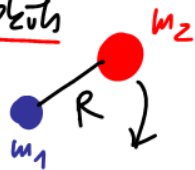


Rotation eines 2-atomigen Moleküls

Trägheitsmoment $I = \mu R^2$



reduzierte Masse $\mu = \frac{m_1 \cdot m_2}{m_1 + m_2}$

Rotationskonstante $\tilde{B} = \frac{h}{8\pi^2 c I}$

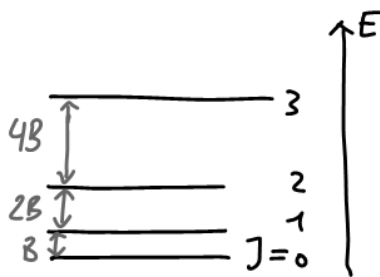
$B = h \cdot c \tilde{B}$

$E_J = B \cdot J(J+1)$

$J \in \{0, 1, 2, \dots\}$

$g_J = 2J+1$

	$\tilde{B} \text{ [cm}^{-1}\text{]}$
H_2	60,85
H^{35}C	10,60
$^{14}\text{N}^{16}\text{O}$	1,705



$$q_R = \sum_J g_J \cdot e^{-\frac{hc\tilde{B}J(J+1)}{kT}}$$

$$= \sum_{J=0}^{\infty} (2J+1) e^{-\frac{hc\tilde{B}J(J+1)}{kT}}$$

Üblicherweise gilt: $\frac{hc\tilde{B}J(J+1)}{kT} \ll 1$

Ersetze $\sum \rightarrow \int$

$$q_R = \int_0^{\infty} (2J+1) e^{-\frac{hc\tilde{B}J(J+1)}{kT}} dJ$$

$$= \frac{kT}{hc\tilde{B}} e^{-\frac{hc\tilde{B}J(J+1)}{kT}} \Big|_0^{\infty}$$

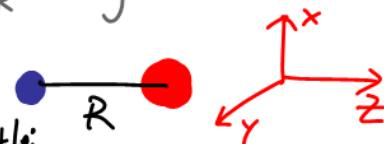
$\hookrightarrow q_R = \frac{kT}{hc\tilde{B}} = \frac{kT}{B} = \frac{T}{\Theta_R}$ linear in T

$\Theta_R = \frac{B}{R}$ (charakt. Rotations-T)

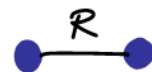
{üblicherweise gilt $\Theta_R \ll T$ }

Rotation um x & y

Rotation um z trägt nicht bei



Symmetrischer homo-Dimer



$q_R = \frac{T}{\sigma \Theta_R}$

σ : Symmetriezahl bei rot. um diese Achse

$\sigma = 1$ hetero-Dimer

$\sigma = 2$ homo-Dimer

folgt aus Symmetrie

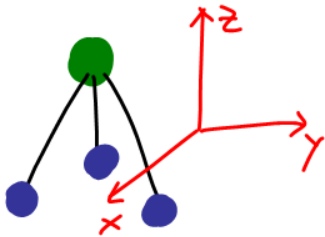
$$U_R = kT^2 \left(\frac{\partial \ln q_R}{\partial T} \right)_V$$

für hetero-dimer:
& homo-dimer

$$U_R = kT^2 \left(\frac{\partial \ln T}{\partial T} \right)_V = kT^2 \cdot \frac{1}{T} = kT$$

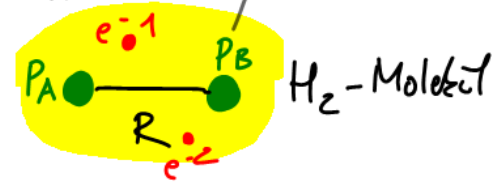
{ 2 Rotationsfreiheitsgrade : $\frac{1}{2} kT$ pro Freiheitsgrad }

im Allgemeinen (mehratomige nicht lineare Moleküle)



$$\begin{aligned} q_R &= q_R^x \cdot q_R^y \cdot q_R^z \\ &= \frac{\sqrt{\pi}}{\sigma} \frac{\sqrt{kT}}{\sqrt{B_x}} \cdot \frac{\sqrt{kT}}{\sqrt{B_y}} \cdot \frac{\sqrt{kT}}{\sqrt{B_z}} \\ &= \frac{\sqrt{\pi}}{\sigma} \frac{(kT)^{3/2}}{\sqrt{B_x B_y B_z}} \end{aligned}$$

Zusatztopic: Wie kommt es zur Symmetrie 15?



Elektronische Wellenfkn. für Grundzustand

$$\psi_e = \frac{1}{\sqrt{2}} \{ 1s_A(1) 1s_B(2) + 1s_B(1) 1s_A(2) \}$$

{ ψ_{e-spin} antisymmetrisch $\downarrow \uparrow$ } Symmetrische Lösung

Rotations-Wellenfkn $Y_{J,m_J}(\theta, \varphi)$ Kugelwellenfkn.

$$\begin{aligned} J &\in \{0, 1, \dots\} \\ m_J &\in \{-J, -J+1, \dots, J\} \end{aligned}$$

$$Y_{00} = \frac{1}{\sqrt{4\pi}}$$

Symmetrisch bei 180° Dreh

$$Y_{10} = \sqrt{\frac{3}{4\pi}} \cos \theta$$

antisymmetrisch bei 180° Dreh
(ebenso Y_{11} & $Y_{1,-1}$)

$$Y_{20} = \sqrt{\frac{5}{16\pi}} (3 \cos^2 \theta - 1)$$

Symmetrisch bei 180° Dreh

generell: $J = 0, 2, 4, \dots$ symmetrisch
 $J = 1, 3, 5, \dots$ antisymmetrisch

Spinwellenfunktionen I $m_I = +1/2 \equiv \alpha$ $m_I = -1/2 \equiv \beta$

$$\psi_{para} = \frac{1}{\sqrt{2}} \{ \alpha(A)\beta(B) - \alpha(B)\beta(A) \}$$

antisymmetrisch **1-β-β**

$$\psi_{ortho} = \frac{1}{\sqrt{2}} \{ \alpha(A)\beta(B) + \alpha(B)\beta(A) \}$$

symmetrisch **3-β-β**

Gesamtwellenfktn $\psi = \psi_e \cdot \psi_r \cdot \psi_s$
 muß antisymmetrisch sein!

also: $\psi_r^{as} \cdot \psi_s^s$

oder: $\psi_r^s \cdot \psi_s^{as}$

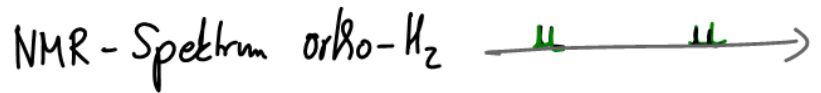
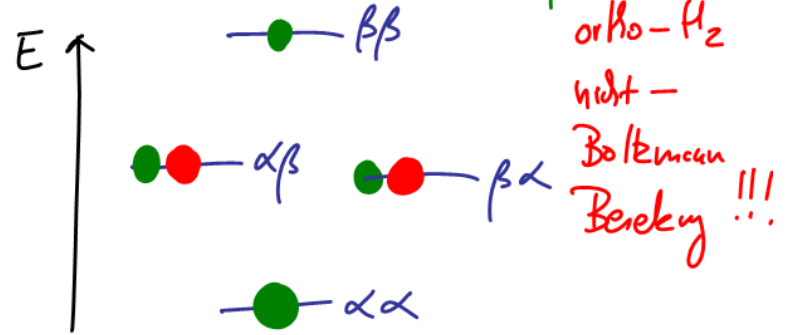
$$g_r = \frac{1}{4} \left\{ 1 \cdot \sum_{j \text{ gerade}} (2j+1) e^{-\frac{Bj(j+1)}{kT}} + 3 \cdot \sum_{j \text{ ungerade}} (2j+1) e^{-\frac{Bj(j+1)}{kT}} \right\}$$

Vorfaktor 6!

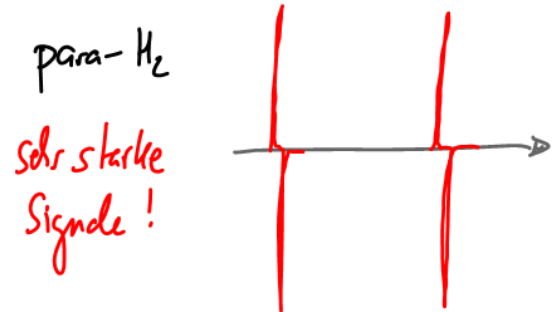
Ortho-H₂: Grundzustand J=1!
 Nullpunktschwingungsenergie

Para-H₂: Spinzustand entweder αβ oder βα
 (nicht αα oder ββ)!

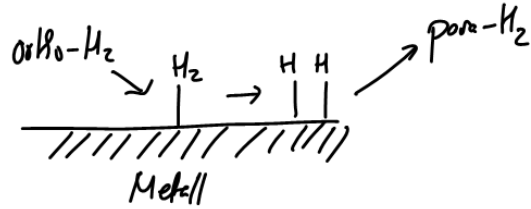
Spin fctn im Magnetfeld B₀:



PHIP

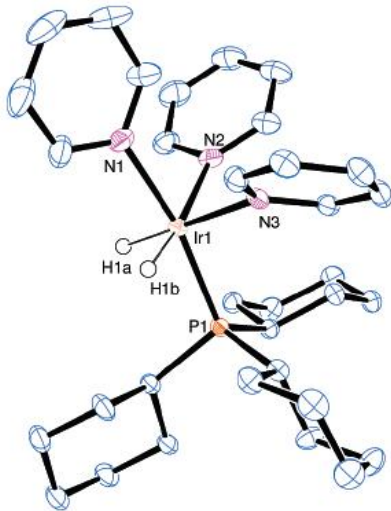


Herstellung von para-H₂:



geht auch mit molekularen Metallkomplexen (L₂)

Wird im MR-Imaging benutzt für Bildkontrast und Intensität!



Kevin D. Atkinson, Michael J. Cowley, Paul I. P. Elliott, Simon B. Duckett*, Gary G. R. Green[‡], Joaquin Lopez-Serrano and Adrian C. Whitwood

J. Am. Chem. Soc., 2009, 131 (37), pp 13362–13368

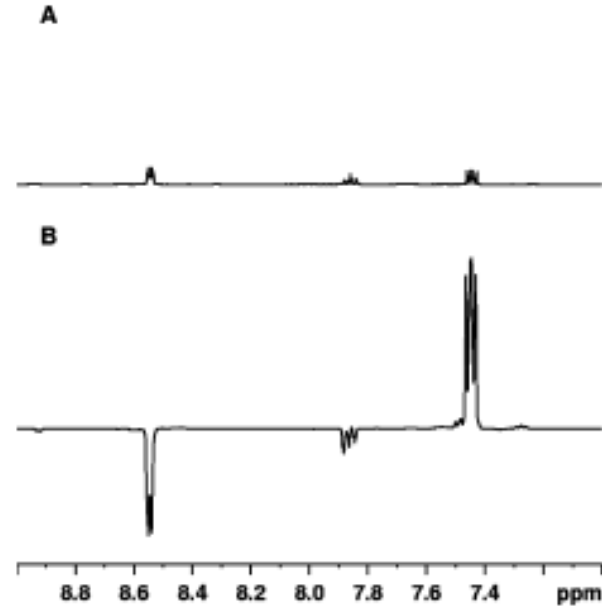
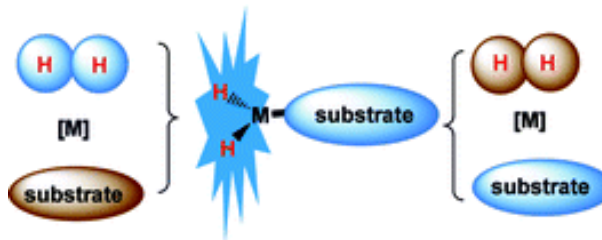


Figure 3. (a) Single scan ¹H NMR spectrum of the aromatic region of a sample of 2 showing three resonances for free pyridine that were obtained prior to polarization, (b) ¹H NMR spectrum recorded immediately after polarization in a 0.5×10^{-4} T field revealing the newly enhanced hydrogen atom signals for free pyridine.



Spontaneous magnetization transfer from parahydrogen to a substrate achieved via a metal template