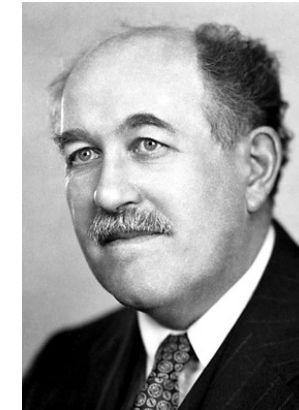
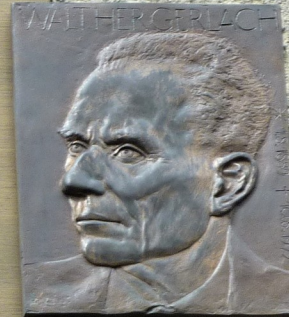
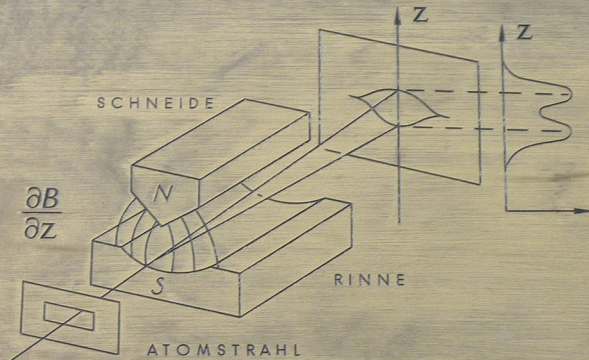


Strukturaufklärung in der molekularen anorganischen Chemie

13. Elektronenspinresonanz- Spektroskopie

Stern-Gerlach-Versuch



Otto Stern
(17.02.1888-
17.08.1969)

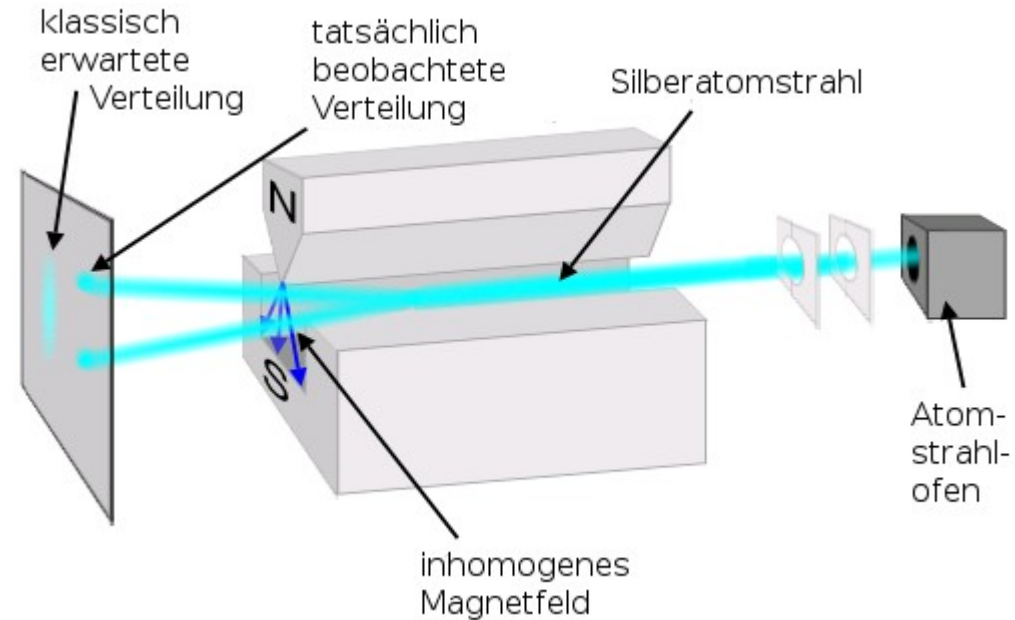
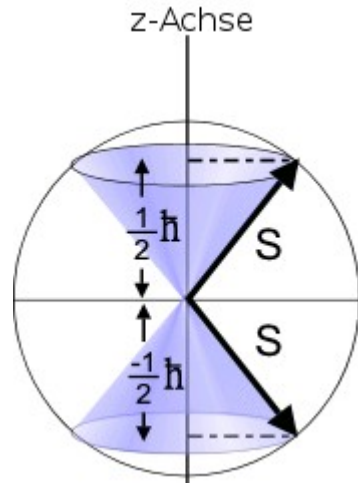


Walther
Gerlach
(01.08.1889-
10.08.1979)

IM FEBRUAR 1922 WURDE IN DIESEM GEBÄUDE DES
PHYSIKALISCHEN VEREINS, FRANKFURT AM MAIN,
VON OTTO STERN UND WALTHER GERLACH DIE
FUNDAMENTALE ENTDECKUNG DER RAUMQUANTISIERUNG
DER MAGNETISCHEN MOMENTE IN ATOMEN GEMACHT.
AUF DEM STERN-GERLACH-EXPERIMENT BERUHEN WICHTIGE
PHYSIKALISCH-TECHNISCHE ENTWICKLUNGEN DES 20. JHDTS.,
WIE KERNSPINRESONANZMETHODE, ATOMUHR ODER LASER.
OTTO STERN WURDE 1943 FÜR DIESE ENTDECKUNG
DER NOBELPREIS VERLIEHEN.

Stern-Gerlach-Versuch

Ag^0 : $[\text{Kr}] 4d^{10} 5s^1$



$$\vec{F} = \nabla (\vec{\mu} \cdot \vec{B}) = \begin{pmatrix} 0 \\ 0 \\ \mu_z \cdot \frac{\partial B}{\partial z} \end{pmatrix}$$

Das Elektron

Eigendrehimpuls $|\mathbf{S}| = \hbar(s(s+1))^{1/2}$ (Spinquantenzahl $s = 1/2$)

Im äußeren Magnetfeld in z-Richtung: $S_z = m_s \hbar$

m_s - Richtungsquantenzahl für den Elektronenspin: $-1/2$ (α), $1/2$ (β)

Klassisch:

Ladung e , Masse m , Bahndrehimpuls $\mathbf{L} \rightarrow$ magnetisches Moment $\boldsymbol{\mu}_L = -e/(2m) \cdot \mathbf{L}$

Analogisch für Spinmagnetismus \rightarrow magnetisches Moment $\boldsymbol{\mu}_s = -e/(2m) \cdot \mathbf{S}$ (Vgl. El. u. Prot.!))

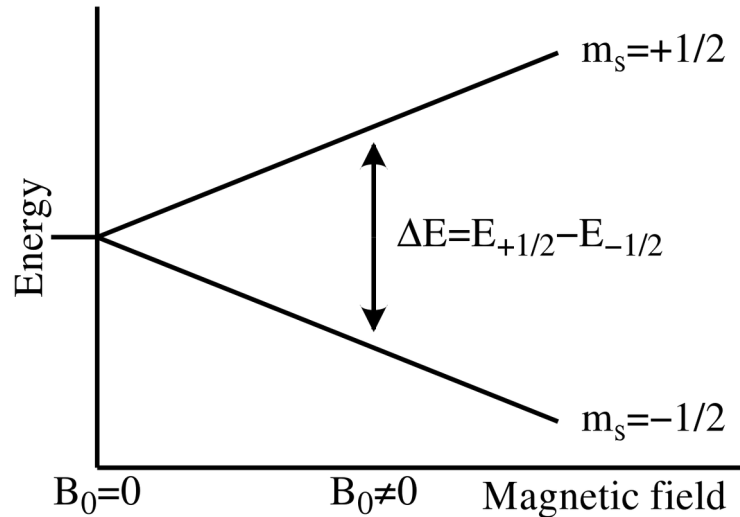
Quantenmechanisch:

Bohr-Magneton: $\mu_B = -\hbar e/(2m_e) = 9,27400915(23) \times 10^{-24}$ [J T⁻¹] (elementare Einheit des magnetisches Bahnmoments in einem äußeren Magnetfeld)

$\boldsymbol{\mu} = g \mu_B \mathbf{S}/\hbar$, g ist der gyromagnetische Faktor (g-Faktor, Landé-Faktor f. Gesamtdrehimpuls)

$g_e = 2,00231930437378(2)$ f. Spinmag. (Vgl. für das Proton $g \approx 5,6$ für das Neutron $g \approx -3,8$)

Das Elektron im Magnetfeld



Zeeman-Effekt:

$$E = m_s g_e \mu_B B_0$$

$$\Delta E = g_e \mu_B B_0$$

$$\gamma_e = -g_e \mu_B / \hbar \text{ (gyromagnetisches Verhältnis f. El.)}$$

$$\gamma_e = -1,76 \times 10^{11} \text{ [rad s}^{-1} \text{ T}^{-1}\text{]}$$

$$\gamma_p = 2,68 \times 10^8 \text{ [rad s}^{-1} \text{ T}^{-1}\text{]} \text{ (für das Proton)}$$

Für das Elektron: 28.025 GHz im Feld von 1 T

(~ 658-mal mehr als für das Proton!)

[1 T = 10^4 G = 10 kG; 1 mT = 10 G; 1 G = 0.1 mT]

EPR: 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
$< 0.1 \text{ \AA}$	5 \AA	100 \AA	2000 \AA			0.7 \mu m	2.5 \mu m	25 \mu m		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
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

λ (wavelength) is indicated by a bracket on the right for the mm-wave and Micro-wave regions.
 $\tilde{\nu} / \text{cm}^{-1}$ (wavenumber) is indicated by a bracket on the right for the Micro-wave region.
 $E / \text{kJ mol}^{-1}$ (energy) is indicated by a bracket on the right for the Micro-wave region.
 E / eV (energy) is indicated by a bracket on the right for the Micro-wave region.
 ν / Hz (frequency) is indicated by a bracket on the right for the Micro-wave region.

Waveband	L	S	C	X	P	K	Q	U	V	E	W	F	D	—	J	—
λ / mm	300	100	75	30	20	12.5	8.5	6	4.6	4	3.2	2.7	2.1	1.6	1.1	0.83
ν / GHz	1	3	4	10	15	24	35	50	65	75	95	111	140	190	285	360
B_0 / T	0.03	0.11	0.14	0.33	0.54	0.86	1.25	1.8	2.3	2.7	3.5	3.9	4.9	6.8	10.2	12.8

Relaxation

EPR Relaxationzeiten sind um den Faktor $\sim 658^2$ kürzer im Vergleich zu NMR.

Spin-Gitter Relaxation T_1

Spin-Spin Relaxation T_2

EPR Relaxationzeiten sind im Bereich von μs (10^{-6} s)

Typischerweise: $T_1 \gg T_2$

EPR

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:

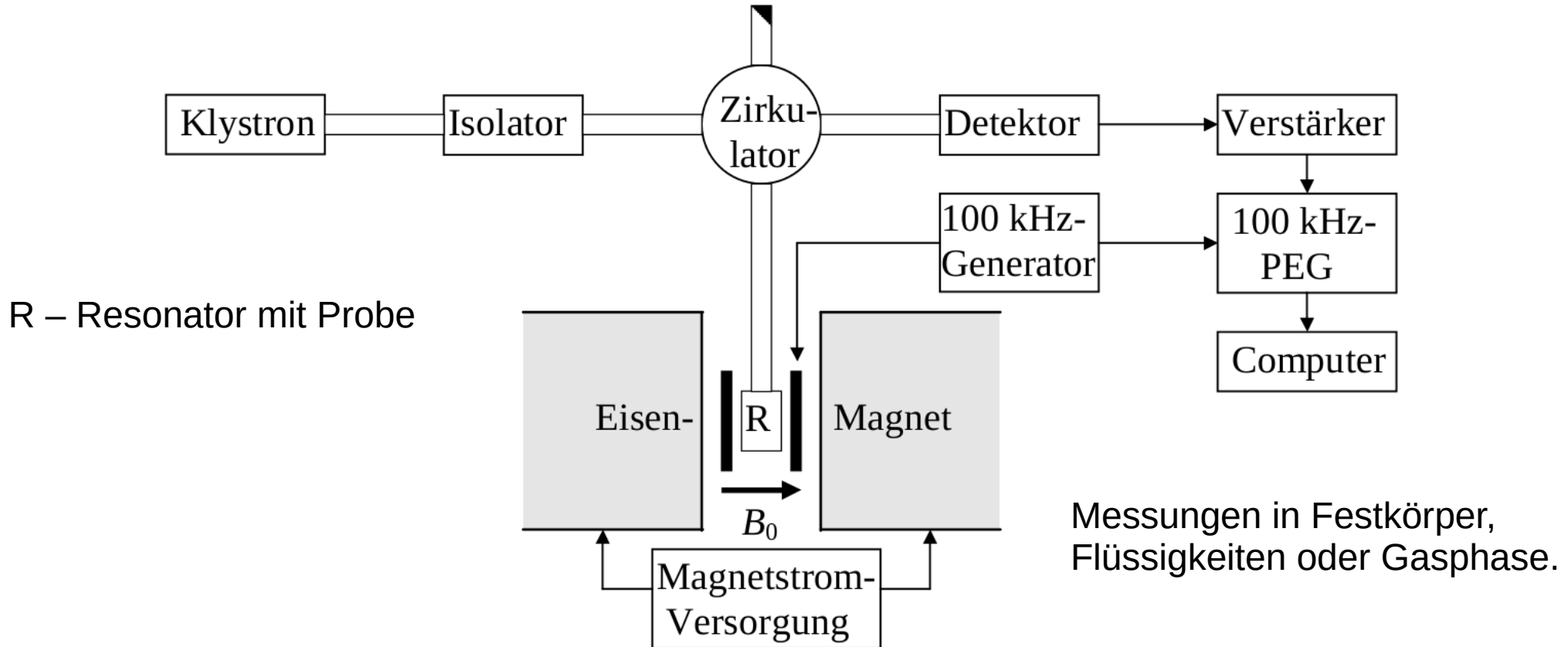
- Langsame Methode
- Mittelschnelle Methode
- Schnelle Methode

Aggregatzustand der Probe:

- Gas
- Flüssigkeit
- Feststoff

Prinzipieller Aufbau

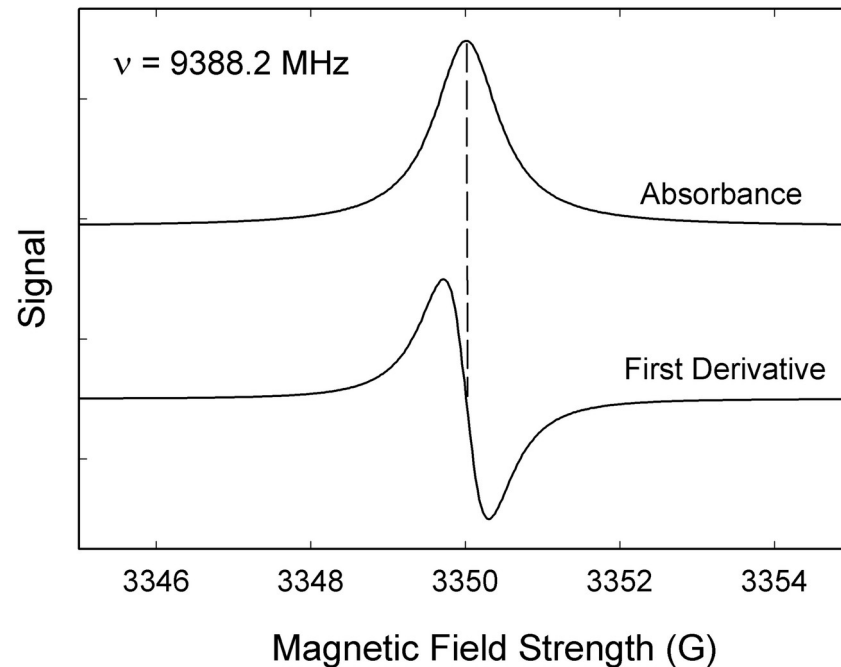
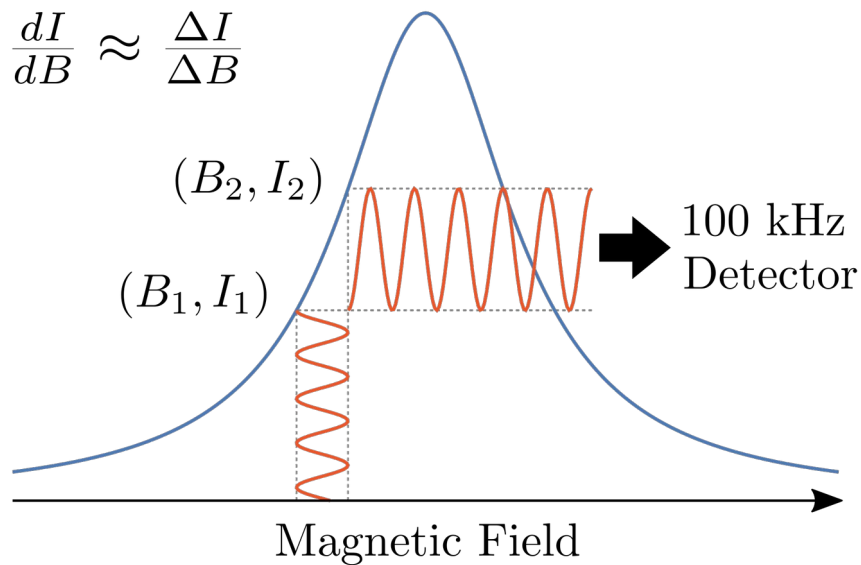
X-Band-EPR-Spektrometer mit 100 kHz Feldmodulation



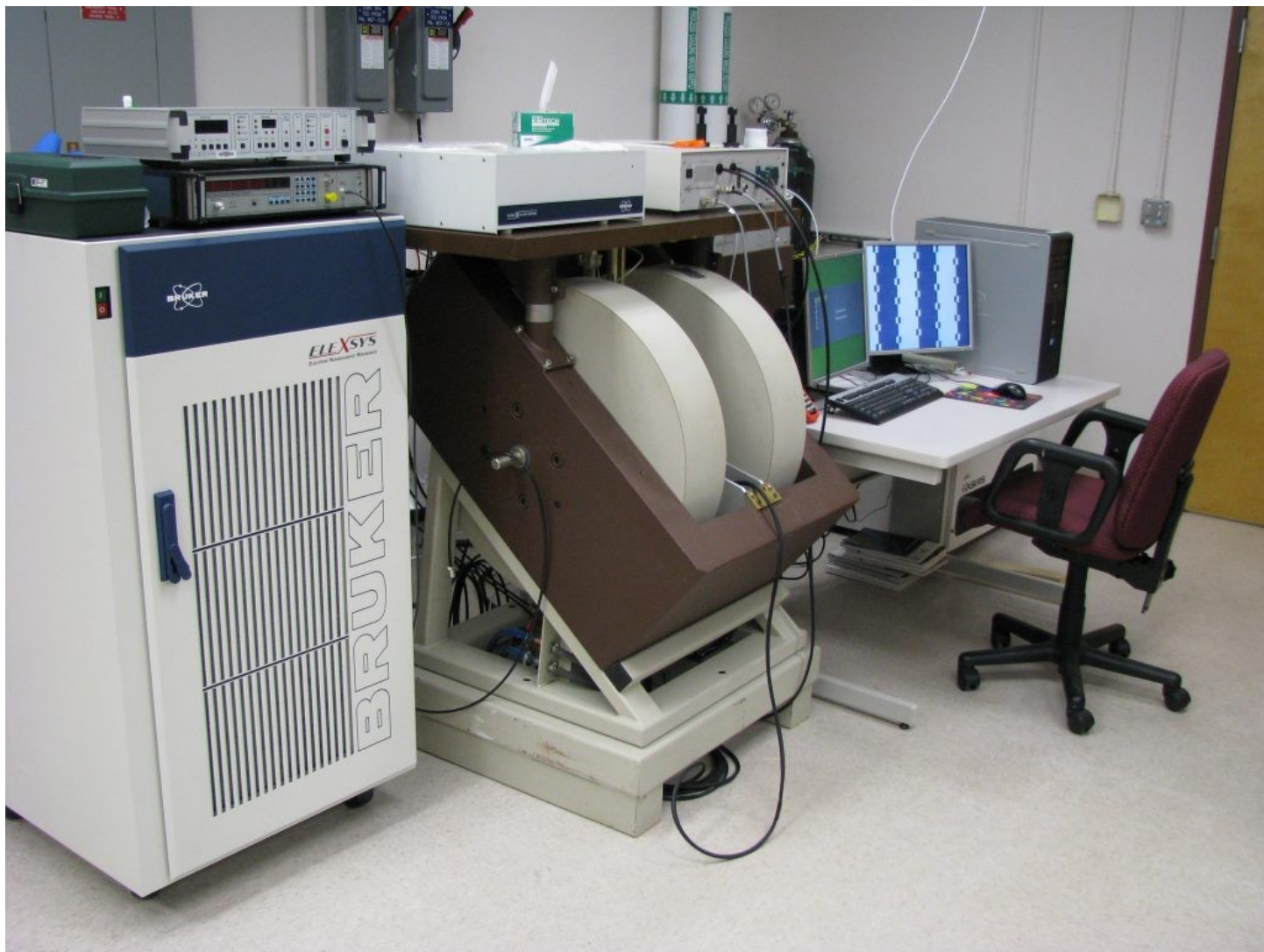
CW EPR

Differentielle Abtastung:

$$\frac{dI}{dB} \approx \frac{\Delta I}{\Delta B}$$



$$B_0 = B_{\text{Anfang}} + \text{const.} \cdot t + B_{\text{Modulation}} \cdot \sin(2\pi \nu_{\text{Modulation}} \cdot t)$$



Bruker E500 X-Band CW EPR Spektrometer (@ North Carolina State University)

g-Faktor

Das freie Elektron: $g = 2,0023$

CH₃ Radikal: $g = 2,0025$

5,5'-(CF₃)₂-2,2'-bipyridin Radikal-Anion: $g = 2,0035$

Cu²⁺-Chloride (*L-S*-Kopplung!):

Compound	g_{av}
(BzlEt ₃ N) ₂ [CuCl ₄] (1)	2.212 ± 0.005
(Me ₃ PhN) ₂ [CuCl ₄] (2)	2.170 ± 0.005
(EtPh ₃ P) ₂ [CuCl ₄] (3)	2.179 ± 0.005
(BzlPh ₃ P) ₂ [CuCl ₄]·2CH ₂ Cl ₂ (4)	2.189 ± 0.005
(Ph ₄ As) ₂ [CuCl ₄] (5)	2.206 ± 0.005

Cu⁰: [Ar] 3d¹⁰ 4s¹

Größenordnung einiger Energien

Orbitalenergie	$> 10^4 \text{ cm}^{-1}$
Energieaufspaltung im Ligandenfeld	$10^2 - 10^4 \text{ cm}^{-1}$
Spin-Bahn-Kopplung für die Atome	B: 10, C: 28, F: 271, Cl: 440, Br: 1842 cm^{-1}
Elektronen-Zeeman-Übergänge im X bzw. Q-Band-Spektrometer:	0,3 bzw. 1 cm^{-1}
Spin-Spin-Kopplung (Nullfeldaufspaltung) für Triplett-Grundzustand-Molek.:	1 cm^{-1}
Elektronenspin-Kernspin-Kopplung (HFS)	$< 10^{-1} \text{ cm}^{-1}$
Zeeman-Übergänge von H-Kernspins im Feld $B_0 = 0,7 \text{ T}$:	10^{-3} cm^{-1}

Elektronenspin-Kernspin-Kopplung

Hyperfein-Kopplung

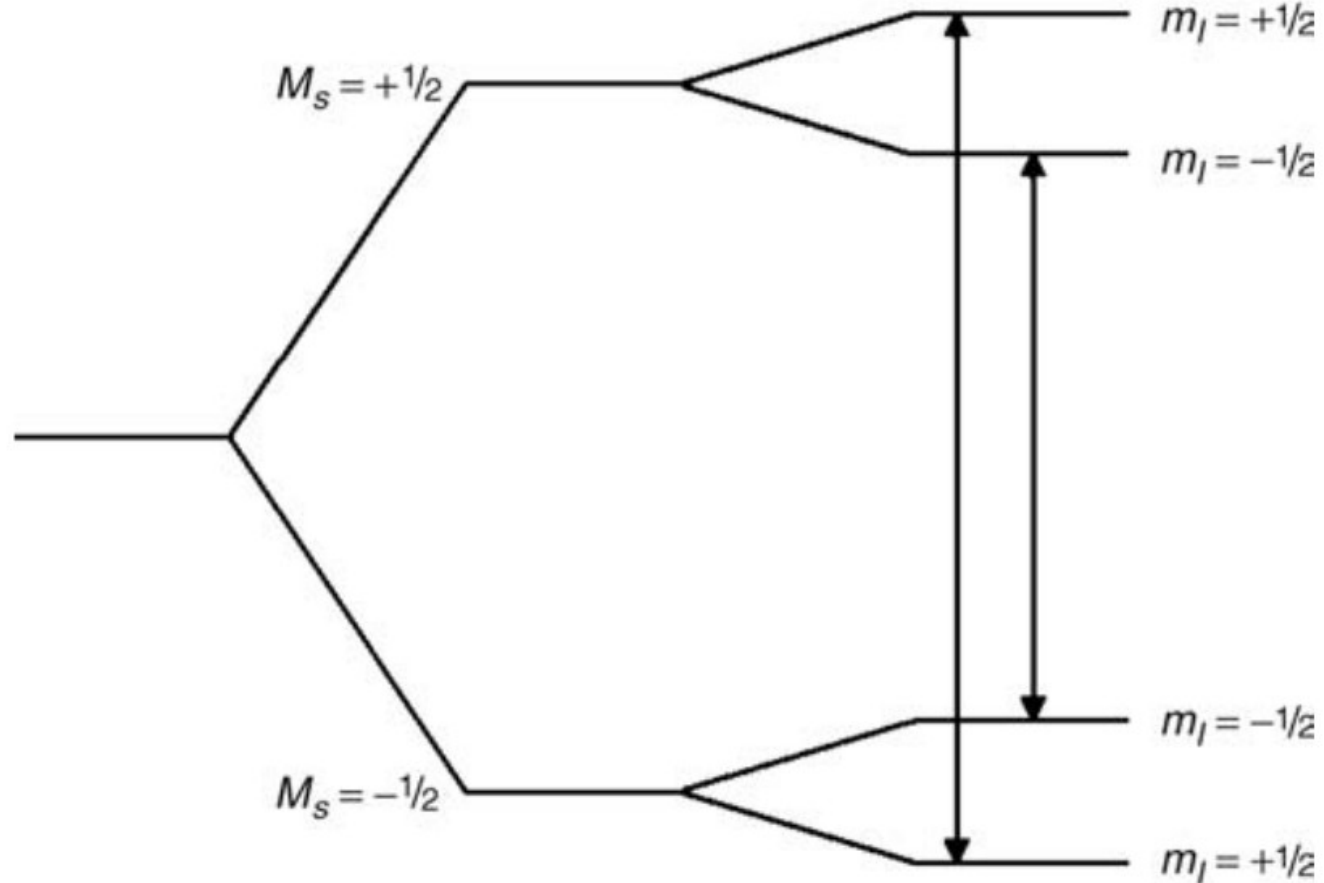
Ein Elektron + Ein Kern mit $s = 1/2$

$$E = m_s g_e \mu_B B_0 + a m_s m_l$$

Auswahlregeln:

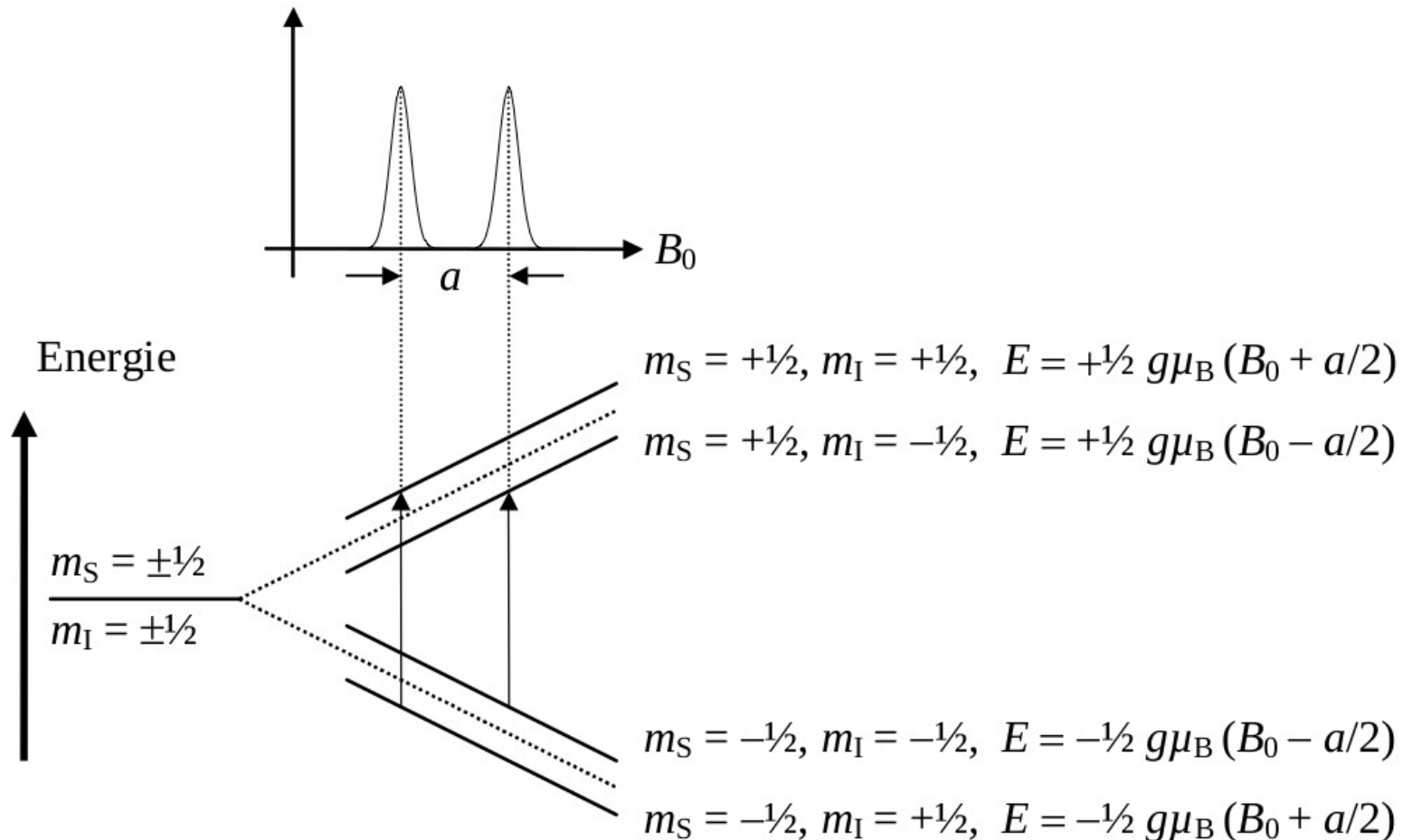
$$\Delta m_s = \pm 1, \Delta m_l = 0$$

a – Hyperfein-Kopplungskonstante (HFC im Engl.)

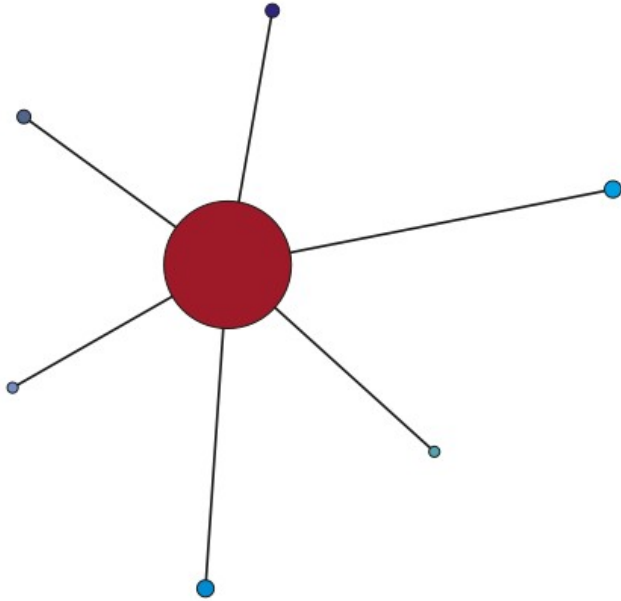


Elektronenspin-Kernspin-Kopplung

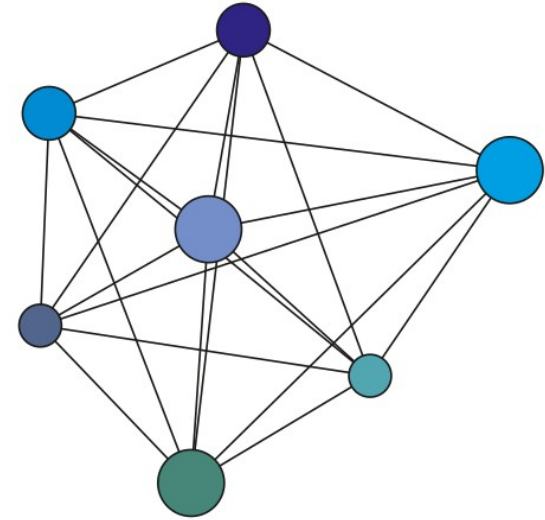
EPR-Absorptionsspektrum



Vergleich mit NMR

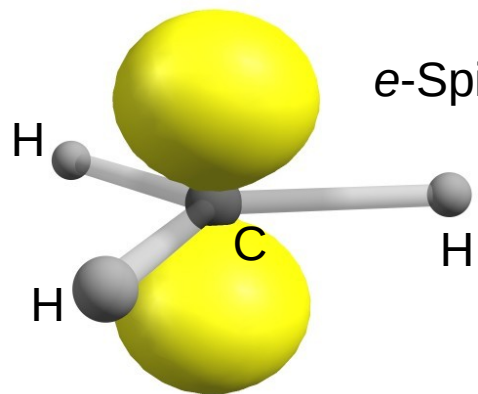


EPR: Hyperfein-Wechselwirkung
(ein Elektron – Kerne)



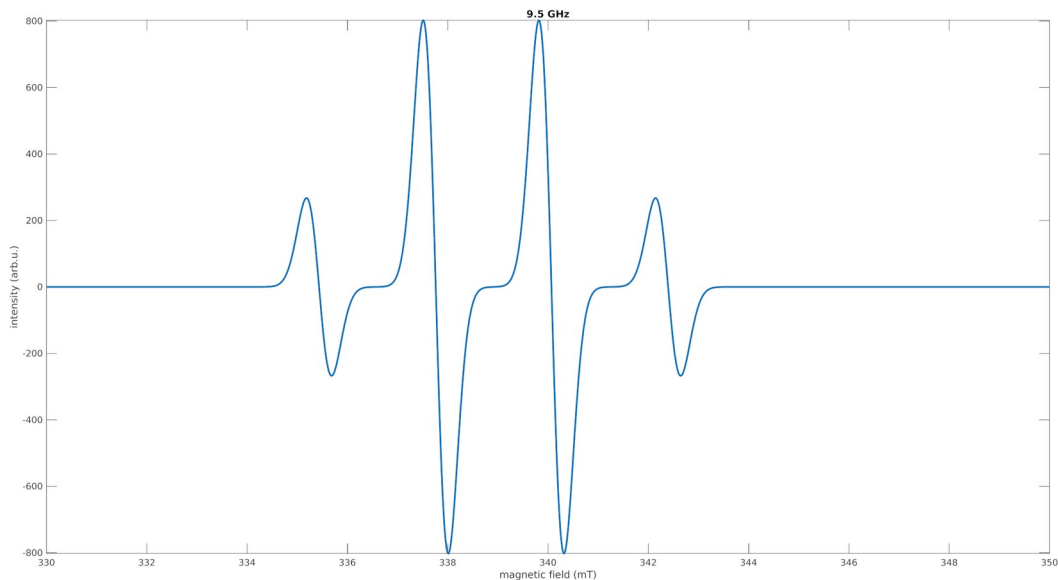
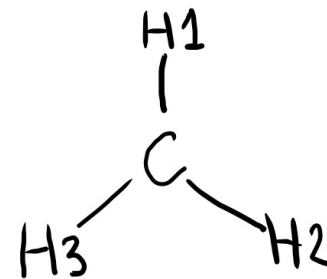
NMR: Kern-Kern-Wechselwirkungen

$^{12}\text{C}^1\text{H}_3$ Radikal

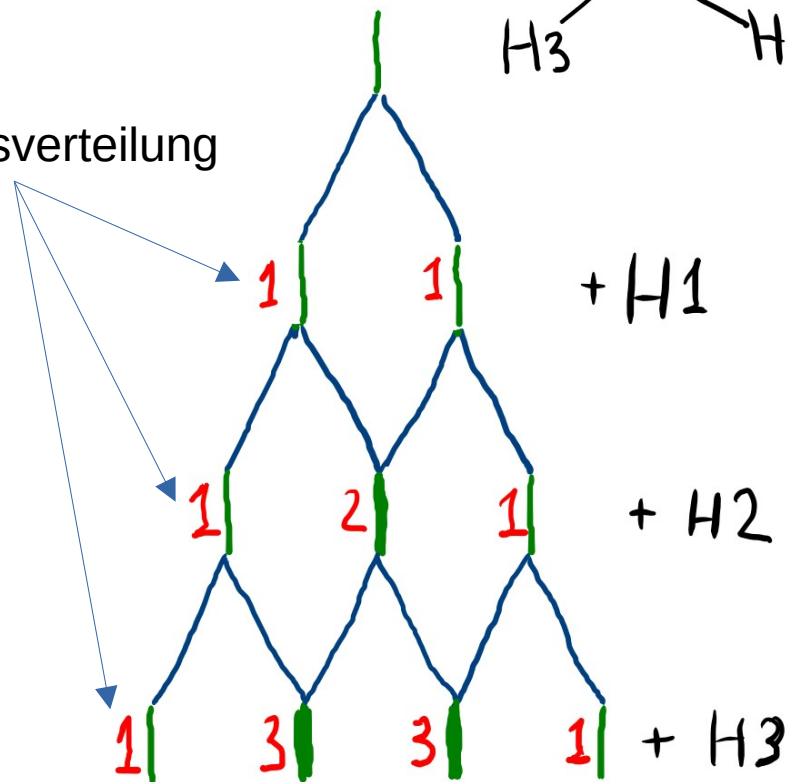


$g = 2.0025$
 $a_{\text{iso}} = -61.8 \text{ MHz}$

Hyperfein-Aufspaltung



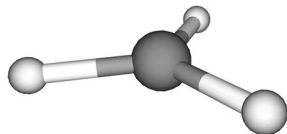
Intensitätsverteilung



CH₃ Geometrie

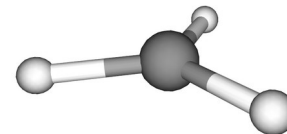
CH₃· Radikal, D_{3h}

Hirota (1982) High-Res IR:
 $r_0(\text{C-H}) = 1.079009(27) \text{ \AA}$
 $r_e(\text{C-H}) = 1.0767 \text{ \AA}$



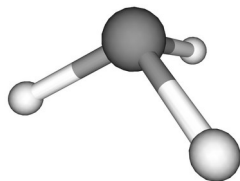
CH₃⁺ Kation, D_{3h}

Crofton (1988) High-Res IR:
 $r_0(\text{C-H}) = 1.095(4) \text{ \AA}$
 $r_e(\text{C-H}) = 1.087 \text{ \AA}$



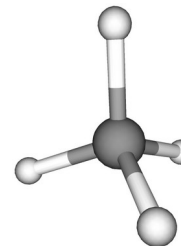
CH₃⁻ Anion, C_{3v}

Theorie, ae-CCSD(T)/cc-pwCVQZ
 $r_e(\text{C-H}) = 1.111 \text{ \AA}$
 $\alpha(\text{H-C-H}) = 104.0^\circ$



CH₄ neutral Singlet, T_d

Stanton (1999) MW, High-Res IR:
 $r_e(\text{C-H}) = 1.0869(3) \text{ \AA}$



Hyperfein-Aufspaltung

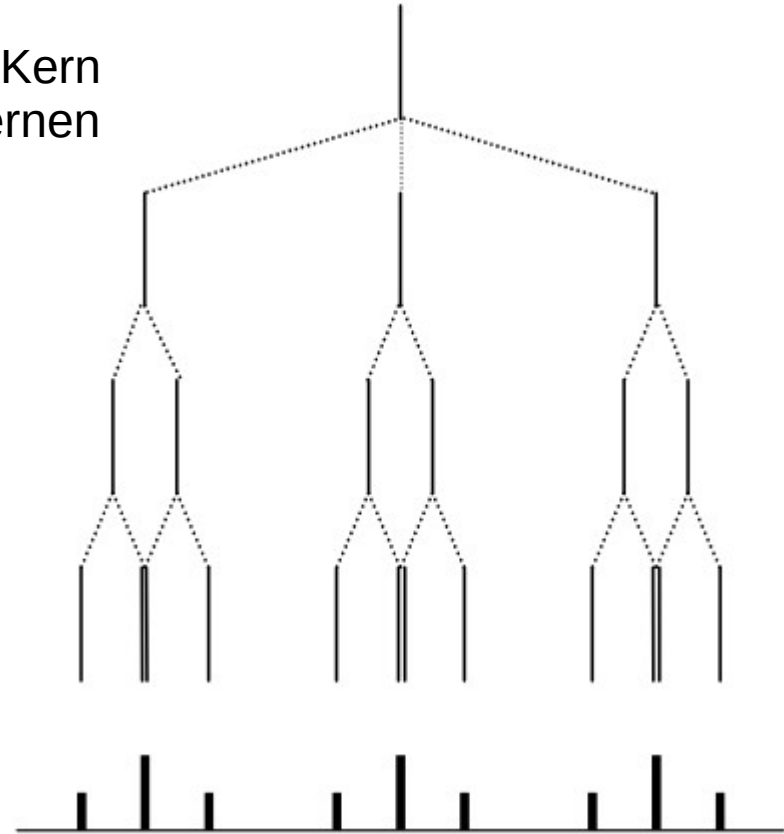
Ein Radikal bestehend aus einem Kern mit $I = 1$ und zwei äquivalenten Kernen mit $I = 1/2$

Im Allgemeinen,

Anzahl von EPR Signale:

$$n_{\text{EPR}} = \prod_i (2k_i I_i + 1)$$

k_i – Anzahl von äquivalenten Kernen mit $I = I_i$ in der Gruppe i



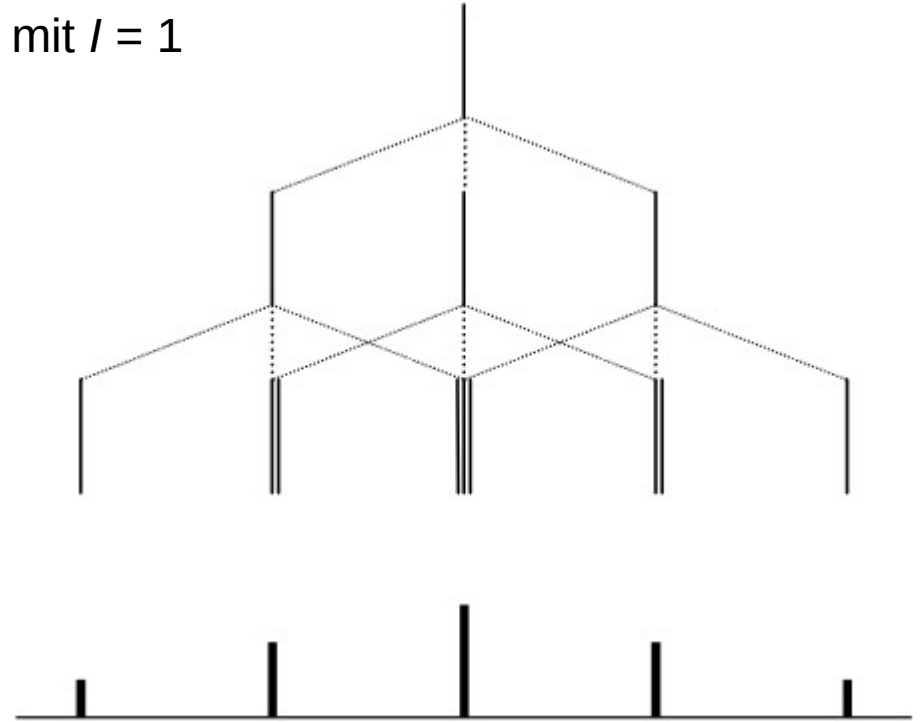
$$n = (2 \cdot 1 \cdot 1 + 1) \cdot (2 \cdot 2 \cdot \frac{1}{2} + 1) = 9$$

Hyperfein-Aufspaltung

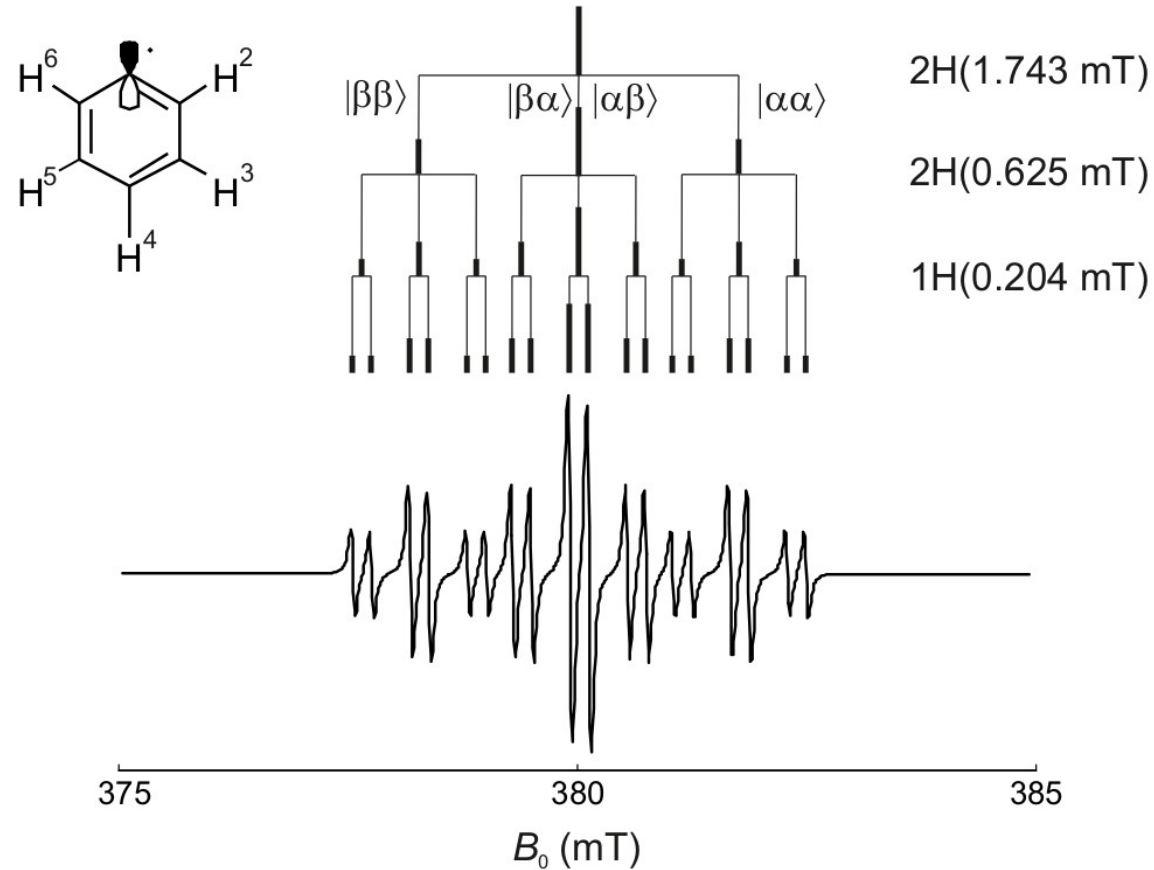
Ein Radikal bestehend aus zwei
äquivalenten Kernen mit $I = 1$

$$n_{\text{EPR}} = \prod_i (2k_i I_i + 1)$$

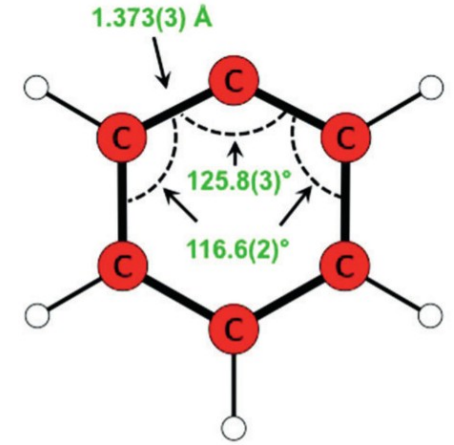
$$n = 2 \cdot 2 \cdot 1 + 1 = 5$$



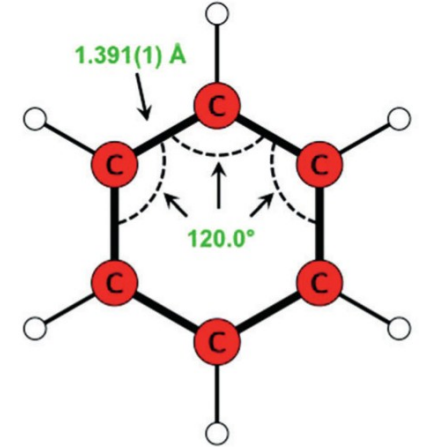
Phenyl-Radikal



Radikal, r_e^{SE} :



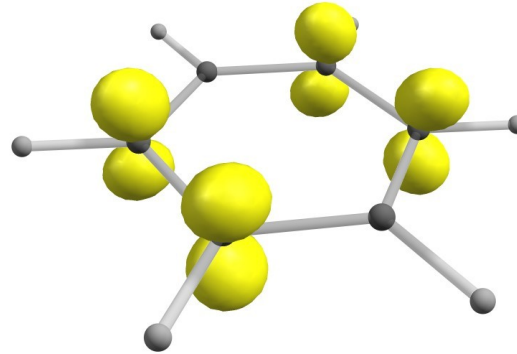
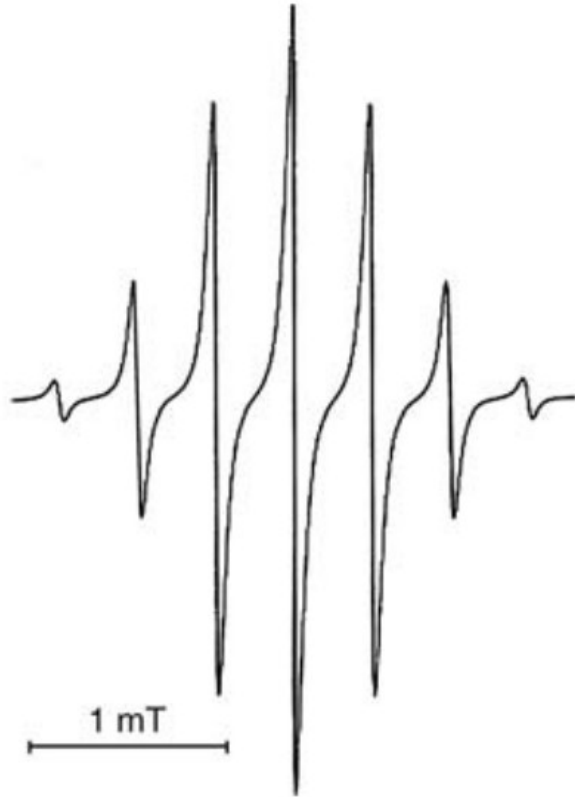
Vgl. Benzol:



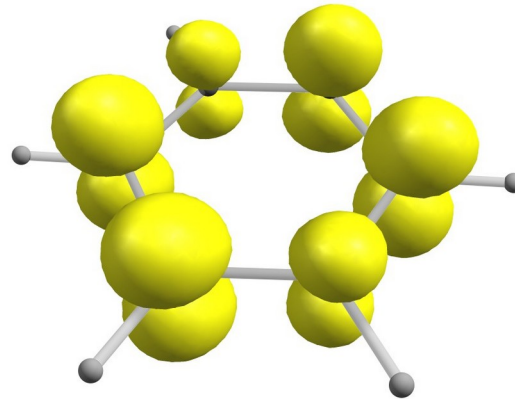
O. Martinez et al., *Angew. Chem. Int. Ed.* 2015, 54, 1808.

Benzol Radikal-Anion

7 Signale wegen $6 \times {}^1\text{H}$



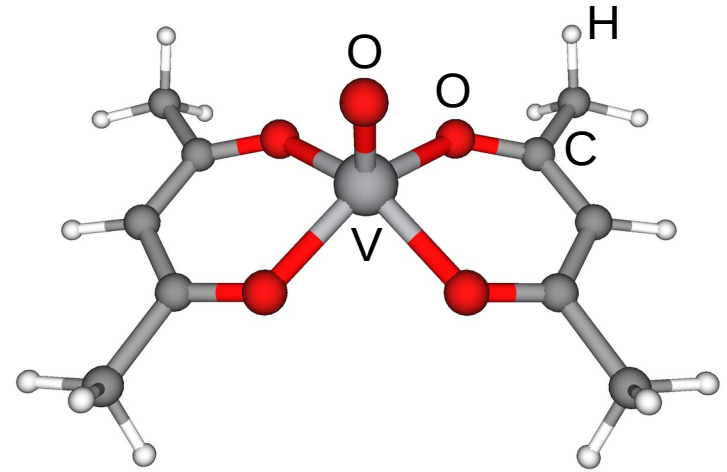
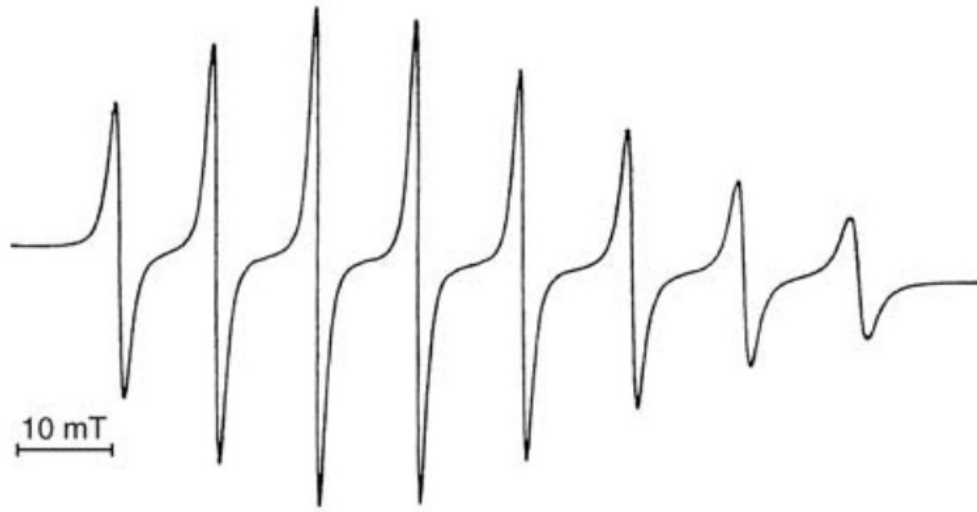
Spindichte (UKS-Theorie)



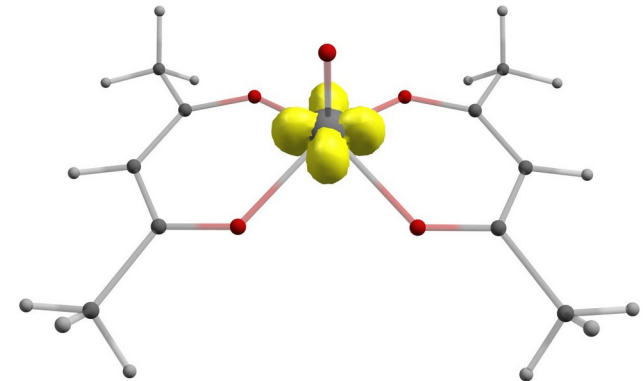
Besser:
FOD (Fractional Occupation
Number Weighted Electron
Density)

$\text{VO}(\text{acac})_2$

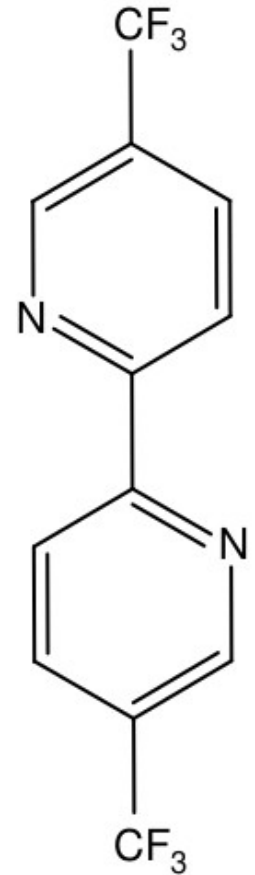
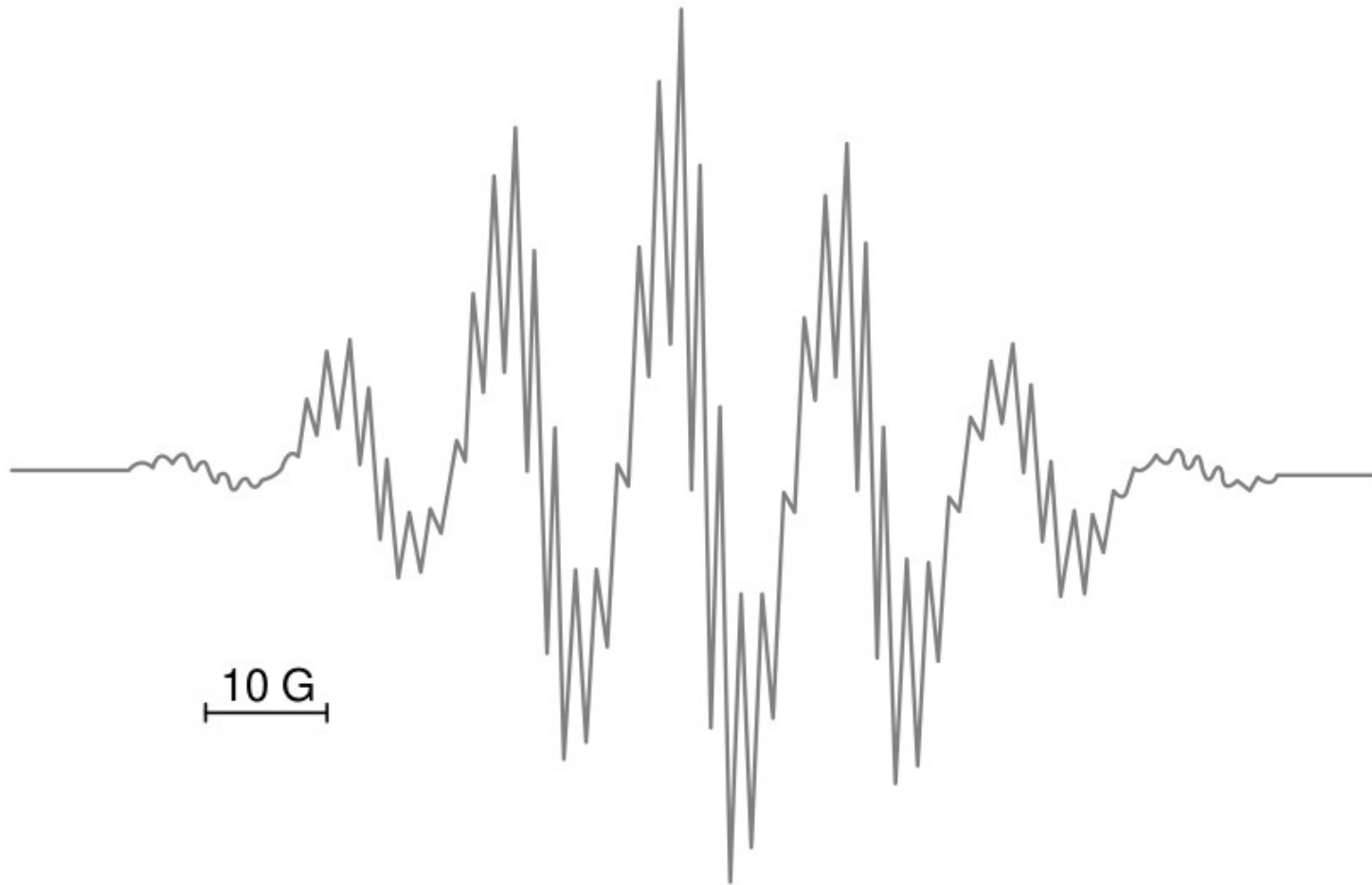
Oktett wegen ^{51}V (100 %), $I = 7/2$



Spindichte:

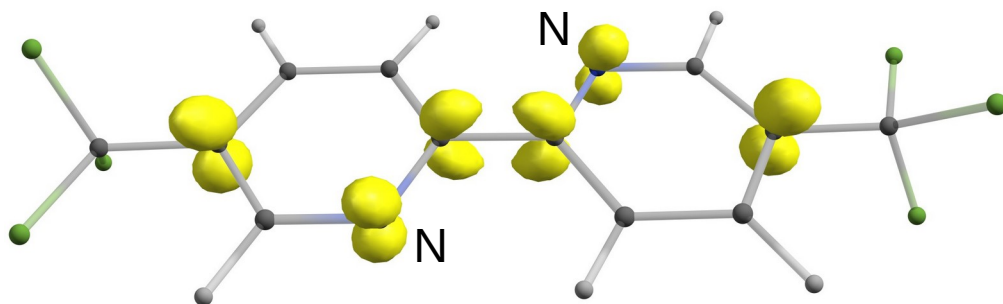


5,5'-(CF₃)₂-2,2'-bipyridin Radikal-Anion

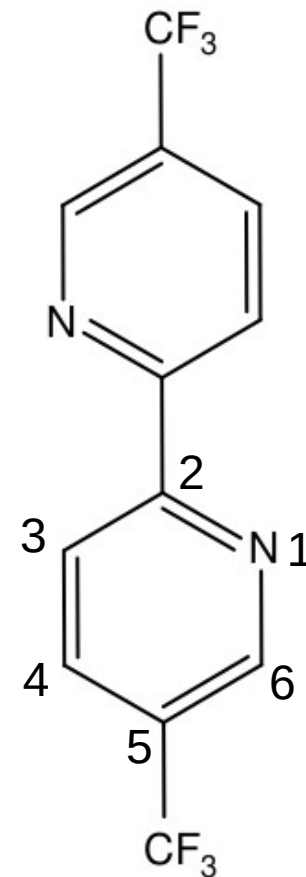


5,5'-(CF₃)₂-2,2'-bipyridin Radikal-Anion

Spindichte:

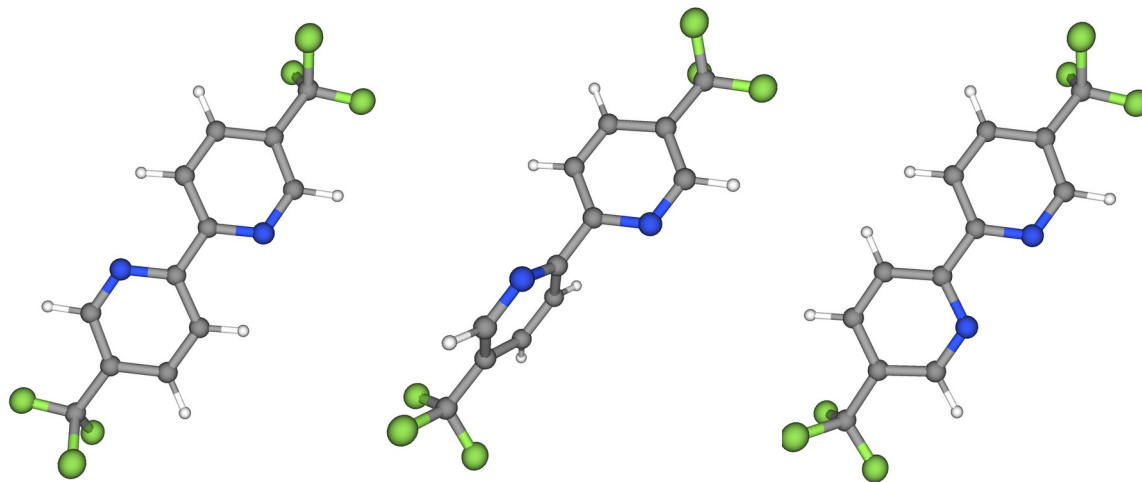


Coupling constant/G	Experimental	Assignment
$a (2 \times {}^{14}\text{N})$	1.61	ring ¹⁴ N
$a (3 \times {}^{19}\text{F})$	13.19	CF ₃ ¹⁹ F
$a (4 \times {}^1\text{H})$	1.61	4,4' ¹ H 3,3' ¹ H
$a (2 \times {}^1\text{H})$	0.52	6,6' ¹ H
g_{iso}	2.0035	

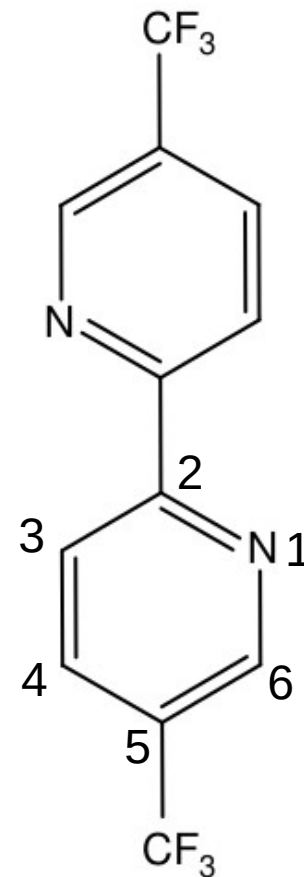


Geometrie-Abhängigkeit

Die 90°-Geometrie kann ausgeschlossen werden, weil:



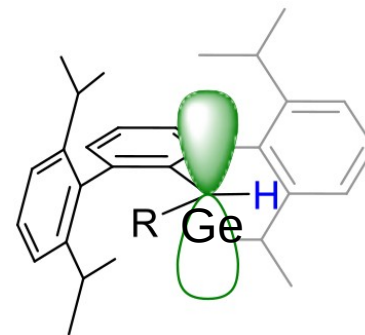
	Gemessen	Gerechnet, anti	Gerechnet, 90°	Gerechnet, syn
$a_{\text{av}} (^{14}\text{N})$	1.61	1.40	3.86	1.43
$a_{\text{av}} (^{19}\text{F})$	13.19	16.17	13.52	16.19
$a (^{1}\text{H}4)$	1.61	-1.29	-4.59	-1.23
$a (^{1}\text{H}3)$		-1.28	1.22	-1.14
$a (^{1}\text{H}6)$	0.52	0.76	0.29	0.72
g_{iso}	2.0035	2.0031	2.0020	2.0031



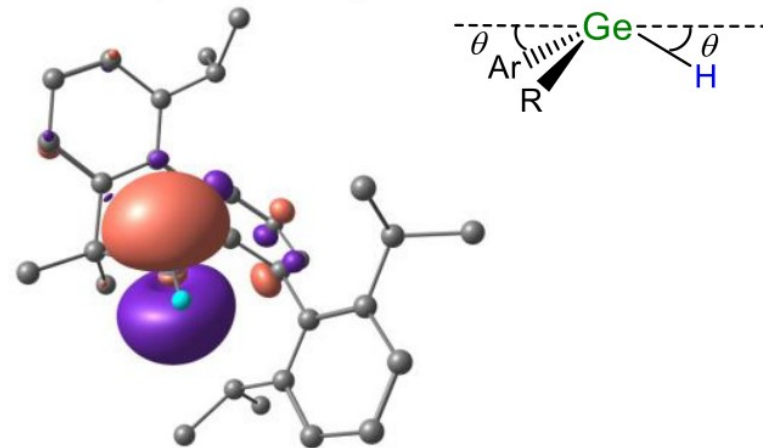
Geometrie-Abhängigkeit: Ar(R)Ge-H

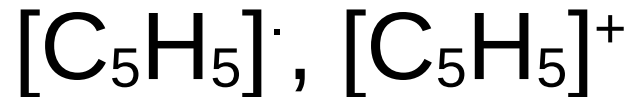
DFT-predicated hyperfine values

Ge geometry	out-of-plane angle (θ)	$A^{73}\text{Ge}$, MHz	$A^{1}\text{H}_{\text{hydride}}$, MHz
pyramidal model	22°	$[-214, -216, -306]$, $a_{\text{iso}} = -245$	$[+101, +108, +112]$, $a_{\text{iso}} = +107$
planar model	0°	$[-46, -162, -49]$, $a_{\text{iso}} = -85.6$	$[-40, -43, -58]$, $a_{\text{iso}} = -47$
exp.	$\approx 0^\circ$	$[-10, -90, -10]$, $a_{\text{iso}} = -36.6$	$[-23.0, -20.5, -31.5]$, $a_{\text{iso}} = -25.0$



SOMO of planar Ge^{III} -hydride model





nature chemistry

Article

<https://doi.org/10.1038/s41557-023-01417-5>

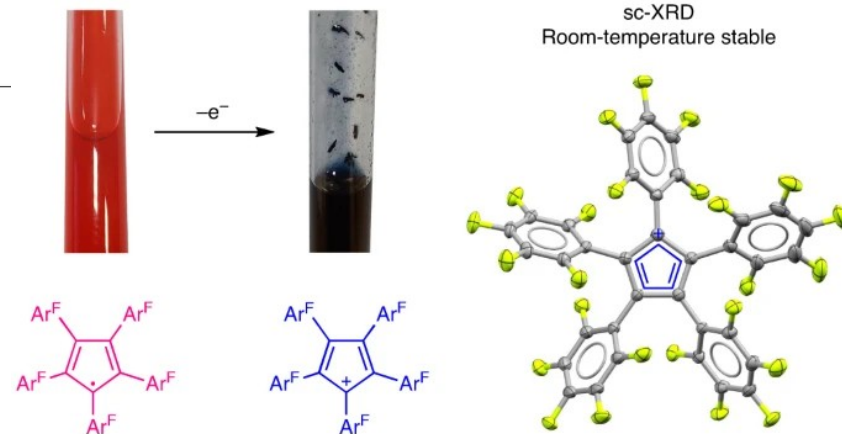
Structural characterization and reactivity of a room-temperature-stable, antiaromatic cyclopentadienyl cation salt

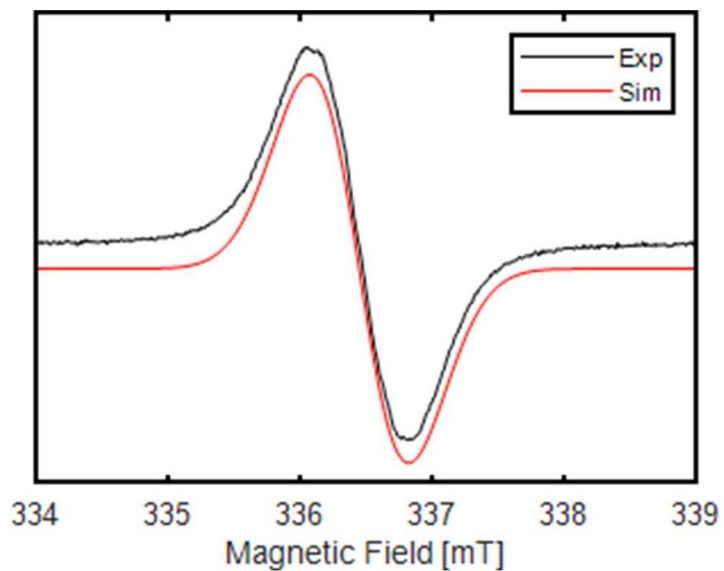
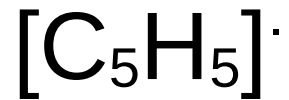
Received: 17 March 2023

Accepted: 7 December 2023

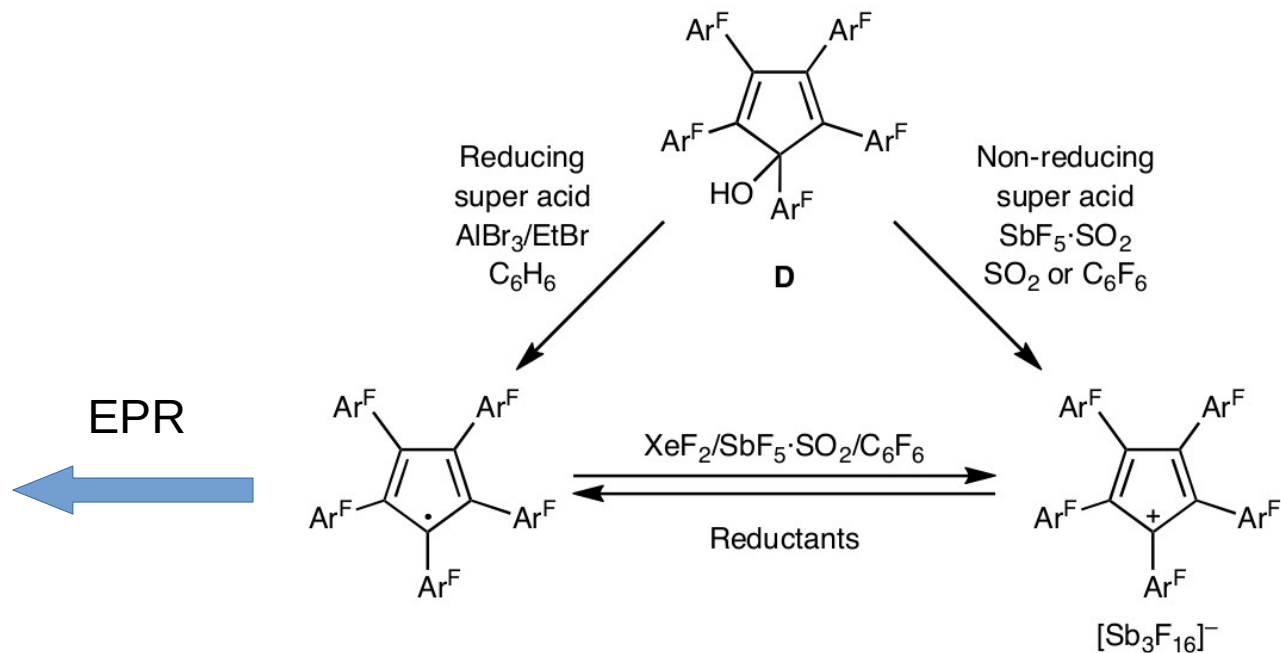
Published online: 15 January 2024

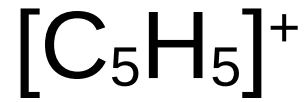
Yannick Schulte¹, Christoph Wölper¹, Susanne M. Rupf²,
Moritz Malischewski², Daniel J. SantaLucia³, Frank Neese³,
Gebhard Haberhauer⁴ & Stephan Schulz^{1,5}



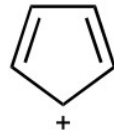
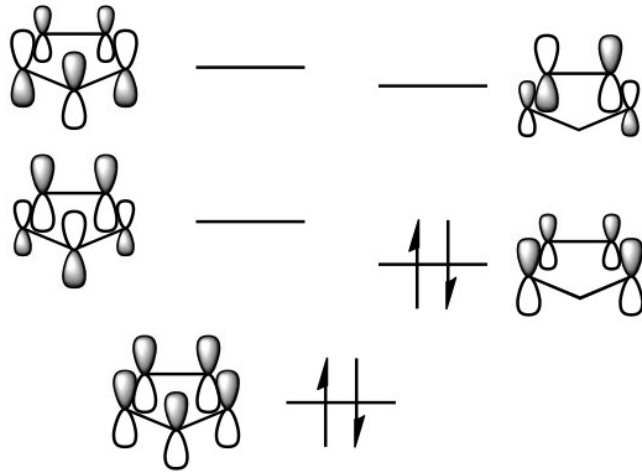


$$g = 2.033$$

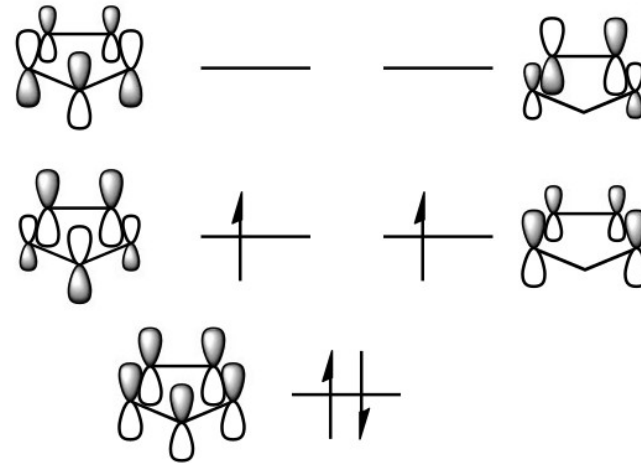




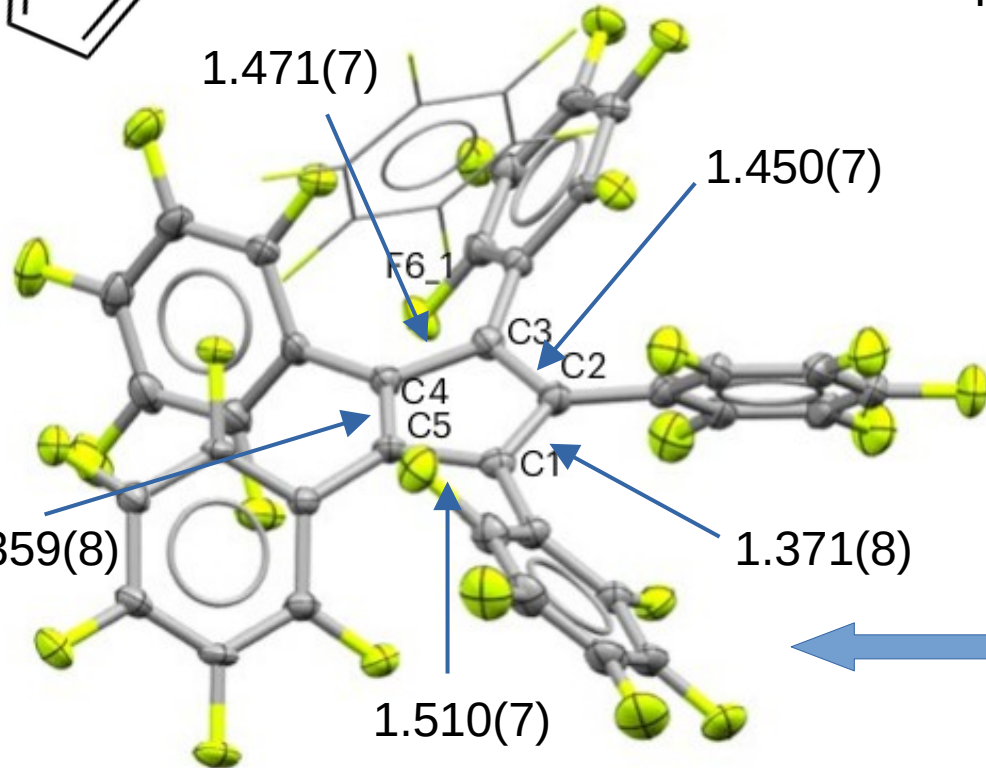
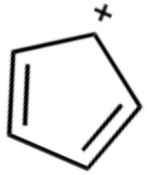
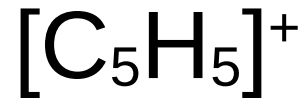
Singlet



Triplet



Das System passt besser zum Experiment, weil es kein EPR Signal ergibt.



Harmonic oscillator model of aromaticity (HOMA)

$$\text{HOMA} = 1 - \frac{\alpha}{n} \sum_i^n (R_{\text{opt}} - R_i)^2$$

α – empirische Konstante 257.7 \AA^{-2}
 R_{opt} – optimal $r(\text{C-C}) = 1.388 \text{ \AA}$

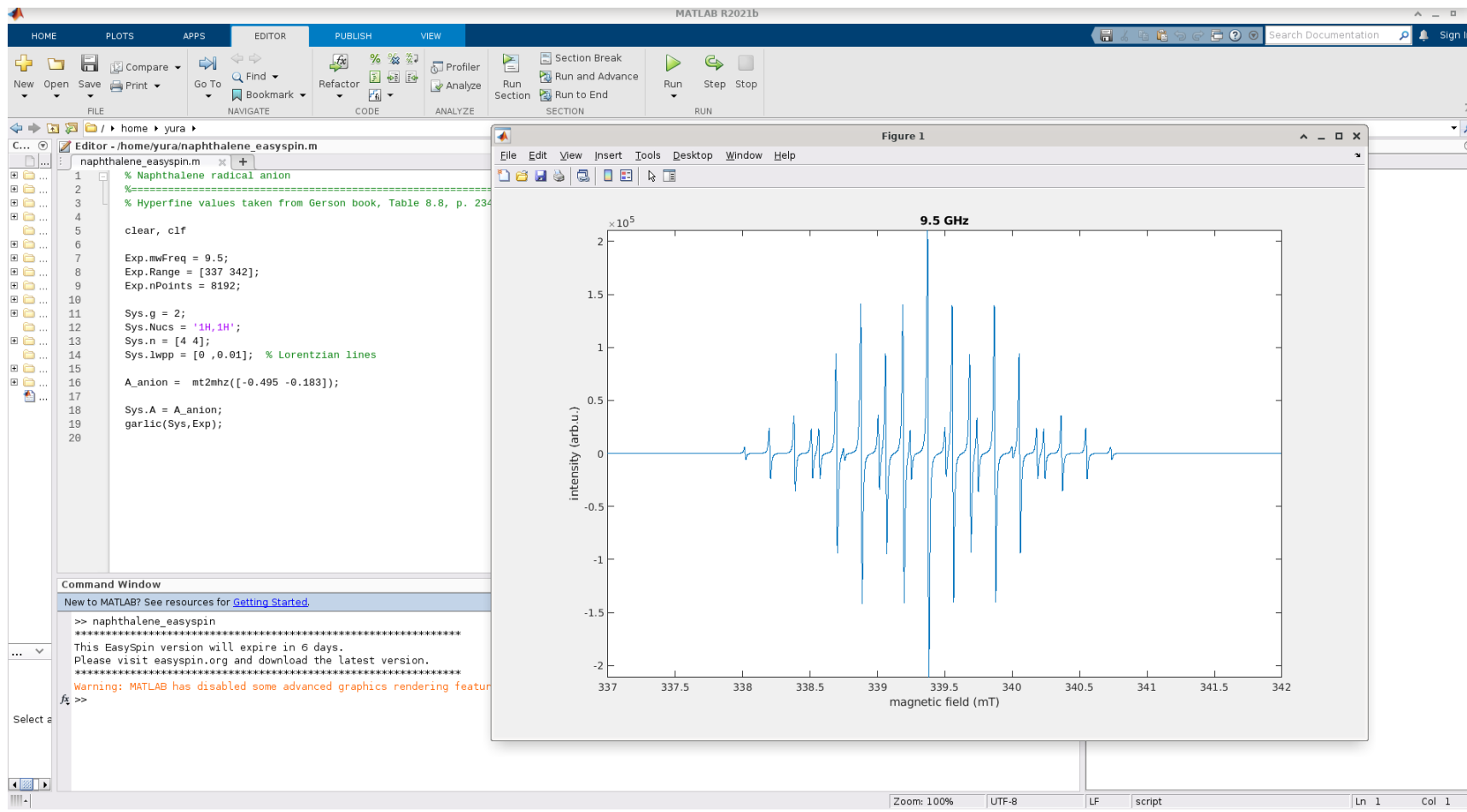
HOMA = 1 für aromatische Systeme
 HOMA = 0 für nichtaromatische Systeme
 HOMA < 0 für antiaromatische Systeme

← HOMA = -0.39

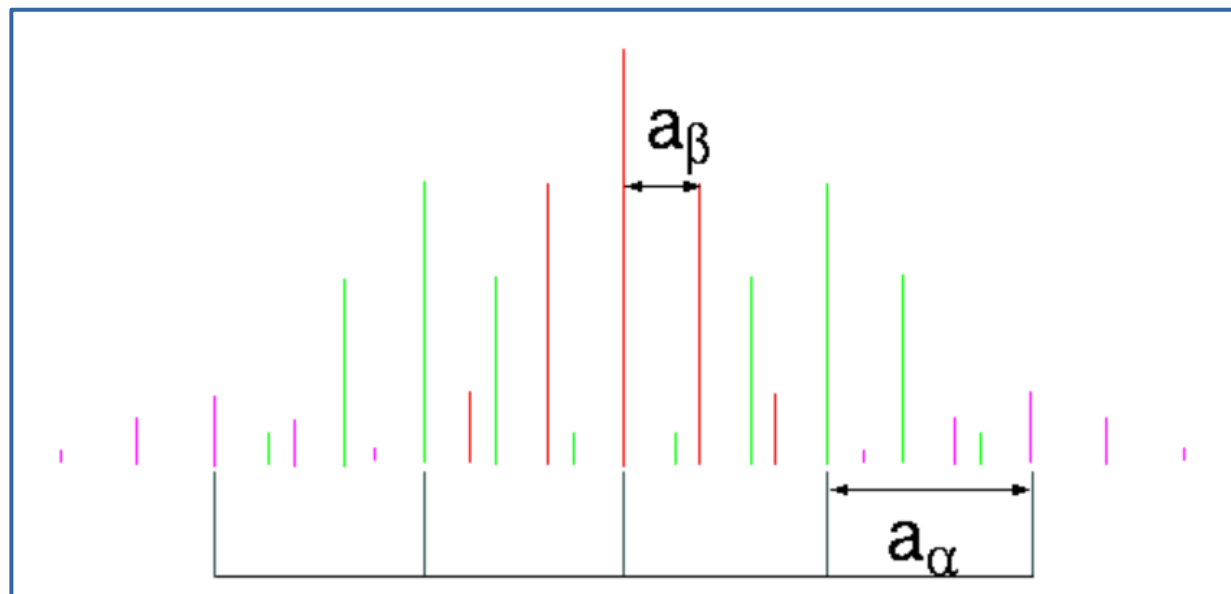
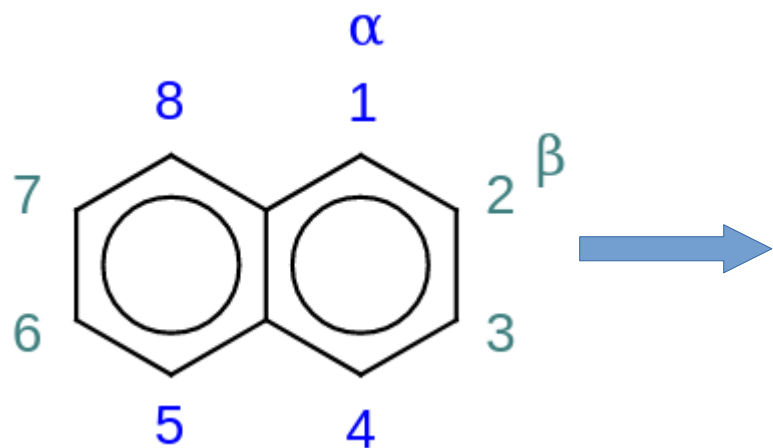
(Es gibt jedoch noch eine weitere
 Kristallmodifikation mit HOMA=0.01)
 (Theor. HOMA für Triplet ist 0.49)

Modellierung / Verfeinerung

EasySpin Software

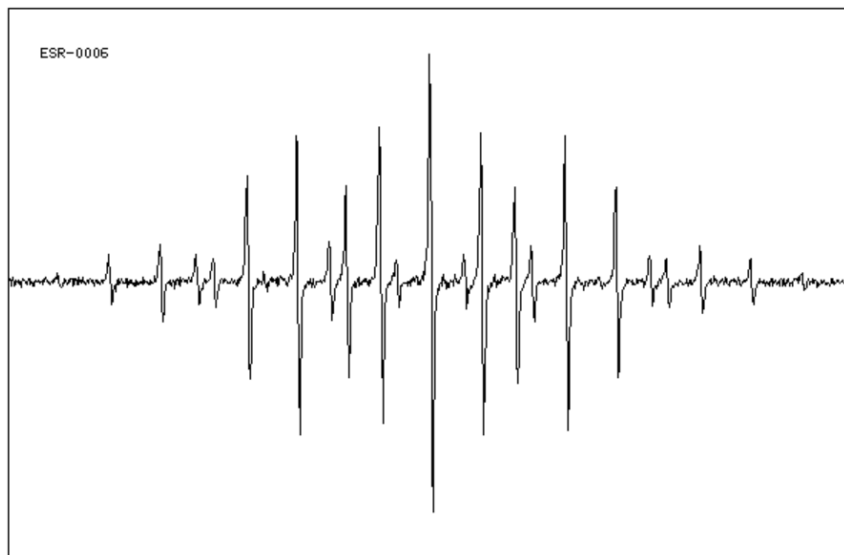


Beispiel: Naphthalin Anion-Radikal

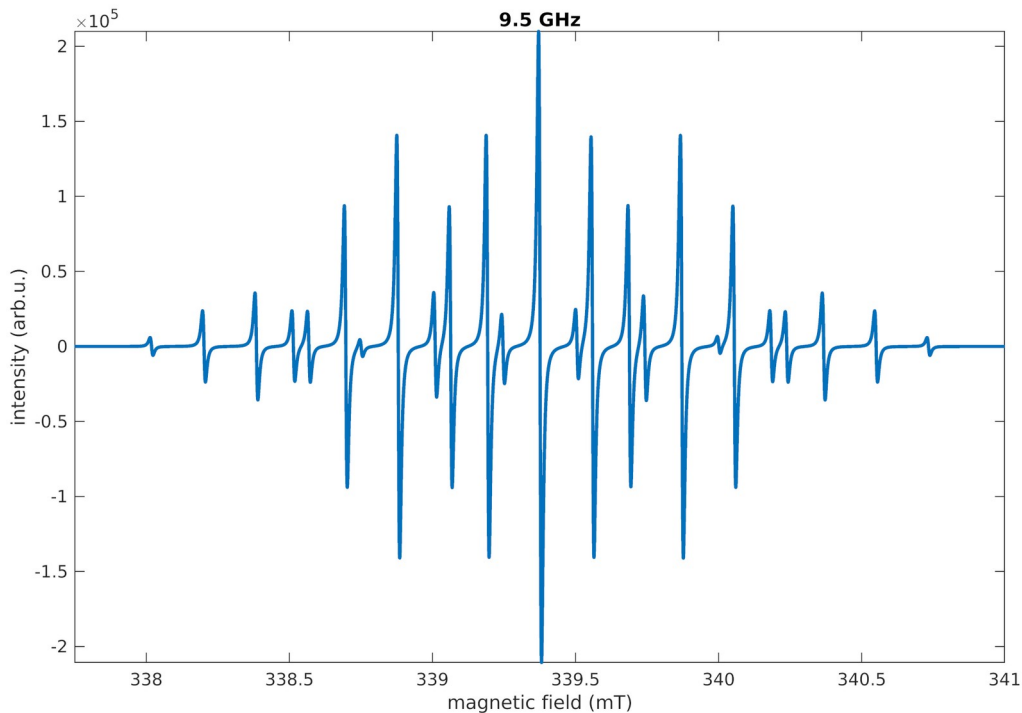


Beispiel: Naphthalin Anion-Radikal

Experiment



Modell: $g = 2.0$, $a_1 = -0.495$ mT, $a_2 = -0.183$ mT



Weitere Themen

In EPR sind auch sehr wichtig:

- Anisotropie
- e-Spin-Spin-Kopplung (Nullfeldaufspaltung)
- Multiresonanz-Methoden

Molekül des Tages: $[\text{Xe}_2]^+$

The Dixenon(1+) Cation: Formation in the Condensed Phases and Characterization by ESR, UV-Visible, and Raman Spectroscopy†

Dean R. Brown,^{1a} Martin J. Clegg,^{1a} Anthony J. Downs,^{*,1a} Richard C. Fowler,^{1a} Alan R. Minihan,^{1a} James R. Norris,^{1b} and Lawrence Stein^{1b}

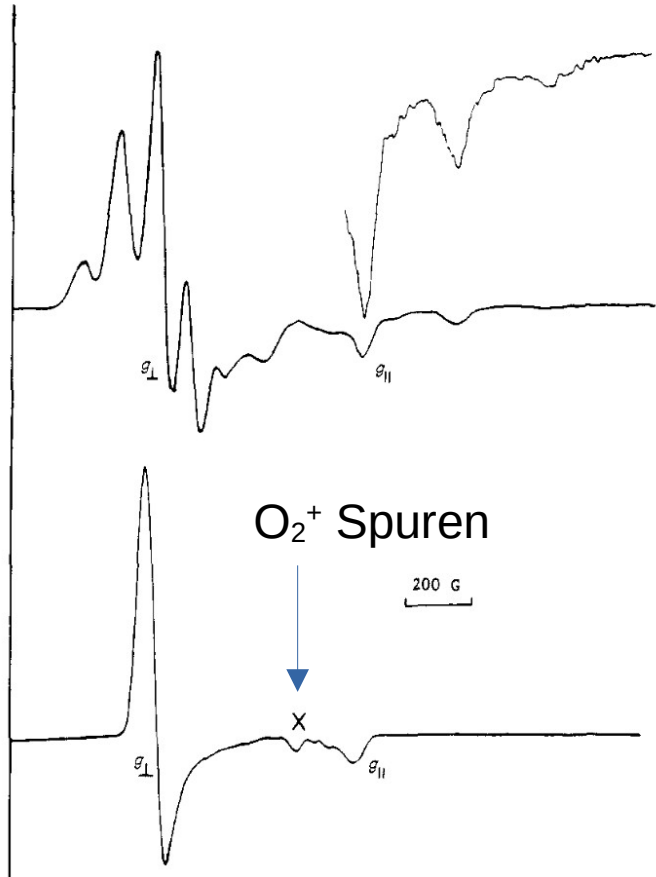
Inorganic Chemistry Laboratory, University of Oxford, Oxford, OX1 3QR, U.K., and Chemistry Division, Argonne National Laboratory, Argonne, Illinois 60439



D. R. Brown, M. J. Clegg, A. J. Downs, R. C. Fowler, A. R. Minihan, J. R. Norris, L. Stein, *Inorg. Chem.* 1992, 31, 5041–5052.

L. Stein, J. R. Norris, A. J. Downs, A. R. Minihan, *J. Chem. Soc., Chem. Commun.* 1978, 502–504.

[Xe₂]⁺: EPR



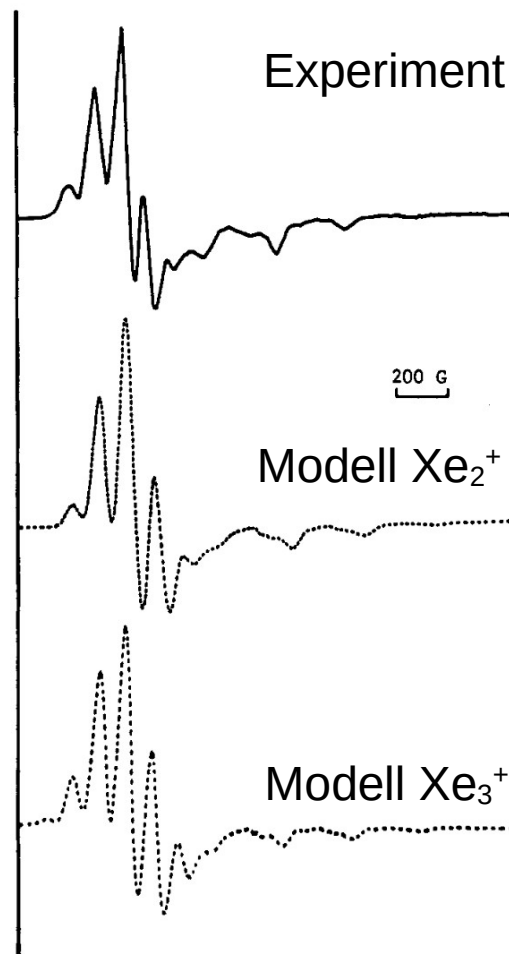
	%	Spin
¹²⁴ Xe	0.09	0
¹²⁶ Xe	0.09	0
Natürliches Gemisch von Xe		
¹²⁸ Xe	1.92	0
¹²⁹ Xe	26.44	1/2
¹³⁰ Xe	4.08	0
¹³¹ Xe	21.18	3/2
¹³² Xe	26.89	0
¹³⁴ Xe	10.44	0
¹³⁶ Xe	8.87	0

Angereichertes ¹³⁶Xe (*I* = 0) wird in Reaktion verwendet

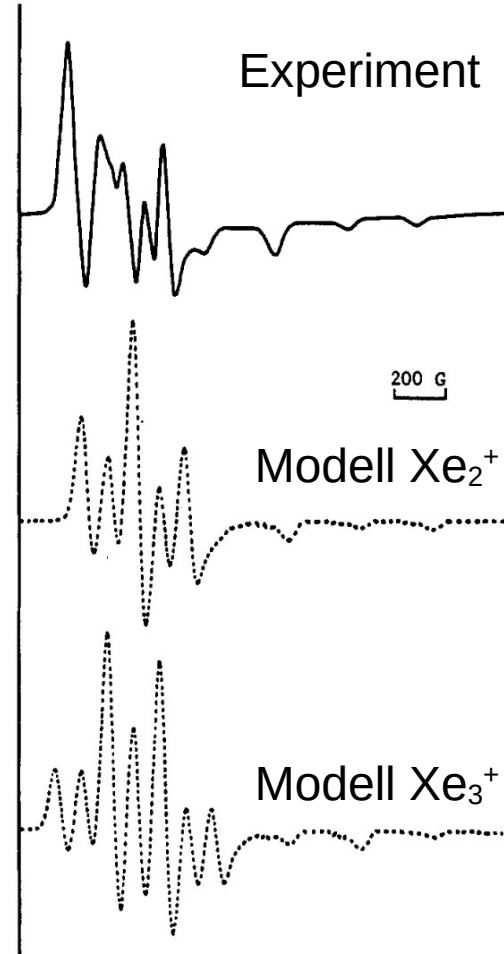
Nur [Xe_{*n*}]⁺ Radikale sind möglich!

$[\text{Xe}_2]^+$: EPR

Natürliches
Gemisch
von Xe



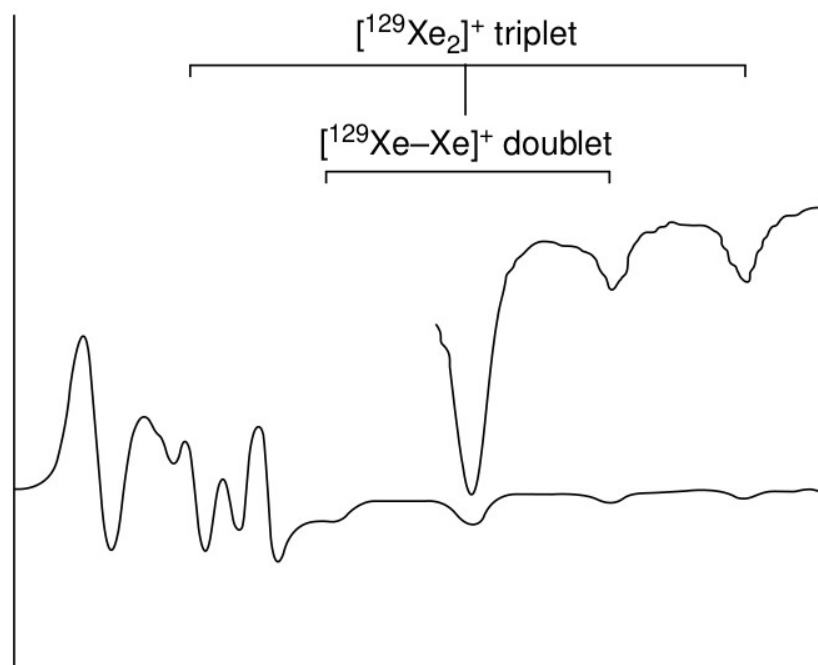
Angereichertes
 ^{129}Xe ($I = 1/2$) wird
in Reaktion
verwendet



$[\text{Xe}_2]^+$: EPR

Angereichertes
 ^{129}Xe ($I = 1/2$) wird
in Reaktion
verwendet

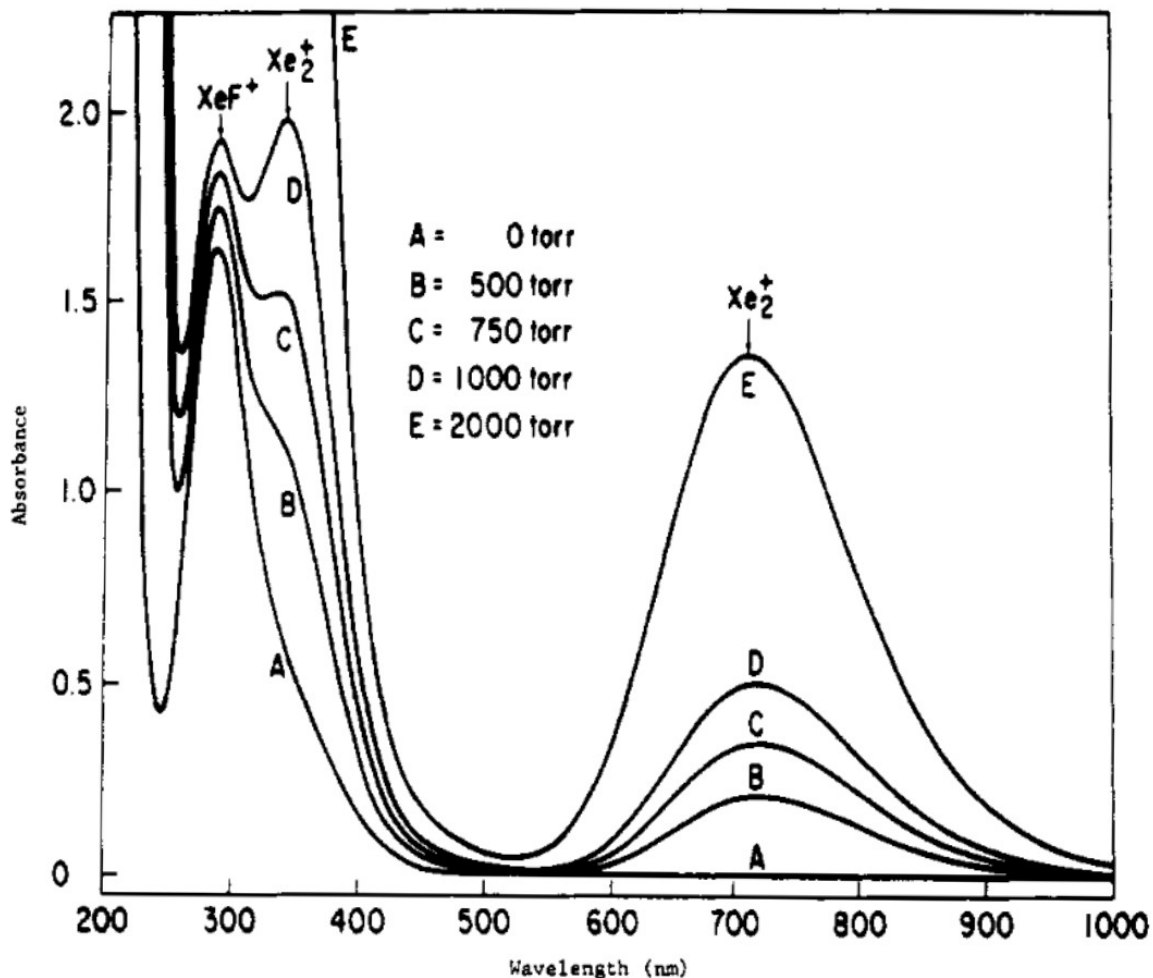
^{129}Xe ($I = 1/2$); ^{131}Xe ($I = 3/2$)



Isotopomer	Natural abundance	EPR multiplicity (g_{\perp})
$^*\text{Xe}^*\text{Xe}$	27.5%	singlet
$^{129}\text{Xe}^*\text{Xe}$	27.7%	doublet
$^{131}\text{Xe}^*\text{Xe}$	22.2%	quartet
$^{129}\text{Xe}^{129}\text{Xe}$	7.0%	triplet
$^{131}\text{Xe}^{131}\text{Xe}$	4.5%	septet
$^{129}\text{Xe}^{131}\text{Xe}$	11.2%	doublet of quartets

*Xe represents all isotopes of xenon with $I = 0$.

$[\text{Xe}_2]^+$: UV-Vis



Lösung von
 $[\text{XeF}]^+[\text{Sb}_2\text{F}_{11}]^-$ in $\text{SbF}_5 + \text{Xe}$ Gas

Neue Banden bei $\lambda = 335$ und 715 nm
herrühren von gleicher Quelle.

[Xe₂]⁺: Raman

In Lösung von [XeF]⁺[Sb₂F₁₁]⁻

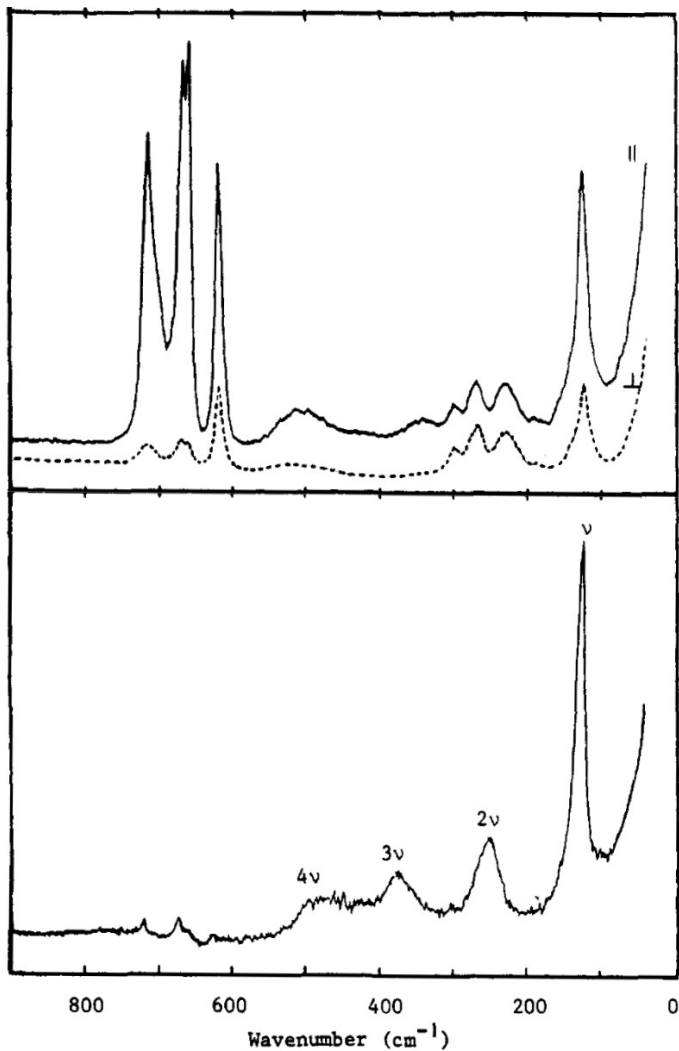
Raman bei $\lambda = 514.5 \text{ nm}$

Streckschwingung bei
 $\nu = 123 \text{ cm}^{-1}$
(+ Obertöne)

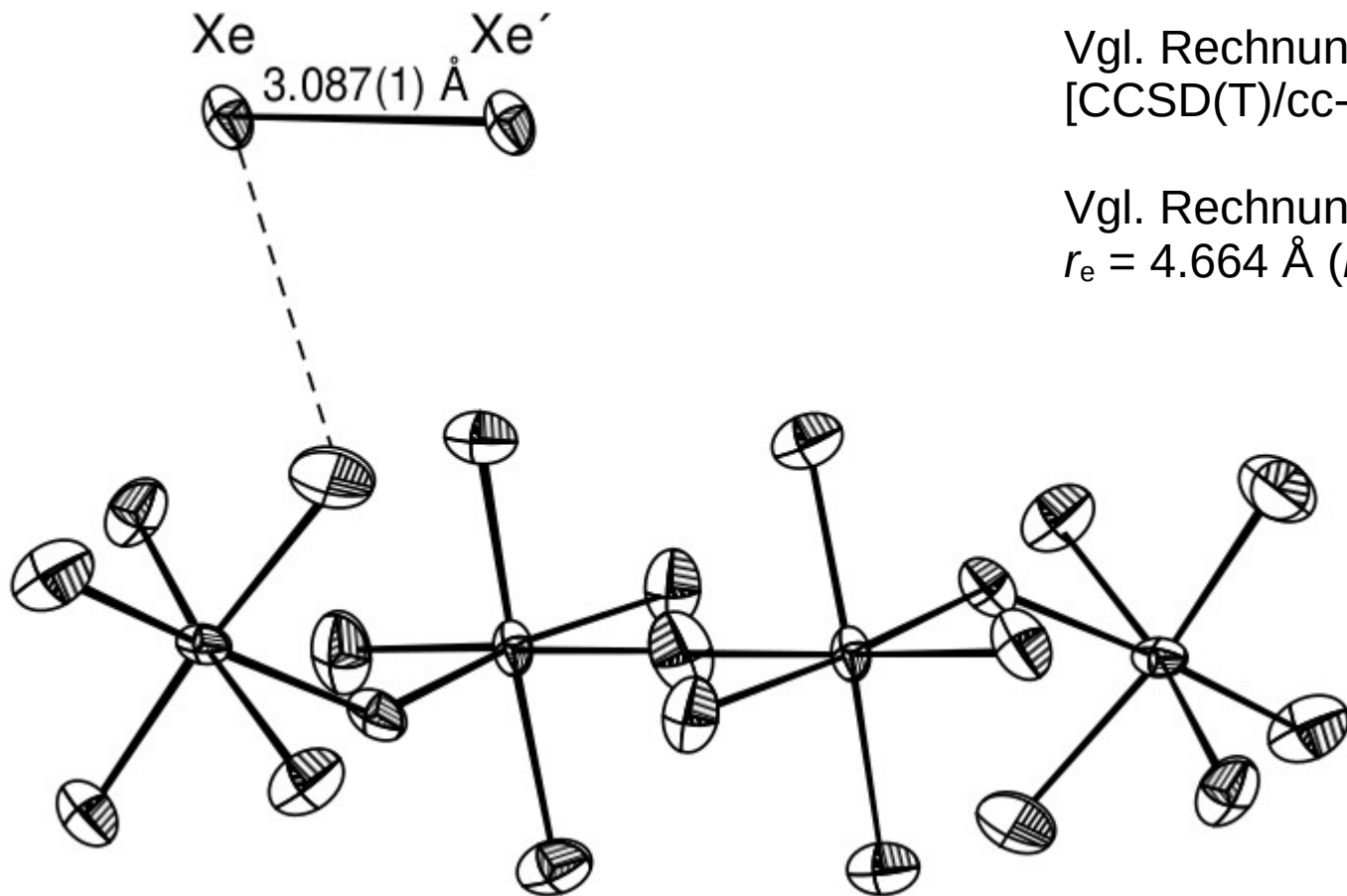
Depolarisation 1:3

Resonanz-Raman
bei $\lambda = 676.4 \text{ nm}$

Isotopeneffekt:
mit ¹³⁶Xe
 $\Delta\nu = 2.4 \pm 0.9 \text{ cm}^{-1}$,
Gerechnet $\Delta\nu = 2.3 \text{ cm}^{-1}$



$[\text{Xe}_2]^+[\text{Sb}_4\text{F}_{21}]^-$: XRD



Vgl. Rechnung (freies $[\text{Xe}_2]^+$) $r_e = 3.068 \text{ \AA}$
[CCSD(T)/cc-pwCVQZ-PP]

Vgl. Rechnung, freies Xe_2 VdW-Komplex:
 $r_e = 4.664 \text{ \AA}$ (r_0 wird noch viel größer!)

T. Drews and K. Seppelt,
Angew. Chem. 109
(1997) 264.

Entwicklung der Geschichte: $[\text{Xe}_4]^+$

DOI: 10.1002/anie.200701688

The Blue Xe_4^+ Cation: Experimental Detection and Theoretical Characterization**

Stefan Seidel, Konrad Seppelt, Christoph van Wüllen,* and Xiao Ying Sun*

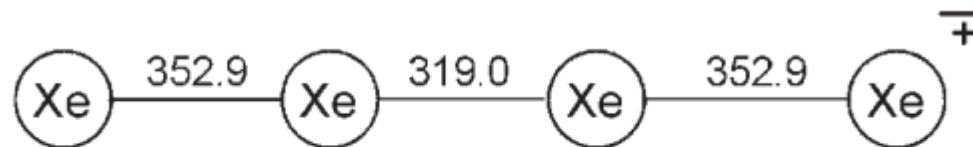
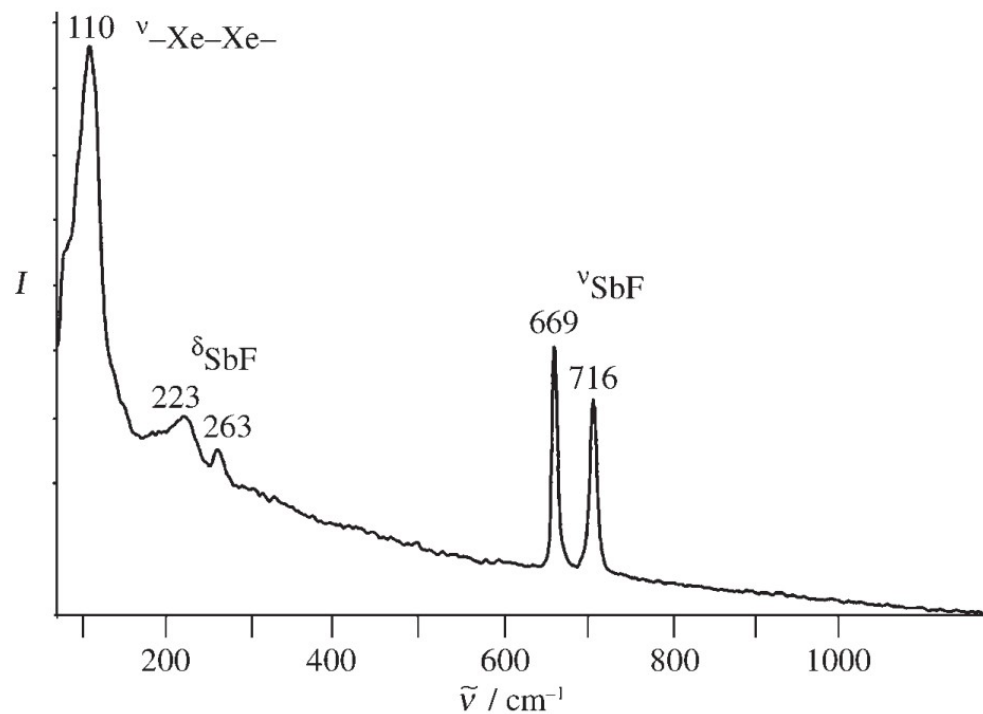
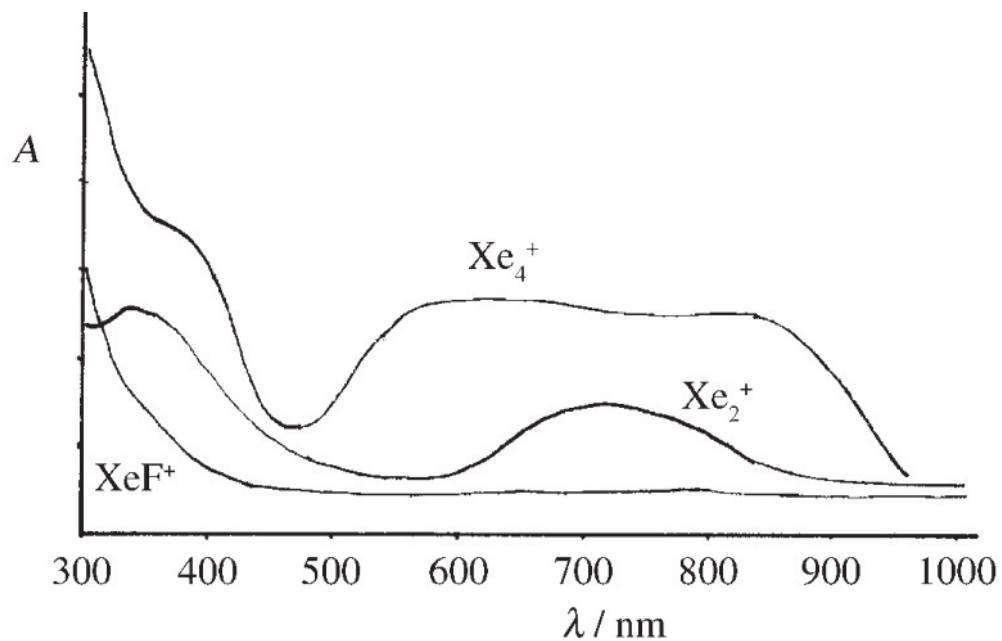
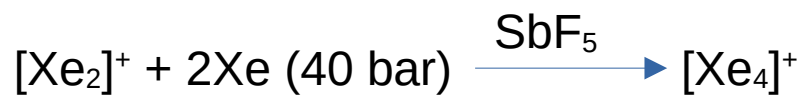
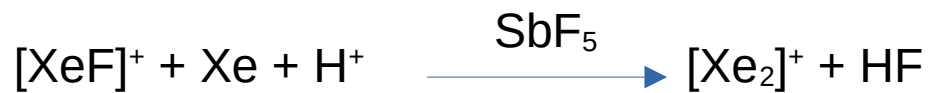


Figure 3. Structure of the Xe_4^+ ion ($D_{\infty h}$) according to our calculations (bond lengths in pm).

$[\text{Xe}_4]^+$



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