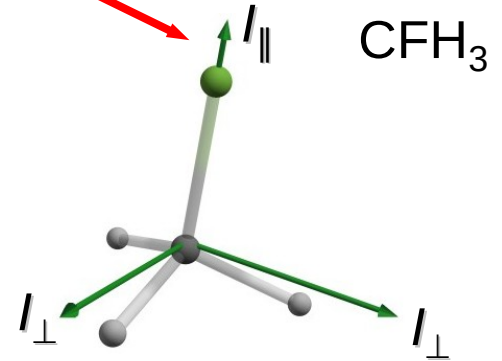
$$I_x = I_y = I_{\perp}$$

$$I_z = I_{\parallel}$$



abgeflacht
(oblate)

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



gestreckt
(prolate)

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

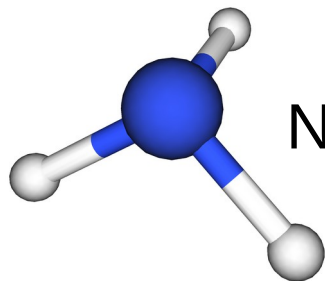
Symmetrische Kreisel

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

oblate

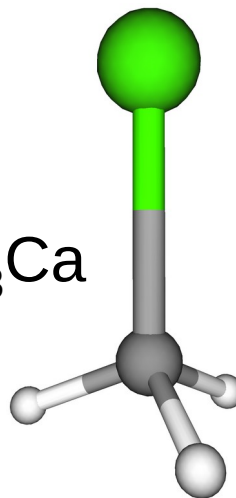
$$I_{\perp} < I_{//}$$

$$I_{//} = I_c$$



NH₃

CH₃Ca



prolate

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

$$I_{//} = I_a$$

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

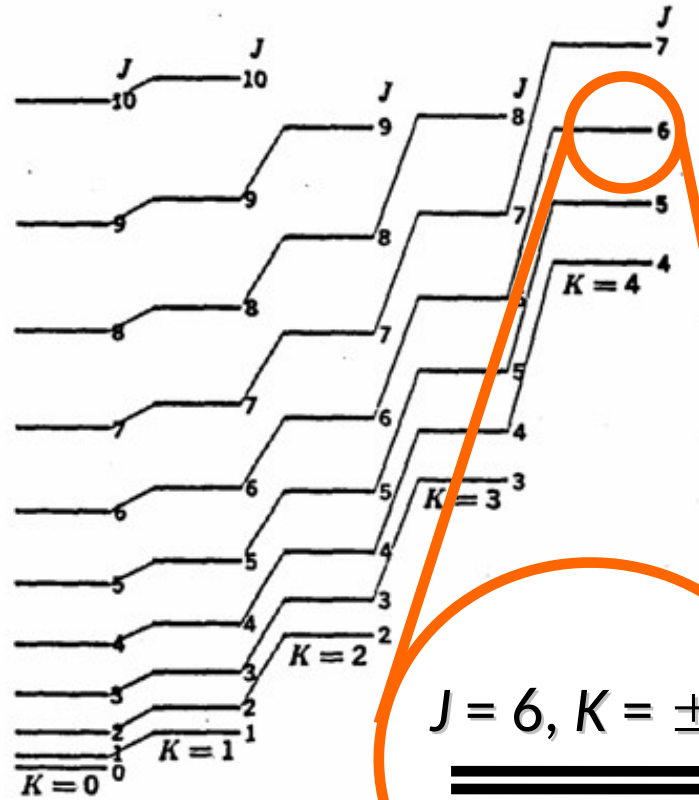
mit $A > B = C$

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

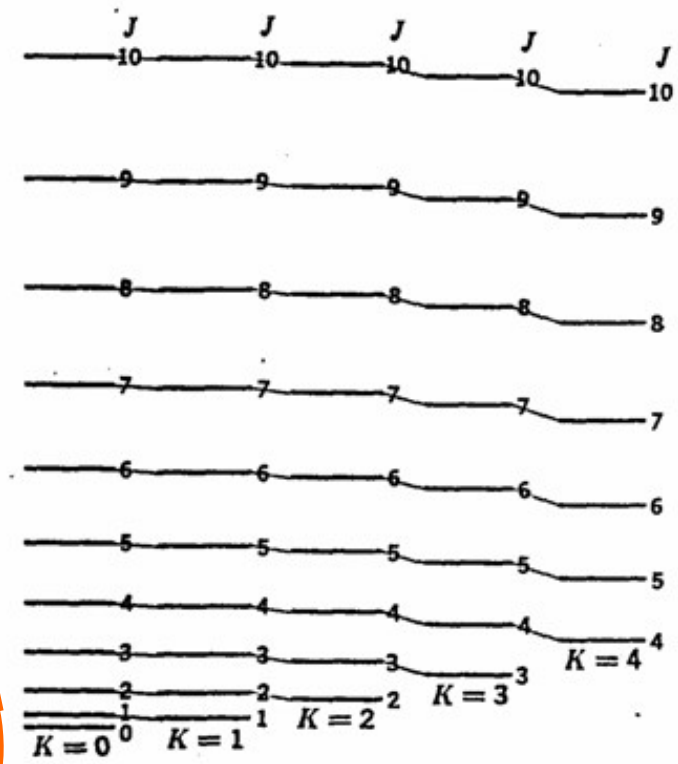
mit $A = B > C$

<0

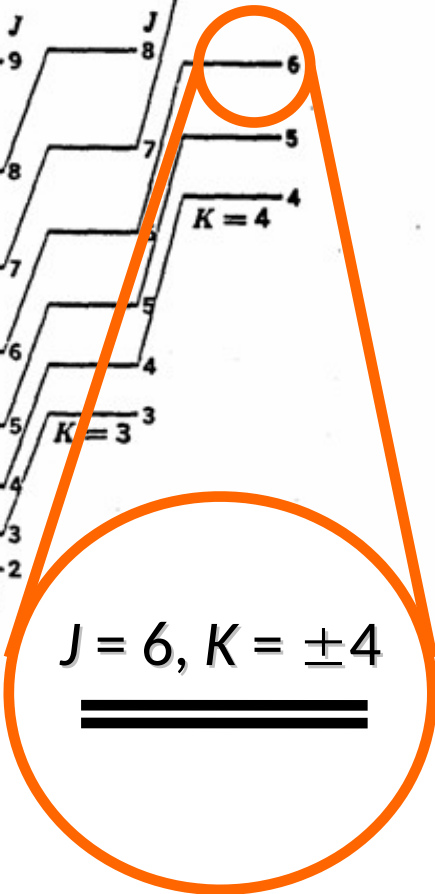
Symmetrische Kreisel - Energieniveaus



$J = 6$ →



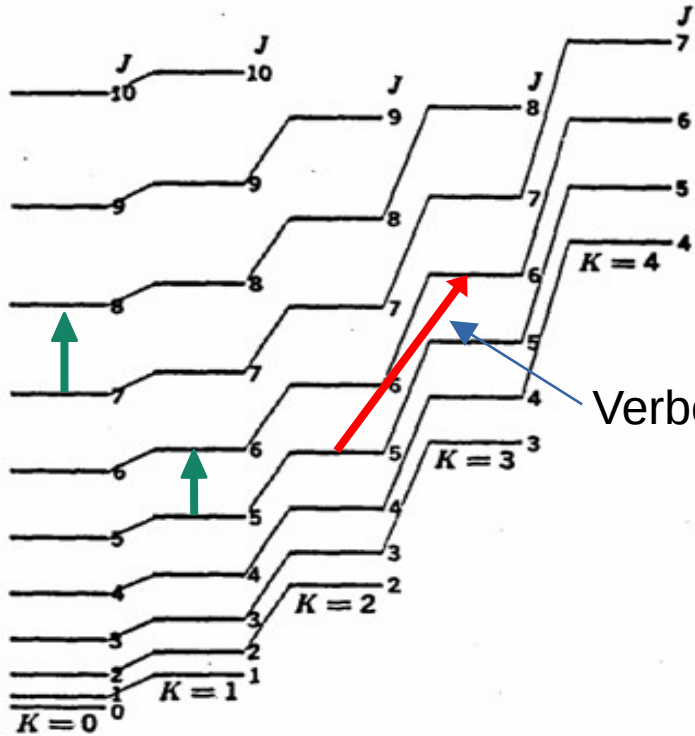
← $J = 6$



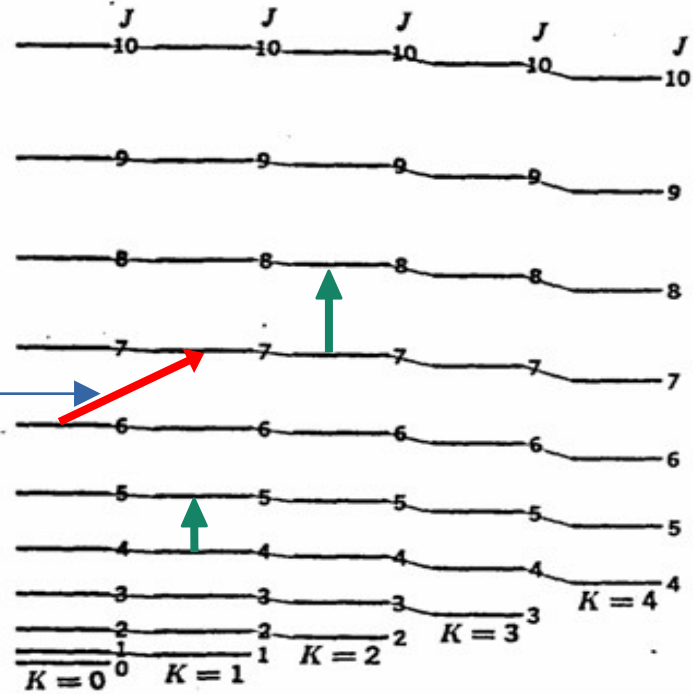
Prolate
 $A > B = C$

Oblate
 $A = B > C$

Symmetrische Kreisel – Auswahlregeln



Prolate
 $A > B = C$



Oblate
 $A = B > C$

Verboten

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

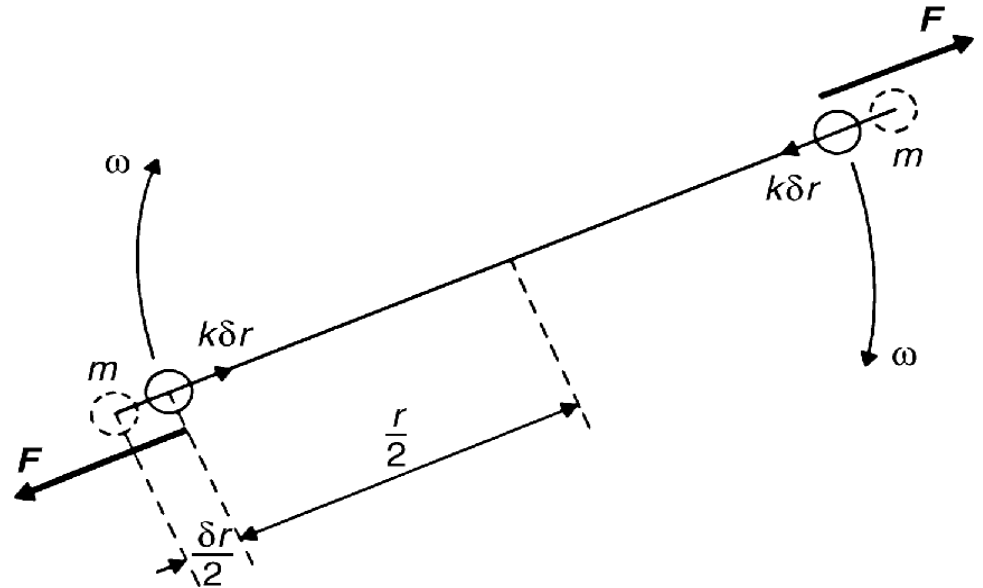
Störung (Distortion)

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

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

quartische Zentrifugal-
Verzerrungs-Konstante

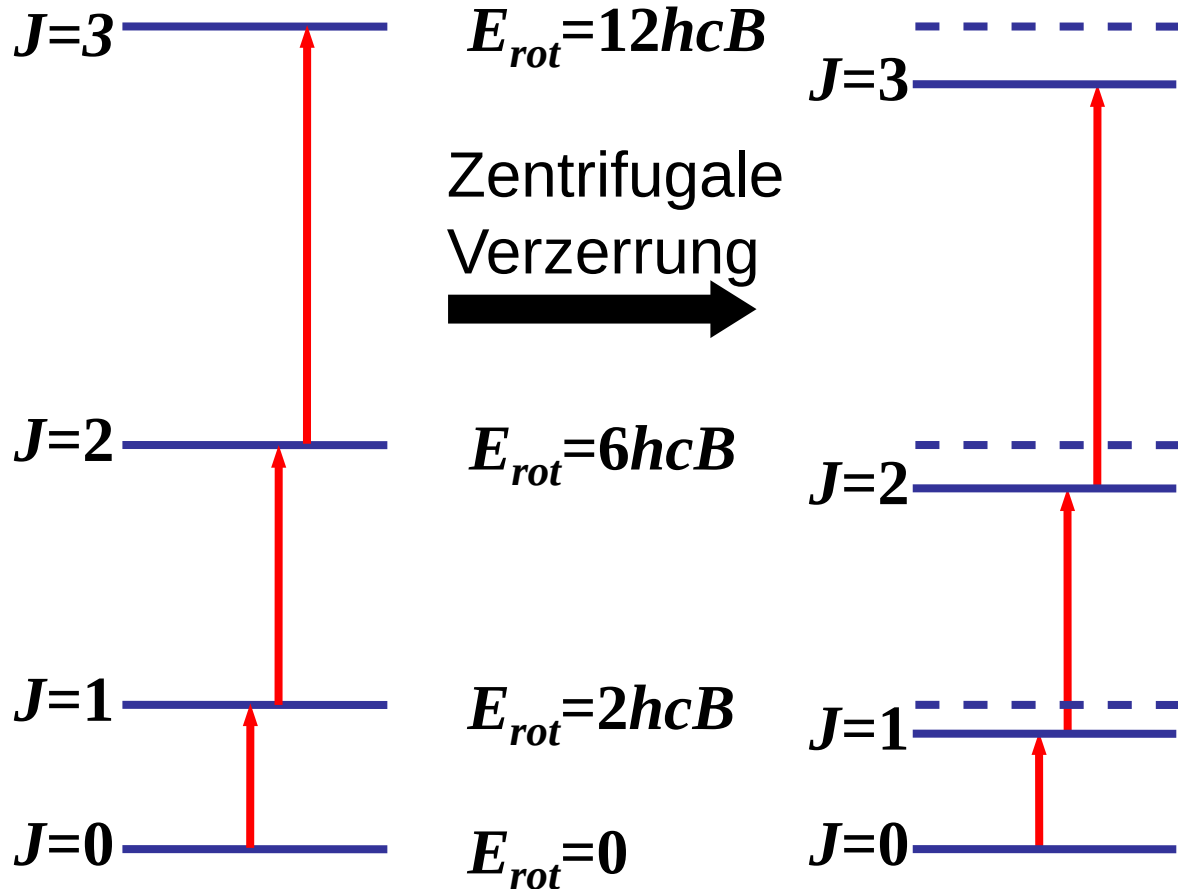
$$D_J = -\frac{\tau_{xxxx}}{4}$$



Zentrifugale Verzerrung: R.-E.-Niveaus

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

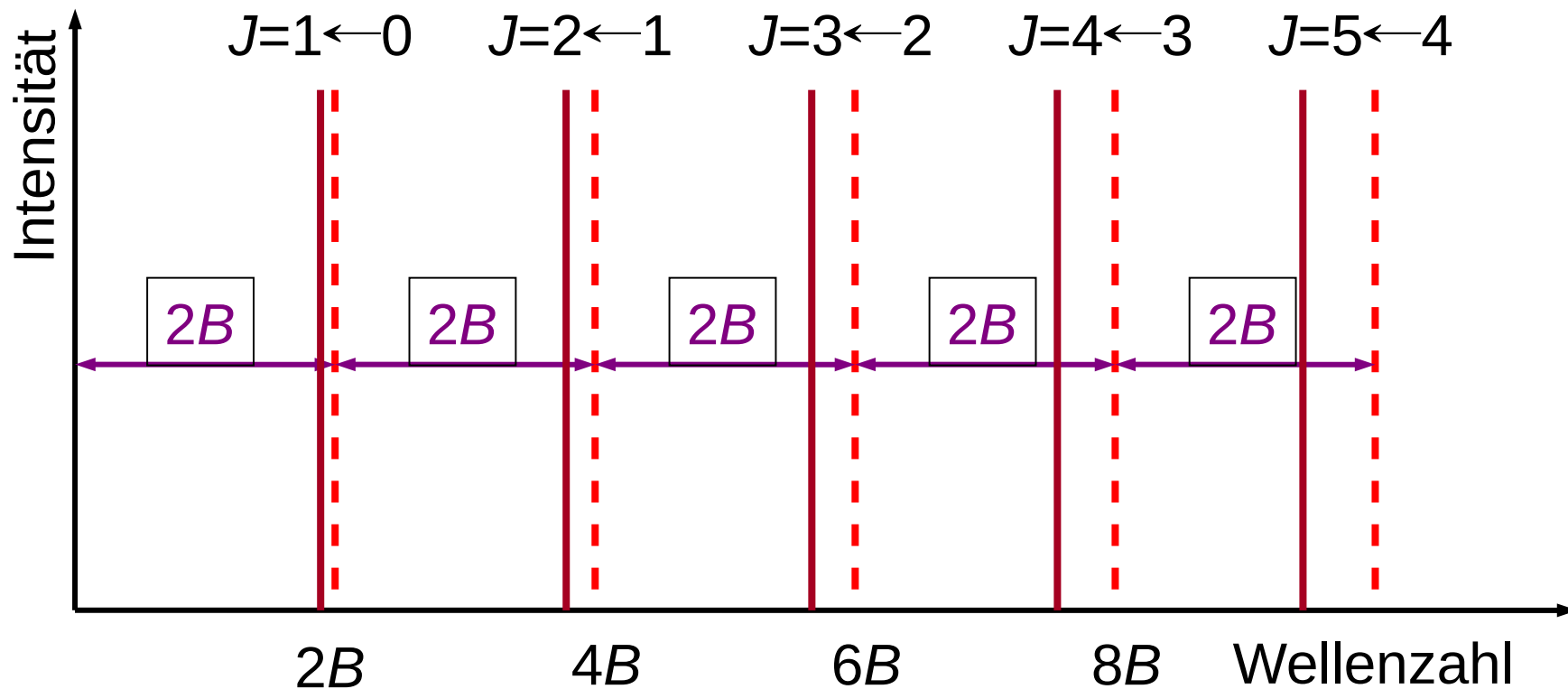
← E. von R.-Zustand!



für lineares Molekül

Zentrifugale Verzerrung: Spektrum

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



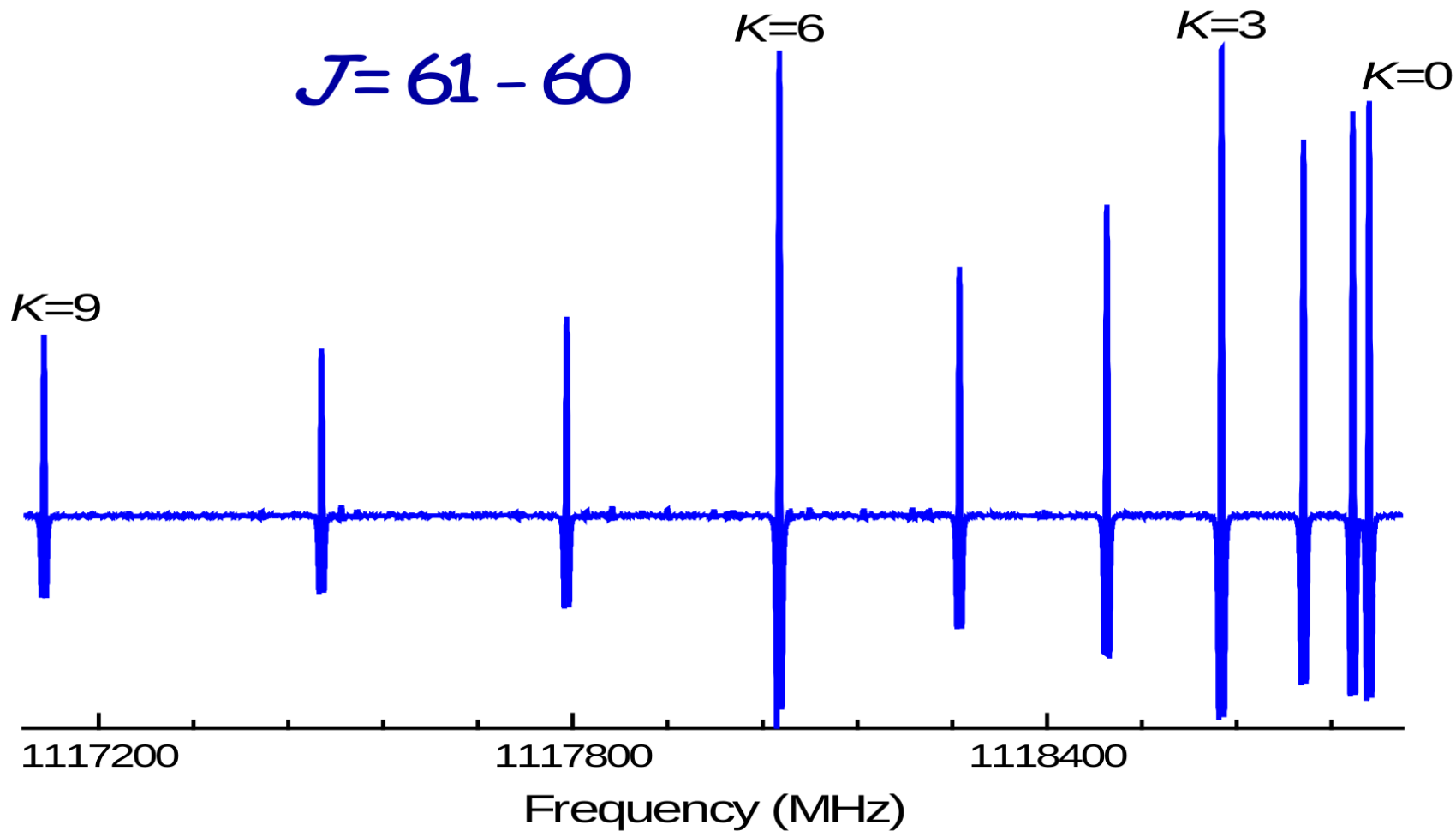
Zentrifugal-Verzerrung: symmetrische Kreisel

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 :

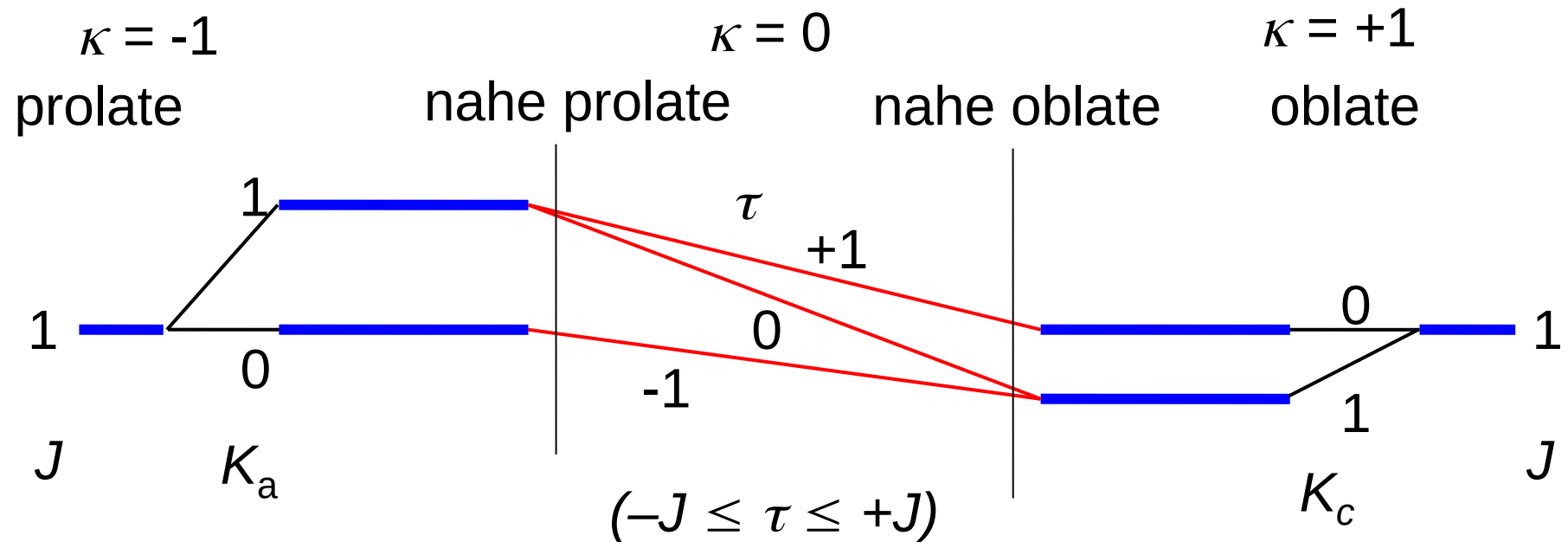
$K_a \rightarrow$ begrenzt den prolaten symmetrischen Kreisel

$K_c \rightarrow$ begrenzt den oblaten symmetrischen Kreisel

Asymmetrische Kreisel: R.-E.-Niveaus

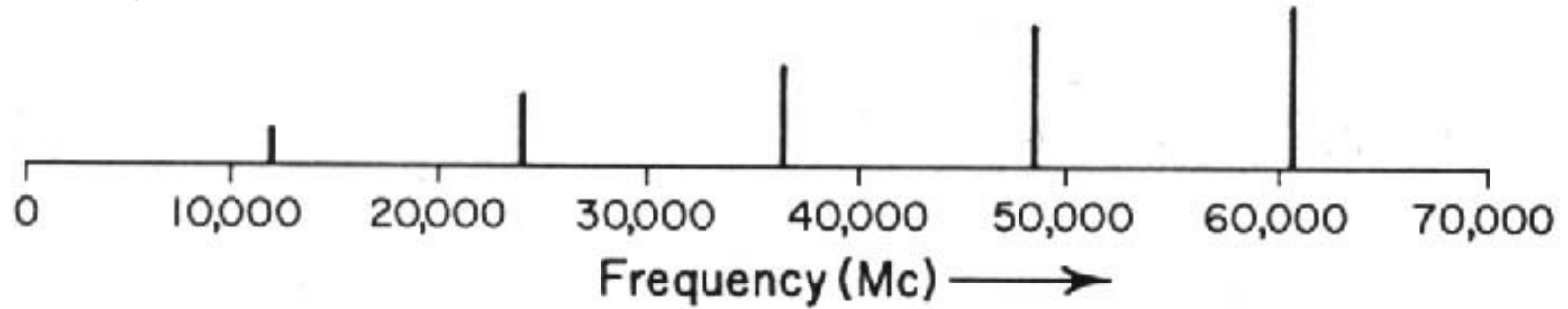
Asymmetrieparameter:
$$\kappa = \frac{2B - A - C}{A - C}$$

2 Notationsschemata: J_{κ_a, κ_c} oder J_τ

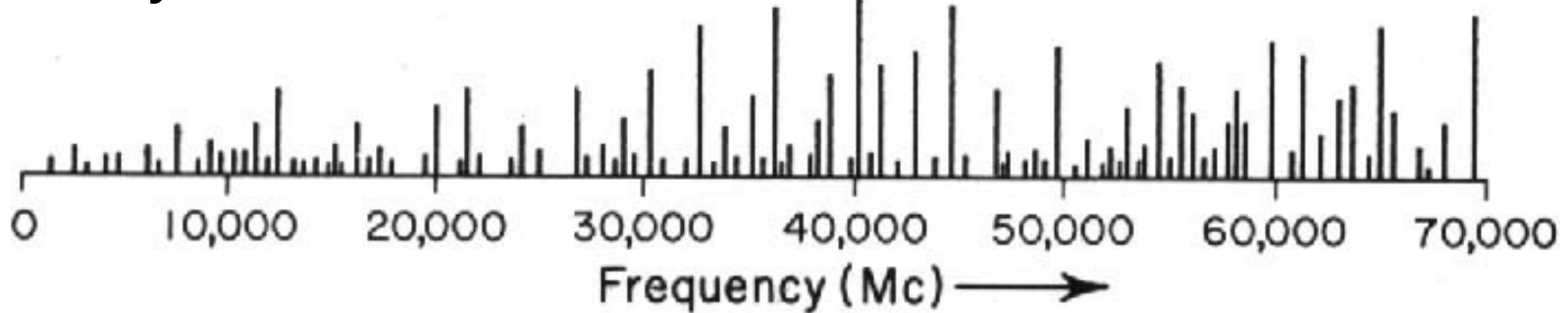


Asymmetrische Kreisel: Spektrum

Symmetrischer Rotor



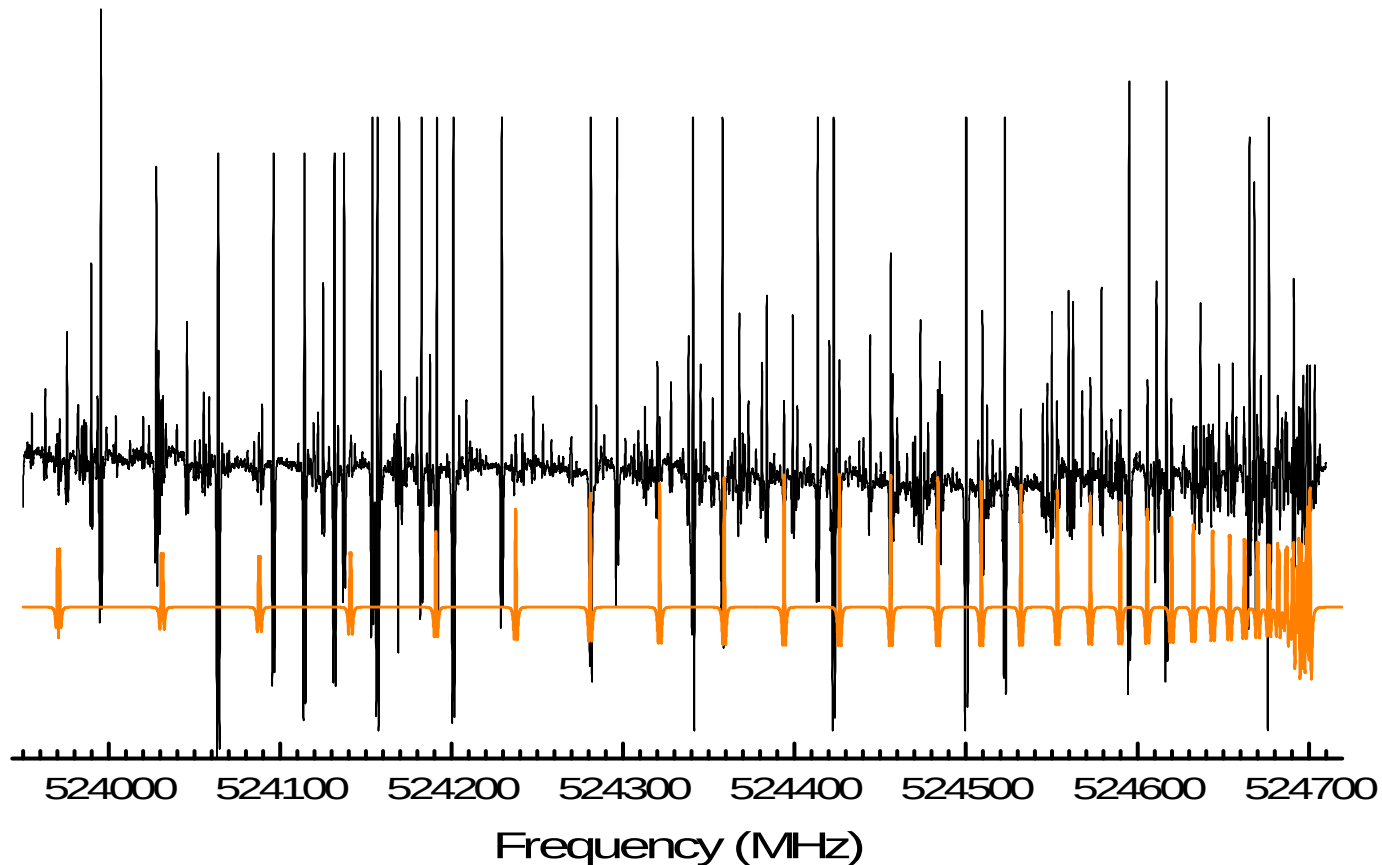
Asymmetrischer Rotor



Asymmetrische Kreisel: Spektrum

kleiner Ausschnitt aus dem Spektrum

trans-CH³⁵Cl=CHF



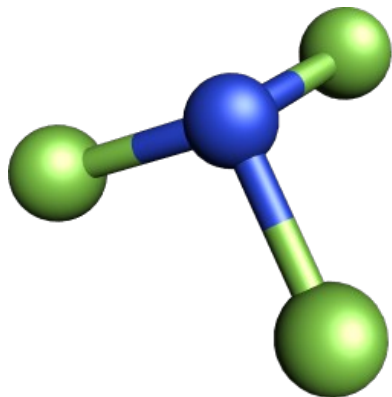
Inertial defect

Inertial defect: $\Delta := I_c - I_a - I_b$

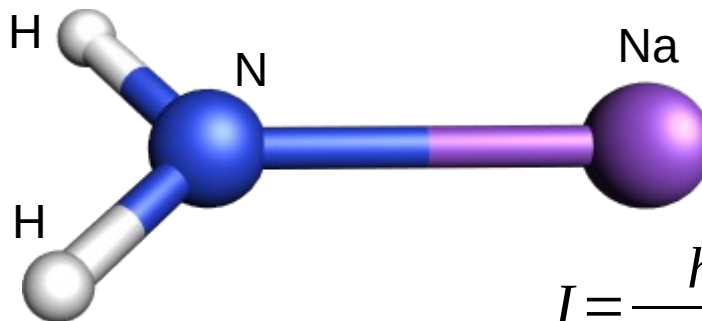
Flache Moleküle: $\Delta = 0$ oder ≈ 0

sonst $\Delta < 0$

NF₃



$$\Delta = -8.11 \text{ amu } \text{Å}^2$$



$$I = \frac{h 10^{14}}{8 \pi^2 k_{amc} B}$$

$$A = 387730 \text{ MHz} \quad \rightarrow \quad I_a = 1.303 \text{ amu } \text{Å}^2$$

$$B = 11250.7326 \text{ MHz} \quad \rightarrow \quad I_b = 44.920 \text{ amu } \text{Å}^2$$

$$C = 10914.8259 \text{ MHz} \quad \rightarrow \quad I_c = 46.302 \text{ amu } \text{Å}^2$$

$$\Delta = I_c - I_a - I_b = 0.078 \text{ amu } \text{Å}^2 \quad \rightarrow \quad \text{NaNH}_2 \text{ ist flach!}$$

$$\text{Vgl. Formaldehyde } \text{H}_2\text{C=O} \quad \Delta = 0.057 \text{ amu } \text{Å}^2$$

J. Xin, M. A. Brewster, L. M. Ziurys, *ApJ* 2000, 530, 323.

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:

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

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

$$\Delta K = 0$$

Symm. Kreisel:

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

Mit Zentrifugalverzerrung:

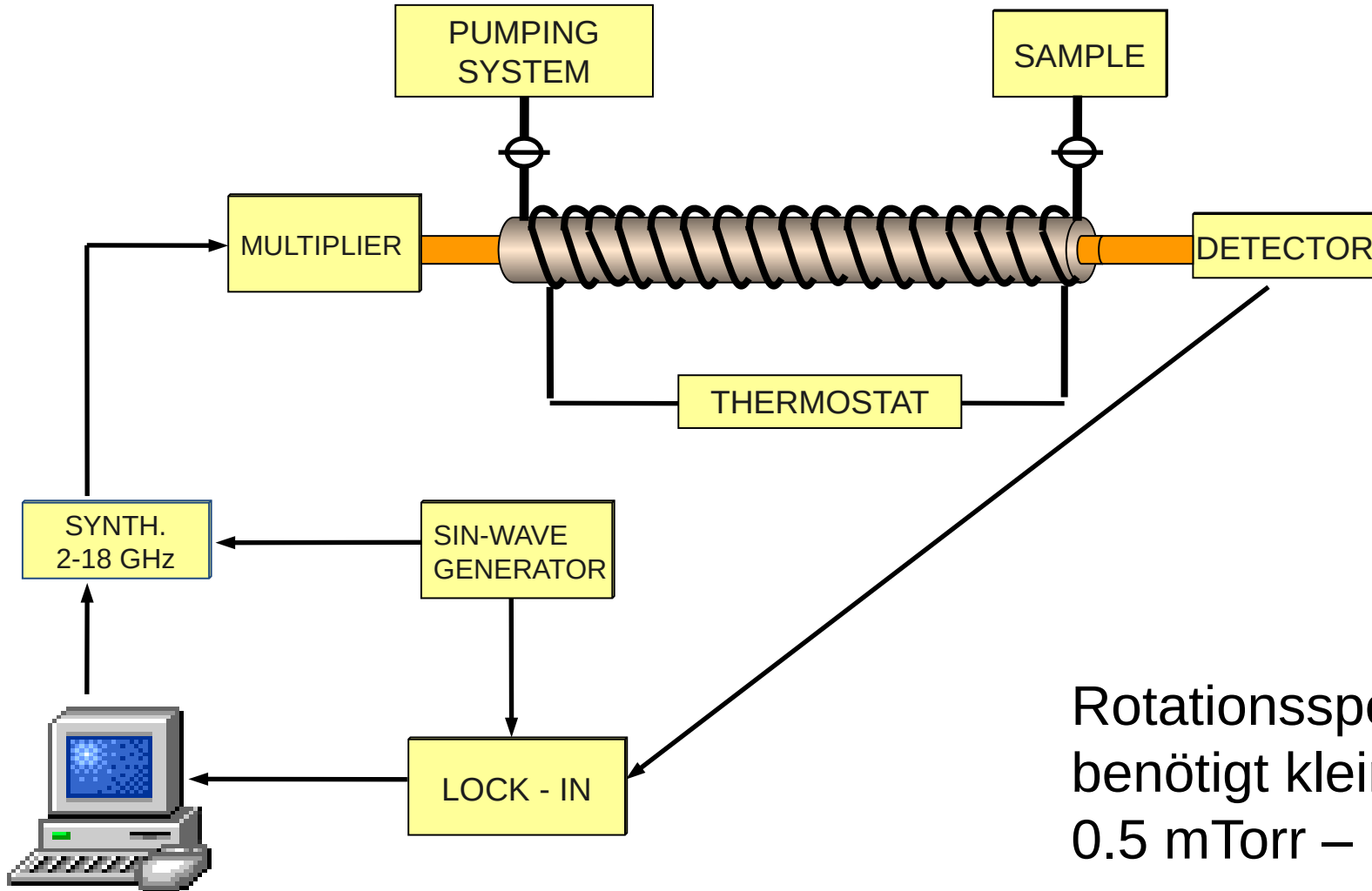
$$E_{\text{rot}} / hc = B(J + 1) + (a - B)K^2 - D_J J^2 (J + 1)^2 - D_{JK} J(J + 1)K - D_K K^4$$

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

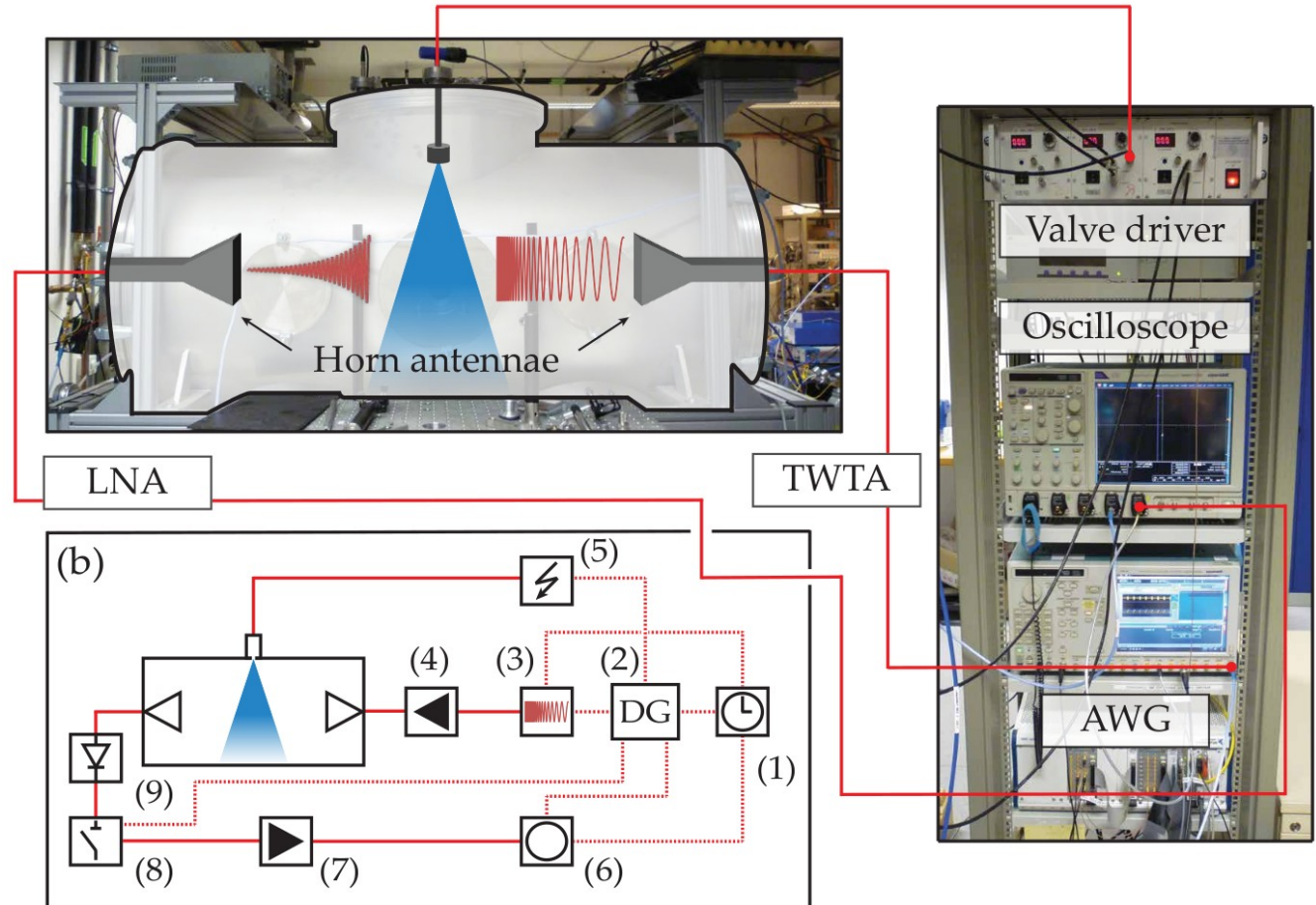
Dissertation @

Max-Planck-Institut für
Struktur und Dynamik der
Materie

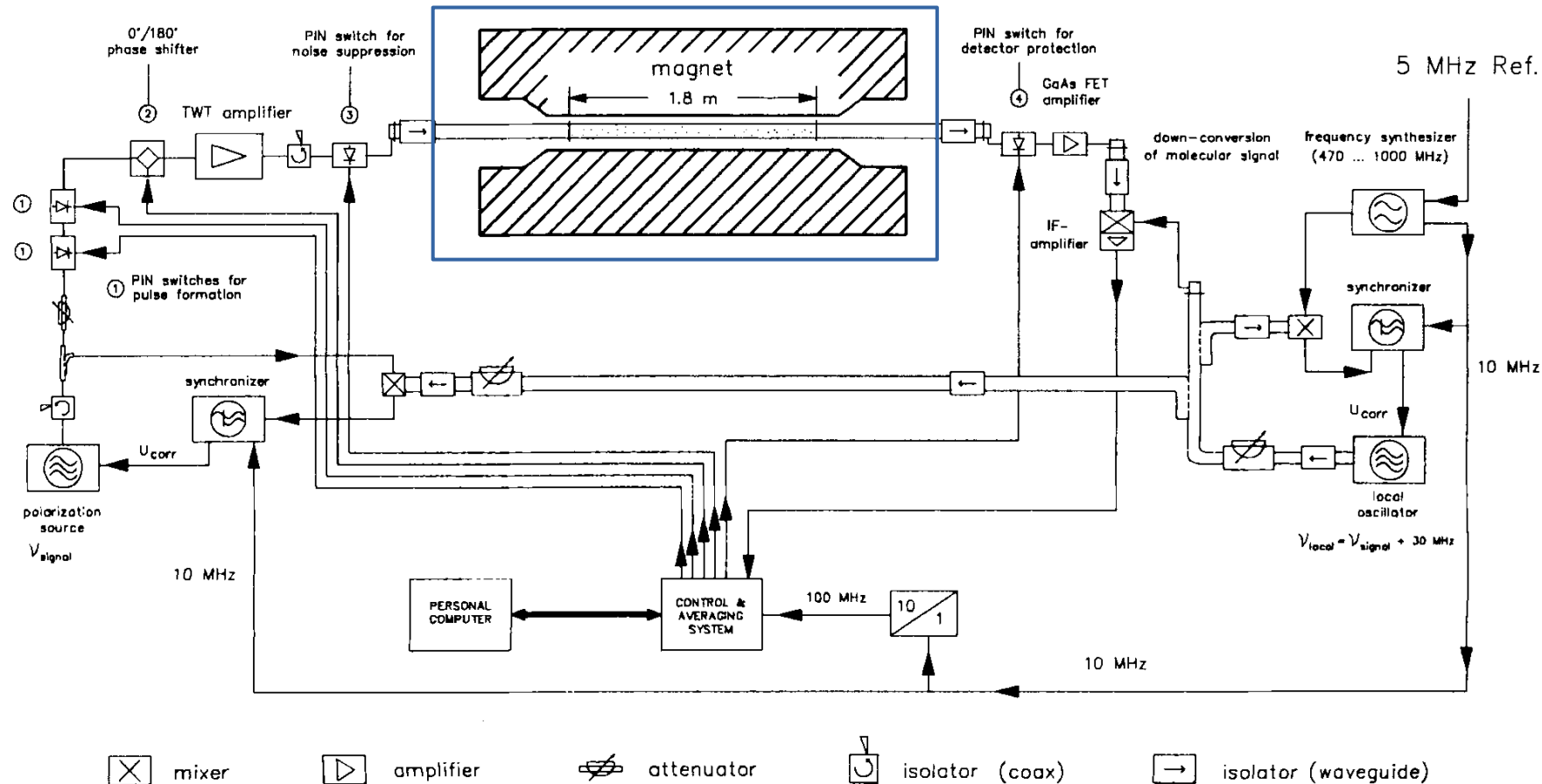
und

Deutsches Elektronen-
Synchrotron,

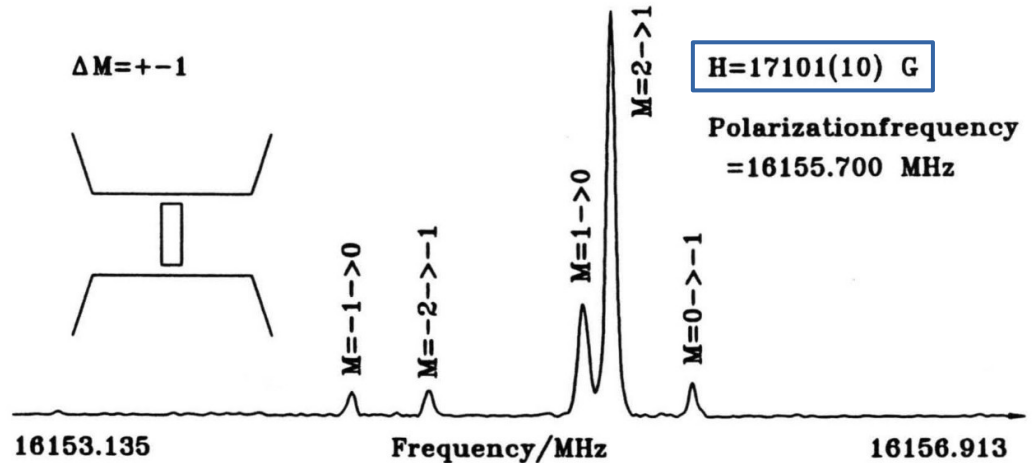
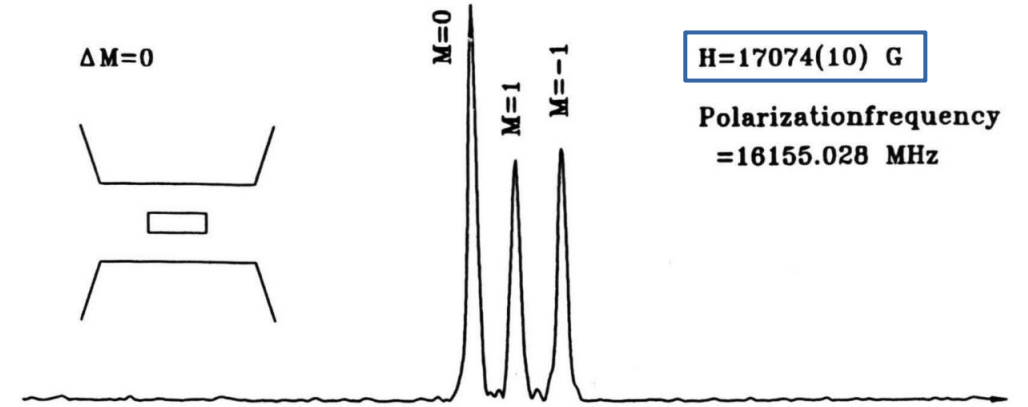
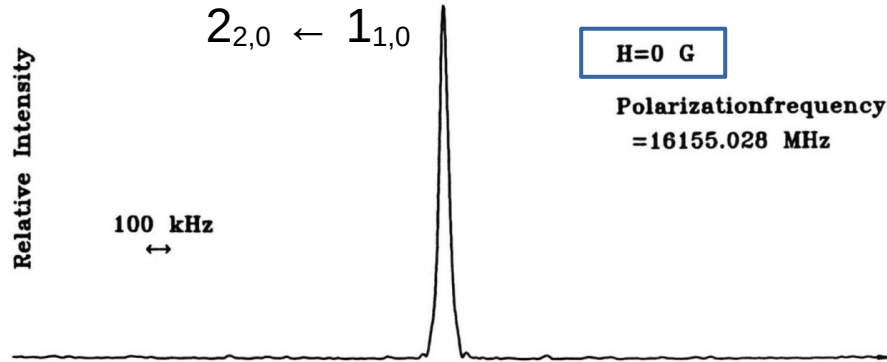
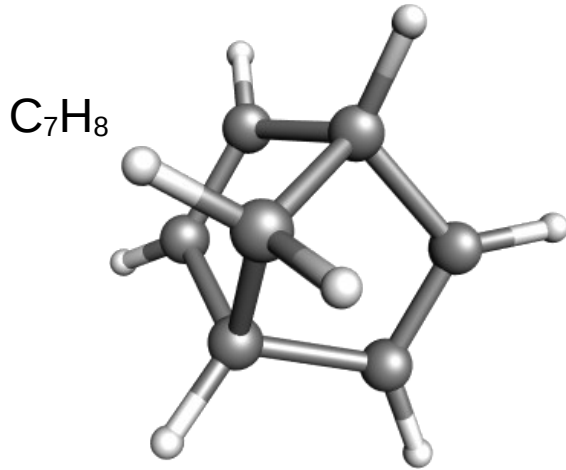
Hamburg



FTMW-Spektrometer mit Magnetfeld



Norbornadien: Zeeman-Effekt










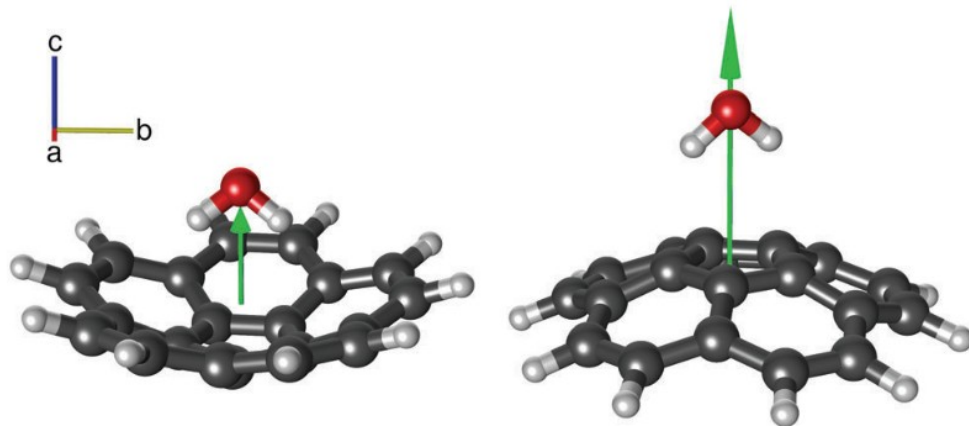
Molekül(e) des Tages

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

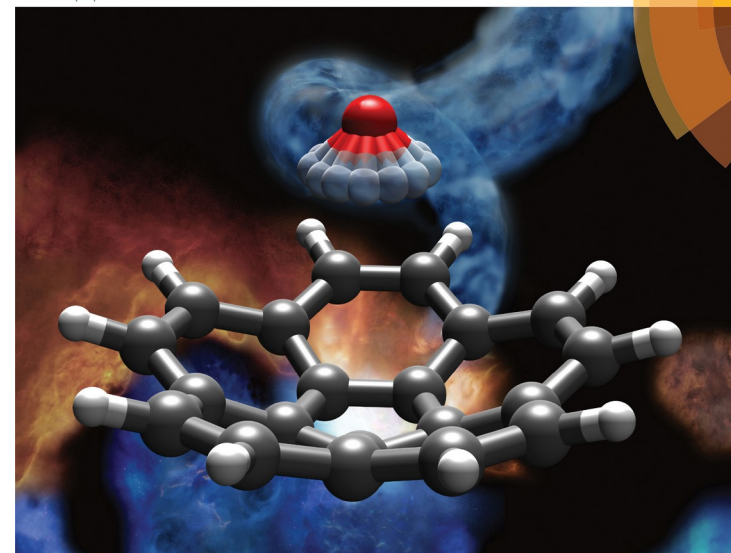
Cite this: *Phys. Chem. Chem. Phys.*,
2017, 19, 14214

Cristóbal Pérez, ^{abc} Amanda L. Steber, ^{abc} Anouk M. Rijs, ^d
Berhane Temelso, ^e George C. Shields, ^e Juan Carlos Lopez,^f
Zbigniew Kisiel ^{*g} and Melanie Schnell ^{*abc}



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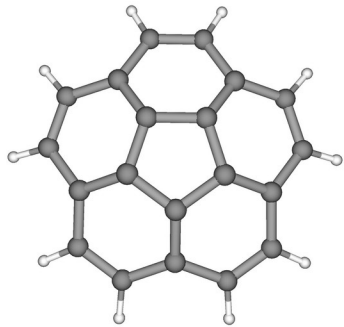
ISSN 1463-9076



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

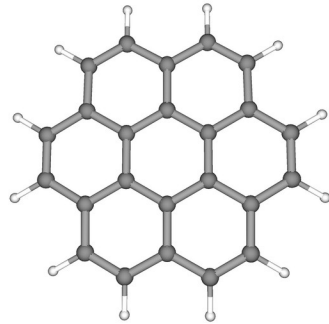
Circulene

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



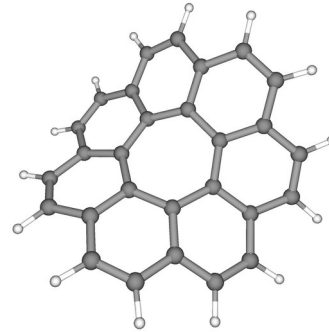
gebogen

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



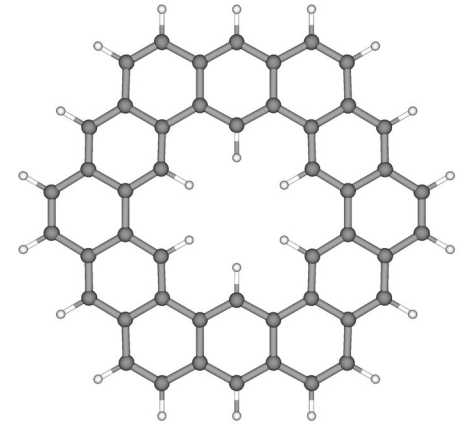
flach

[7]circulen (C_s)

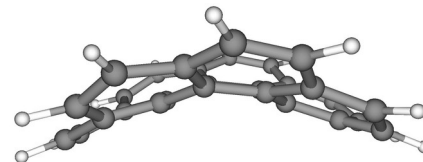
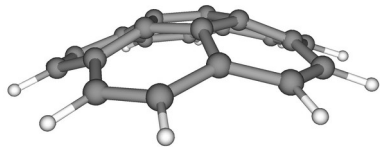


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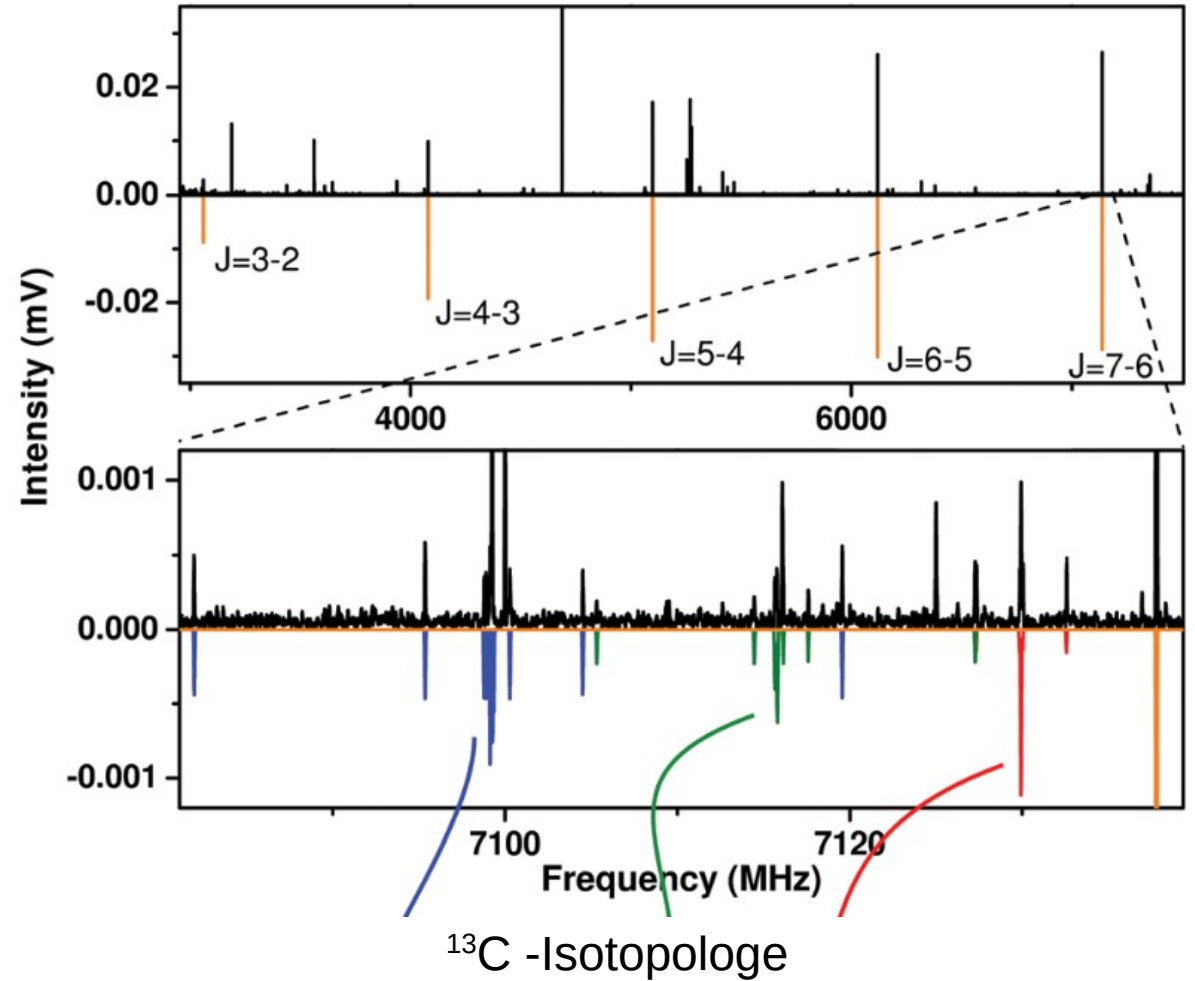
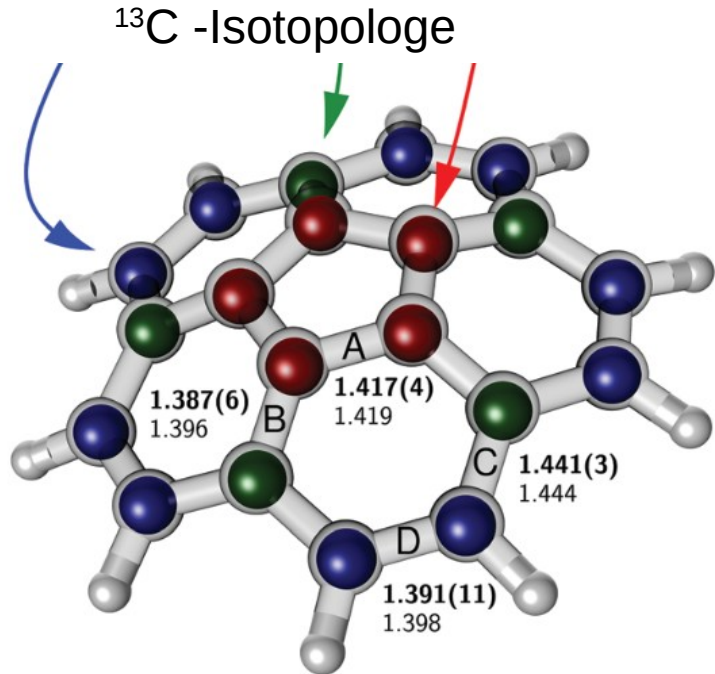
[12]circulen
Kekulen (D_{6h})



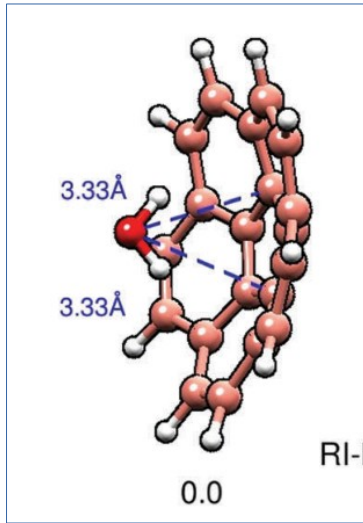
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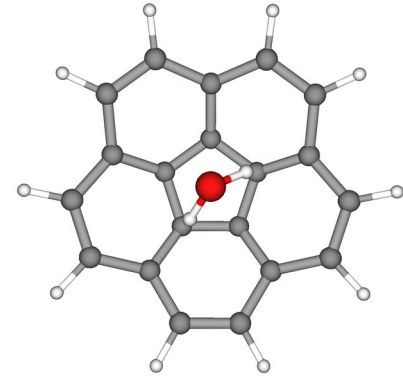
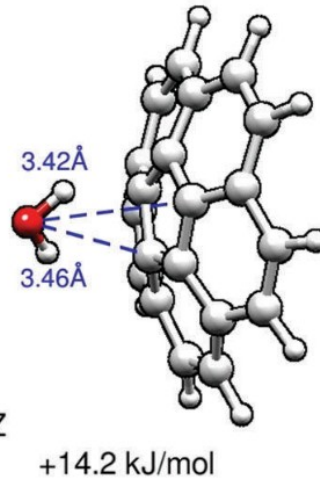
Corannulen, MW Spektrum



Corannulen-H₂O



RI-MP2/aug-cc-pVTZ

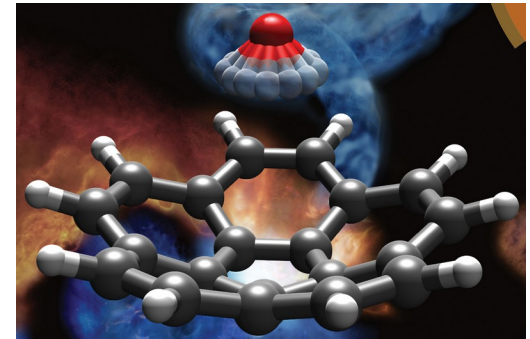


Aber: Spektrum eines symmetrischen Kreisel!
(Charakteristische Zeiten!)

$$B = 455 \text{ MHz} \rightarrow t = 1 \text{ ns} (10^{-9} \text{ s})$$

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

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



Quellen/Literatur

- D. W. H. Rankin, N. W. Mitzel, C. A. Morrison, *Structural Methods in Molecular Inorganic Chemistry*, John Wiley & Sons, Chichester, 2013.
- J.-U. Grabow, W. Caminati, “*Chapter 14 - Microwave Spectroscopy: Experimental Techniques*”. In: J. Laane, editor. *Frontiers of Molecular Spectroscopy*. Elsevier, Amsterdam, 2009. Pp. 383–454.
- 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.
- W. Gordy, R. L. Cook, *Microwave Molecular Spectra*, Wiley, New York, 1984.

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

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

$$A\mathbf{J}_A^2 + B\mathbf{J}_B^2 + C\mathbf{J}_C^2$$

Rotationskonstanten

Spin-Rotations-
Wechsel-
wirkung

$$\sum_K I_K C_K J$$

Kopplung: $I + J = F$

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

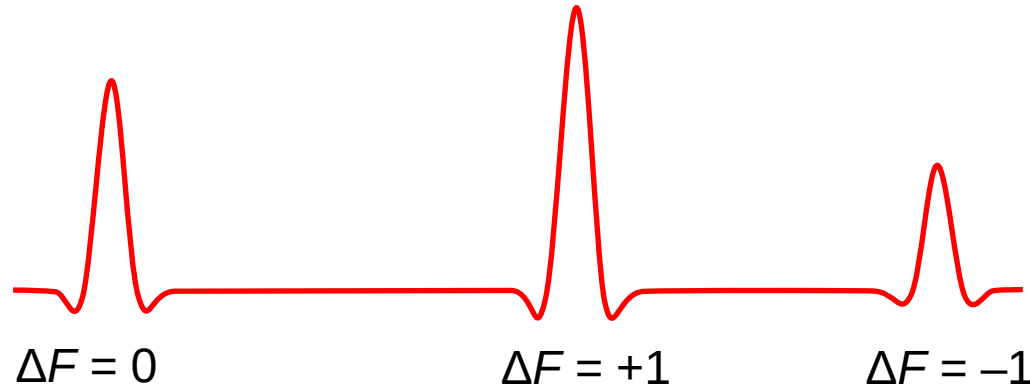
Kern-Quadrupol-Kopplung

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

Kern-Quadrupol-Kopplung

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

E \rightarrow $F =$

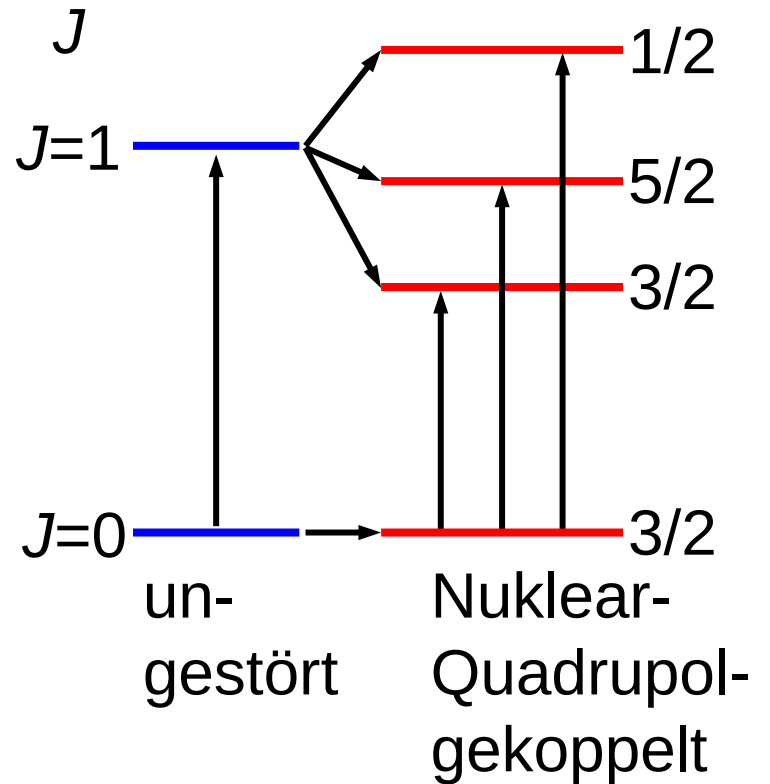


$J=1-0$

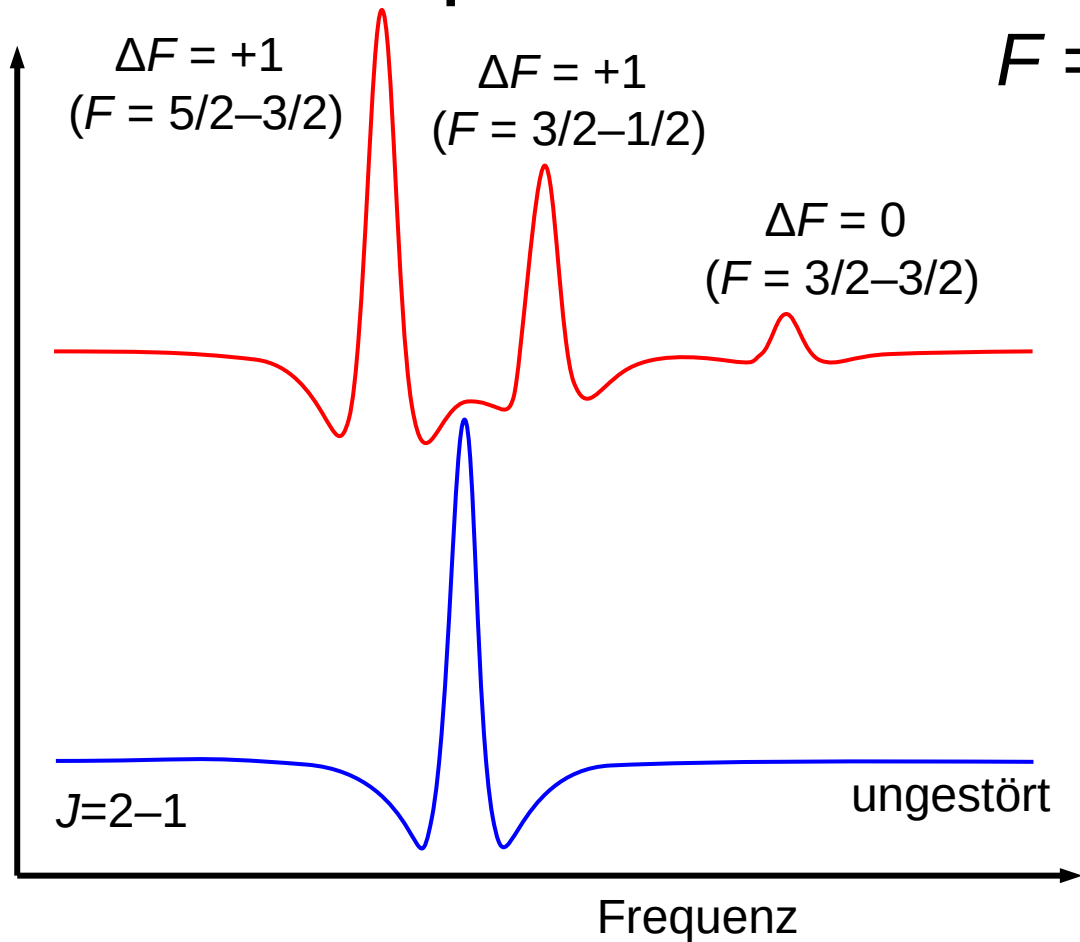
ungestört

Frequenz

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



Spin-Rotations-Wechselwirkung



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

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

E

