

Strukturaufklärung in der molekularen anorganischen Chemie

12. Kernresonanz-Spektroskopie

Energiebereich

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
$\leftarrow < 0.1 \text{ \AA}$	5 \AA	100 \AA	2000 \AA			0.7 μm	2.5 μm	25 μm		1 mm		10 cm \rightarrow
		10 nm	200 nm	400 nm	700 nm	2500 nm						
$> 10^9$	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

$\left. \begin{array}{l} \lambda \\ \tilde{\nu} / \text{cm}^{-1} \\ E / \text{kJ mol}^{-1} \\ E / \text{eV} \\ \nu / \text{Hz} \end{array} \right\}$

$$\nu = 60 - 1000 \text{ MHz}$$

Charakteristische Zeit = Relaxationszeit ($\sim 0.1 - 100$ Sekunden)

NMR

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

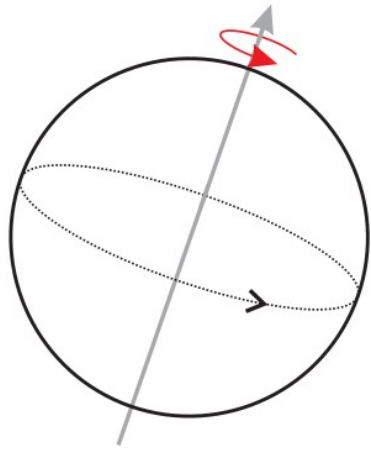
Charakteristische Zeit:

- Langsame Methode
- Mittelschnelle Methode
- Schnelle Methode

Aggregatzustand der Probe:

- Gas
- Flüssigkeit
- Feststoff

Atomkern Eigendrehimpuls



Eigendrehimpuls $|\vec{P}| = \sqrt{I(I+1)}\hbar$

magnetisches Moment $\mu = \gamma\sqrt{I(I+1)}\hbar$

γ – gyromagnetisches Verhältnis

I – Kernspinquantenzahl

Für ${}^1\text{H}^+$ (Proton): $\mu = 14.1 \times 10^{-27} \text{ J}\cdot\text{T}^{-1}$

Kernspinquantenzahl

- *gg*-Kerne, also Atomkerne mit einer geraden Kernladungszahl (erstes *g*) und einer geraden Massenzahl (zweites *g*) haben eine Kernspinquantenzahl $I = 0$
- *uu*-Kerne (ungerade Kernladung, ungerade Masse) haben $I = 1/2, 3/2, \dots$
- *ug*-Kerne haben eine ganzzahlige Kernspinquantenzahl ($I = 1, 2, 3, \dots$)
- *gu*-Kerne haben wieder halbe Kernspins $I = 1/2, 3/2, \dots$

Kern	Kernspinquantenz.	γ [$10^8 \frac{\text{rad}}{\text{Tesla}\cdot\text{s}}$]	natürliche Häufigkeit
^1H	$\frac{1}{2}$	2.68	99.98%
D [^2H]	1	0.41	0.015%
^{12}C	0	-	98.9%
^{13}C	$\frac{1}{2}$	0.67	1.1%
^{16}O	0	-	99.96%
^{17}O	$\frac{5}{2}$	-0.36	0.037%
^{14}N	1	0.19	99.6%
^{15}N	$\frac{1}{2}$	-0.27	0.4%
^{19}F	$\frac{1}{2}$	2.52	100%
^{29}Si	$\frac{1}{2}$	-0.54	4.7%
^{31}P	$\frac{1}{2}$	1.08	100%

Kernspinquantenzahl

Nuclear Spins for Main Elemental Isotopes that Undergo NMR

1A 1 H																	8A 2 He						
3 Li	2A 4 Be																	3A 5 B	4A 6 C	5A 7 N	6A 8 O	7A 9 F	10 Ne
11 Na	12 Mg																	13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
19 K	20 Ca	3B 21 Sc	4B 22 Ti	5B 23 V	6B 24 Cr	7B 25 Mn	8B 26 Fe		27 Co	28 Ni	1B 29 Cu	2B 30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr					
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe						
55 Cs	56 Ba	57-71 Lanthanides	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn						
87 Fr	88 Ra	89-103 Actinides	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Uut	114 Fl	115 Uup	116 Lv	117 Uus	118 Uuo						

Lanthanides	57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
Actinides	89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

Nuclear Spin

■ 1/2	■ 3/2	■ 7/2	■ 5
■ 1	■ 5/2	■ 9/2	■ 8

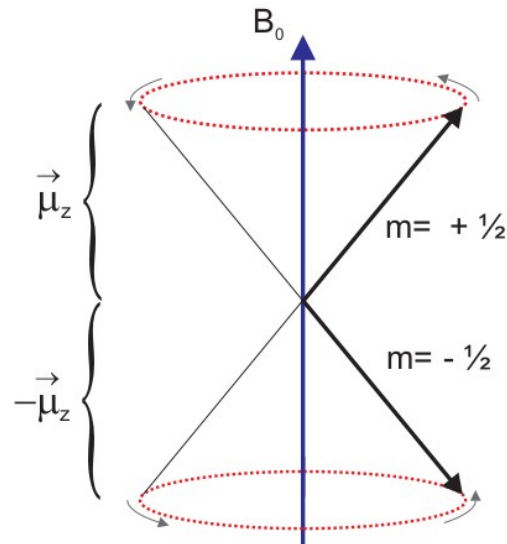
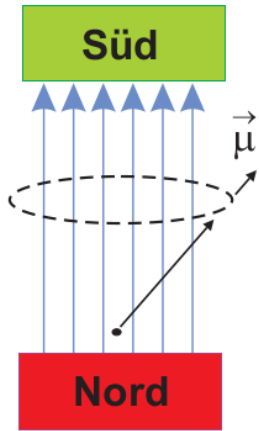
No data for synthetic elements ≥ 103

Atomkern im Magnetfeld

Drehimpuls-Komponente in Feldrichtung $P_z = m\hbar$

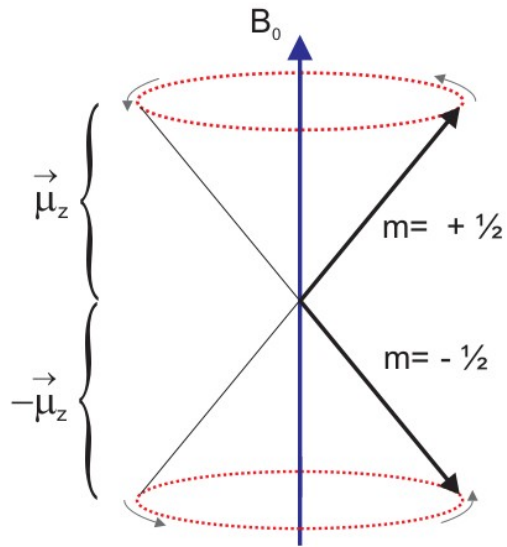
Magnetquantenzahl $m = -l, -l+1, \dots, l-1, l$ ($2l+1$ Orientierungen möglich)

Magnetisches Moment in z-Richtung $\mu_z = \gamma m\hbar$



Doppelpräzessionskegel der
Bewegung eines ^1H -Kerndipols im
Magnetfeld B_0

Larmorfrequenz



Drehmoment $\vec{L} = -\vec{\mu} \times \vec{B}_0$

$$= \frac{d\vec{P}}{dt} = \omega \vec{P}$$

$$\omega \vec{P} = -\vec{\mu} \times \vec{B}_0 = -\gamma \vec{P} \times \vec{B}_0$$

Larmorgeschwindigkeit $\omega = \gamma B_0$

Larmorfrequenz $\nu_L = \left| \frac{\gamma}{2\pi} \right| B_0$

Energie der Kerne im Magnetfeld

$$E = -\mu_z B_0$$

$$E = -m \gamma \hbar B_0$$

$$\Delta m = \pm 1$$

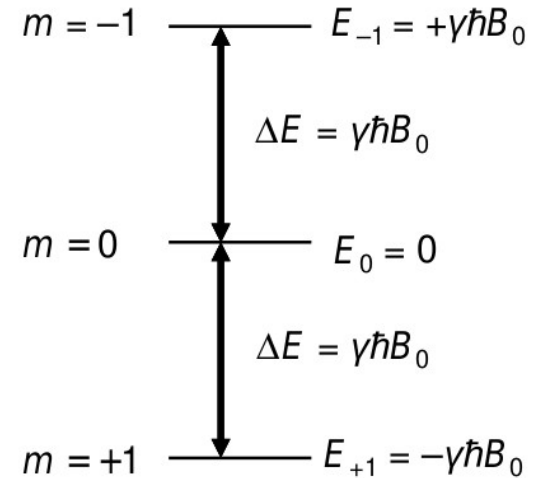
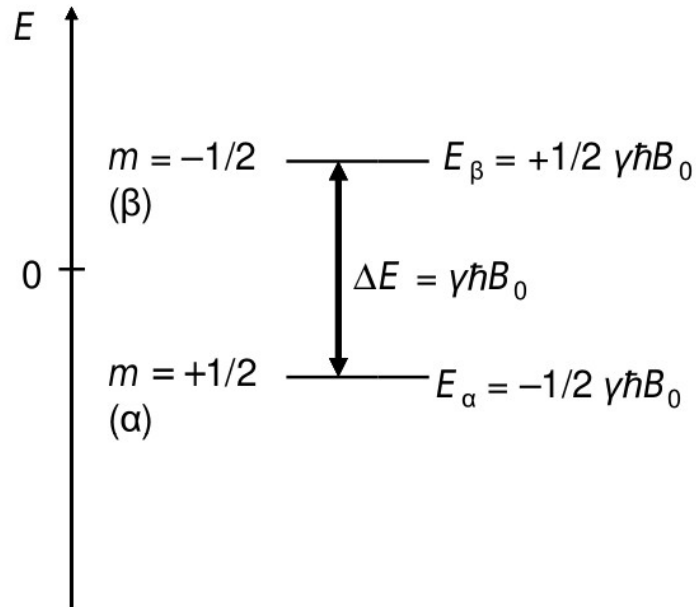
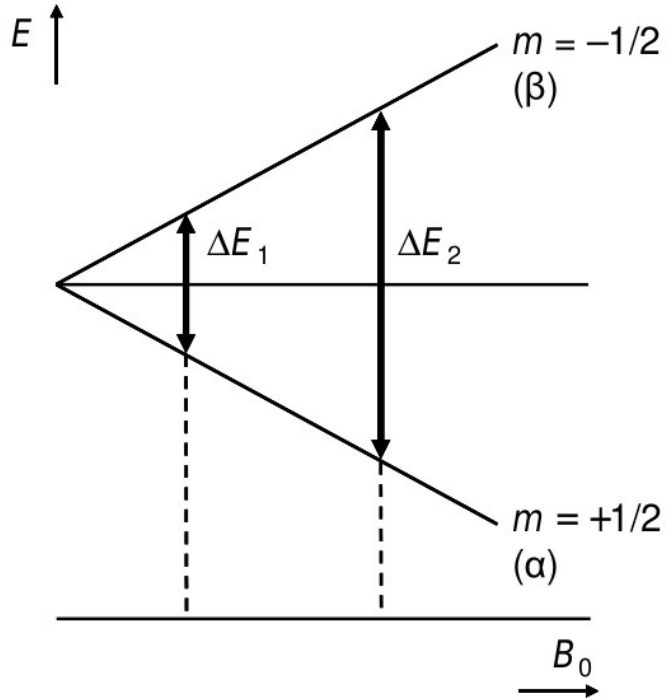
$$\Delta E = \hbar \gamma B_0 = h \nu_L$$

$$I = 1/2$$

e.g. ^1H , ^{19}F

$$I = 1$$

e.g. ^2H , ^{14}N



Kern-Zeemann-Niveaus

Boltzmann-Statistik

$$\Delta E = \hbar\gamma B_0 = h \nu_L$$

$$\frac{N_\alpha}{N_\beta} = \exp(-\hbar\gamma B_0/kT) \approx 1 - \frac{\hbar\gamma B_0}{kT}$$

z.B. ^1H : $B_0 = 4.7 \text{ T} \rightarrow \nu_L = 200 \text{ MHz} \rightarrow \Delta E = 1.3 \times 10^{-25} \text{ J [0.08 J/mol]} \rightarrow$

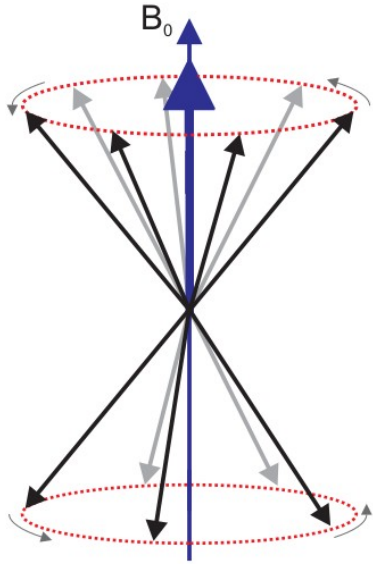
$\rightarrow N_\alpha/N_\beta = 0.99997 @ T = 293.15 \text{ K} \rightarrow \Delta N \propto 1.6 \times 10^{-5} \text{ [z.B. } \Delta N = 16 @ \Sigma N = 10^6]$

z.B. ^1H : $B_0 = 19 \text{ T} \rightarrow \nu_L = 810 \text{ MHz} \rightarrow \Delta E = 5.4 \times 10^{-25} \text{ J [0.3 J/mol]} \rightarrow$

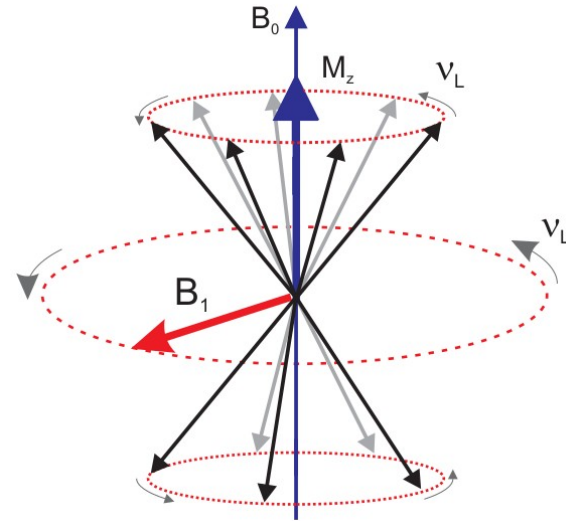
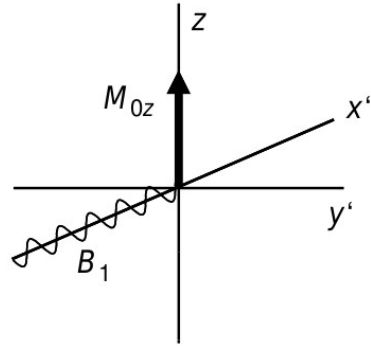
$\rightarrow N_\alpha/N_\beta = 0.99987 @ T = 293.15 \text{ K} \rightarrow \Delta N \propto 6.6 \times 10^{-5} \text{ [z.B. } \Delta N = 66 @ \Sigma N = 10^6]$

WW von Kerndipol und elektromagn. Welle

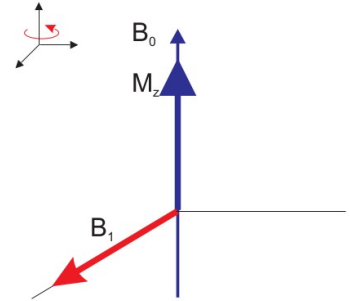
Im Magnetfeld B_0



Ein Impuls mit B_1 kommt

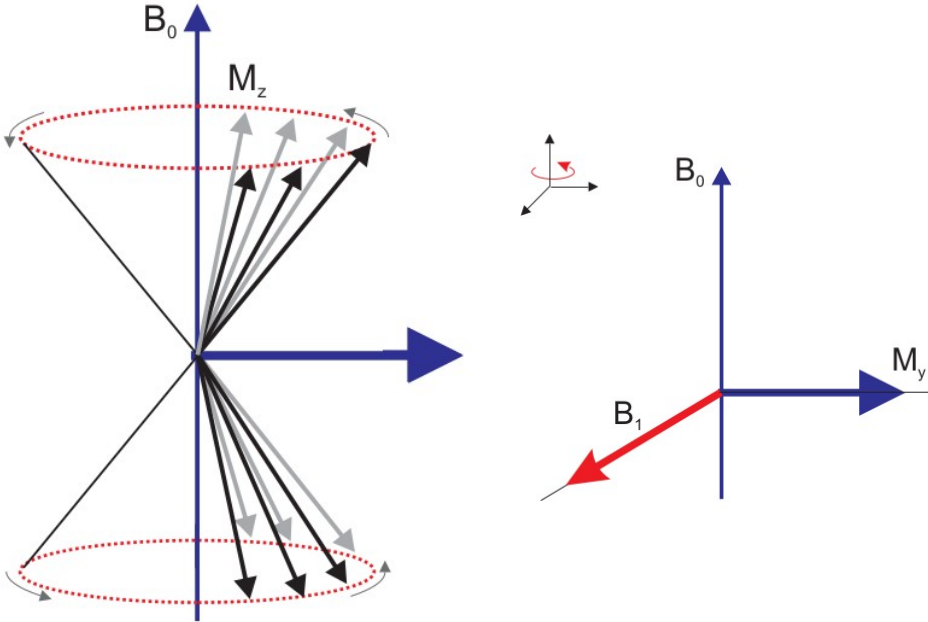


(x',y',z) System

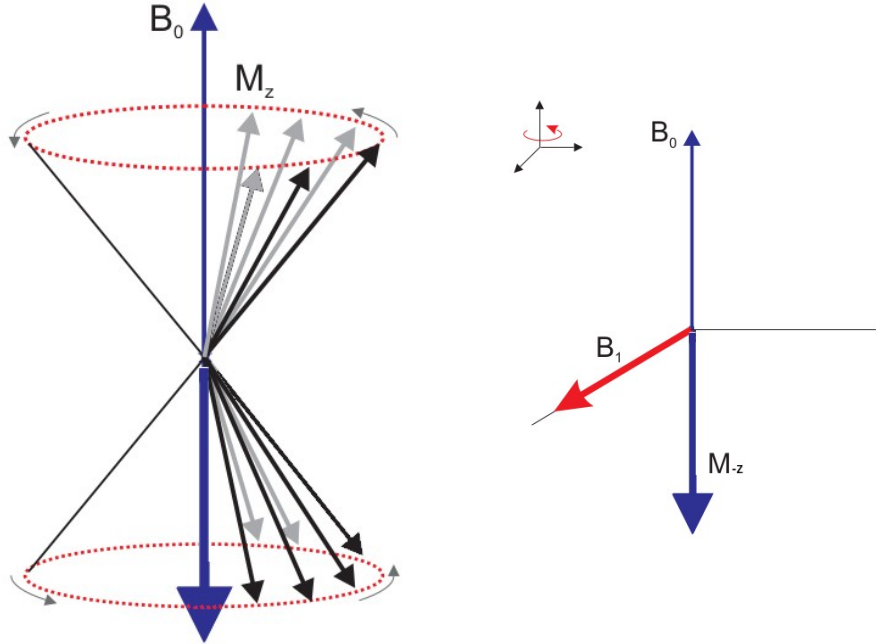


90- und 180-Puls

90°



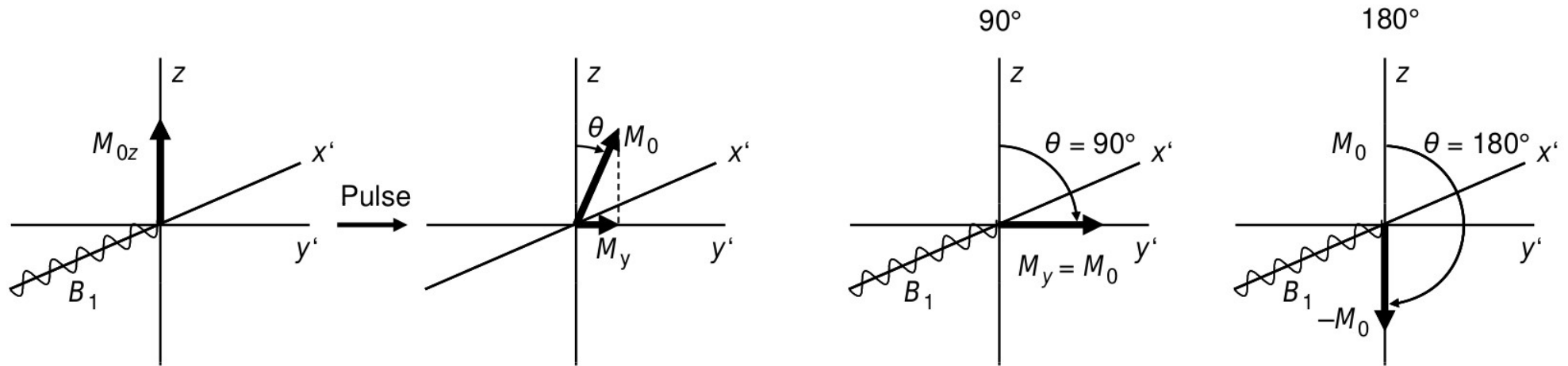
180°



Der Impulswinkel

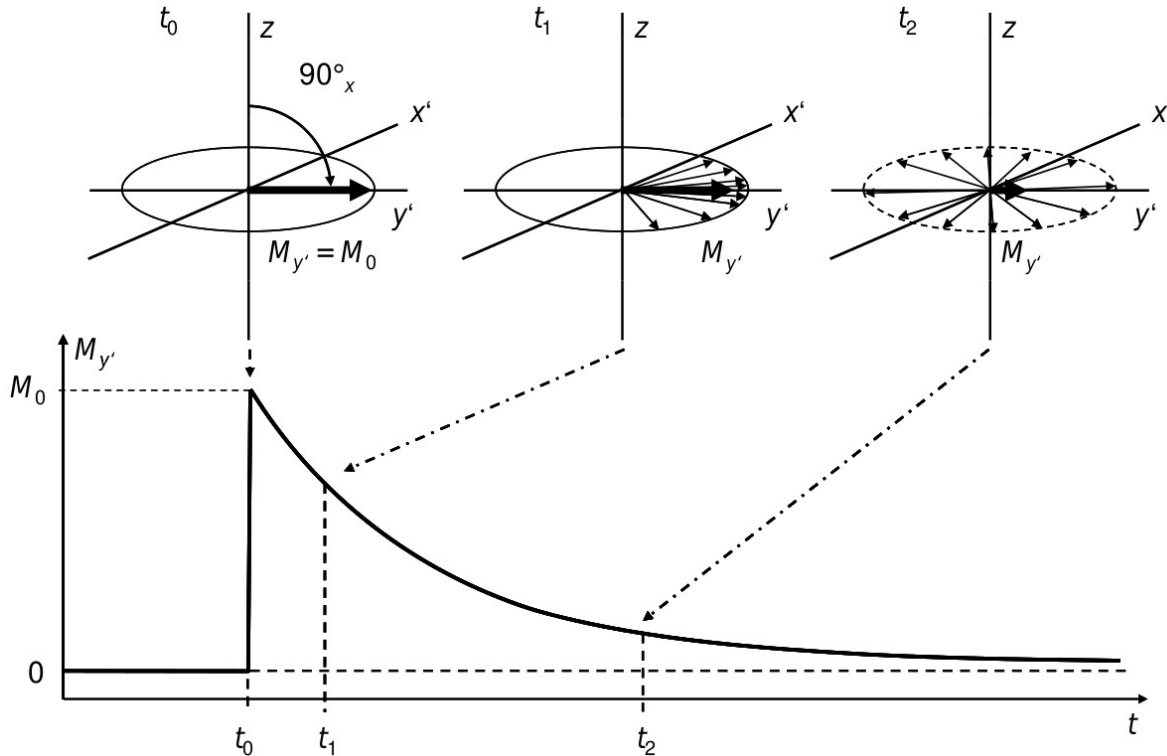
Impulswinkel $\theta = \gamma B_1 \tau_P$

τ_P – Impulslänge



Nach dem Puls: Relaxation

Spin-Spin (transversale) Relaxation T_2



Spin-Gitter (longitudinale) Relaxation T_1

Die thermische Boltzmann-Verteilung der Kernspins stellt sich wieder ein.

$$T_2 < T_1$$

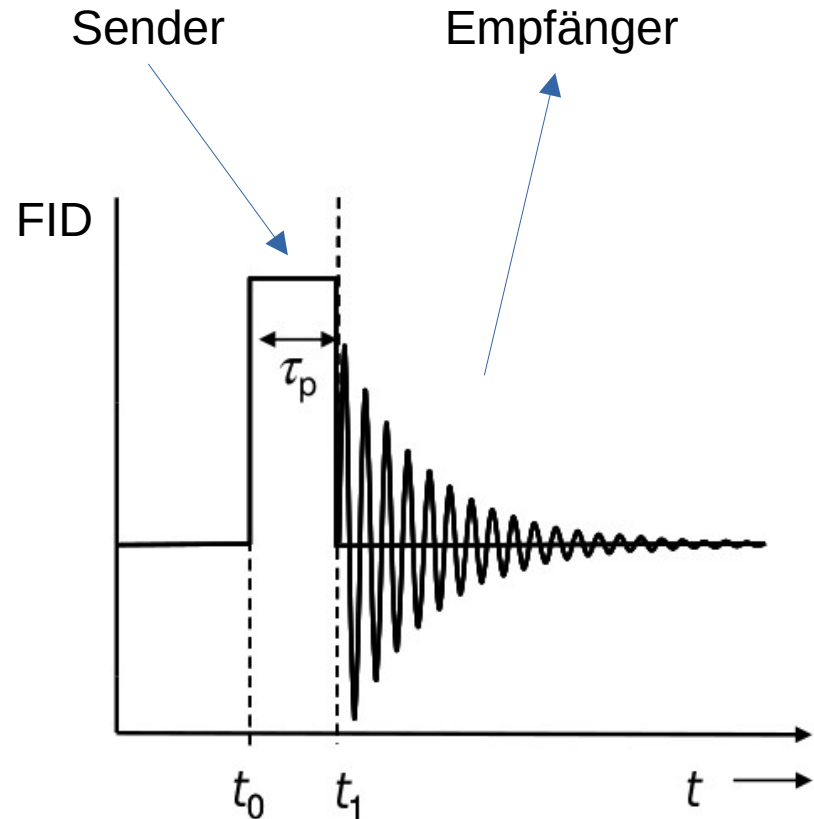
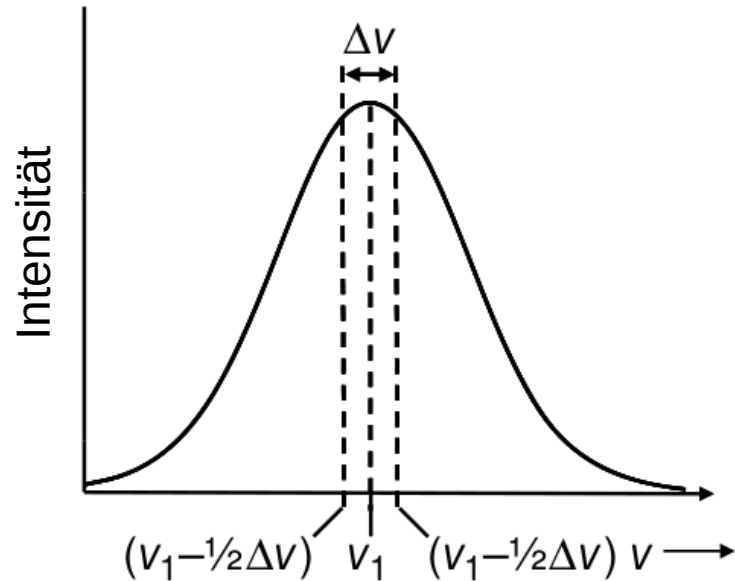
^1H : $T_1 \sim 1$ Sek.

^{13}C : $T_1 \sim 0.1 - 100$ Sek.

Charakteristische Zeit!
(s. PF₅ als Beispiel in 1. Einführung)

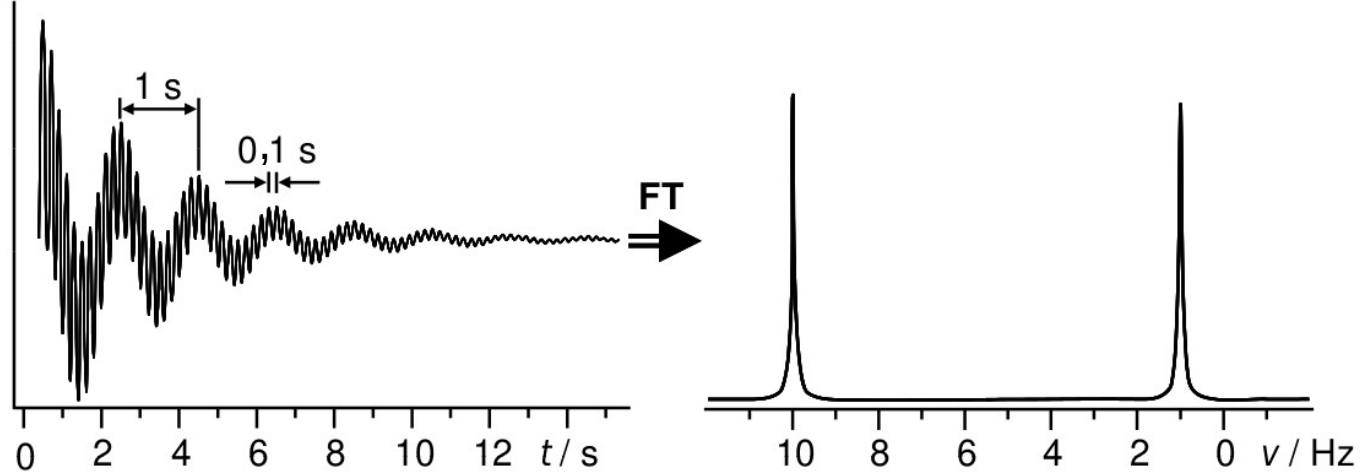
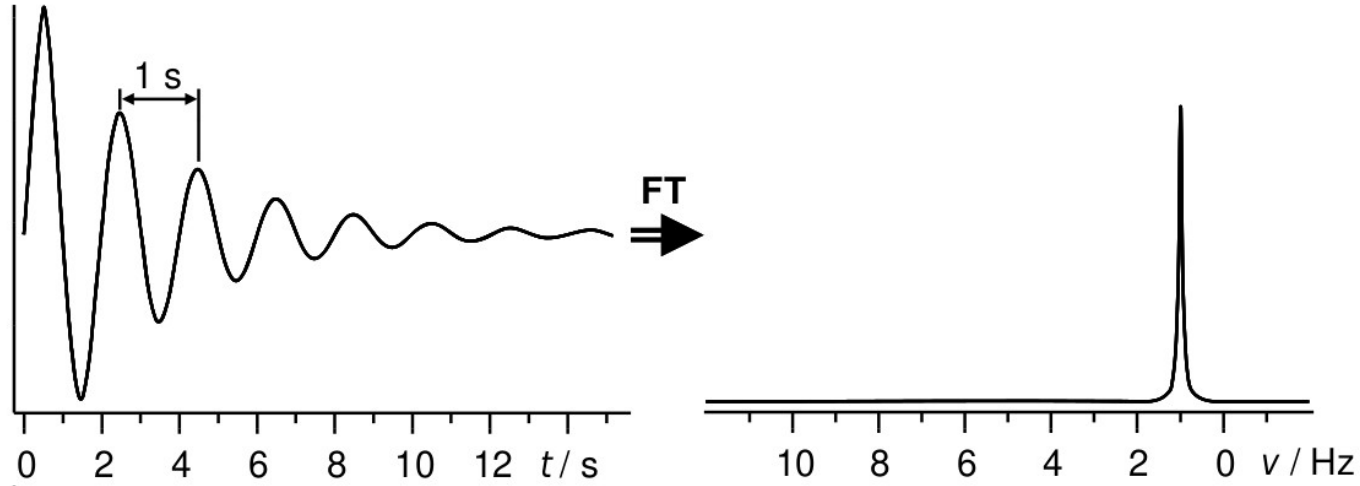
Puls-Fourier-Transform NMR

$$\theta = \gamma B_1 \tau_P$$



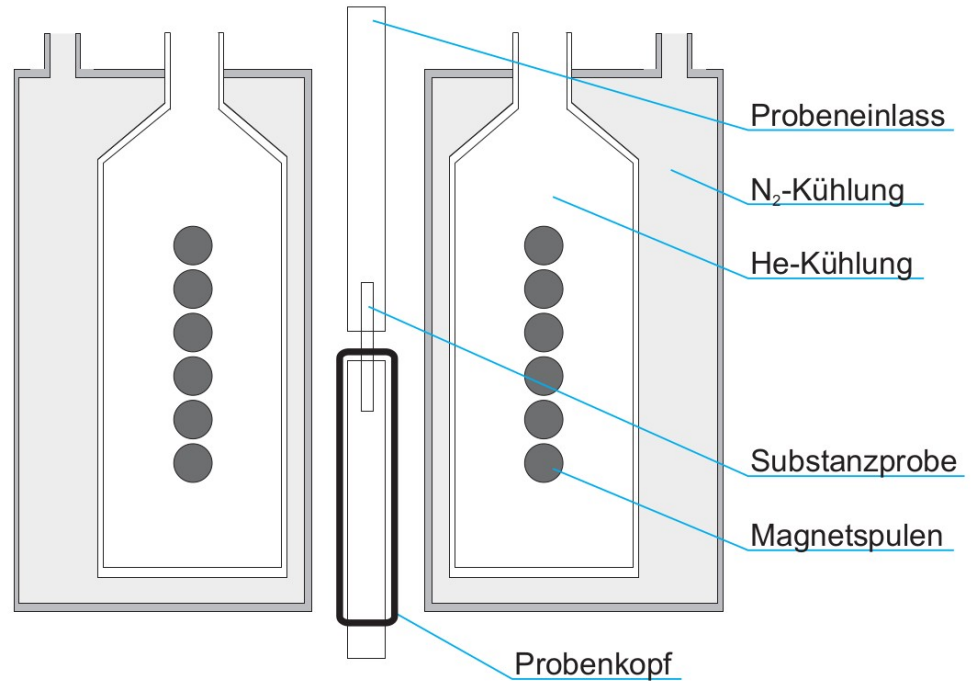
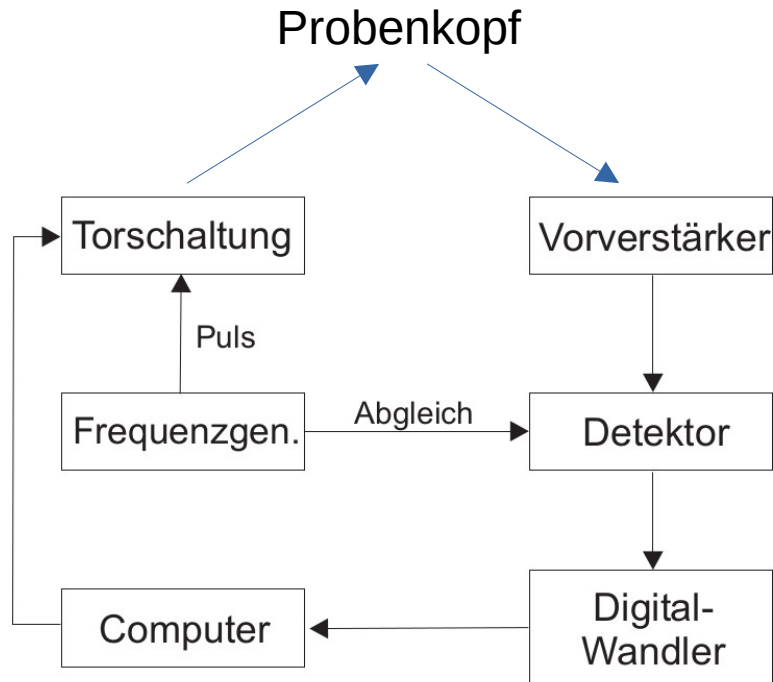
Freier Induktionszerfall (FID)

Free induction decay (FID)
(Spannung in Detektionsspule)



Differenzen von Frequenzen:
[in Spannung des Spindektors] –
[in Spannung wegen Präzession der
Magnetisierung M_y]

NMR-Spektrometer



1.41T → 60 MHz für ¹H
4.7T → 200 MHz für ¹H
19T → 800 MHz für ¹H

NMR-Spektrometer



Chemische Verschiebung

Effektives Feld $B_{eff} = B_0(1 - \sigma)$

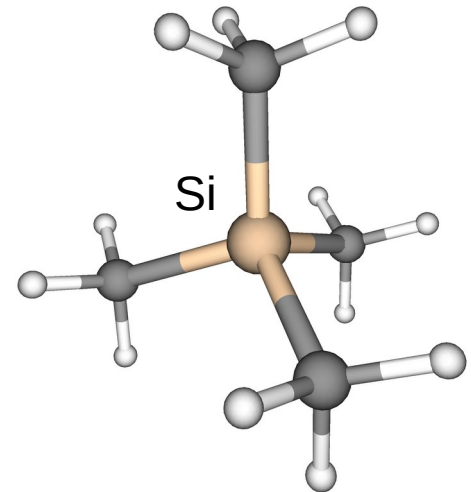
σ – Abschirmungskonstante (abhängig von der Kern-Umgebung)

Resonanzfrequenz $\nu_1 = \left| \frac{\gamma}{2\pi} \right| (1 - \sigma) B_0$

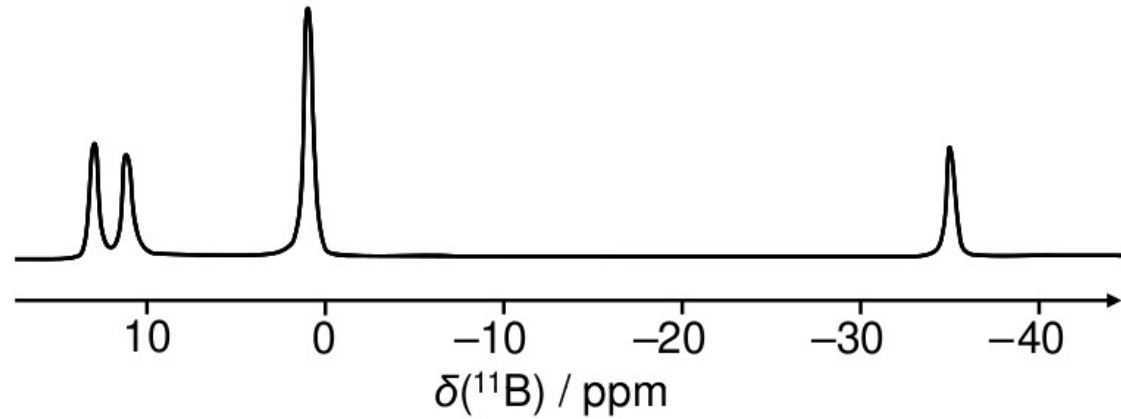
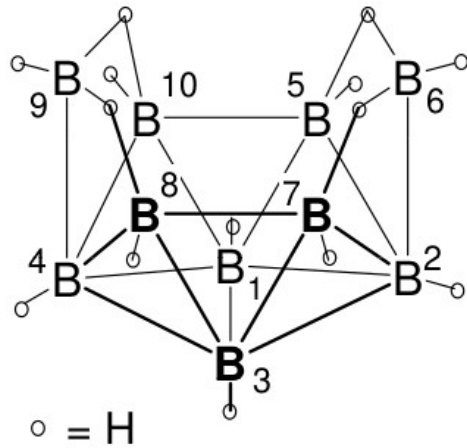
Chemische Verschiebung (ppm) $\delta = \frac{\nu_{Substanz} - \nu_{Referenz}}{\nu_{Referenz}} \cdot 10^6$

Referenz-Standard z.B. für ^1H , ^{13}C , ^{29}Si : SiMe_4 (TMS)

$$\delta(TMS) = 0$$



Chemische Verschiebung



Abschirmungskonstante σ zunimmt



Nachbargruppeneffekte

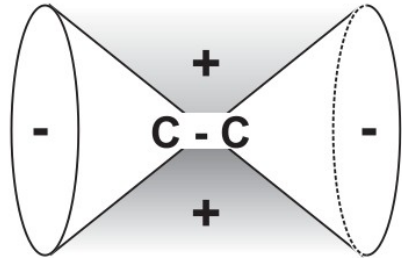
$\delta(^1\text{H}) / \text{ppm}$

	E = C	E = Si	E = Ge
EH_4	0.1	3.2	3.1
EH_3I	2.0	3.4	3.5
EH_3Cl	2.5	4.2	4.5
EH_3Br	2.8	4.6	5.1
$\text{O}(\text{EH}_3)_2$	3.2	4.6	5.3
EH_3F	4.1	4.8	5.7

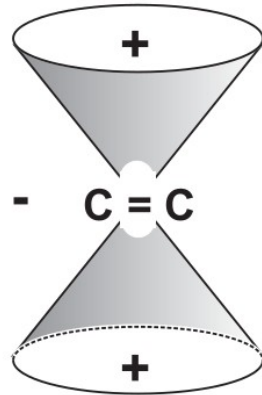
Magnetische Anisotropie

Abschirmung

größer



kleiner

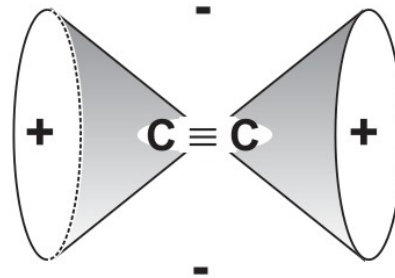
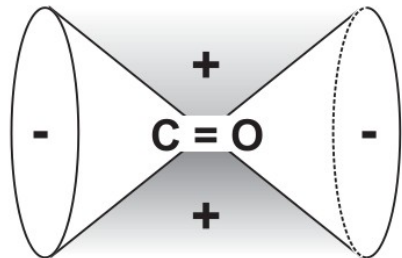
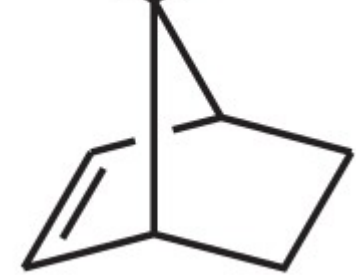


z.B.

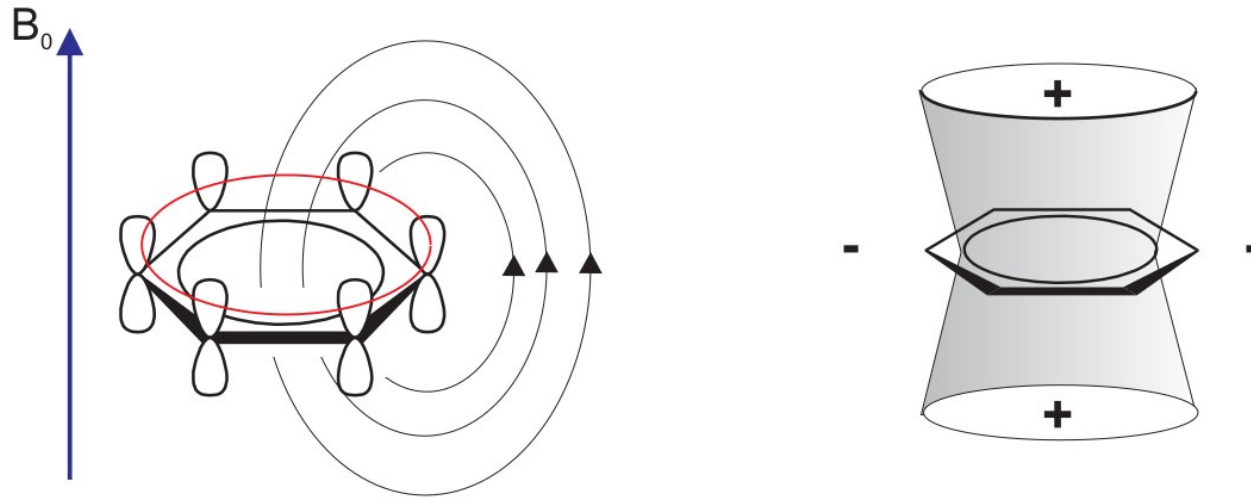
0.42 ppm

1.42 ppm

H_a H_b



Der Ringstromeffekt

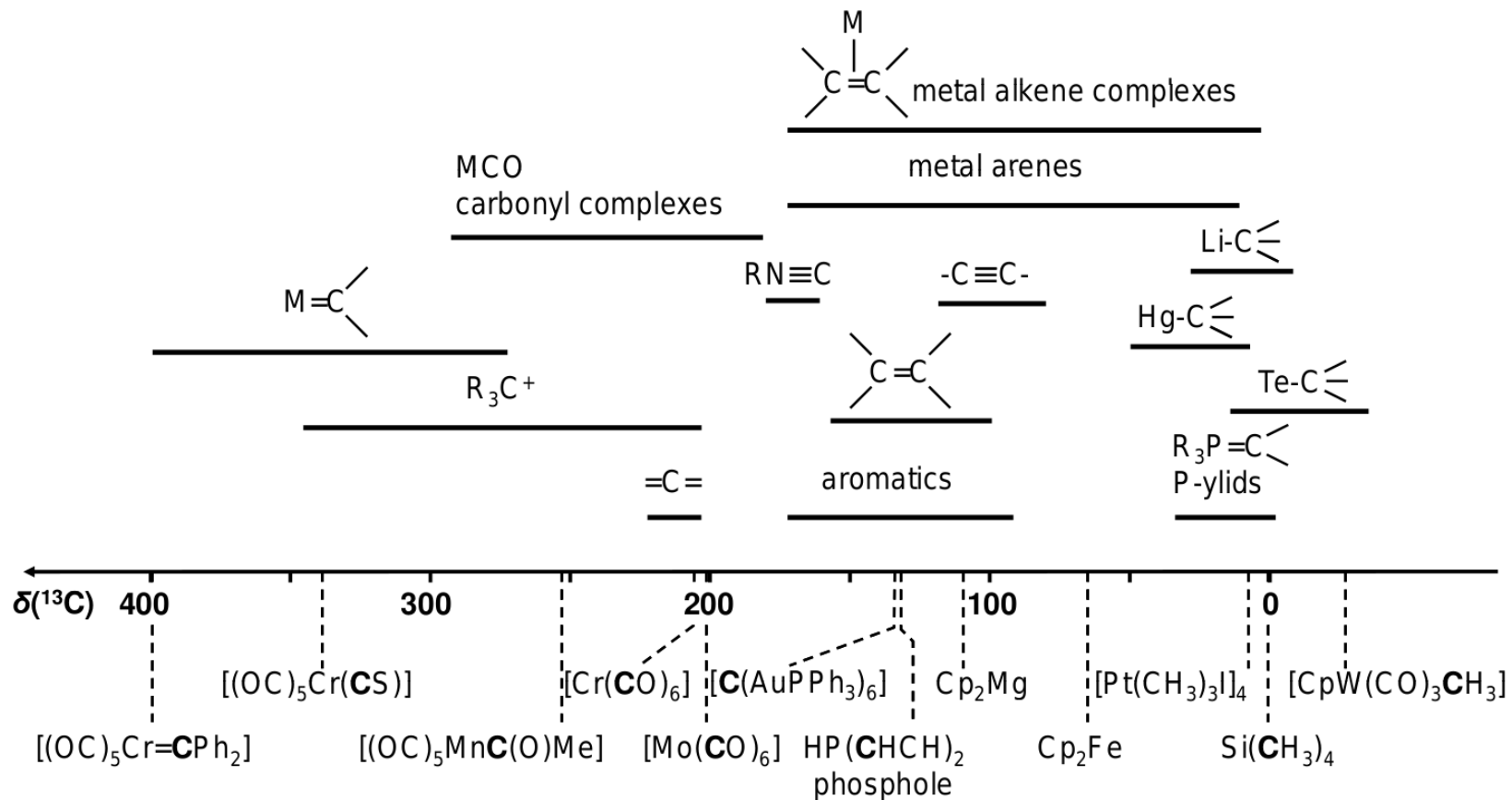


$\delta(^1\text{H}) = 7.3 \text{ ppm}$ in Benzol (vgl. 5.3 ppm in Ethylen)

Chemische Verschiebungen: ^1H

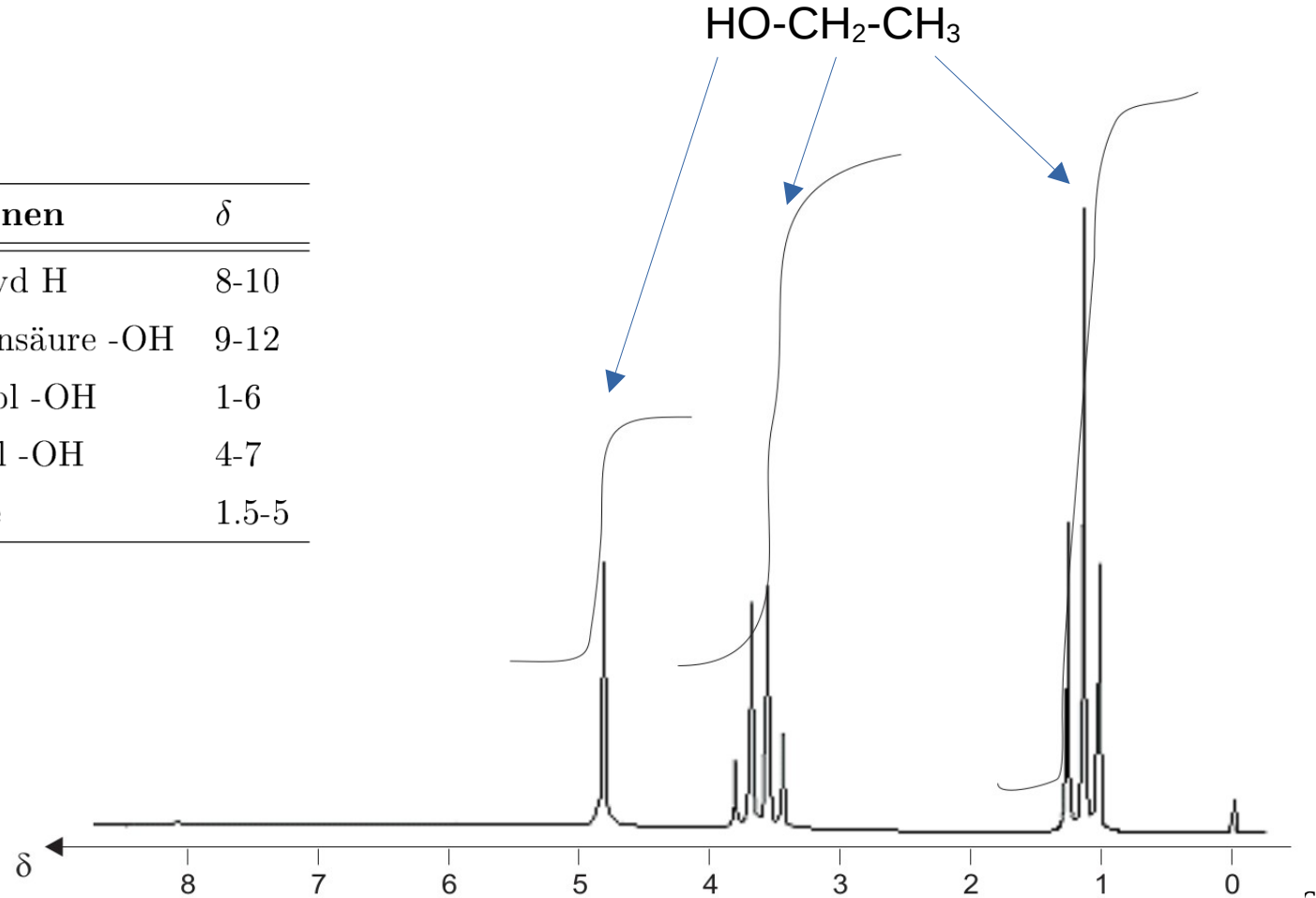
Protonen	δ	Protonen	δ
-CH ₃	1-1.5	Aldehyd H	8-10
-CH ₂	1-4.5	Carbonsäure -OH	9-12
oleph. H	5-6.5	Alkohol -OH	1-6
aromat. H	6.5-8	Phenol -OH	4-7
Benzol	7.3	Amine	1.5-5

Chemische Verschiebungen: ^{13}C



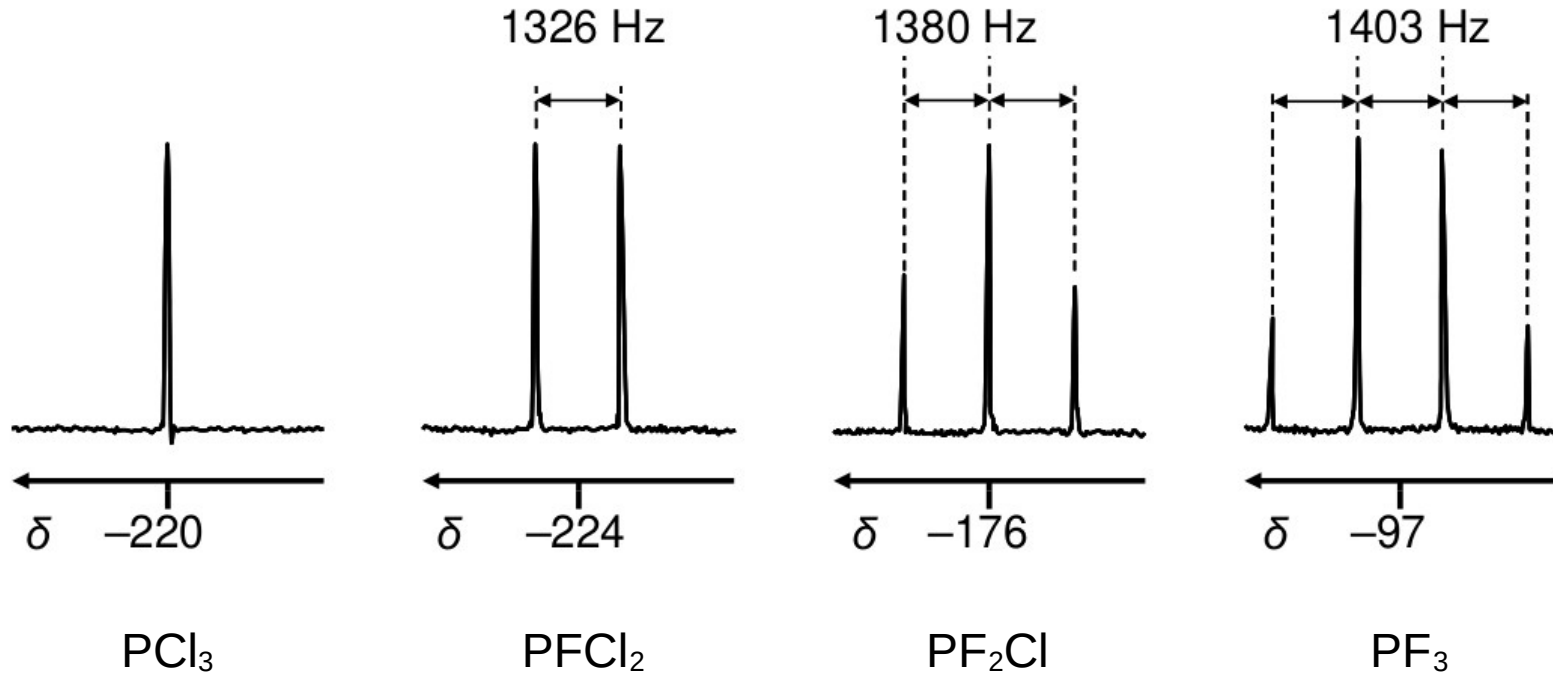
Chemische Verschiebungen: ^1H

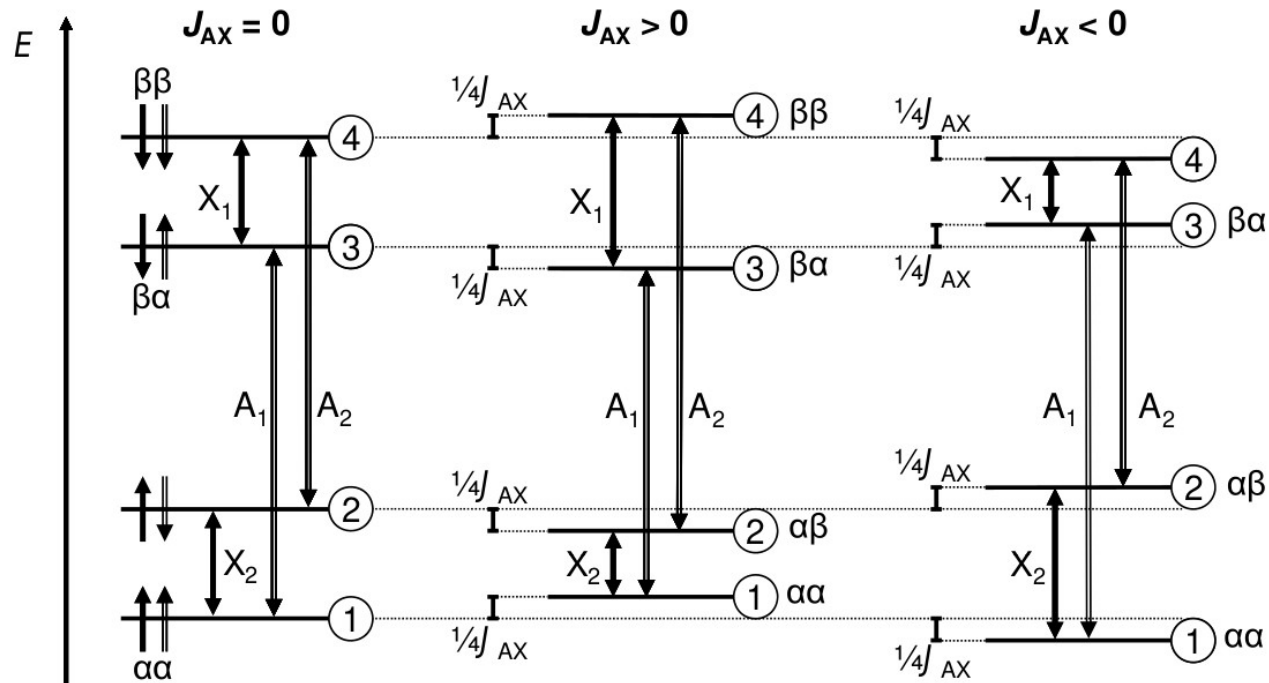
Protonen	δ	Protonen	δ
-CH ₃	1-1.5	Aldehyd H	8-10
-CH ₂	1-4.5	Carbonsäure -OH	9-12
oleph. H	5-6.5	Alkohol -OH	1-6
aromat. H	6.5-8	Phenol -OH	4-7
Benzol	7.3	Amine	1.5-5



Spin-Spin-Kopplungen

^{31}P NMR

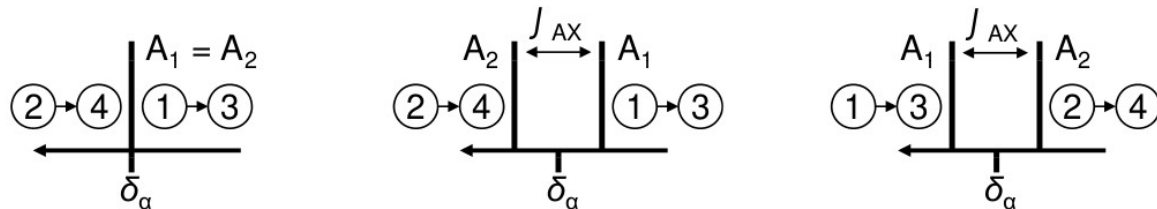




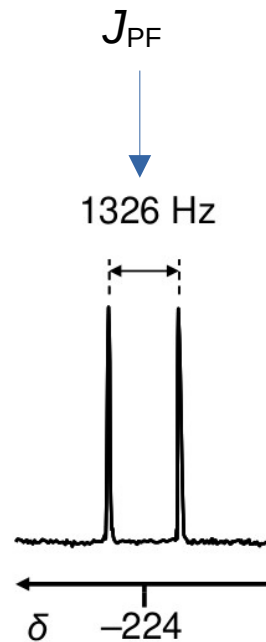
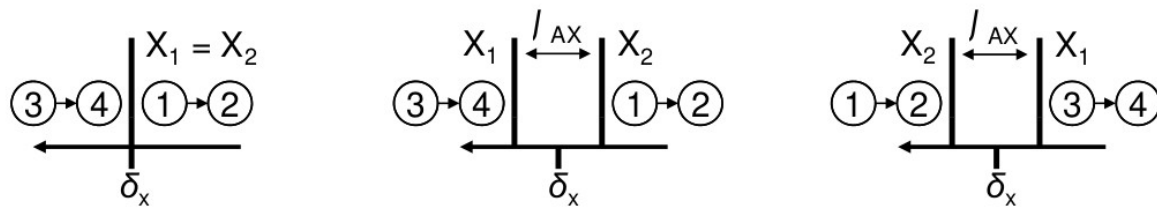
Kopplung mit einem Nachbarkern
(AX-Spinsysteme)

z.B: ^{31}P NMR in PFCl_2

spectrum A

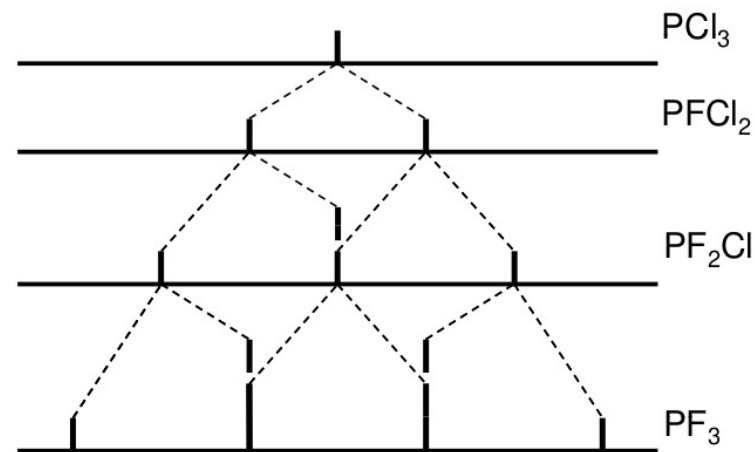
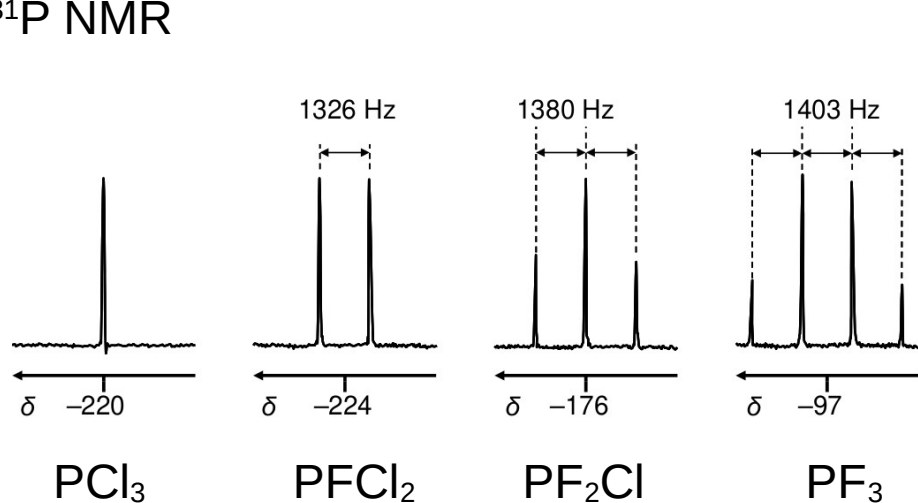


spectrum X



Spin-Spin-Kopplungen

³¹P NMR



Für AX_n-Spinsystemen M Signale:

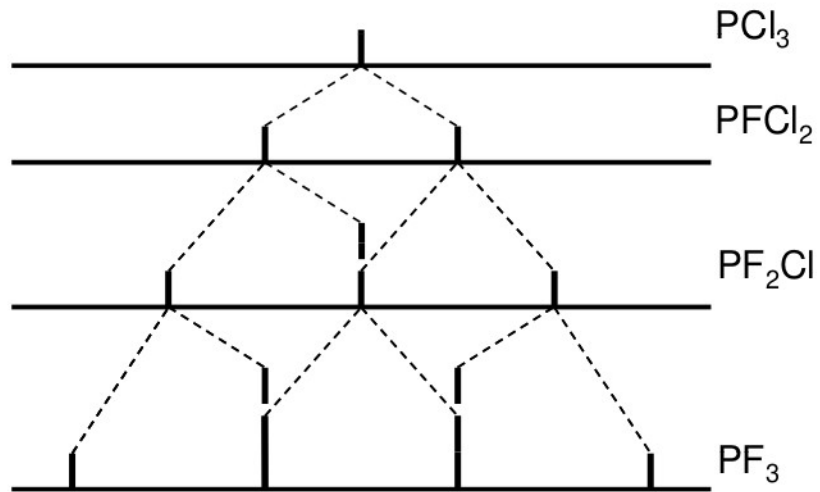
$$M = 2In + 1$$

$$M = n + 1 \quad \text{wenn } I = 1/2$$

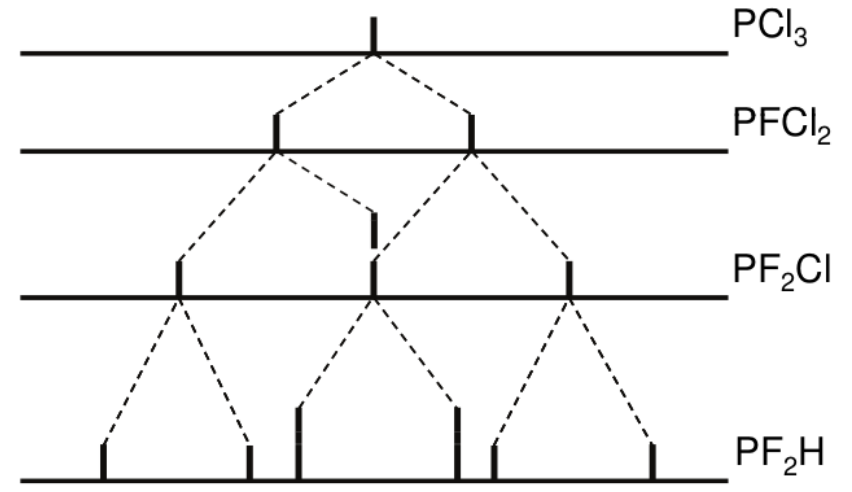
n=0			1			Singulett
n=1			1	1		Dublett
n=2		1	2	1		Triplet
n=3	1	3	3	1		Quartett
n=4	1	4	6	4	1	Quintett
...			...			

Spin-Spin-Kopplungen

^{31}P NMR

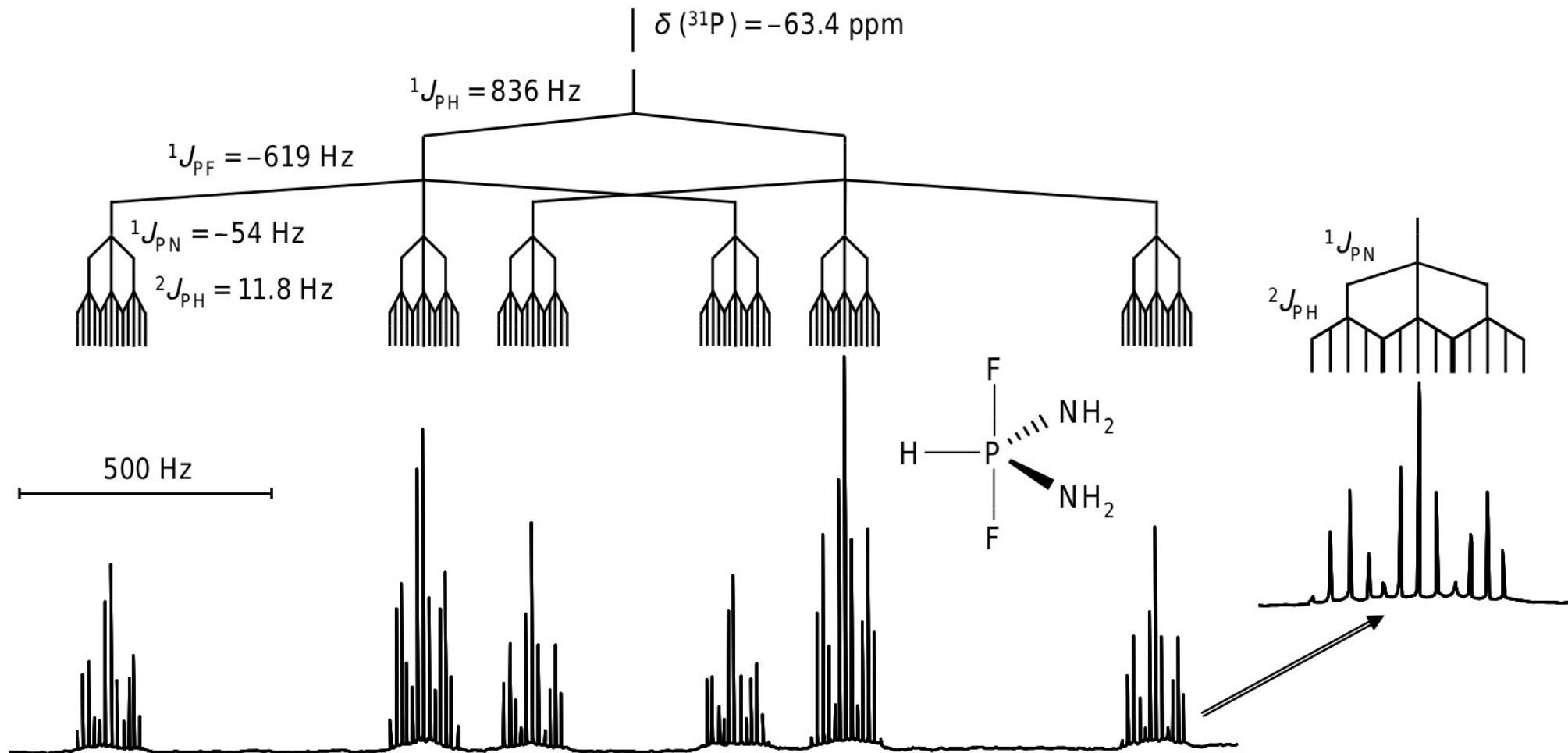


Quartett



Triplett von Dubletts

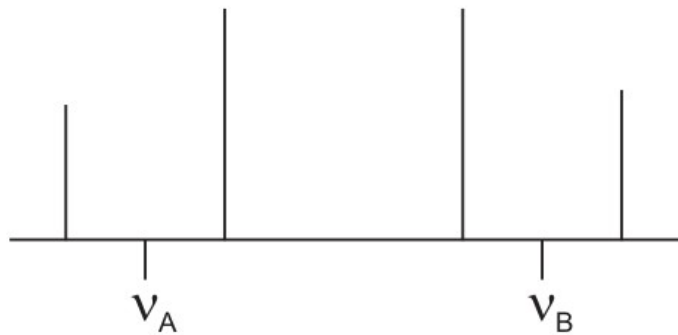
^{31}P NMR von $\text{PF}_2\text{H}(\text{}^{15}\text{NH}_2)_2$



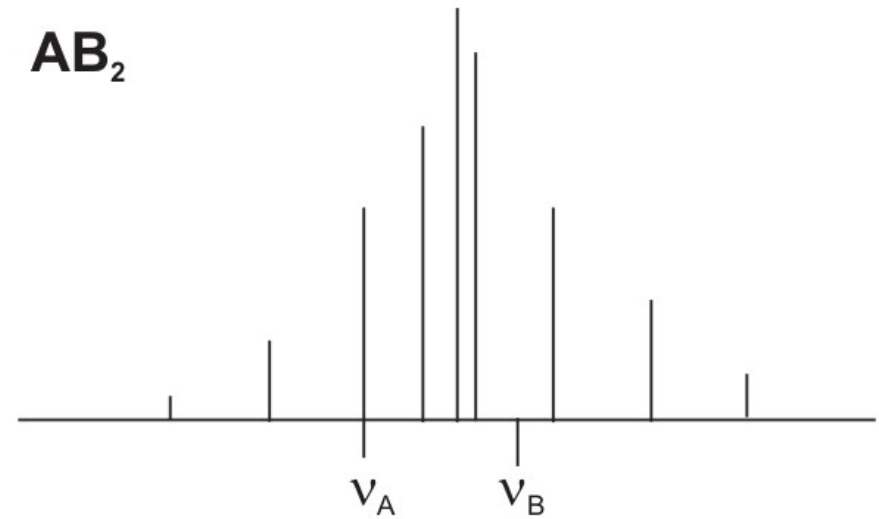
Weitere Spinsysteme

Wenn $\Delta\nu \approx J_{AB}$

AB

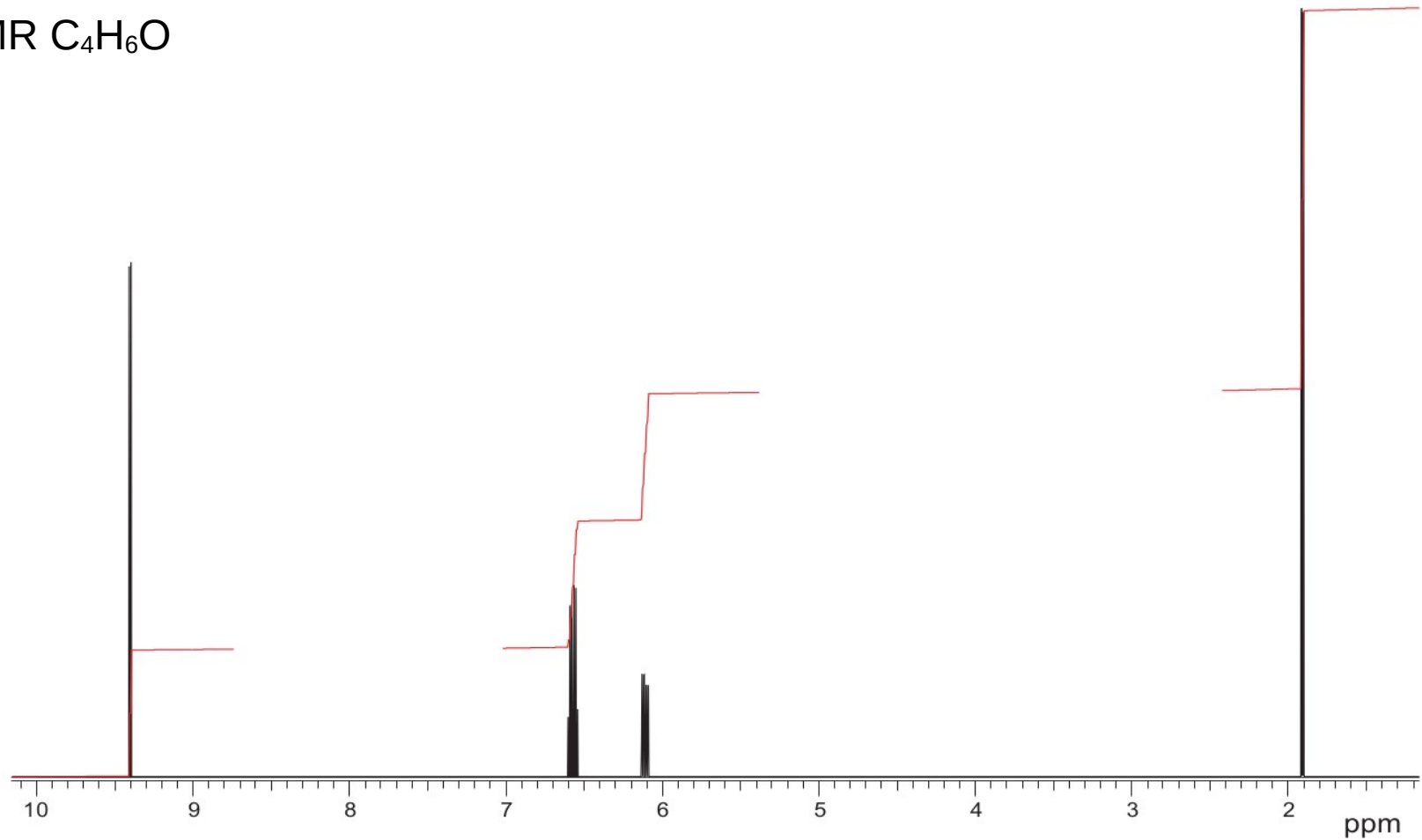


AB₂



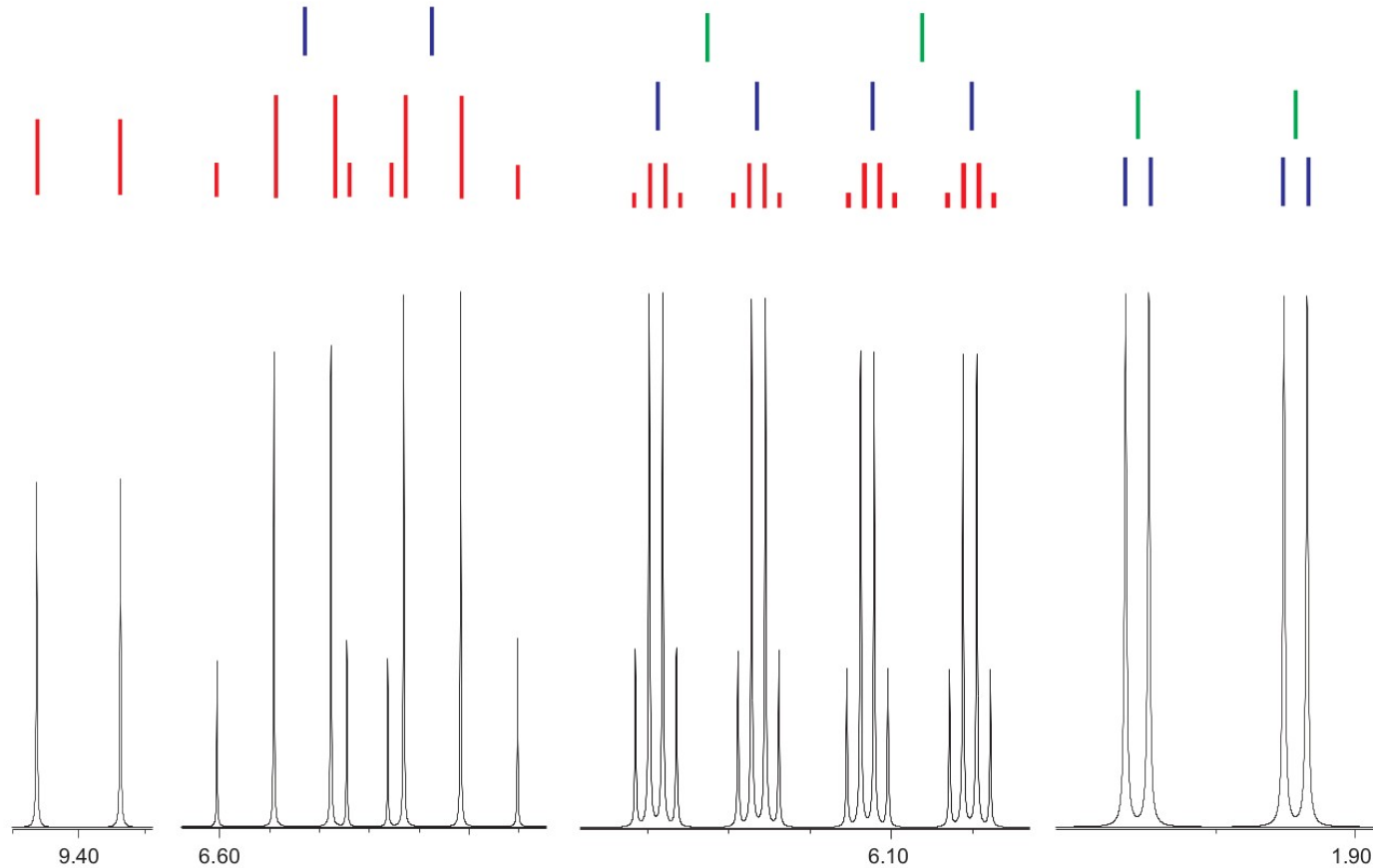
Spektreninterpretation

^1H NMR $\text{C}_4\text{H}_6\text{O}$



Spektreninterpretation

^1H NMR $\text{C}_4\text{H}_6\text{O}$



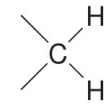
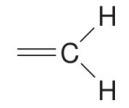
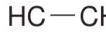
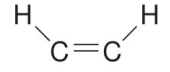
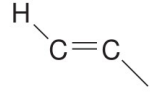
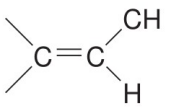
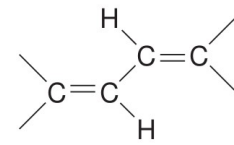
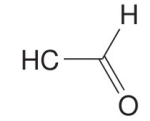
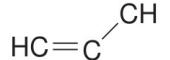

Spektreninterpretation

$^1\text{H NMR C}_4\text{H}_6\text{O}$

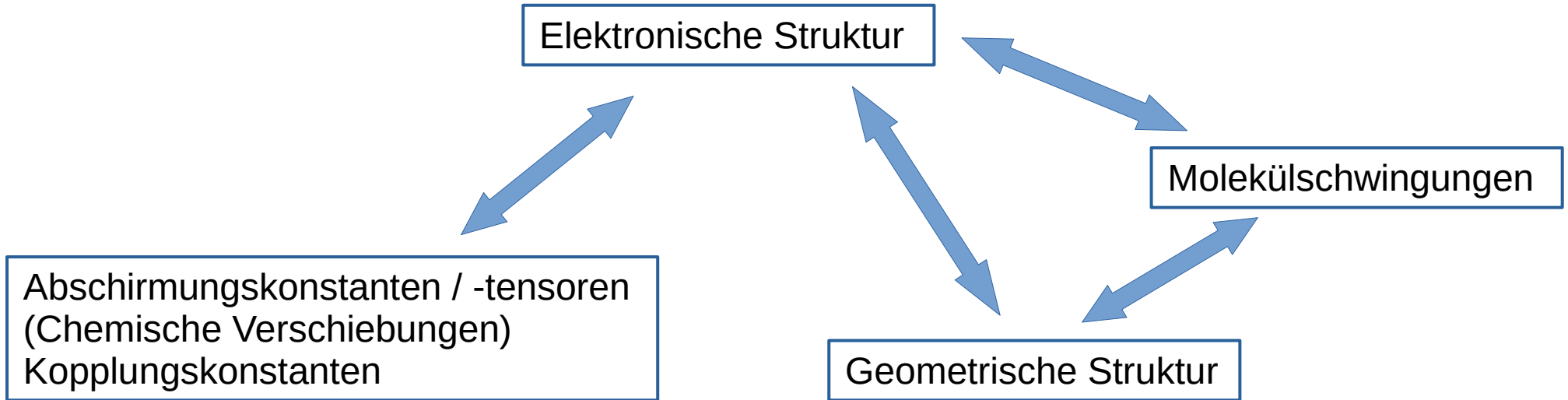
δ [ppm]	Integral	Multiplizität	J [Hz]
1.91	3	Dublett	6.9
		Dublett	1.65
6.11	1	Dublett	15.8
		Dublett	7.6
		Quartett	1.65
6.57	1	Dublett	15.8
		Quartett	6.9
9.40	1	Dublett	7.6

Welche Verbindung ist das?

Zur Info:

^2J	 12-20	 0-3.5	
^3J	 2-9 (≈ 7)	 6-14	 11-18
^4J	 4-10	 10-13	 3-7
	 1-3	 2-3	

Wechselbeziehungen



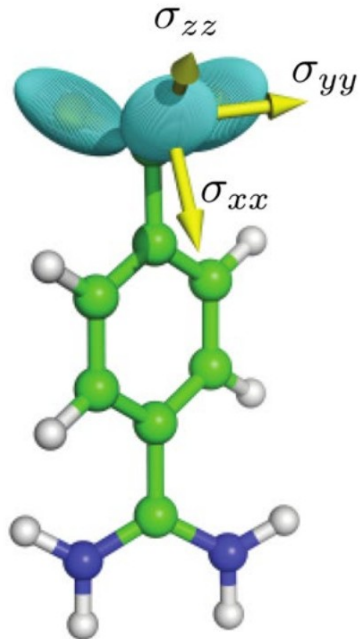
Abschirmtensor ↔ Elektronische Struktur

$$\sigma = \begin{bmatrix} \sigma_{xx} & \sigma_{xy} & \sigma_{xz} \\ \sigma_{yx} & \sigma_{yy} & \sigma_{yz} \\ \sigma_{zx} & \sigma_{zy} & \sigma_{zz} \end{bmatrix}$$

$$\sigma_{\gamma\beta} = \frac{\partial^2 E}{\partial B_\beta \partial \mu_\gamma} \quad \sigma_{iso} = \frac{1}{3} (\sigma_{xx} + \sigma_{yy} + \sigma_{zz}) \quad \sigma_{\gamma\beta} = \sigma_{\gamma\beta}^{dia} + \sigma_{\gamma\beta}^{para}$$

$$\sigma_{zz}^{dia} = \frac{\alpha^2}{2} \int \frac{x^2 + y^2}{r^3} \rho(\vec{r}) d\vec{r} = \frac{\alpha^2}{2} \int \frac{\sin^2 \theta}{r} \rho(\vec{r}) d\vec{r} \geq 0$$

$$\sigma_{zz}^{para} = -\alpha^2 \sum_{I \neq 0} \frac{\langle \Psi_0 | \hat{L}_z / r^3 | \Psi_I \rangle \langle \Psi_I | \hat{L}_z | \Psi_0 \rangle}{E_I - E_0}$$



α – Feinstrukturkonstante

ρ – Elektronendichte

L_z – Drehimpulsoperator

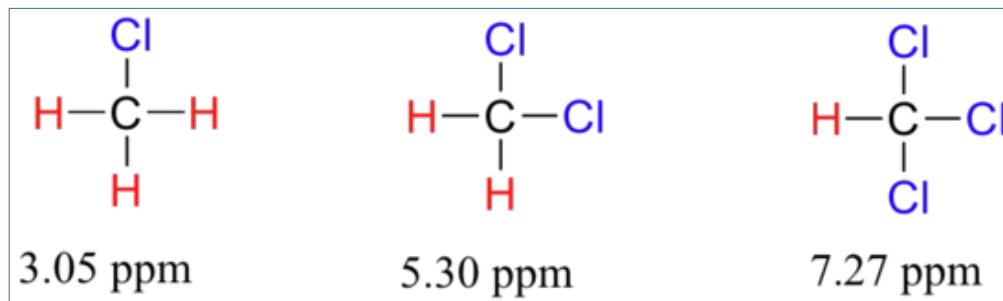
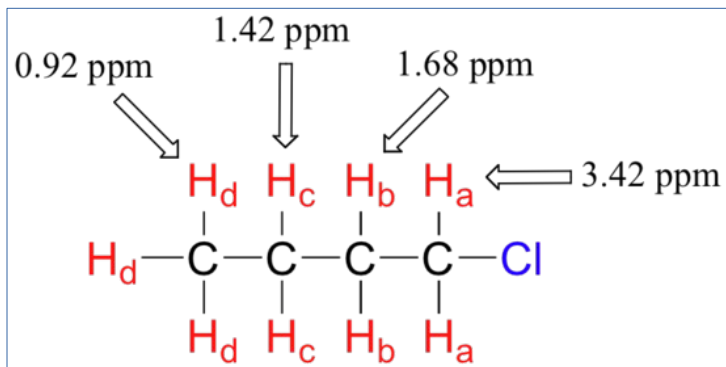
Ψ_0, Ψ_I – Wellenfunktion im Grund- und angeregten Zustand

E_0, E_I – Energien vom Grund- und angeregten Zustand

s. z.B.: F. Plasser et al., *Eur. J. Org. Chem.* 2021, 2021, 2529.

Elektronegativität $\leftrightarrow \sigma^{\text{dia}}$

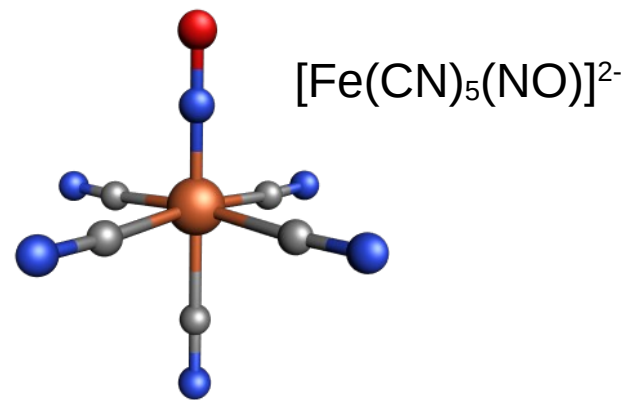
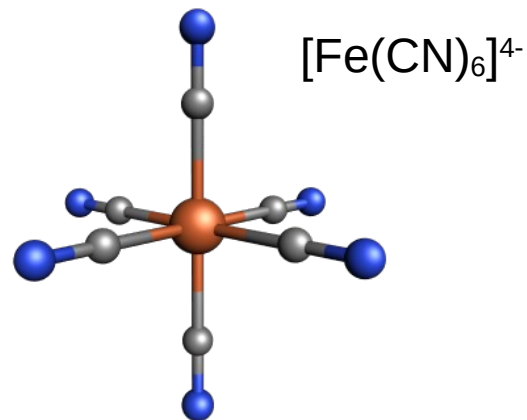
$$\sigma_{zz}^{\text{dia}} = \frac{\alpha^2}{2} \int \frac{x^2 + y^2}{r^3} \rho(\vec{r}) d\vec{r} = \frac{\alpha^2}{2} \int \frac{\sin^2 \theta}{r} \rho(\vec{r}) d\vec{r} \geq 0$$



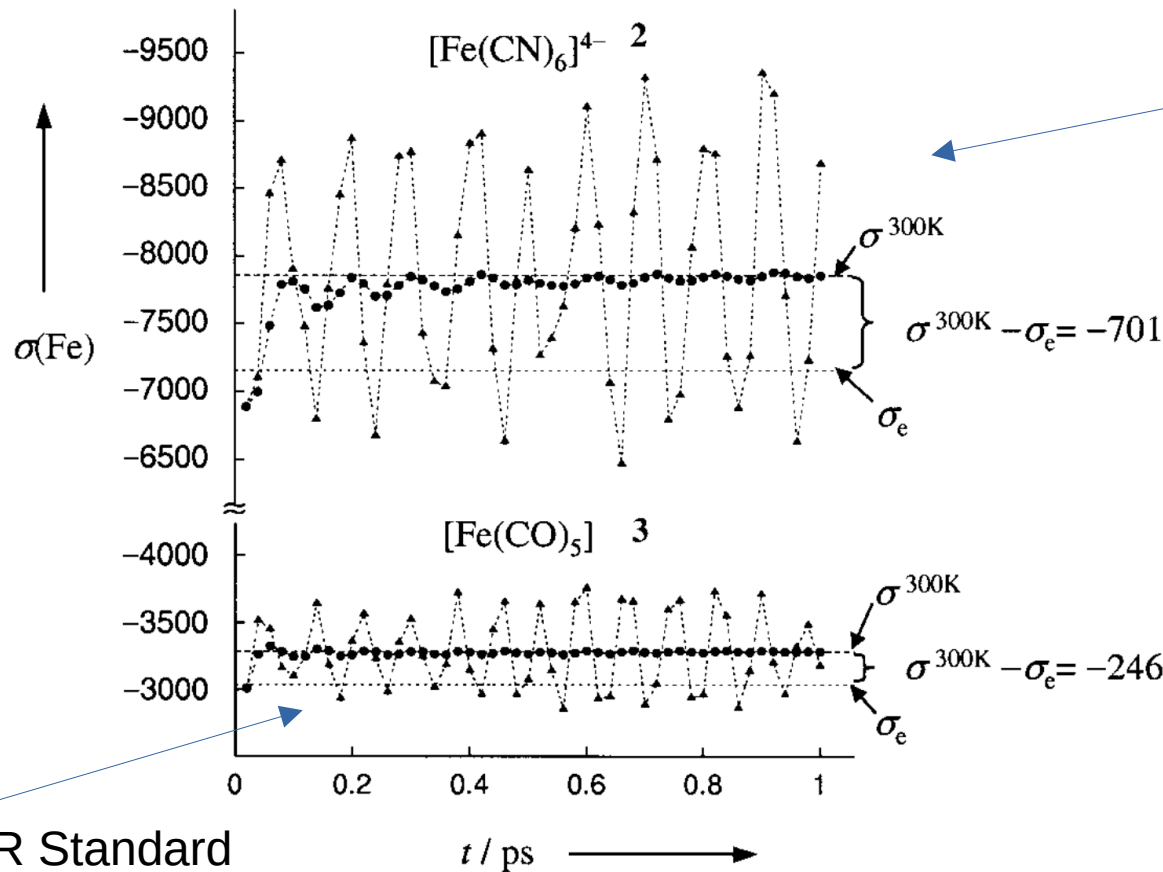
σ^{para} : ein Beispiel einer $\delta(^{57}\text{Fe})$ Untersuchung

Remarkably Large Geometry Dependence of ^{57}Fe NMR Chemical Shifts**

Michael Bühl,* Frank T. Mauschick, Frank Terstegen,
and Bernd Wrackmeyer



$\sigma(^{57}\text{Fe}) \leftrightarrow$ Moleküldynamik



Effekte der thermischen Mittelung der Geometrie (Molekülschwingungen!)

^{57}Fe NMR Standard

$$\delta(^{57}\text{Fe}) \leftrightarrow r(\text{Fe-C})$$

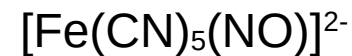
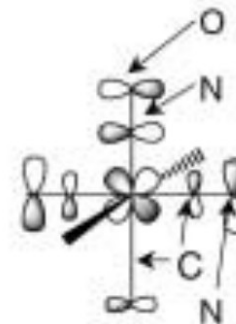
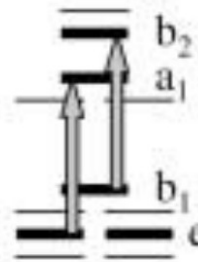
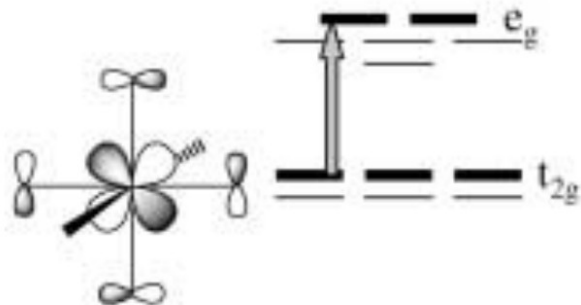
Simulationen:	Level of approximation	[Fe(CN) ₆] ⁴⁻	[Fe(CN) ₅ (NO)] ²⁻
		2	1
[a] Gleichgewicht, isolierte Mol.	δ_e (//QM-opt) ^[a]	4120	2254
	$\delta^{300\text{K}}$ (//MD) ^[b]	4575	2466
	$\delta^{300\text{K}}$ (//MD/H ₂ O) ^[c]	2593	2076
[b] MD, isolierte Mol.	$\delta_{\text{Experiment/H}_2\text{O}}$ ^[d]	2455	2004
	r_e (QM-opt) ^[a]	1.973	1.955 ^[e]
[c] MD in H ₂ O	$r^{300\text{K}}$ (MD) ^[b]	1.987	1.969 ^[e]
	$r^{300\text{K}}$ (MD/H ₂ O) ^[c]	1.924	1.943 ^[e]

Durchschnitts- $n(\text{H-O-H} \text{ ---- } \text{X}[\text{Ligand}])$: 15.3 für **2** und 7.4 für **1** → Δr

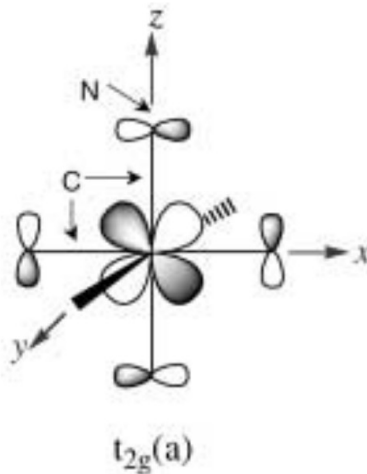
Wichtig: mit Geometrien aus MD/H₂O Simulationen aber ohne H₂O gerechnete $\delta(^{57}\text{Fe})$:
2448 ppm für **2** und 2140 ppm für **1**.

$\delta(^{57}\text{Fe}) \leftrightarrow$ Elektronische Struktur

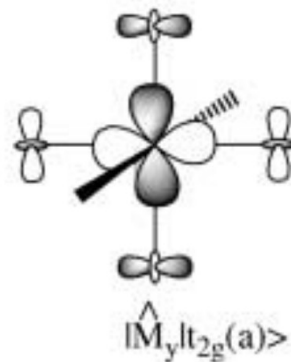
$\delta(^{57}\text{Fe})$ sind sehr stark entschirmt wegen $\sigma(\text{para})$:



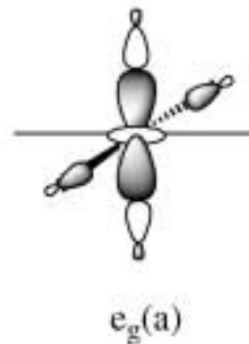
Beispiel
für $[\text{Fe}(\text{CN})_6]^{4-}$:



HOMO



*Drehimpulsoperator



LUMO+n

Gute Überlappung
→ große negative
 $\sigma(\text{para})$

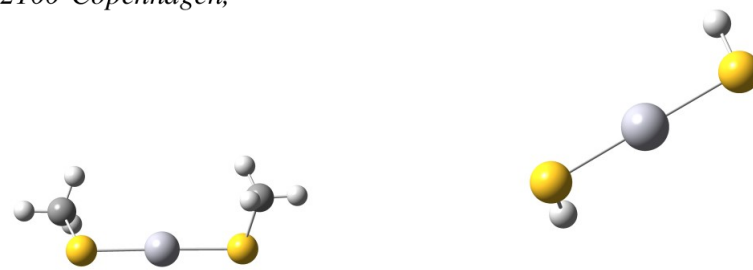
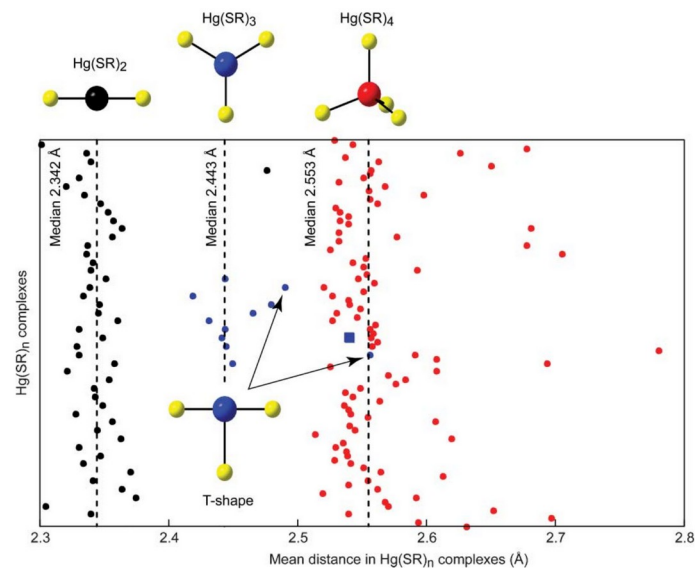
Bevorzugt für große
 $r(\text{Fe-C})$, weil d-
Orbitale weniger
verzerrt sind!

σ^{para} : ein Beispiel einer $\delta(^{199}\text{Hg})$ Untersuchung

On the Geometry Dependence of the NMR Chemical Shift of Mercury in Thiolate Complexes: A Relativistic DFT Study

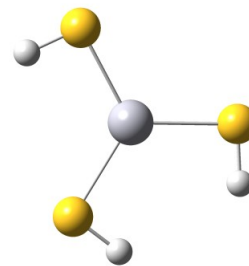
Haide Wu,^{1, a)} Lars Hemmingsen,¹ and Stephan P. A. Sauer¹

Department of Chemistry, University of Copenhagen, Universitetsparken 5, DK-2100 Copenhagen, Denmark

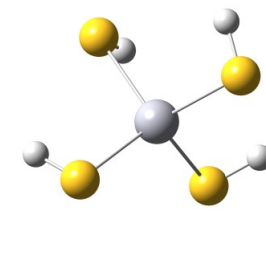


(a) Hg(SCH₃)₂

(b) Hg(SH)₂

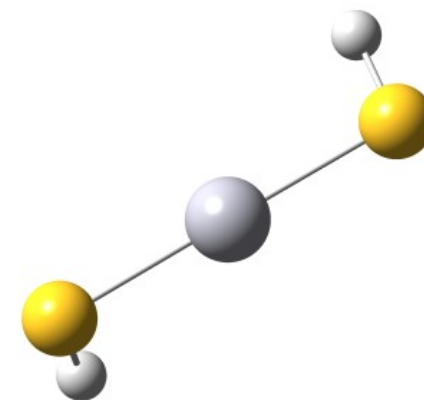
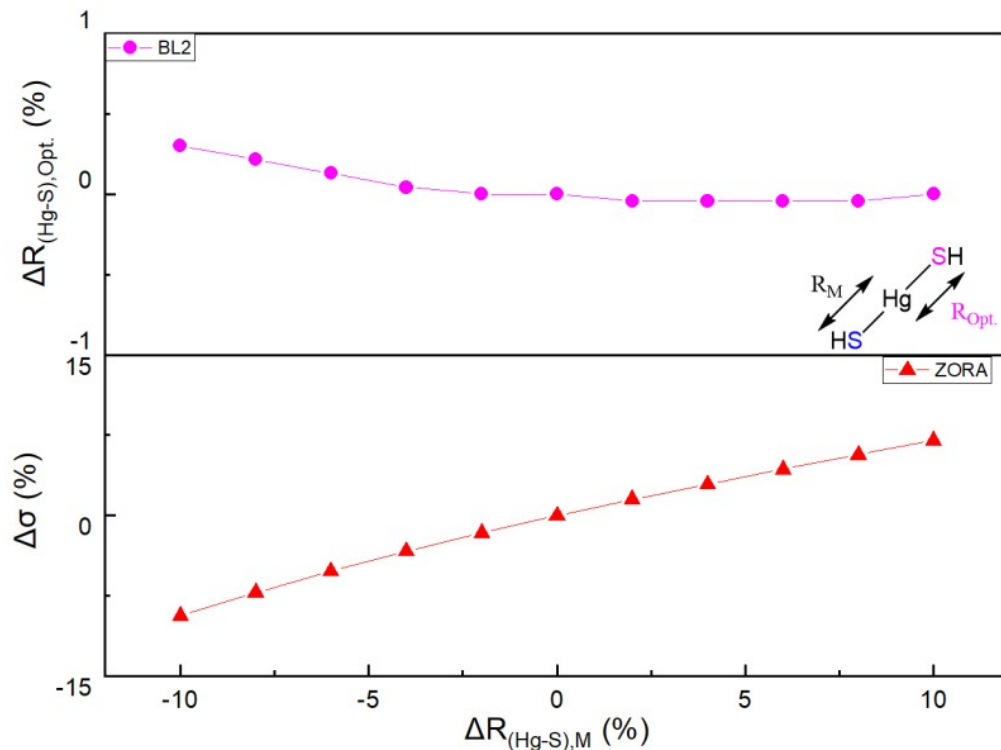


(c) [Hg(SH)₃]⁻



(d) [Hg(SH)₄]²⁻

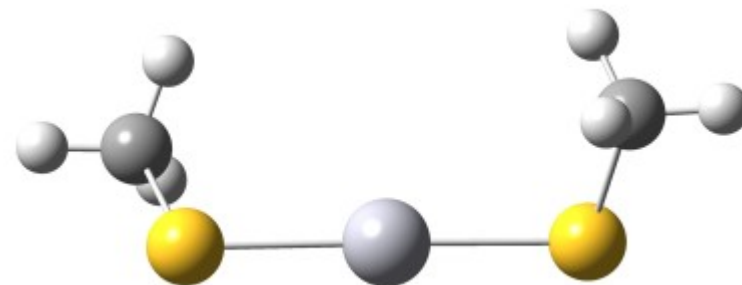
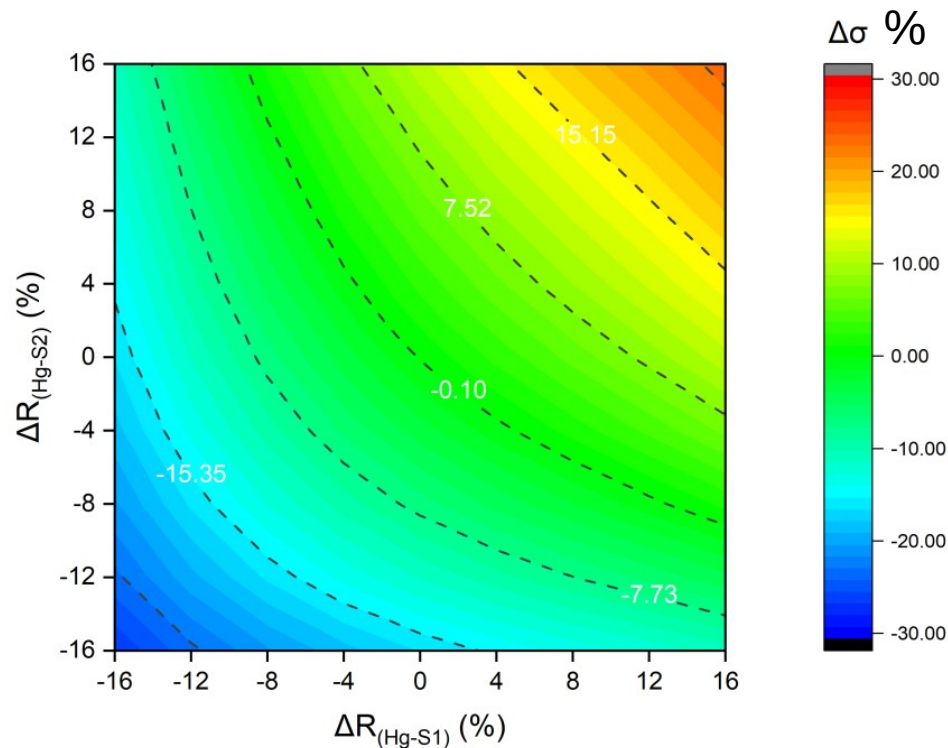
$$\delta(^{199}\text{Hg}) \leftrightarrow r(\text{Hg-S})$$



Starke Abhängigkeit!

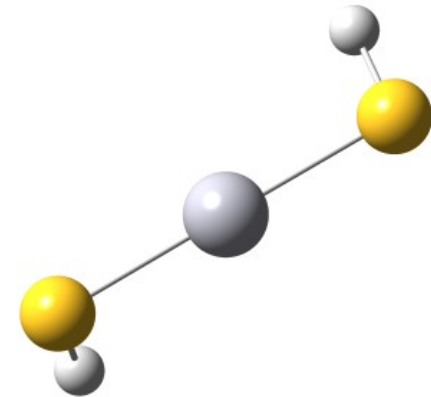
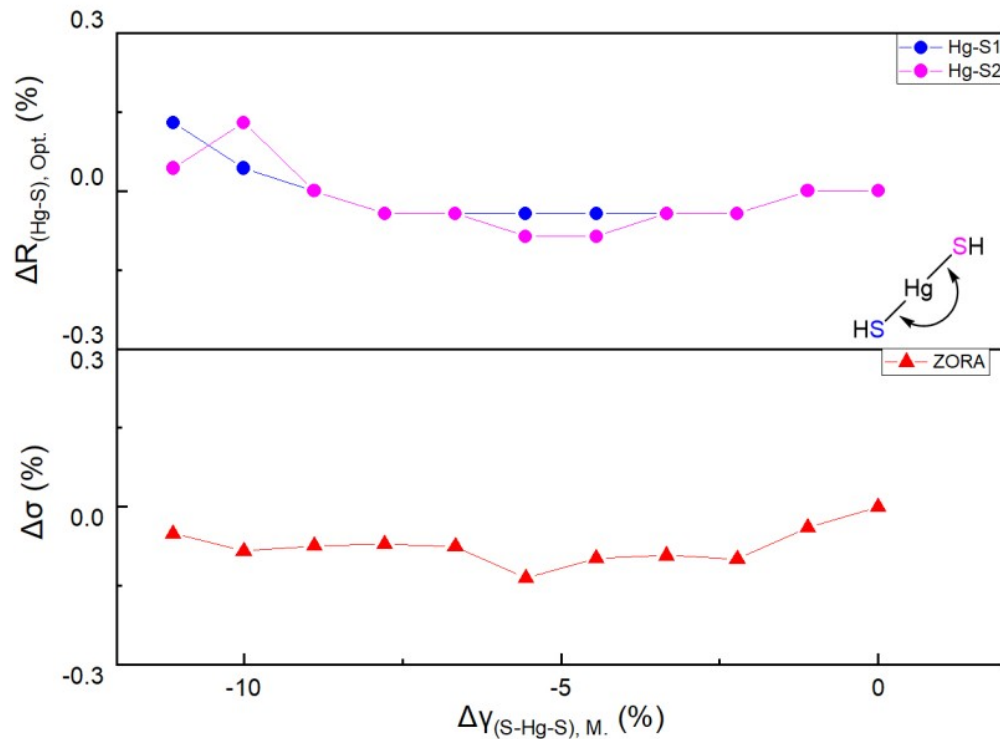
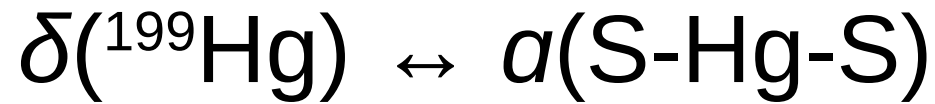
FIG. 9: $\text{Hg}(\text{SH})_2$: $\sigma(^{199}\text{Hg})$ isotropic shielding constant variation vs. changes in the Hg-S bond length calculated at the ZORA/PBE0/QZ4P level of theory.

$$\delta(^{199}\text{Hg}) \leftrightarrow r(\text{Hg-S})$$



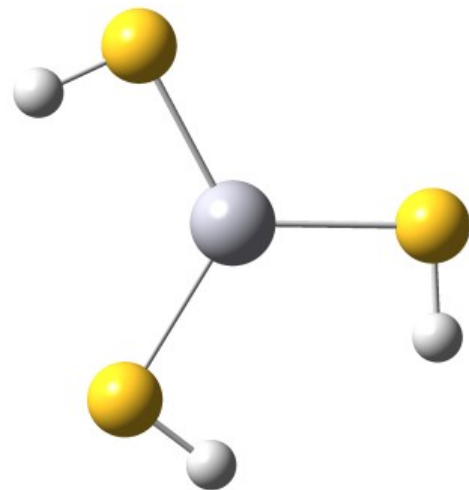
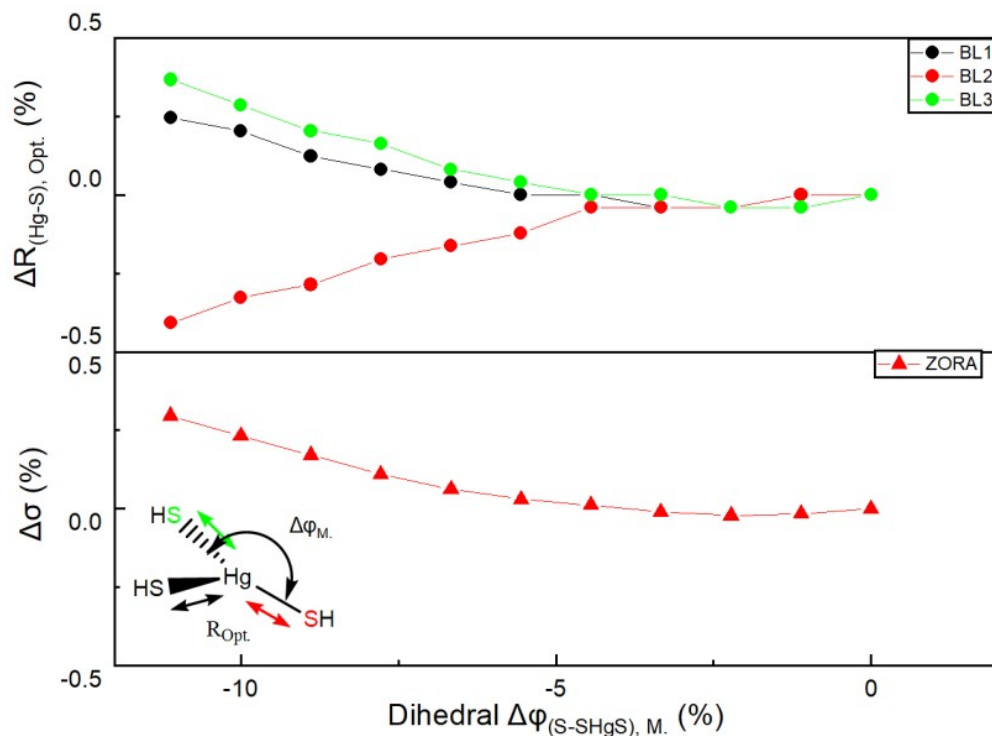
Starke Abhängigkeit!

FIG. 16: $\text{Hg}(\text{SMe})_2$: Contour plot of the effect of changes in both Hg-S bond lengths on the $\sigma(^{199}\text{Hg})$ isotropic shielding constant calculated at ZORA/PBE0 level of theory.



Schwache Abhängigkeit!

FIG. 11: $\text{Hg}(\text{SH})_2$: $\sigma(^{199}\text{Hg})$ isotropic shielding constant variation vs. changes in the S-Hg-S bond angle, calculated at the ZORA/PBE0/QZ4P level of theory.



Schwache Abhängigkeit!

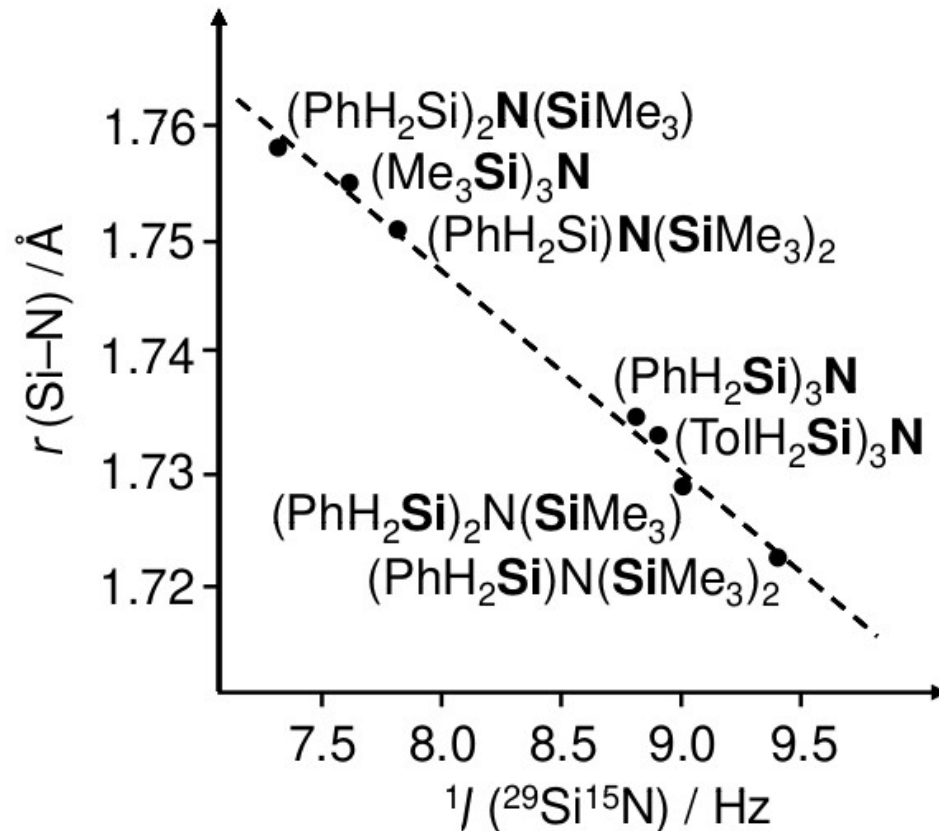
FIG. 21: $[\text{Hg}(\text{SH})_3]^-$: $\sigma(^{199}\text{Hg})$ isotropic shielding constant variation vs. changes in the S-SHgS dihedral angle calculated at the ZORA/PBE0/QZ4P level of theory.

Kopplungskonstanten ↔ Geometrie

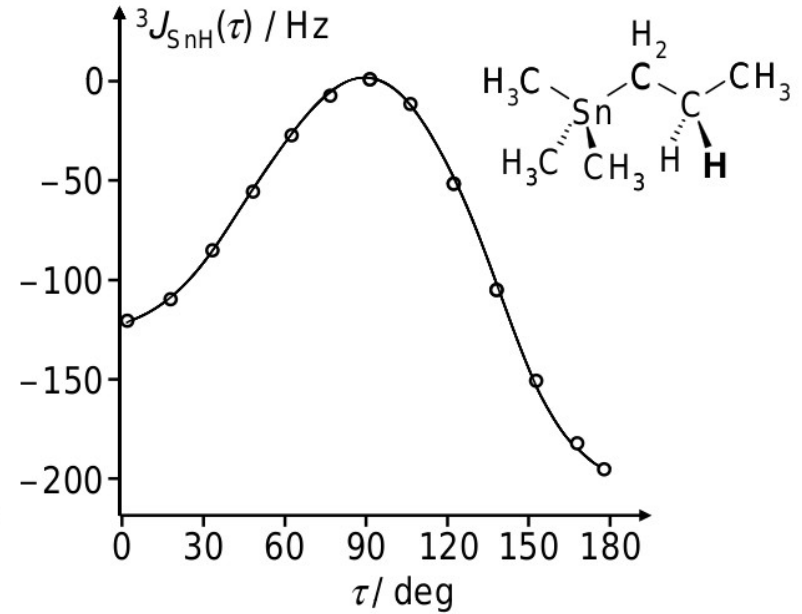
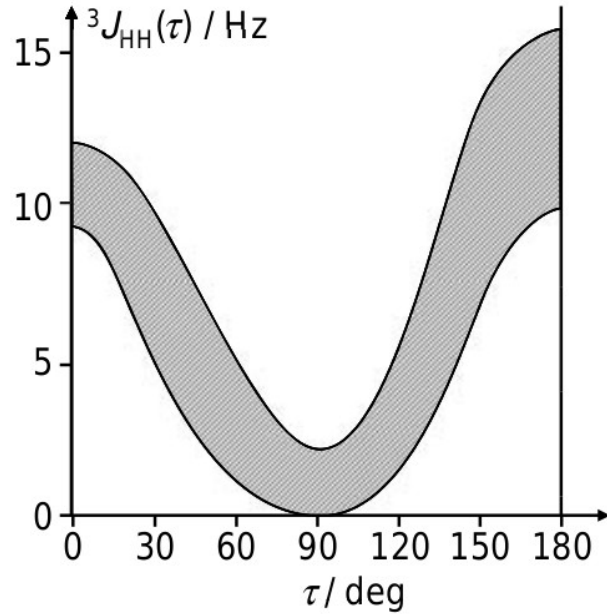
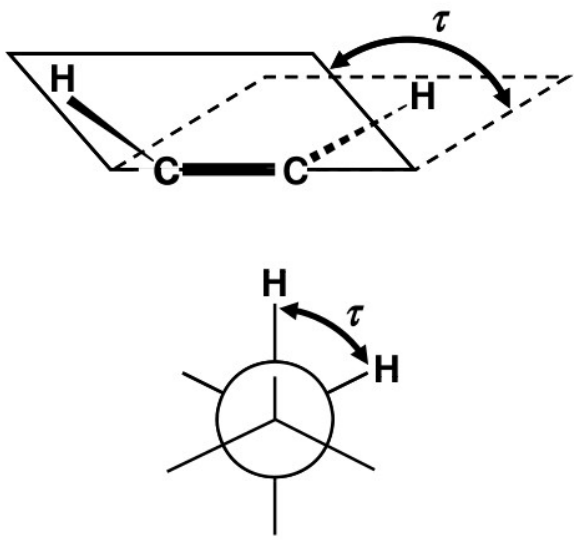
Kopplungskonstanten sind abhängig von:

- Hybridisierung der an der Kopplung beteiligten Atome
- Valenz- und Torsionswinkel
- Bindungslängen
- Substituenteneffekte

Z.B.: $^1J(^{29}\text{Si}^{15}\text{N})$ gegen $r(\text{Si-N})$ in XRD:



Kopplungskonstanten ↔ Torsionswinkel



Molekül des Tages: Bullvalen

156. Comparison of ^{13}C - and ^1H -Magnetic Resonance Spectroscopy as Techniques for the Quantitative Investigation of Dynamic Processes. The Cope Rearrangement in Bullvalene

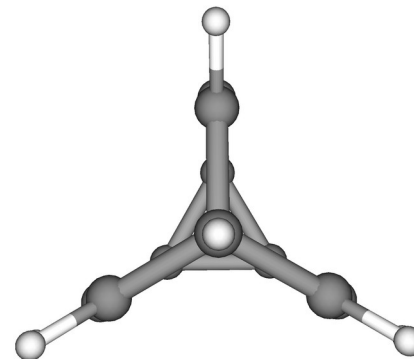
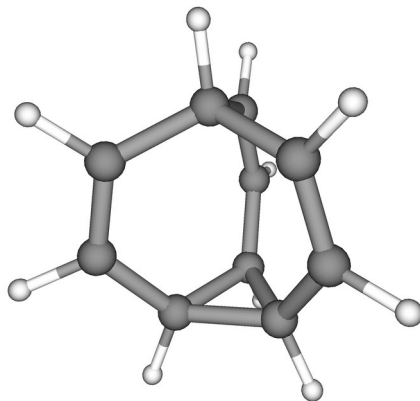
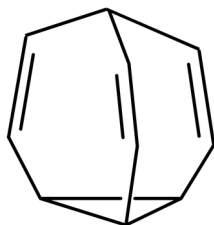
by **Jean F. M. Oth, Klaus Müllen, Jean-Marie Gilles** and **Gerhard Schröder**

Laboratory for organic chemistry, E.T.H., CH-8006 Zürich

Institute for organic chemistry, University of Karlsruhe, D-7500 Karlsruhe

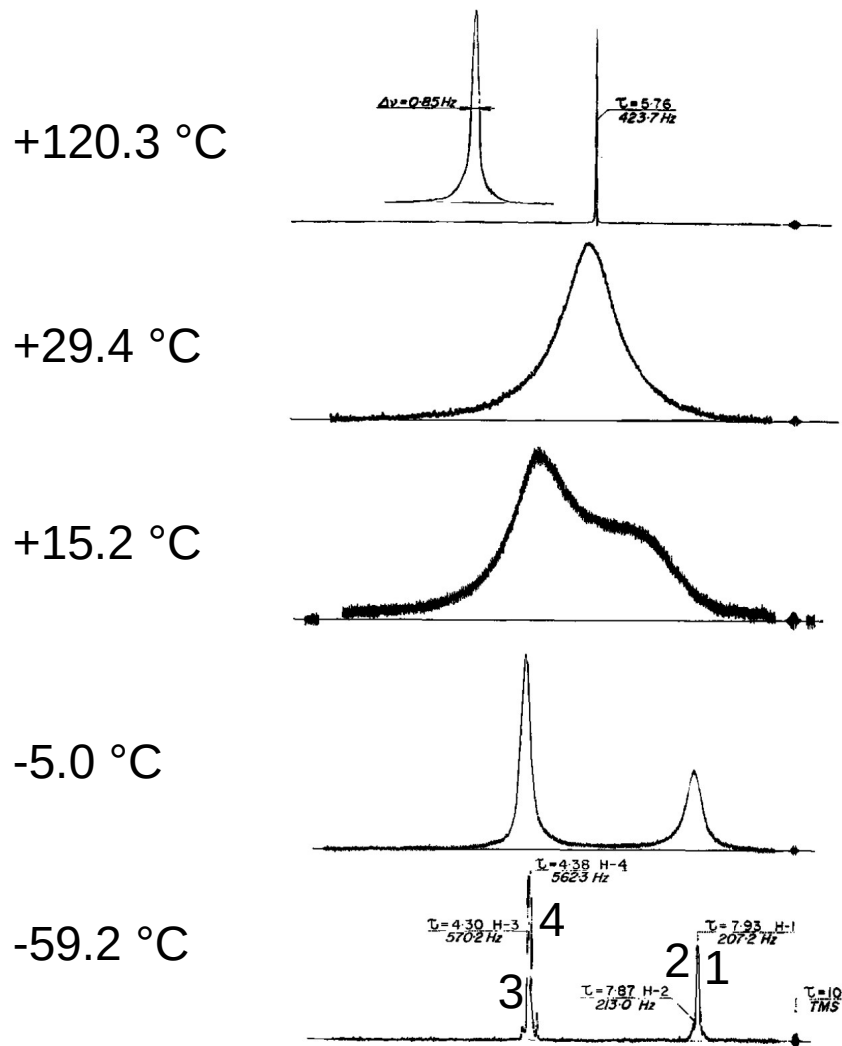
Helv. Chim. Acta 1974, 57, 1415–1433

Bullvalen: $(\text{CH})_{10}$

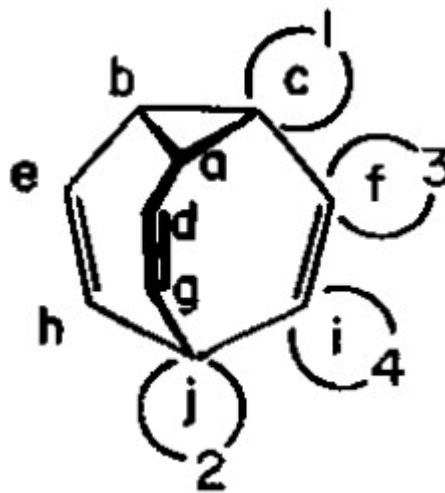


C_{3v} Symmetrie

Bullvalen: ^1H NMR

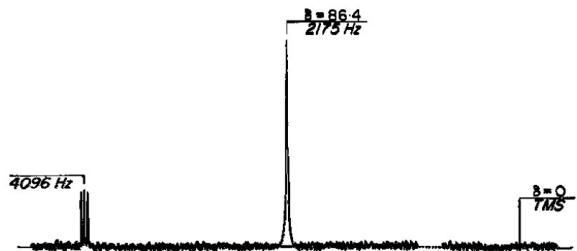


Sites 1, 2, 3, 4:

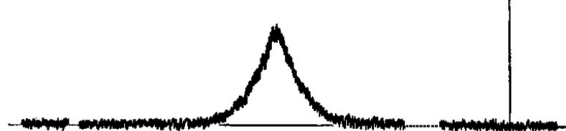


Bullvalen: ^{13}C NMR

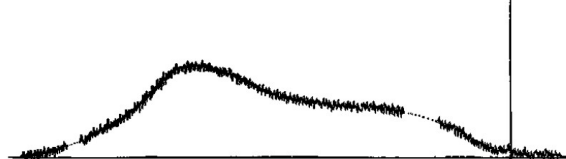
+140.8 °C



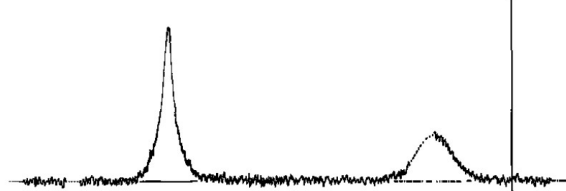
+70.3 °C



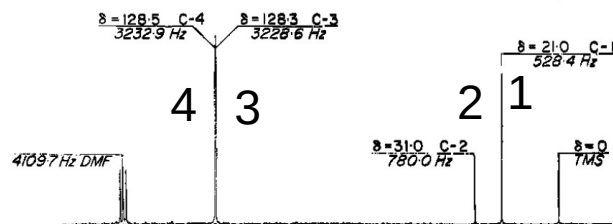
+39.9 °C



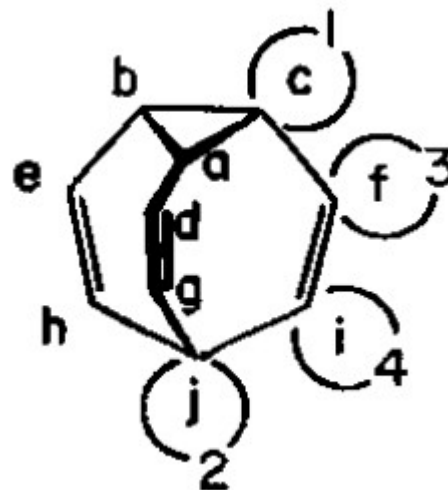
+14.1 °C



-59.9 °C

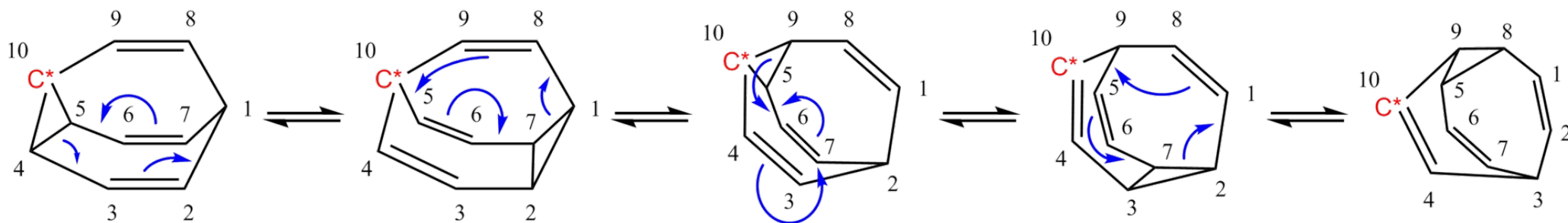


Sites 1, 2, 3, 4:



Bullvalen: Cope-Umlagerung

Cope-Umlagerung:



1,2 Millionen Valenzisomeren (genau $10!/3 = 1.209.600$ Möglichkeiten)

(s. Animation)

Quellen/Literatur

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- C. Merten, J. Willmann, Physikalische Grundlagen der Spektroskopie, Uni-Bremen, 2005.
- <https://mriquestions.com/predict-nuclear-spin-i.html>
- M. Holz, B. Knüttel, “Gepulste Kernspinresonanz: Der heutige Stand einer physikalischen Methode mit einer Vielzahl von Anwendungsmöglichkeiten”, *Physikalische Blätter*, 38 (1982) 368–374.
- J. F. M. Oth, K. Müllen, J.-M. Gilles, G. Schröder, “Comparison of ^{13}C - and ^1H -Magnetic Resonance Spectroscopy as Techniques for the Quantitative Investigation of Dynamic Processes. The cope rearrangement in bullvalene”, *Helv. Chim. Acta*, 57 (1974) 1415–1433.