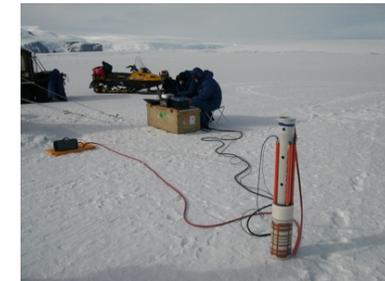
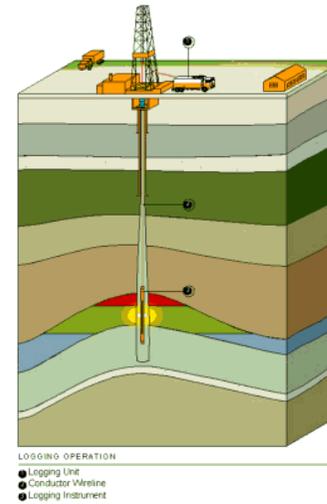
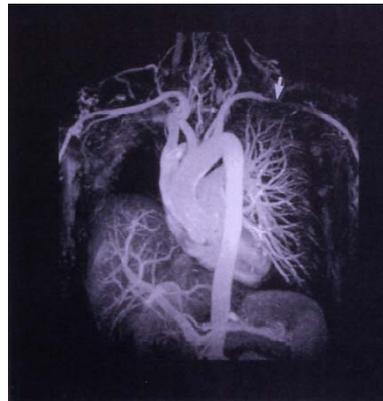
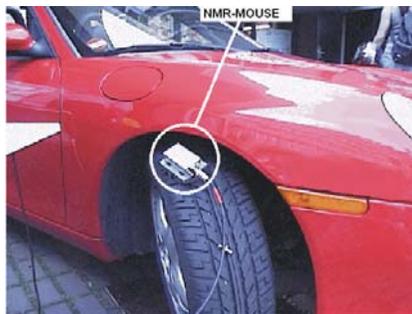
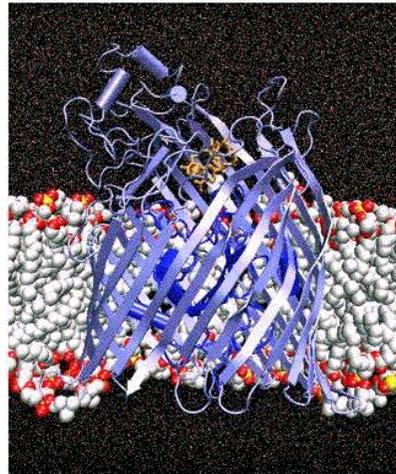
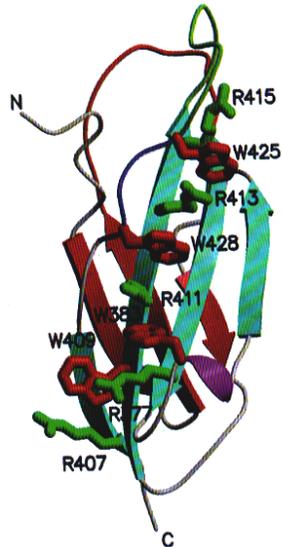




## **Festkörper NMR**

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**Nuclear Magnetic Resonance: Kernmagnetische Resonanz**



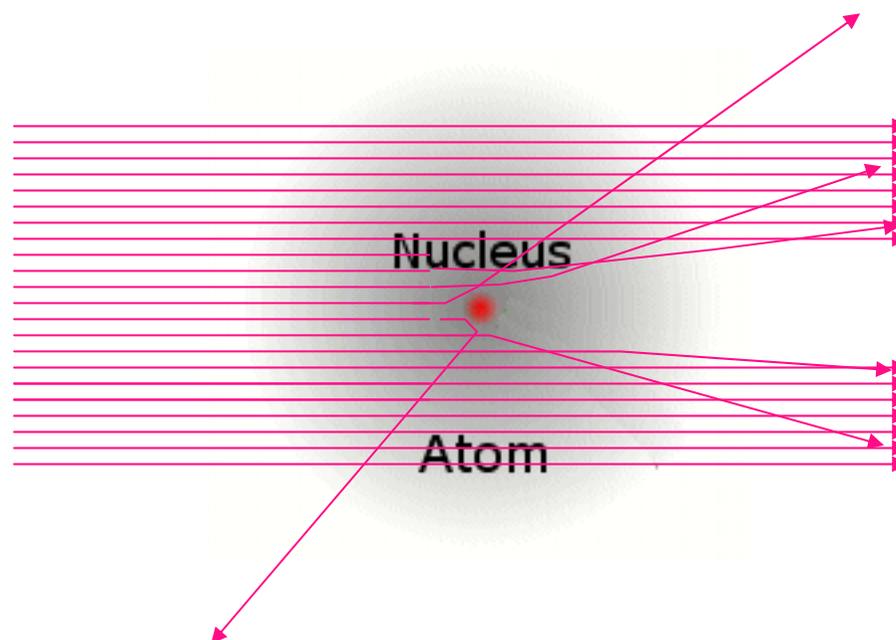
Input register	Output register
$a_1  000\rangle$	$a_1 F 1000\rangle$
$+ a_2  001\rangle$	$+ a_2 F 001\rangle$
$+ a_3  010\rangle$	$+ a_3 F 1010\rangle$
$+ a_4  011\rangle$	$+ a_4 F 011\rangle$
$+ a_5  100\rangle$	$+ a_5 F 1100\rangle$
$+ a_6  101\rangle$	$+ a_6 F 101\rangle$
$+ a_7  110\rangle$	$+ a_7 F 1110\rangle$
$+ a_8  111\rangle$	$+ a_8 F 111\rangle$

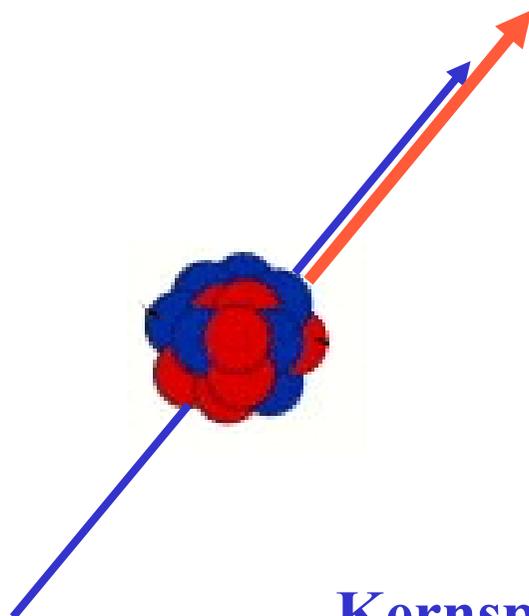
# Nuclear Magnetic Resonance: Kernmagnetische Resonanz



- 1. Einleitung und Überblick**
- 2. NMR an nicht-orientierten Proben**
- 3. NMR an orientierten Proben**







**Kernspin  
und Kernmagnetismus**



Wofgang Pauli

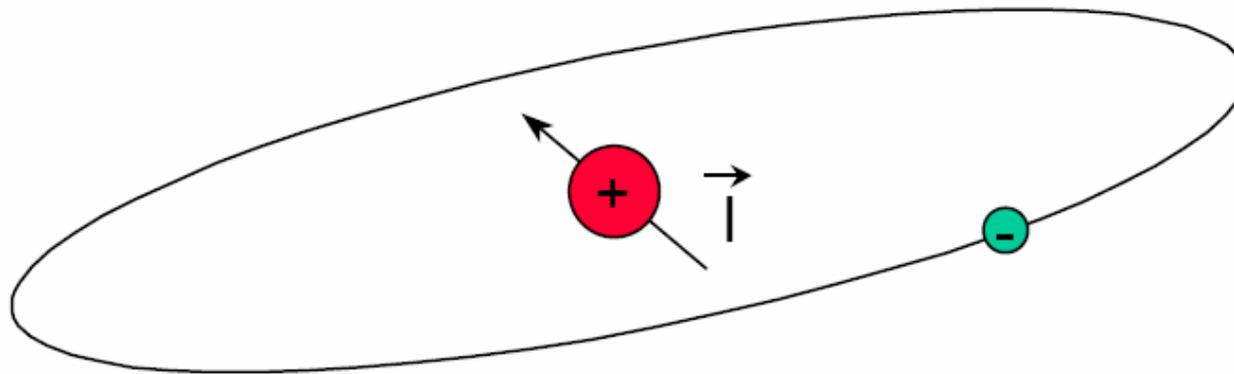
1924, Vorhersage des Kernspins

**Nobelpreis für Physik, 1945**





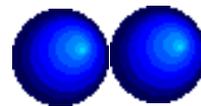
Drehimpuls  $\vec{l}$   
für  $\vec{l} \neq 0$ : magnetisches Moment  $\vec{\mu}$



$$\vec{\mu} = \gamma \vec{l} \hbar$$

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## Mikroskopische Magnete



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## Mikroskopische Magnete in makroskopischen Magneten



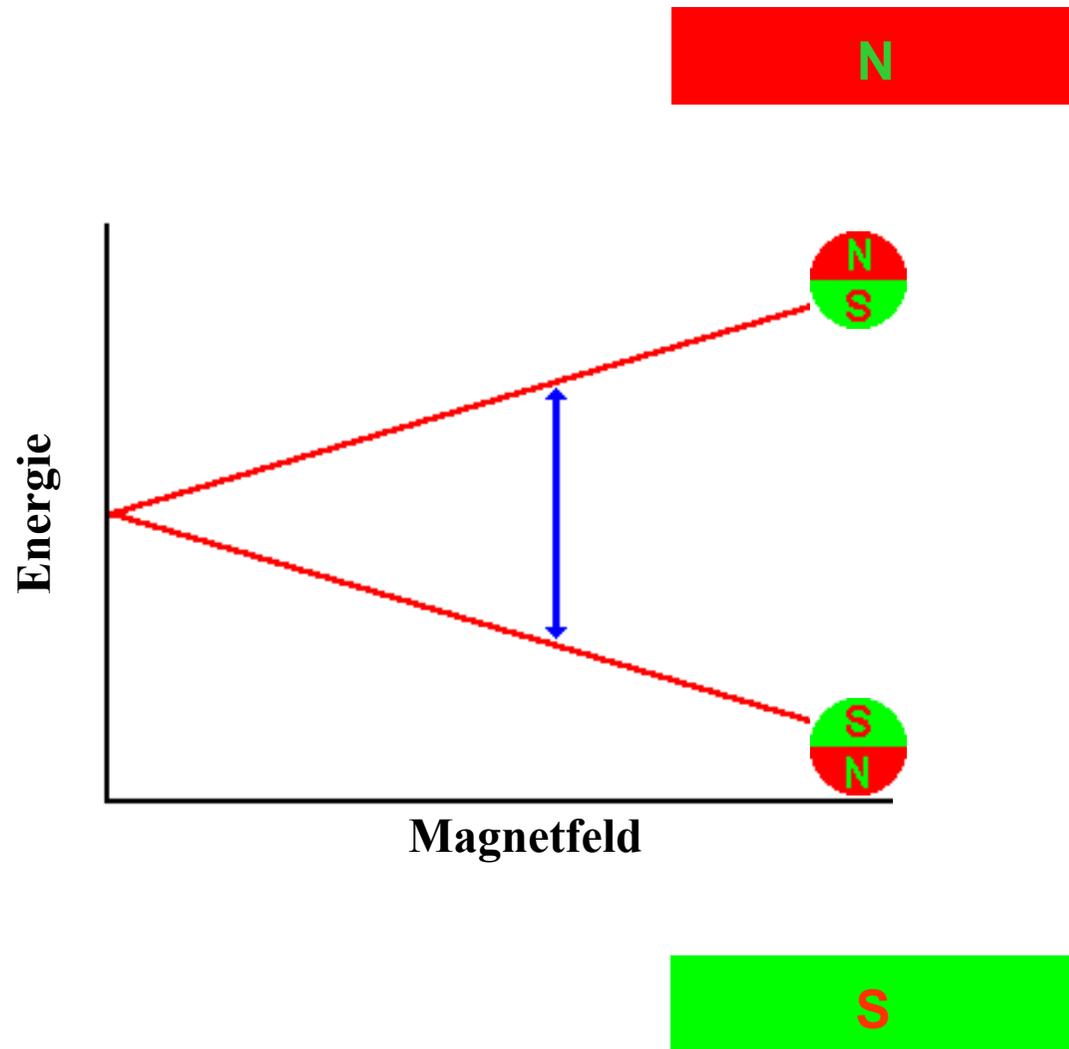
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## Mikroskopische Magnete in makroskopischen Magneten

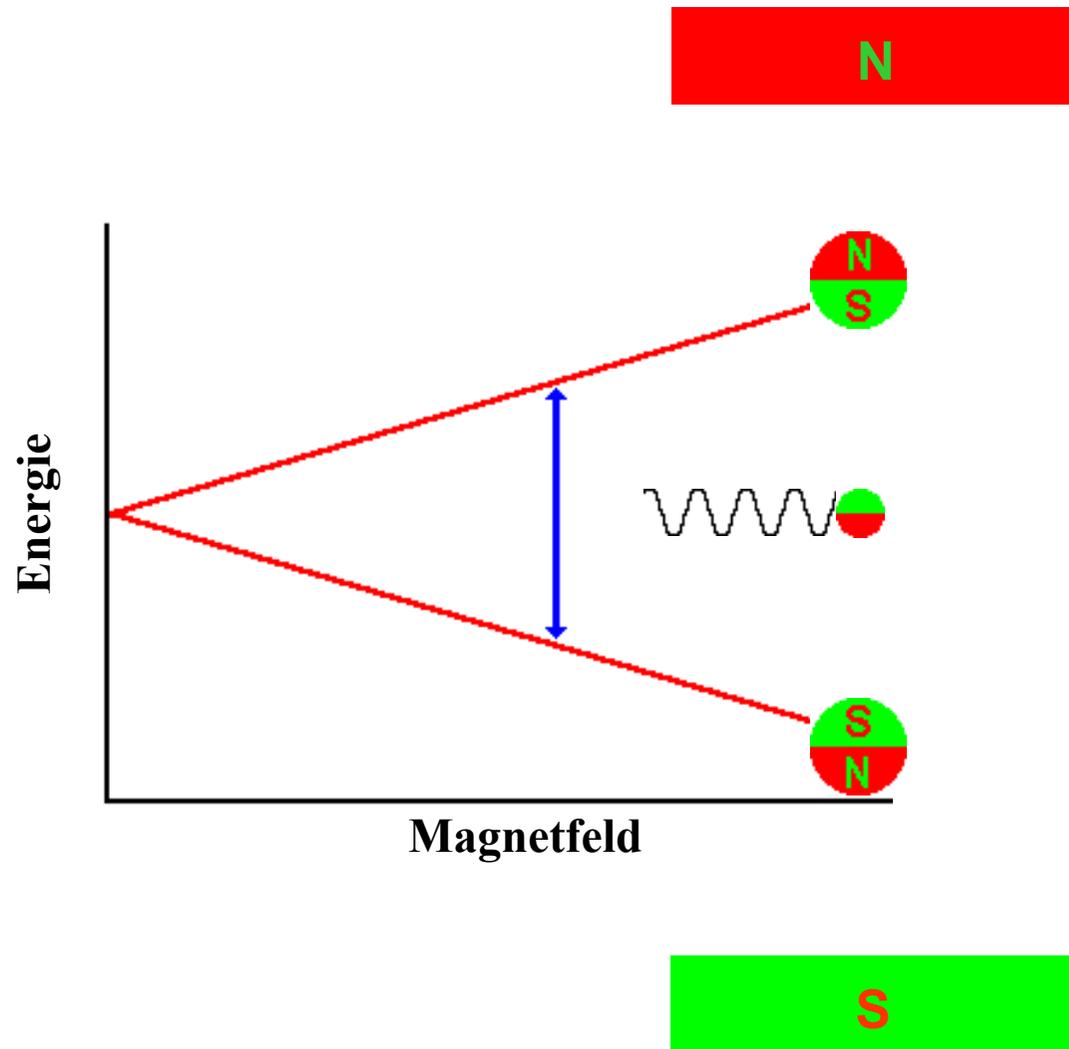


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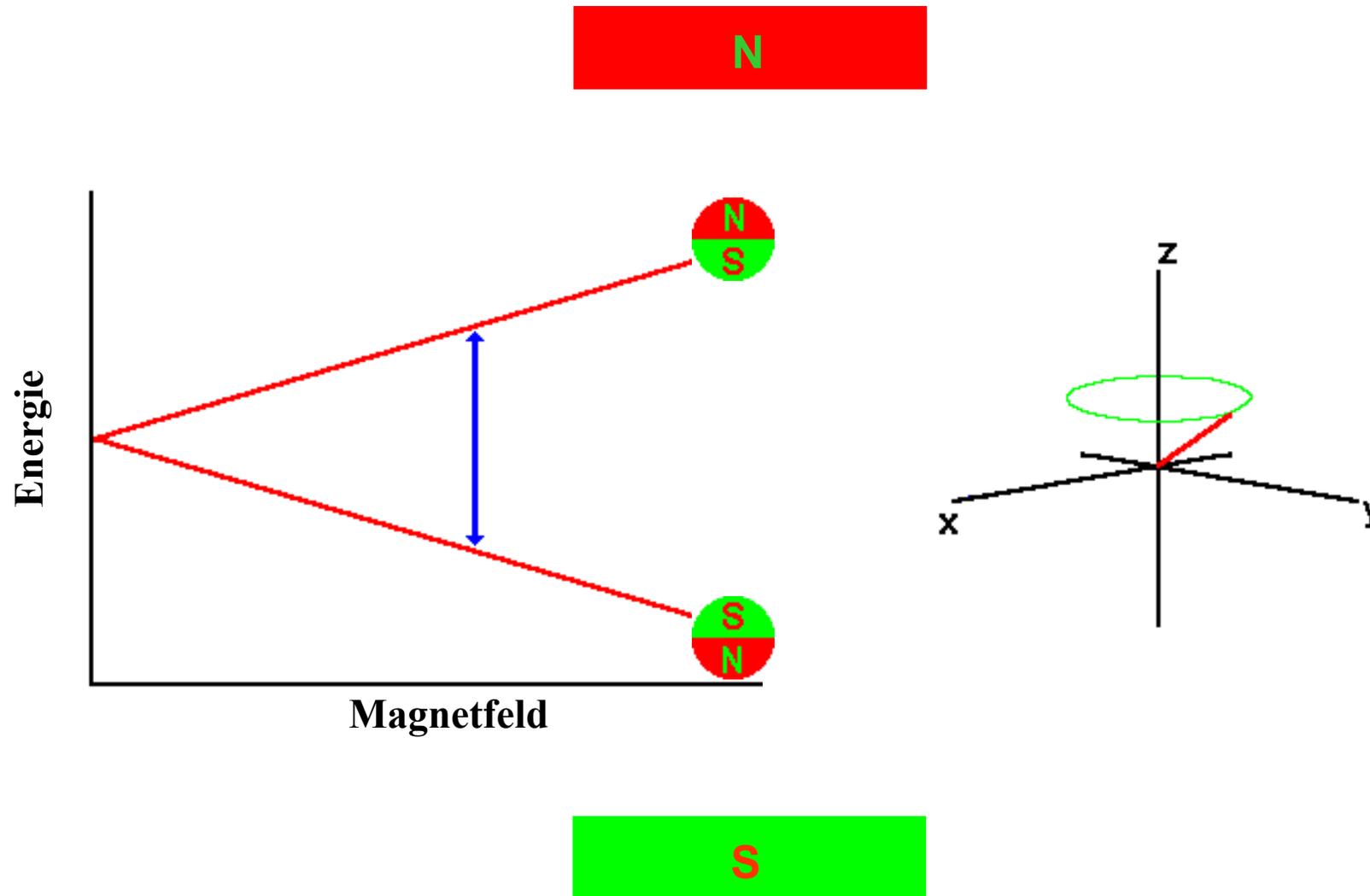
## Mikroskopische Magnete in makroskopischen Magneten



Mikroskopische Magnete in makroskopischen Magneten



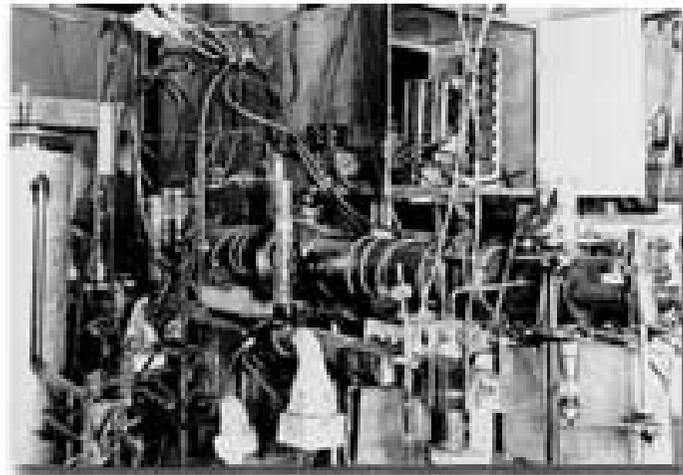
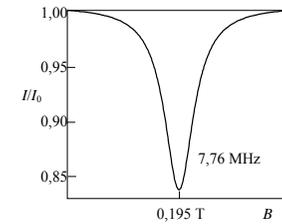
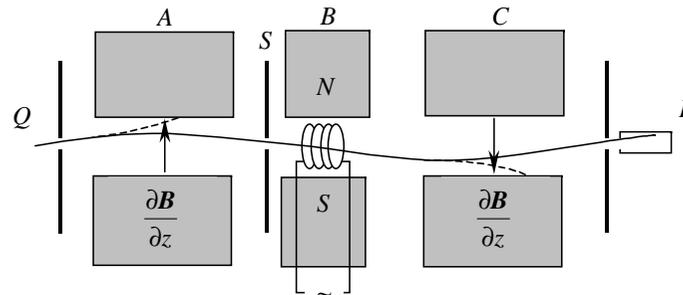
## Mikroskopische Magnete in makroskopischen Magneten



## Mikroskopische Magnete in makroskopischen Magneten



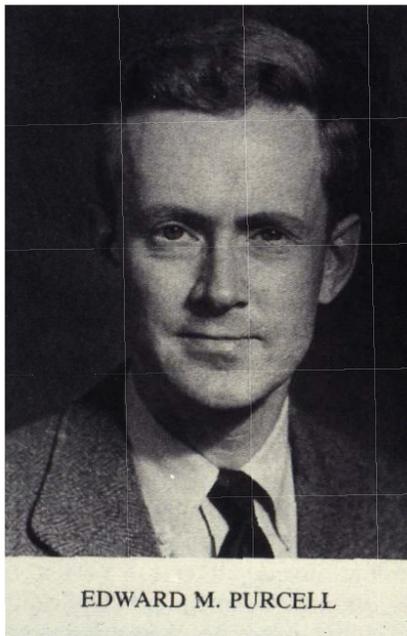
Isidor Rabi



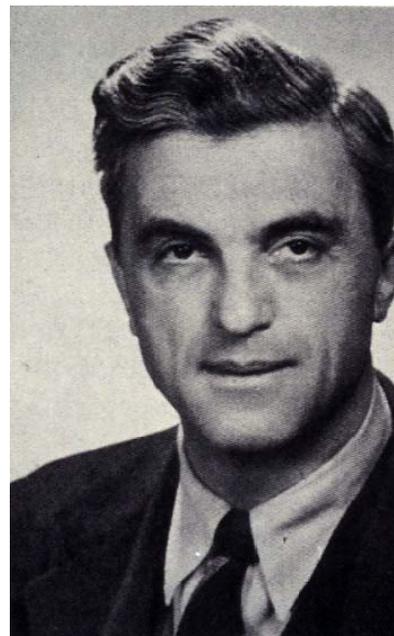
1933, Resonanzmethode für magnetische Eigenschaften der Kerne

**Nobelpreis, 1944**

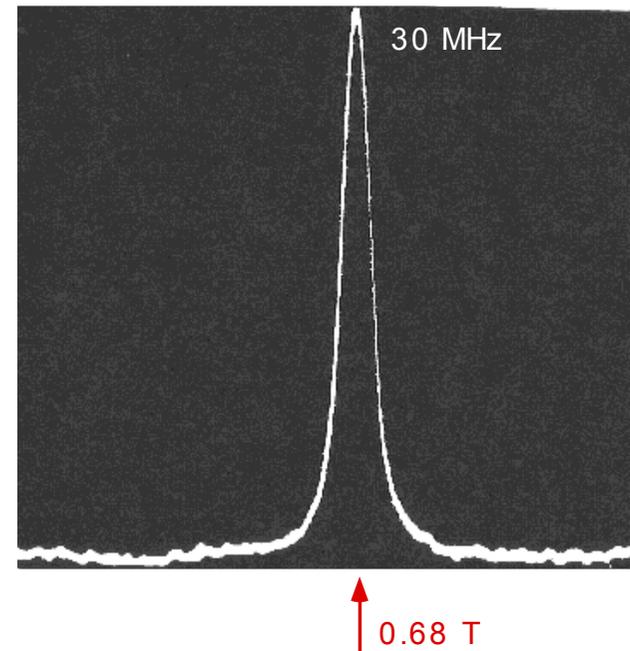




Edward Purcell  
*at Harvard*



Felix Bloch  
*at Stanford*



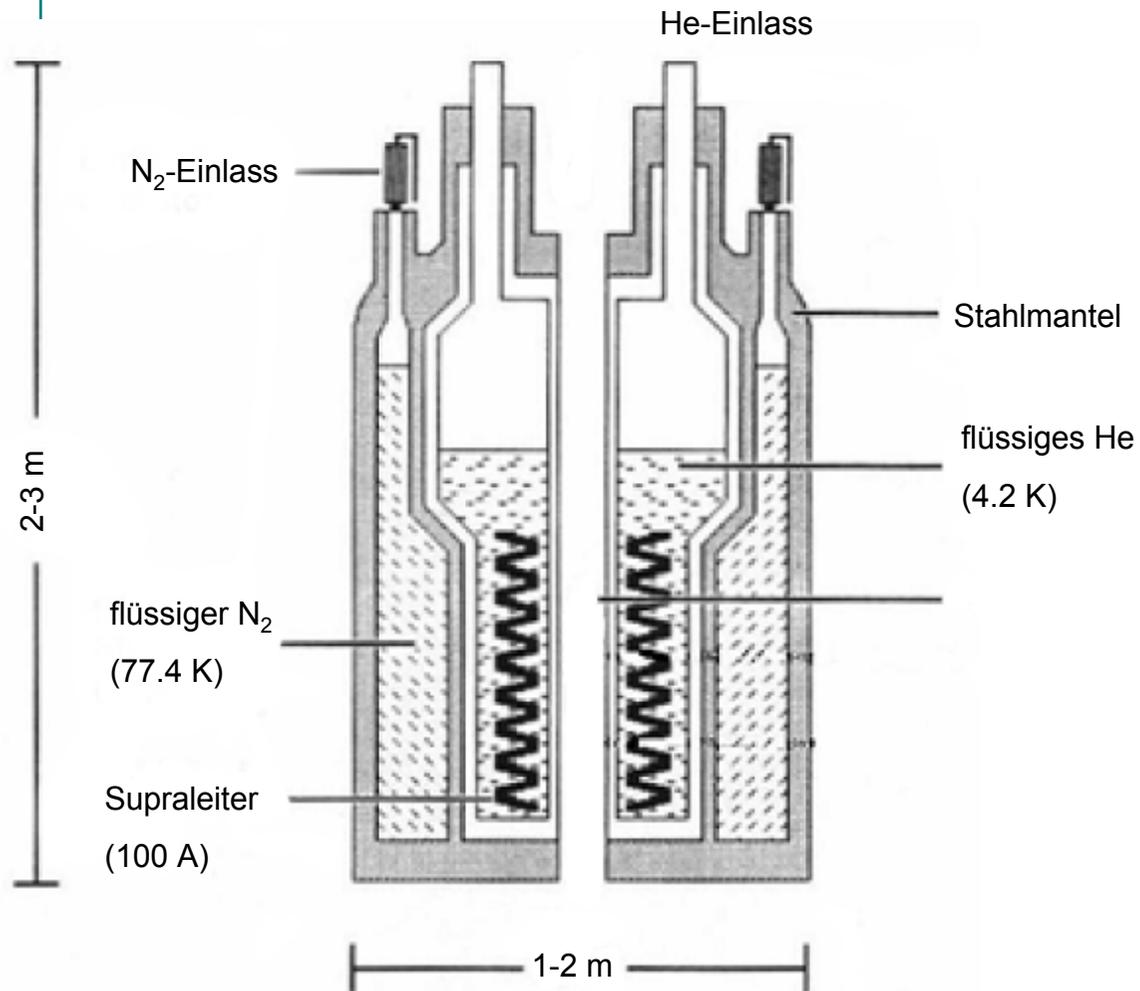
proton resonance in water

*Phys Rev* **73**, 679 (1948)

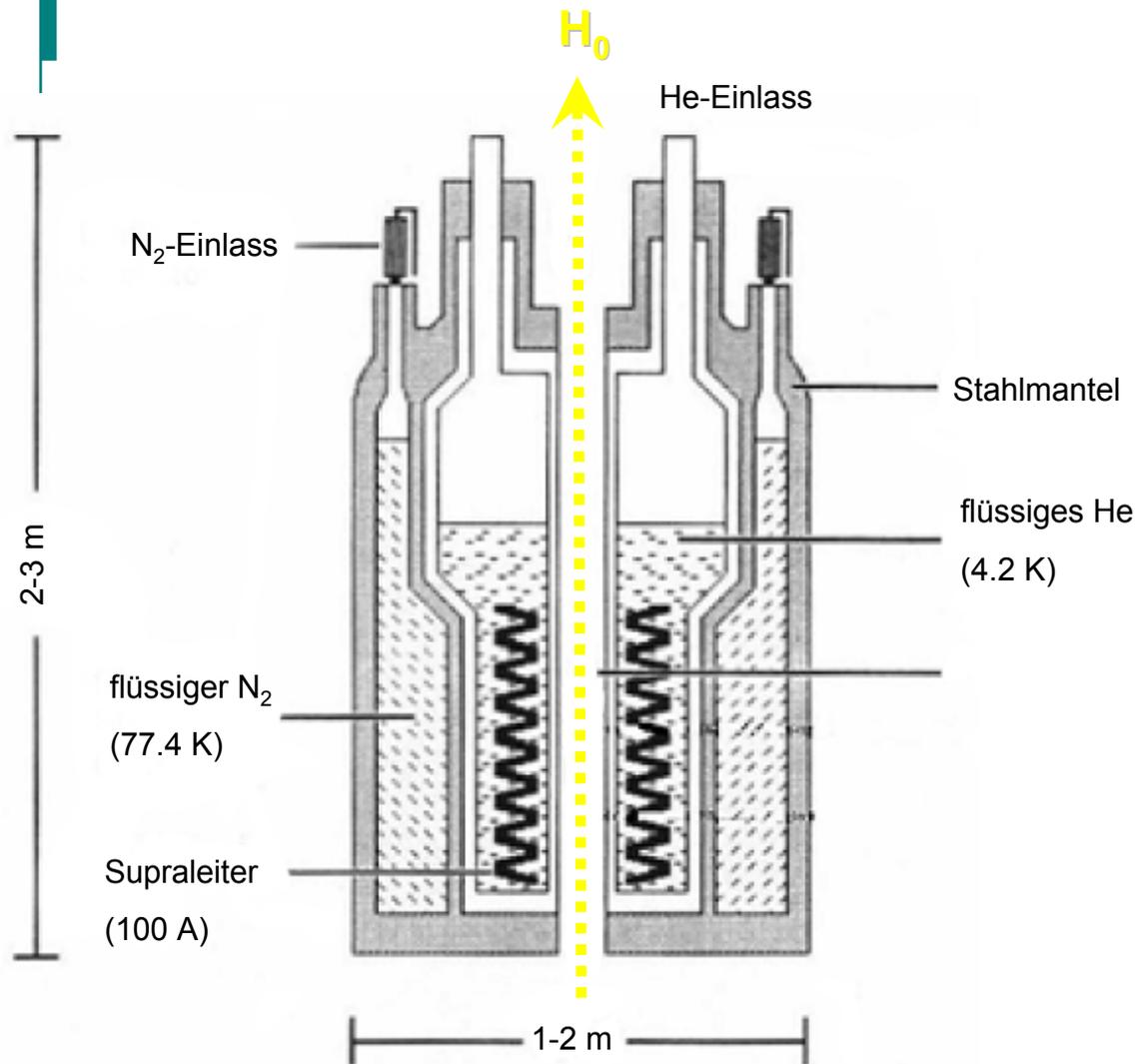
1945, Resonanzmethode für magnetische Eigenschaften der Kerne



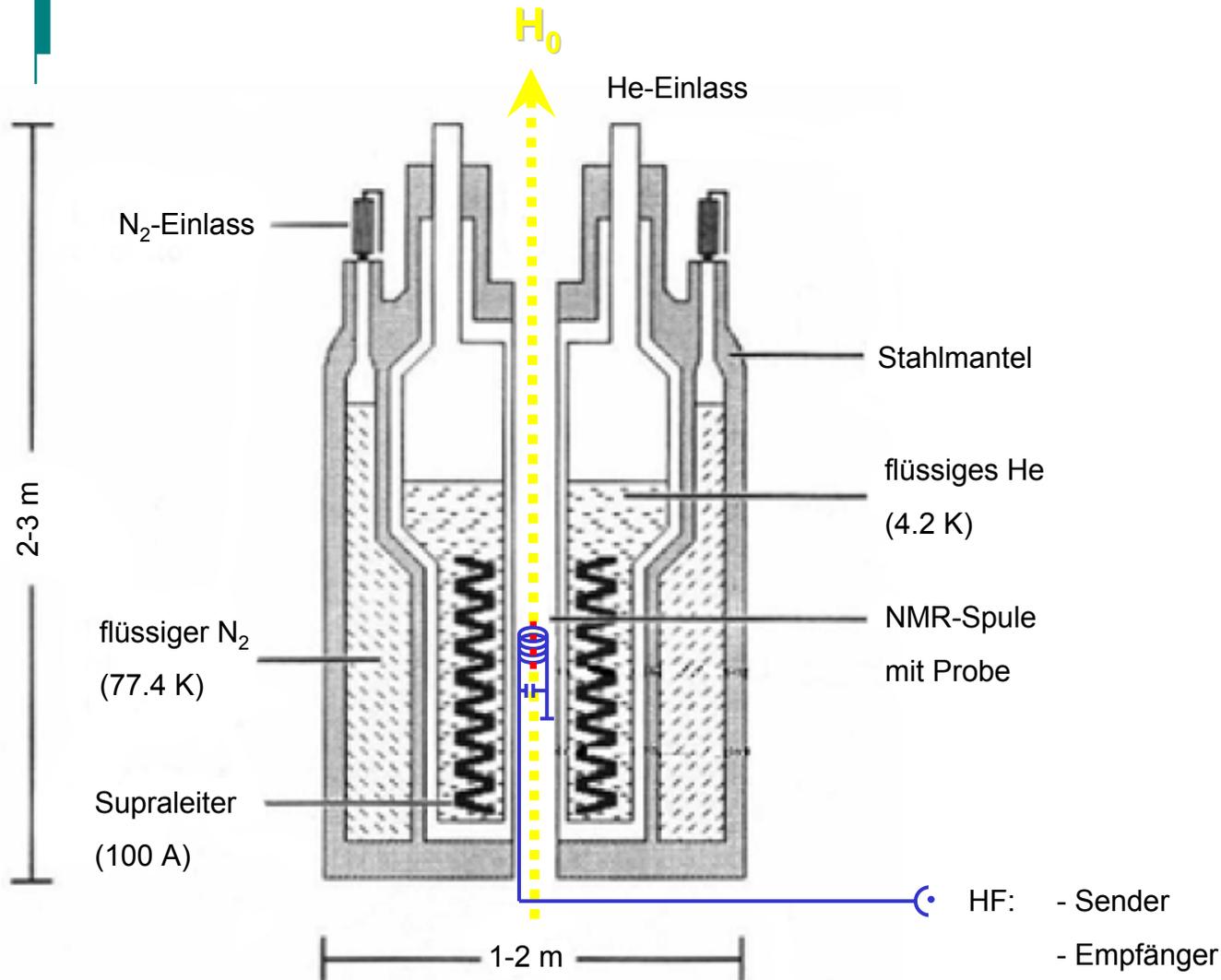
**Nobelpreis für Physik 1952**



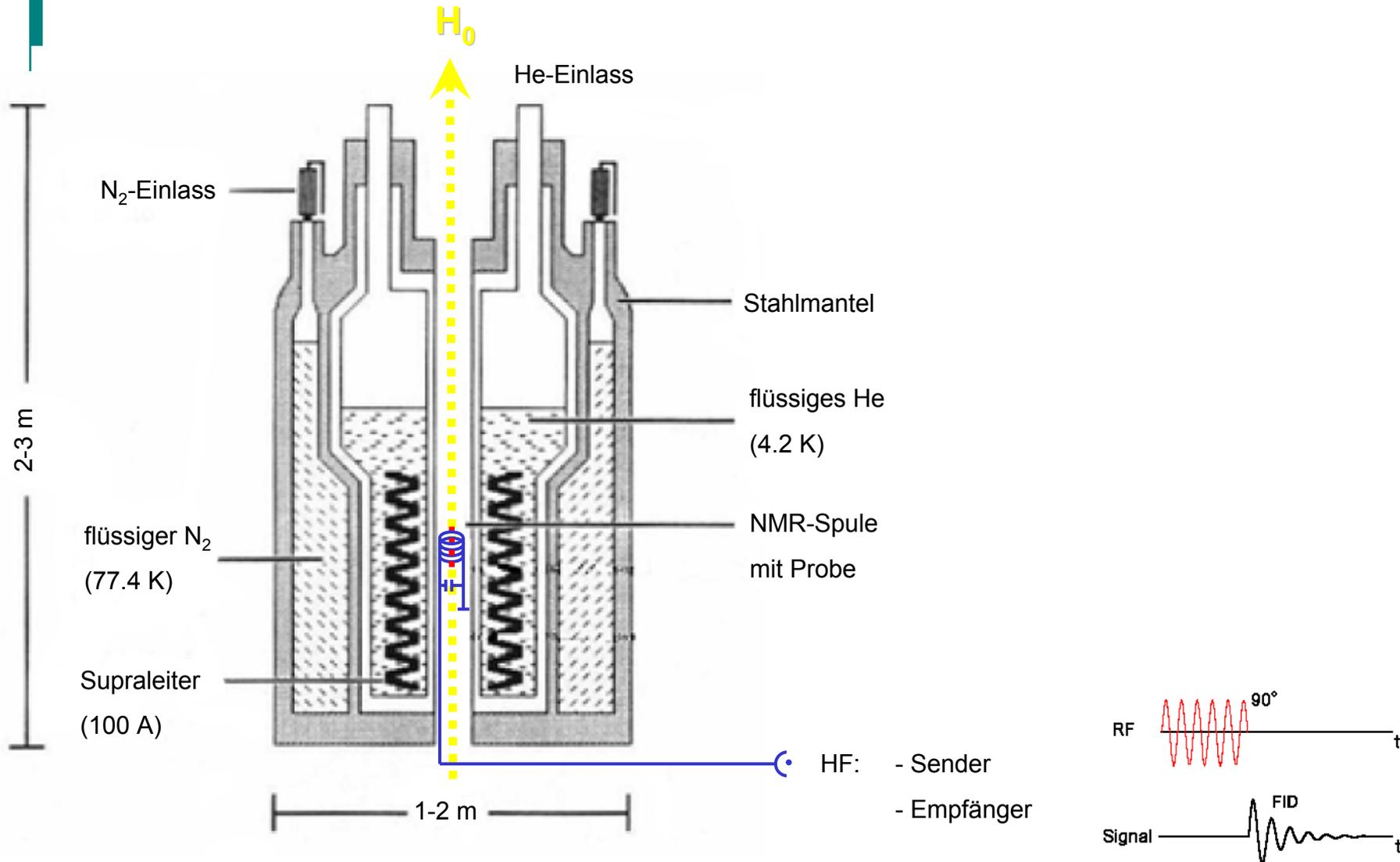
## Prinzip des NMR-Experiments



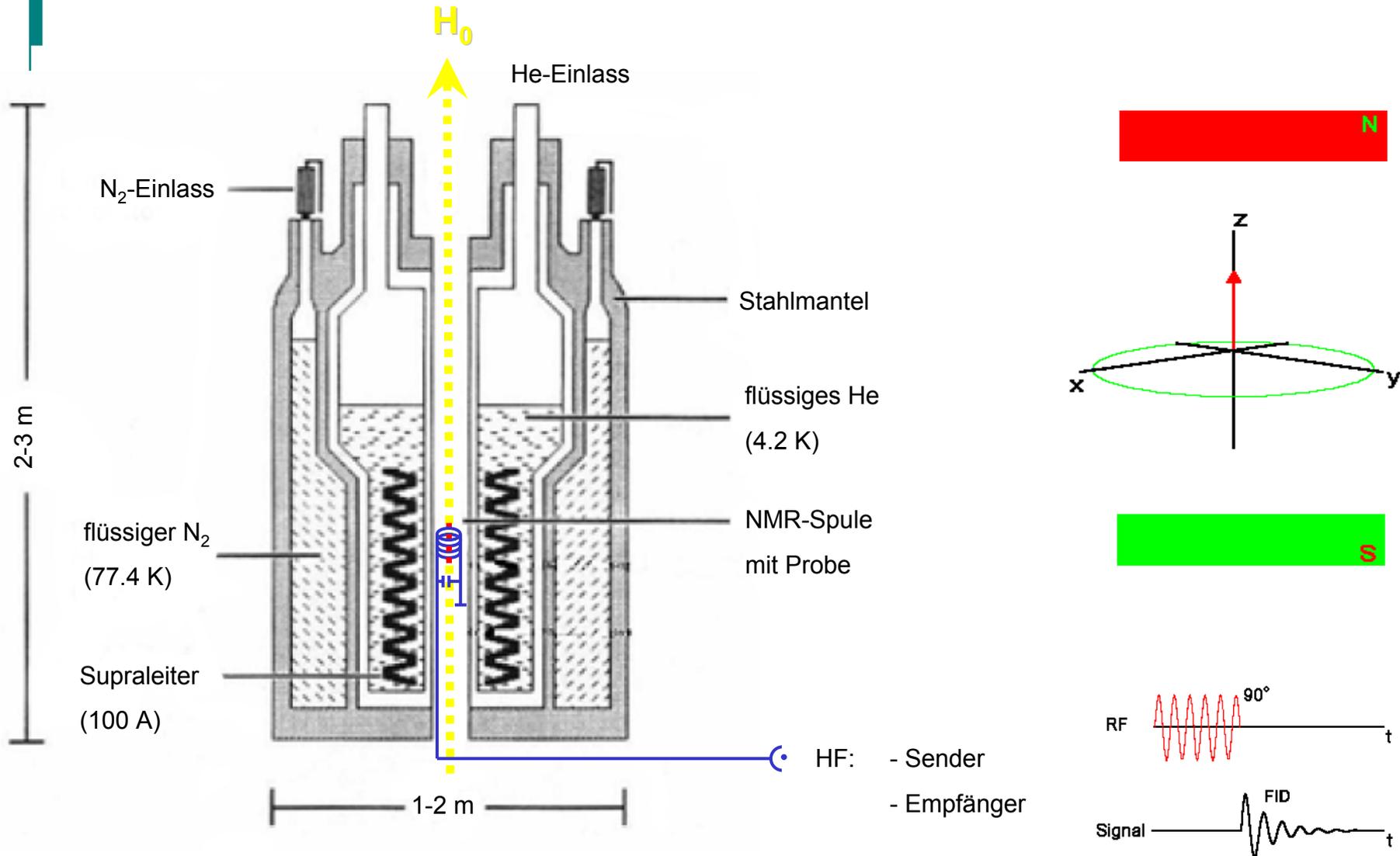
## Prinzip des NMR-Experiments



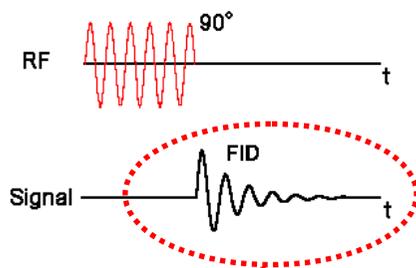
## Prinzip des NMR-Experiments



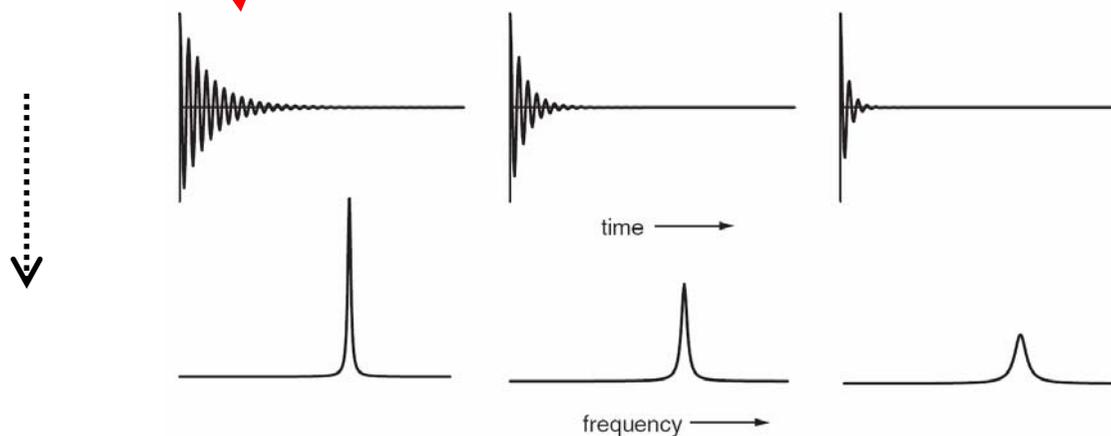
## Prinzip des NMR-Experiments



## Prinzip des NMR-Experiments



Fourier-  
transformation



Frequenzspektrum



## Dependence of the $F^{19}$ Nuclear Resonance Position on Chemical Compound\*

W. C. DICKINSON

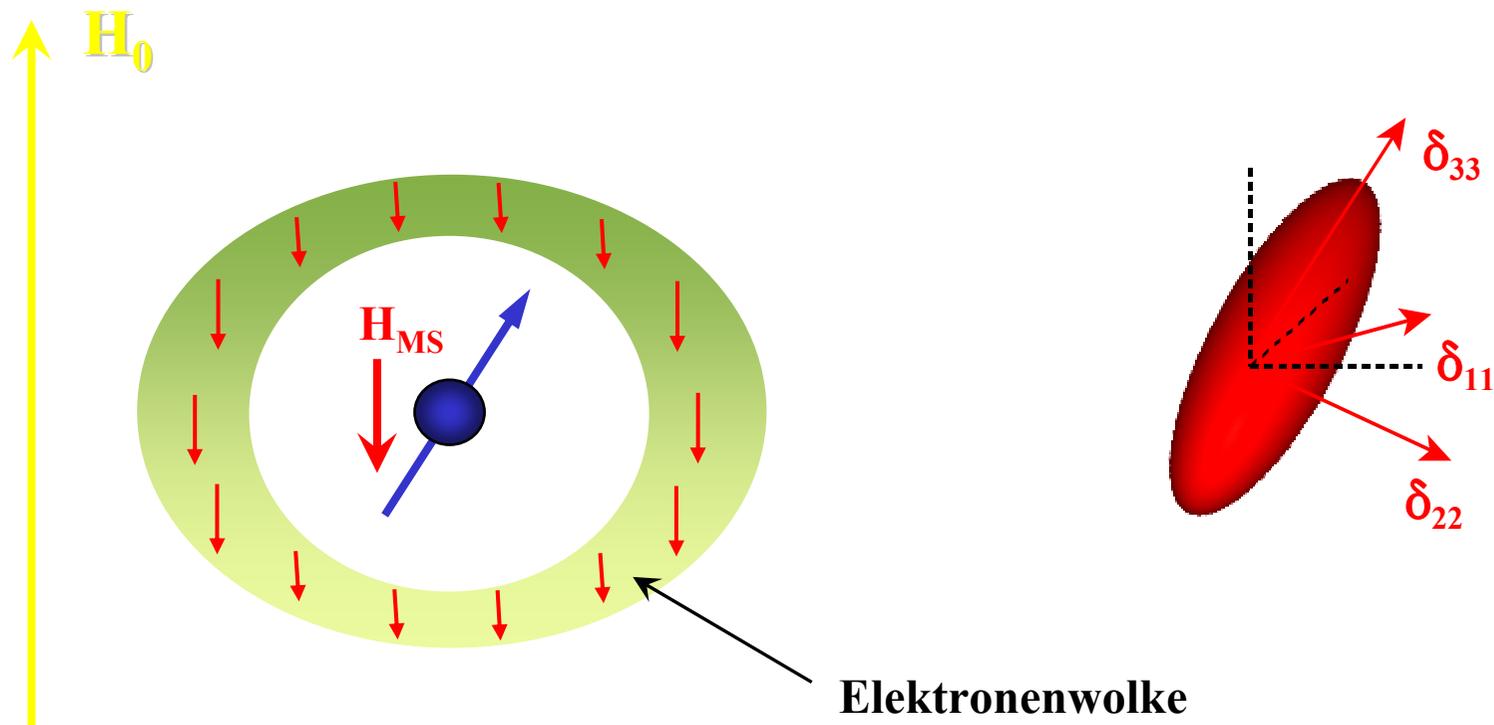
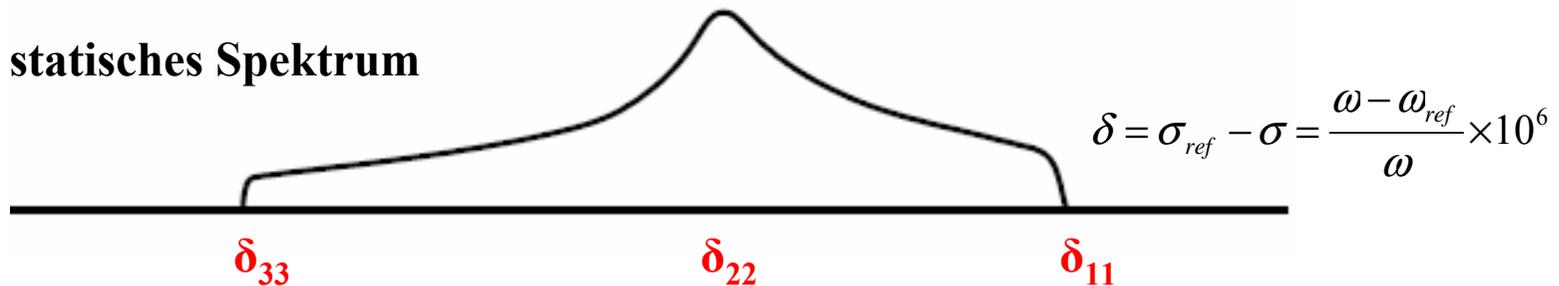
*Research Laboratory of Electronics, Massachusetts Institute of Technology,  
Cambridge, Massachusetts*

January 9, 1950

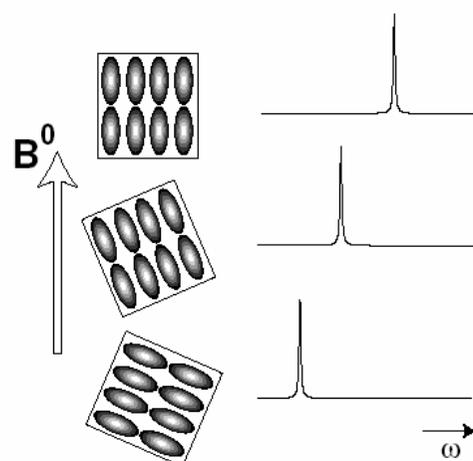
**M**OST unexpectedly, it has been found that for  $F^{19}$  the value of the applied magnetic field  $H_0$  for nuclear magnetic resonance at a fixed radiofrequency depends on the chemical compound containing the fluorine nucleus. The assumption has generally been made that the time average of all internal magnetic fields is zero, excluding of course the small diamagnetic field at the nucleus due to the Larmor precession of its atomic electrons in  $H_0$ . Nuclear resonance shifts in metals,<sup>1</sup> interpreted as being due to the conduction electrons, are larger by about an order of magnitude than those reported here.<sup>2</sup>



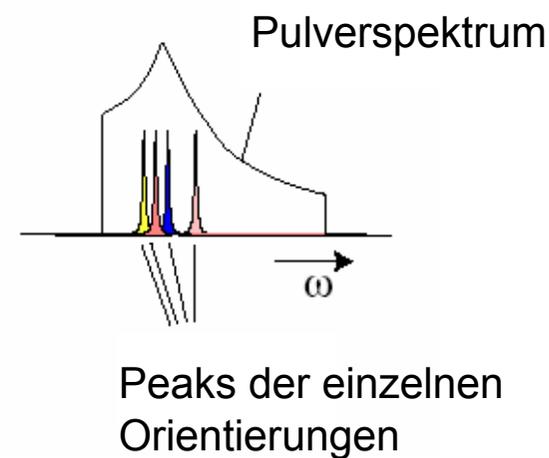
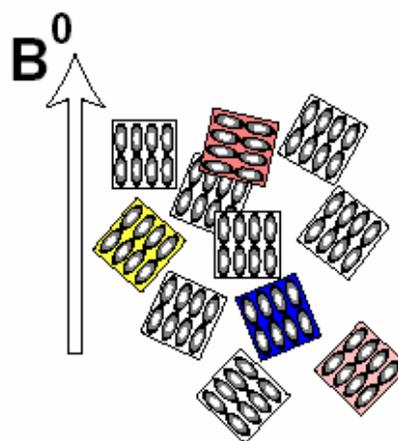
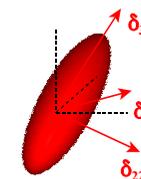
statisches Spektrum



Chemische Verschiebung



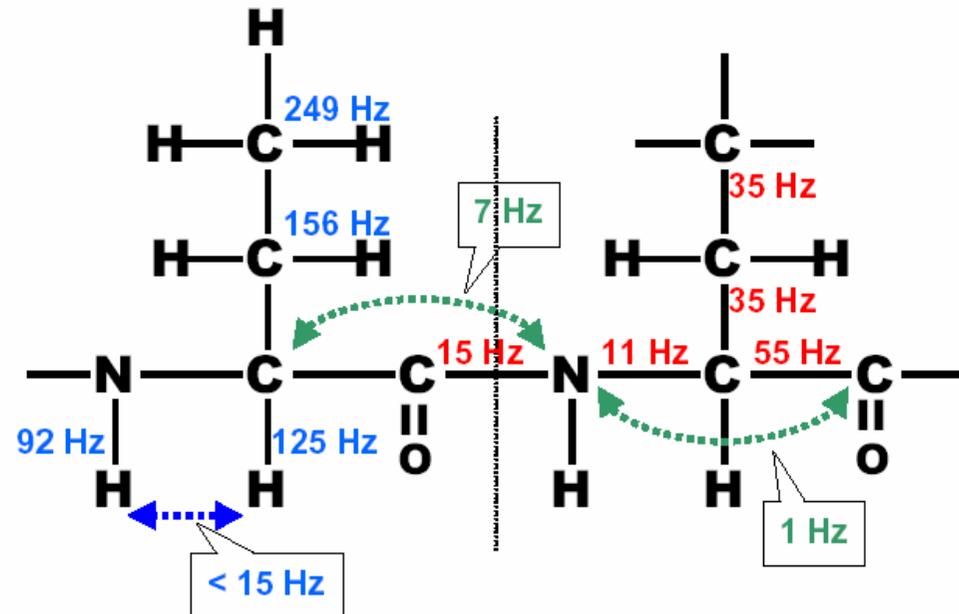
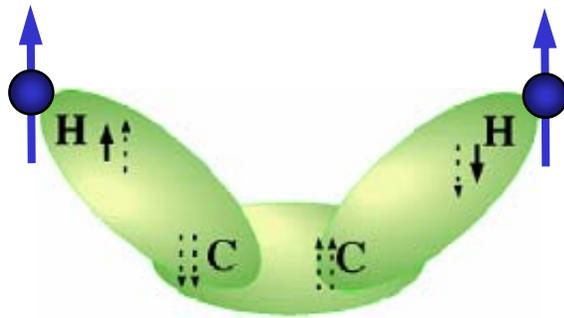
Zu jeder Orientierung des Tensors der chemischen Verschiebung gehört ein Peak.



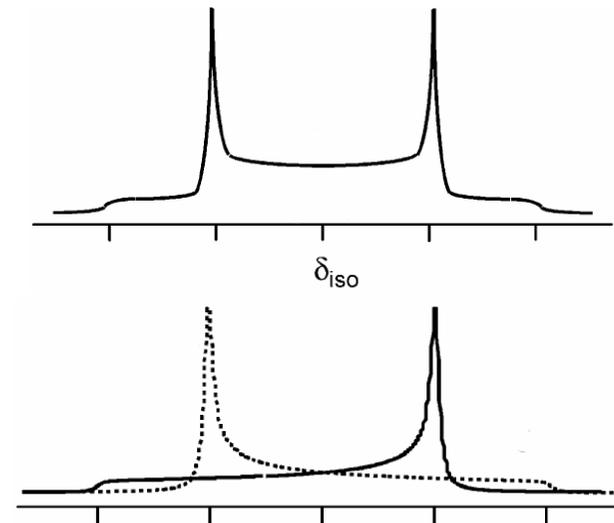
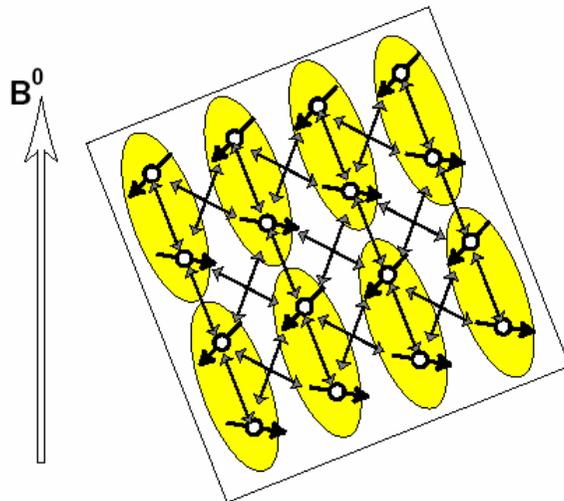
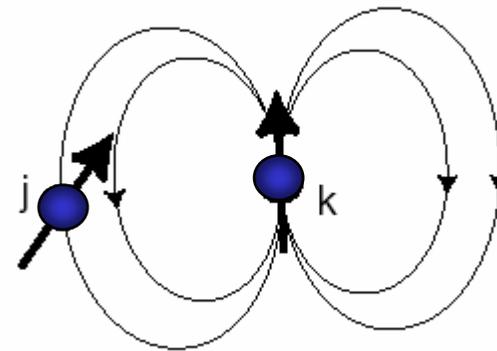
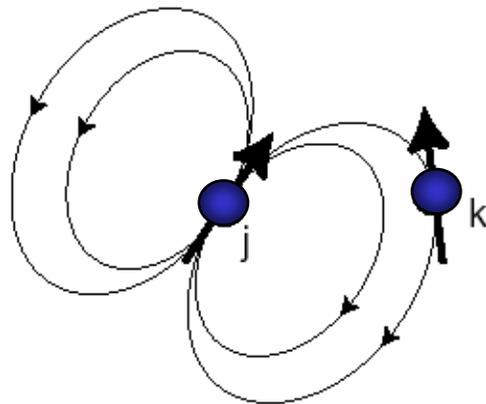
## Pulver Spektrum



## J-Kopplung in Peptiden



Kopplung über die Bindung

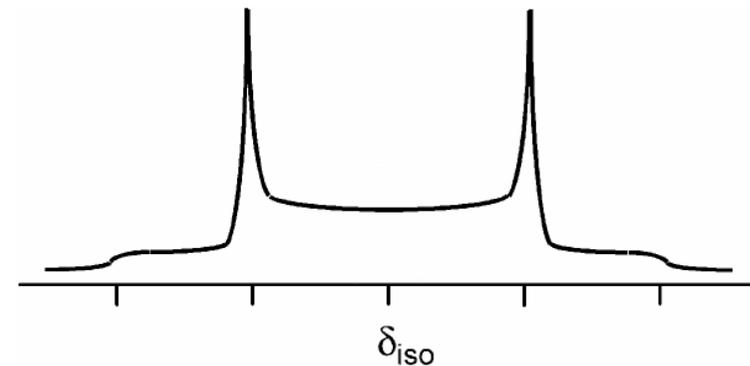
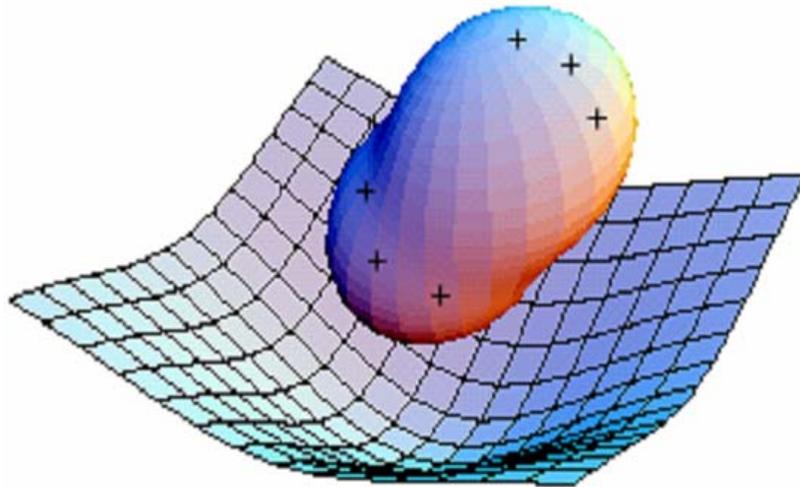


statisches Pulverspektrum

## Dipolare Kopplung



zigarrenförmige oder  
linsenförmige Kerne haben ein  
**Quadrupolmoment** ( $I > 1/2$ )



statisches Pulverspektrum ( $I=1$ )

elektrisches Potential der Elektronenverteilung  
(Wechselwirkung des Quadrupolmomentes mit dem **elektrischen  
Feldgradienten**)

## Quadrupolkopplung



i-ter Spin-Hamiltonian

$$H_i = -\gamma B_0 I_{iz} - \mathcal{A}_i \cdot \underline{\underline{\delta}} \cdot \mathbf{B}_0 - \sum_j J_{ij} \mathbf{I}_i \cdot \mathbf{I}_j - \mathbf{I}_i \cdot \underline{\underline{Q}} \cdot \mathbf{I}_i - \sum_j \mathbf{I}_j \cdot \underline{\underline{D}}_{ij} \cdot \mathbf{I}_i$$

Zeeman  
~100e MHz

isotrope  
+ anisotrope  
Chemische  
Verschiebung  
~kHz  
+ ~kHz\*Y<sub>2</sub><sup>m</sup>(θ,φ)

Spin-Spin  
Kopplung  
~Hz

quadrupolare-  
und dipolare  
Kopplung  
~100 kHz\*Y<sub>2</sub><sup>m</sup>(θ,φ)

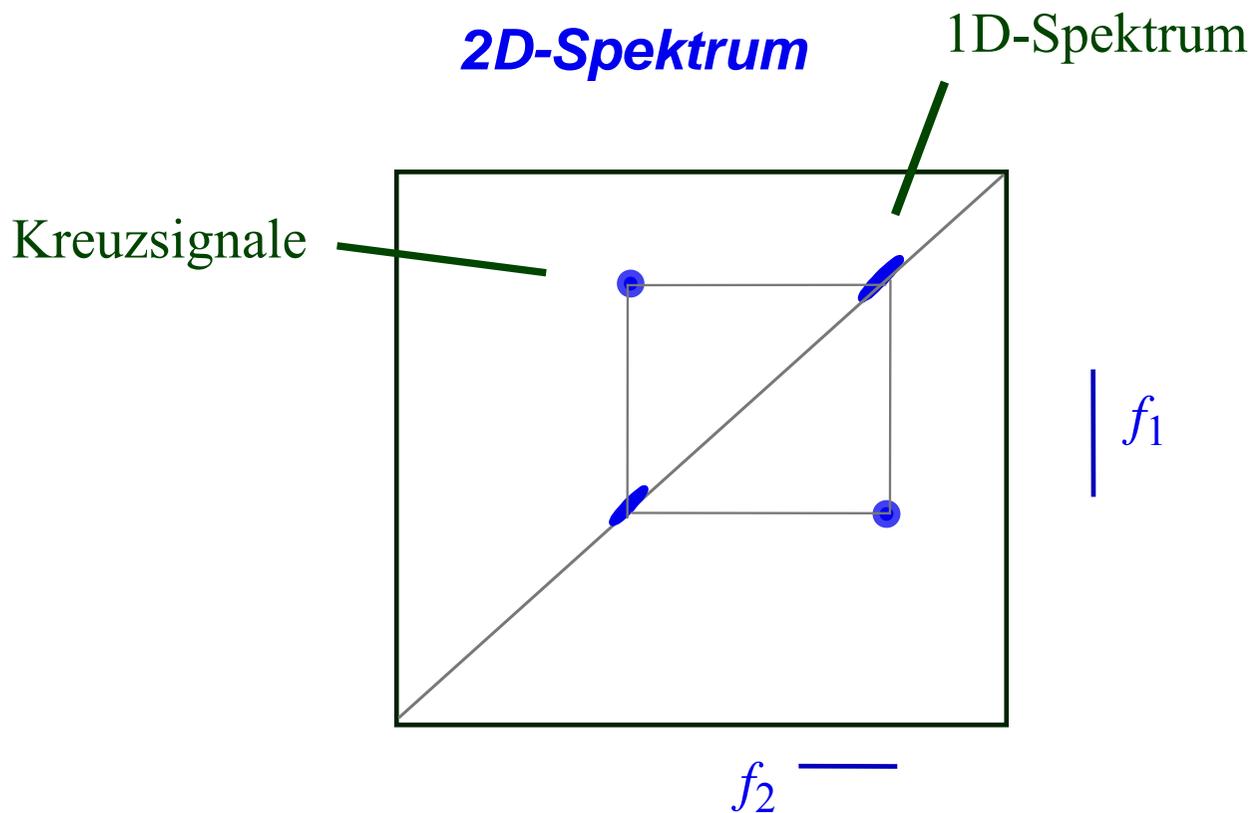
## NMR-Hamiltonian (Energieoperator)



$$\psi = \frac{\text{Signal}}{\text{Rauschen}} \propto I(I+1) \cdot N \cdot \gamma^3$$

$$\frac{\psi_{^1\text{H}}}{\psi_{^{13}\text{C}}} = \frac{99.985\%}{1.1\%} \cdot \left( \frac{100\text{MHz}}{25.145\text{MHz}} \right)^3 = 5717$$

$^2\text{D}$	$^{13}\text{C}$	$^{15}\text{N}$	$^{19}\text{F}$	$^{31}\text{P}$
$1.8 \cdot 10^6$	$5.7 \cdot 10^3$	$262 \cdot 10^3$	1.2	15.1



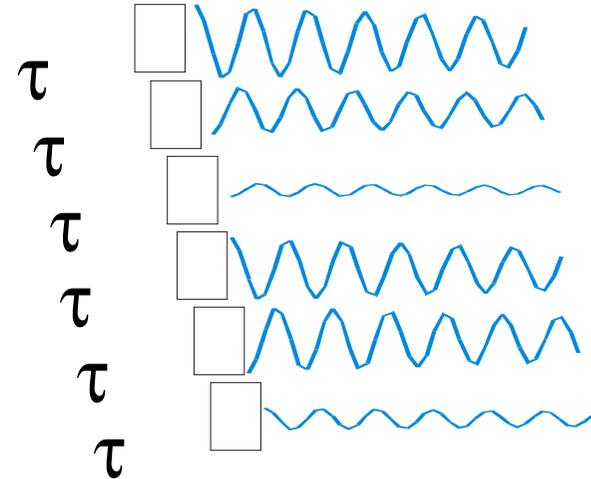
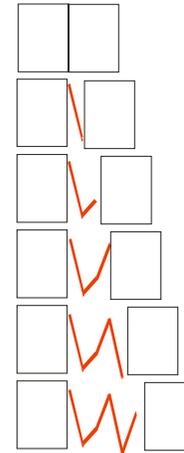
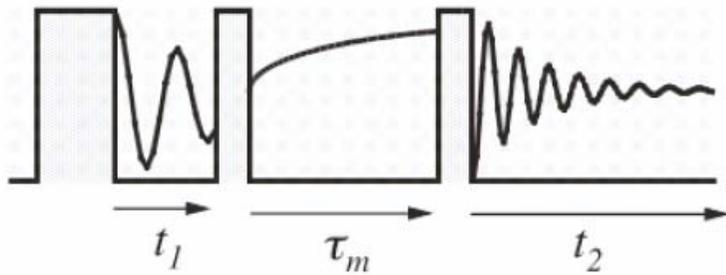
Jean Jeener

Jean Jeener, *Ampere Summer School*, Basko Polje 1971

## Doppelte Fouriertransformation

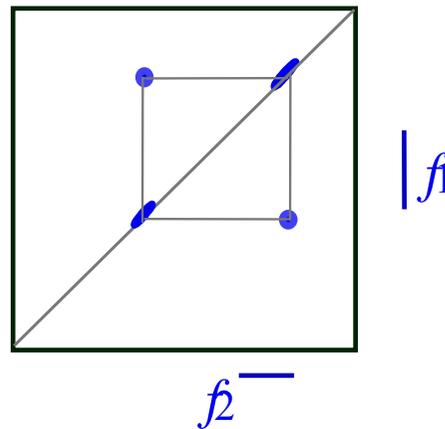


### 2D-Experiment



**Satz von FIDs**

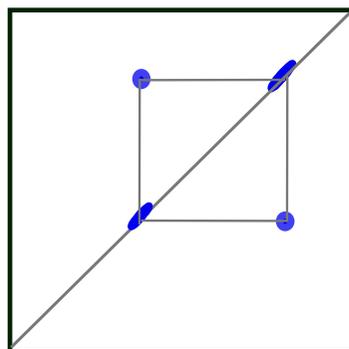
### 2D-Spektrum



## 2D-NMR



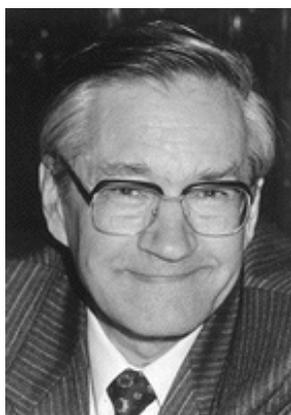
## 2D-Spektrum



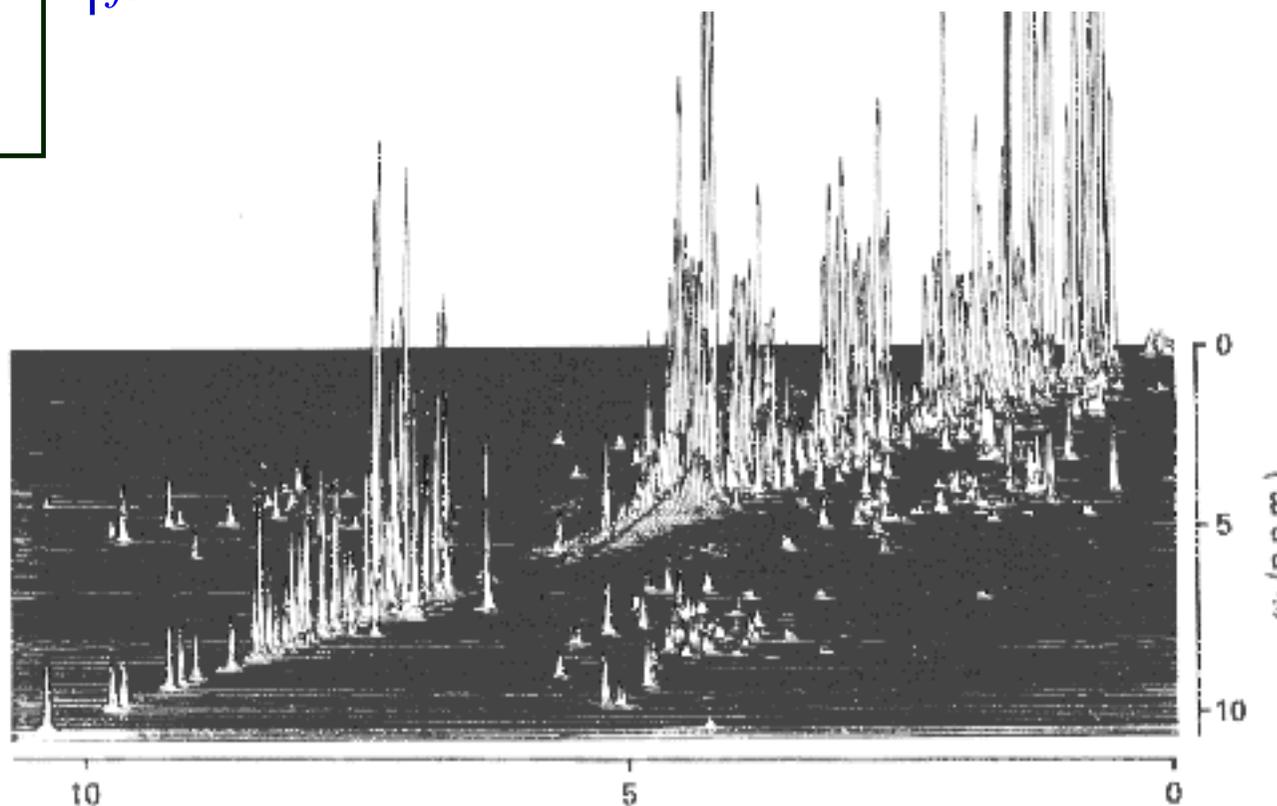
$f_1$

$f_2$

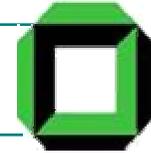
*Struktur und Konnektivitäten  
von komplexen Molekülen*



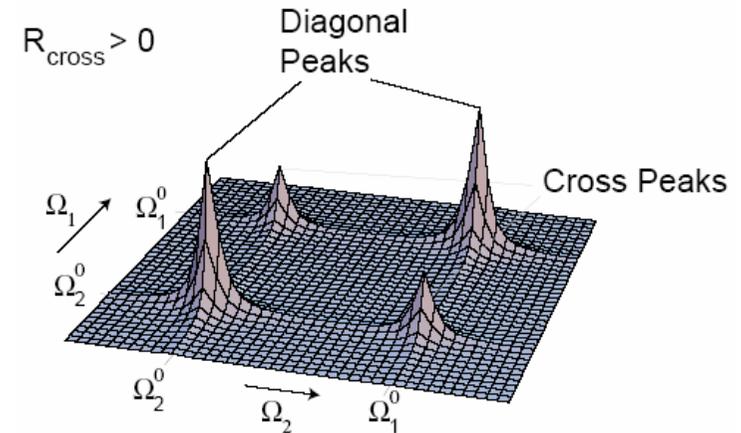
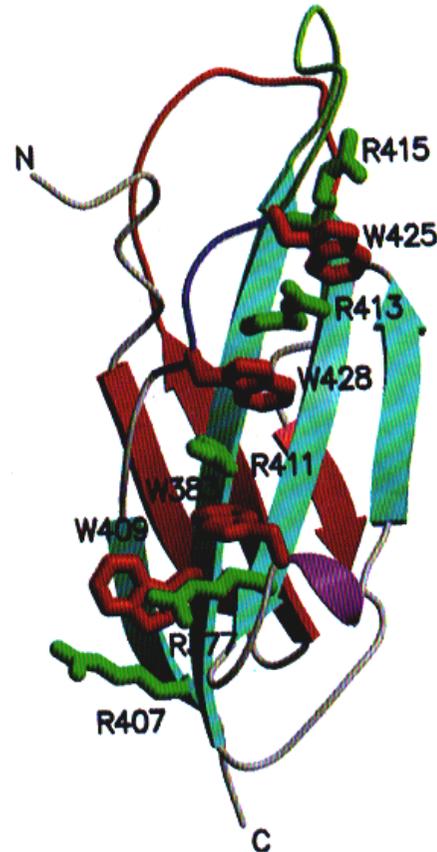
Richard R Ernst



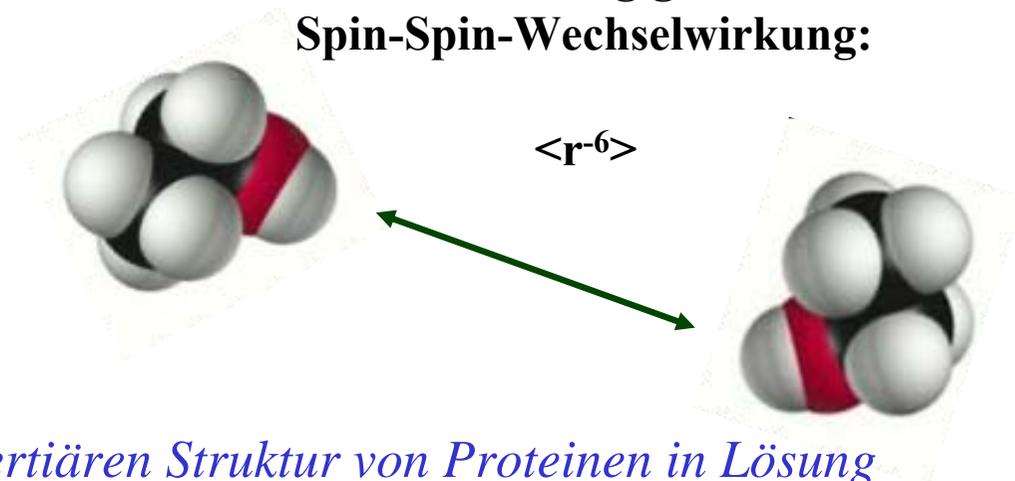
**Nobelpreis für Chemie, 1991**



Kurt Wüthrich



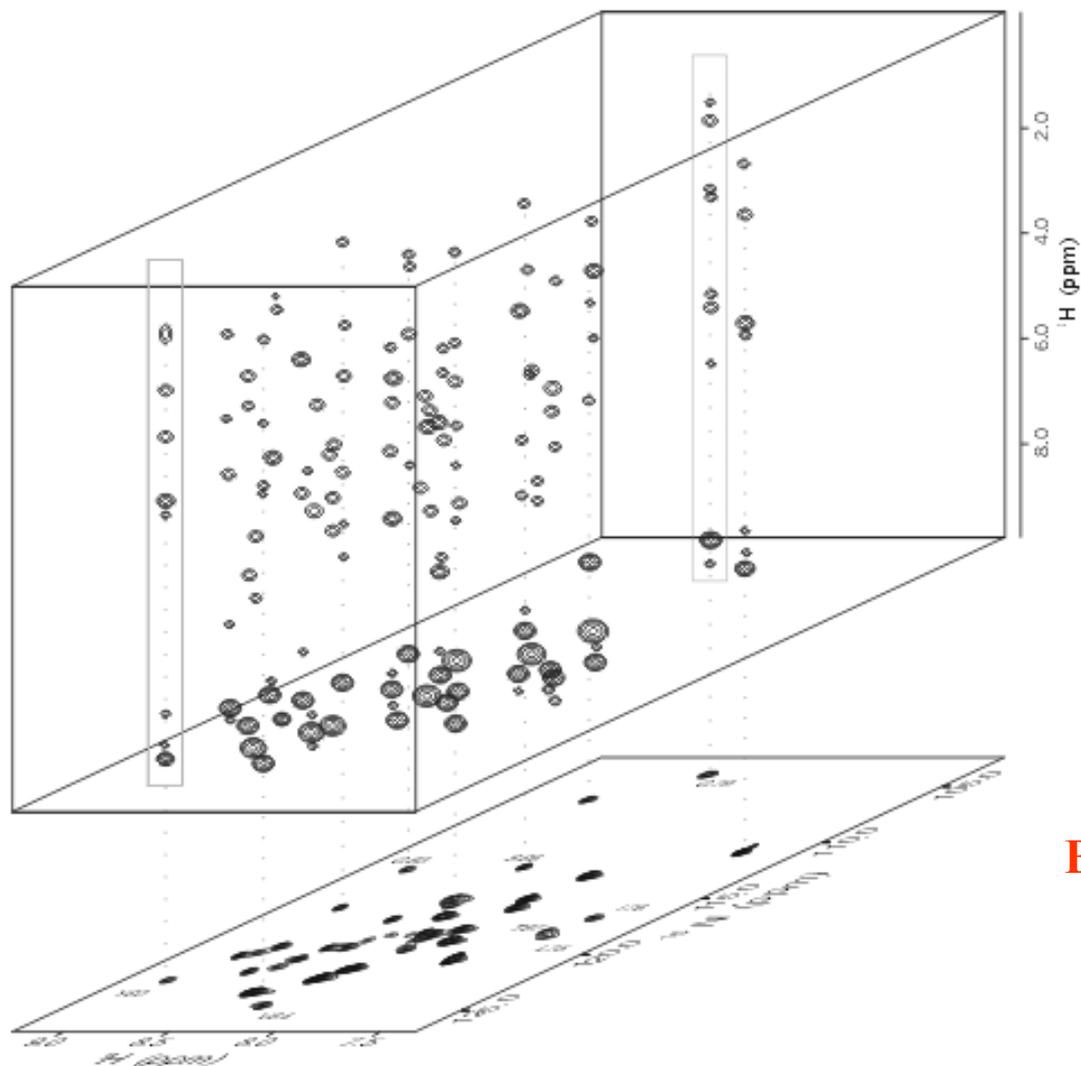
Abstandsabhängigkeit der NOE  
Spin-Spin-Wechselwirkung:



*Aufklärung der sekundären und tertiären Struktur von Proteinen in Lösung*

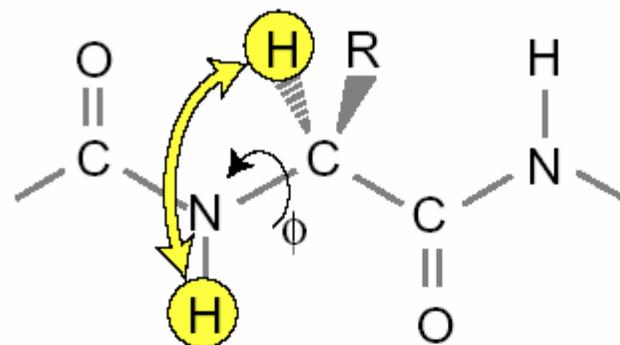
**Nobelpreis für Chemie, 2002**





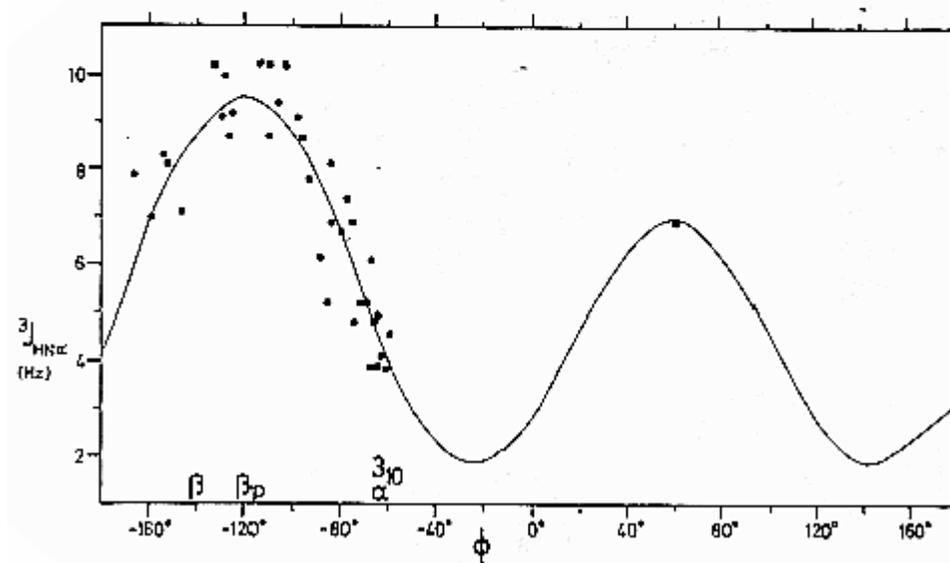
**Beispiel:**  
drei Zeitabhängige  
und somit  
drei Frequenzachsen.

## Mehrdimensionale NMR



Karplus Relation:

$$J_{HNCH}^3(\theta) = A \cos^2(\theta) + B \cos(\theta) + C$$



## Karplus Relation



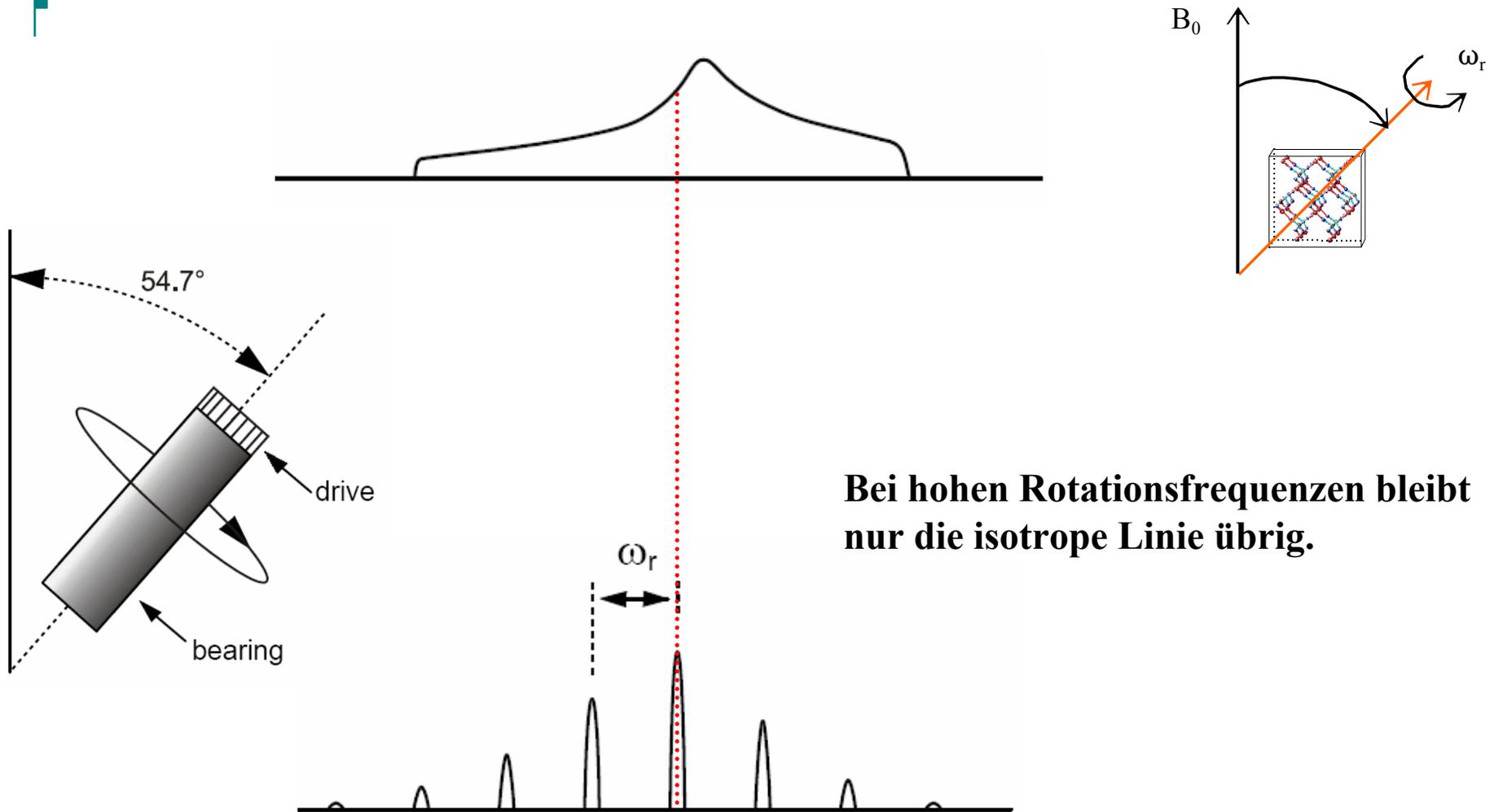
## *Aufklärung der sekundären und tertiären Struktur von Proteinen*

Kern	$\alpha$ -Helix	$\beta$ -strand
$^1\text{H}\alpha$	-0.38	0.38
$^1\text{HN}$	-0.19	0.29
$^{13}\text{C}\alpha$	2.6	-1.4
$^{13}\text{C}'$	1.7	-1.4
$^{15}\text{N}$	-1.7	1.2

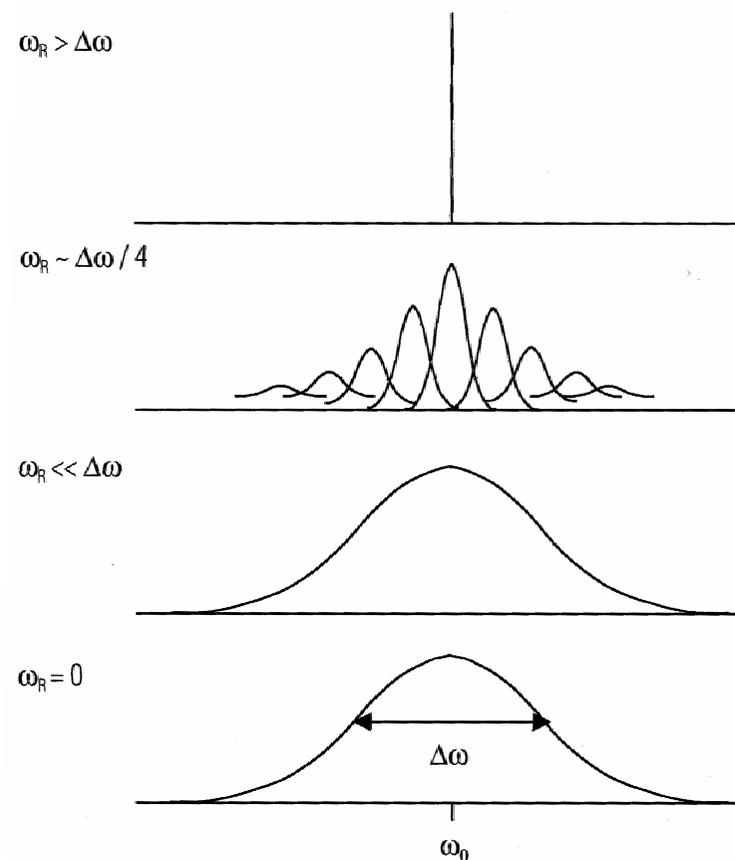
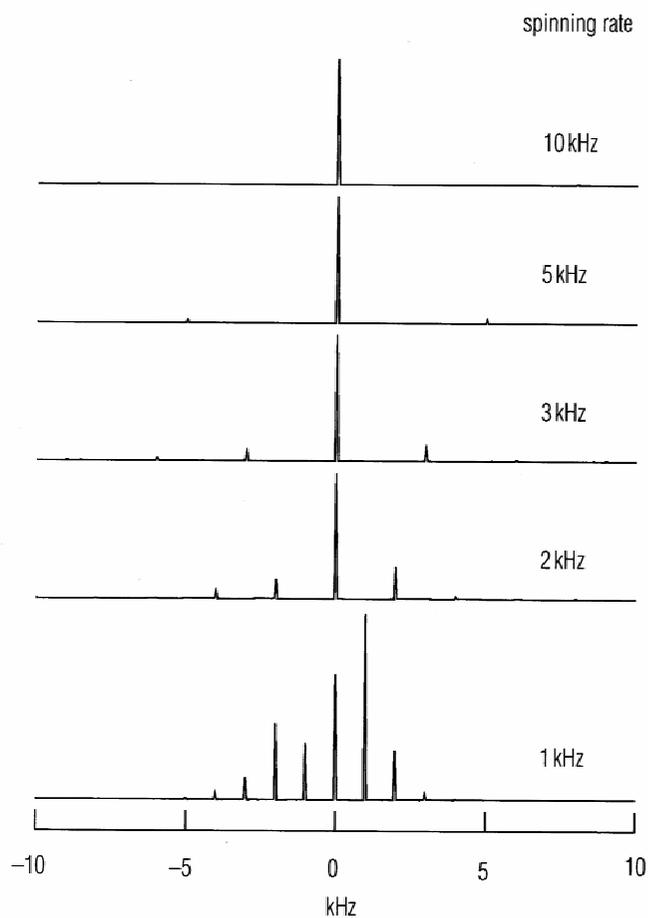
Gemittelte isotrope chemische Verschiebungen (in ppm) relativ zu Werten von Aminosäuren in "Random-Coil-Konformation".

Wishart and Sykes "Chemical shifts as a tool for structure determination" Methods in Enzymology 239, pp 363-392 (1994).

## CSI: Chemical Shift Index



## MAS: Magic Angle Spinning

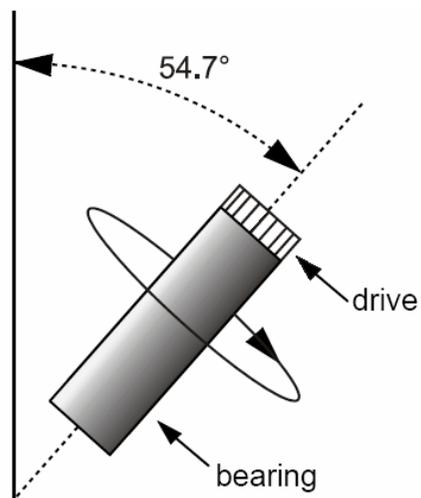


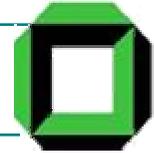
**Ausmittlung der Anisotropie: Rotationsfrequenz > Anisotropie**



## Festkörper NMR

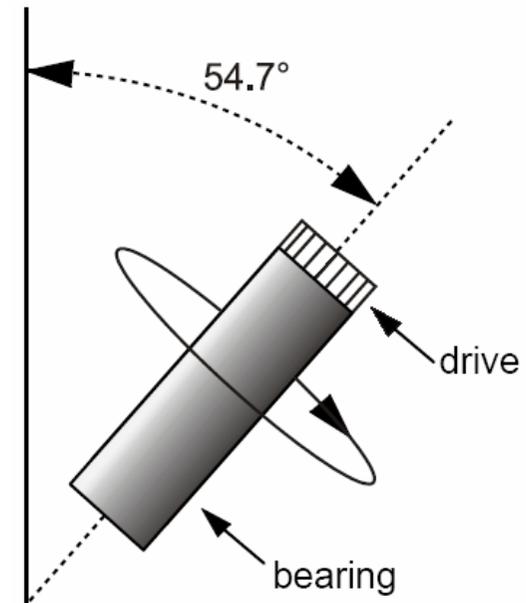
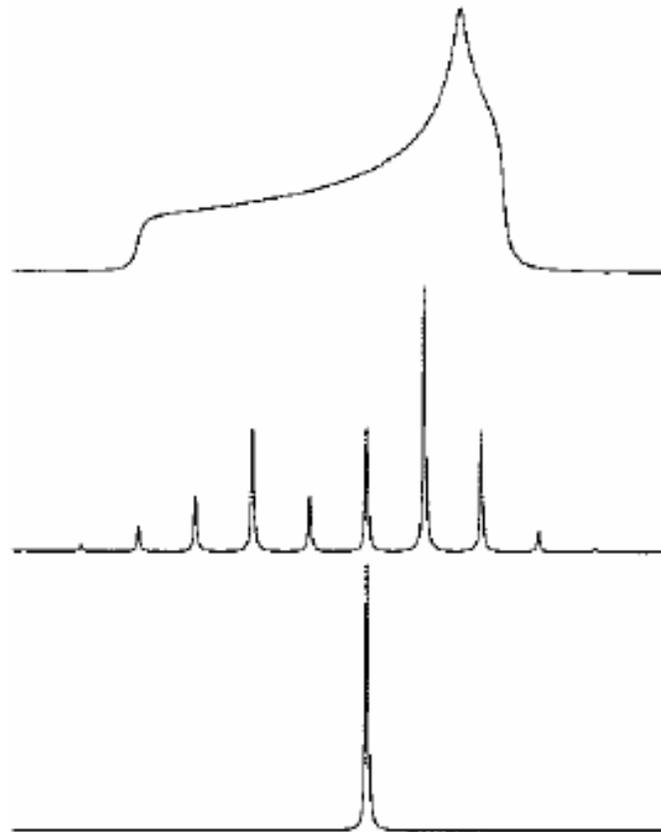
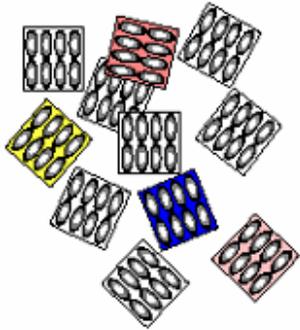
### 2. NMR an makroskopisch nicht-orientierten Proben





# **Auflösungserhöhung**

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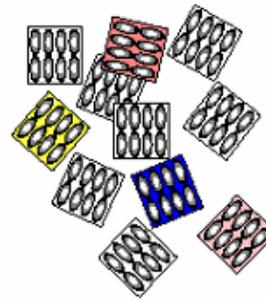
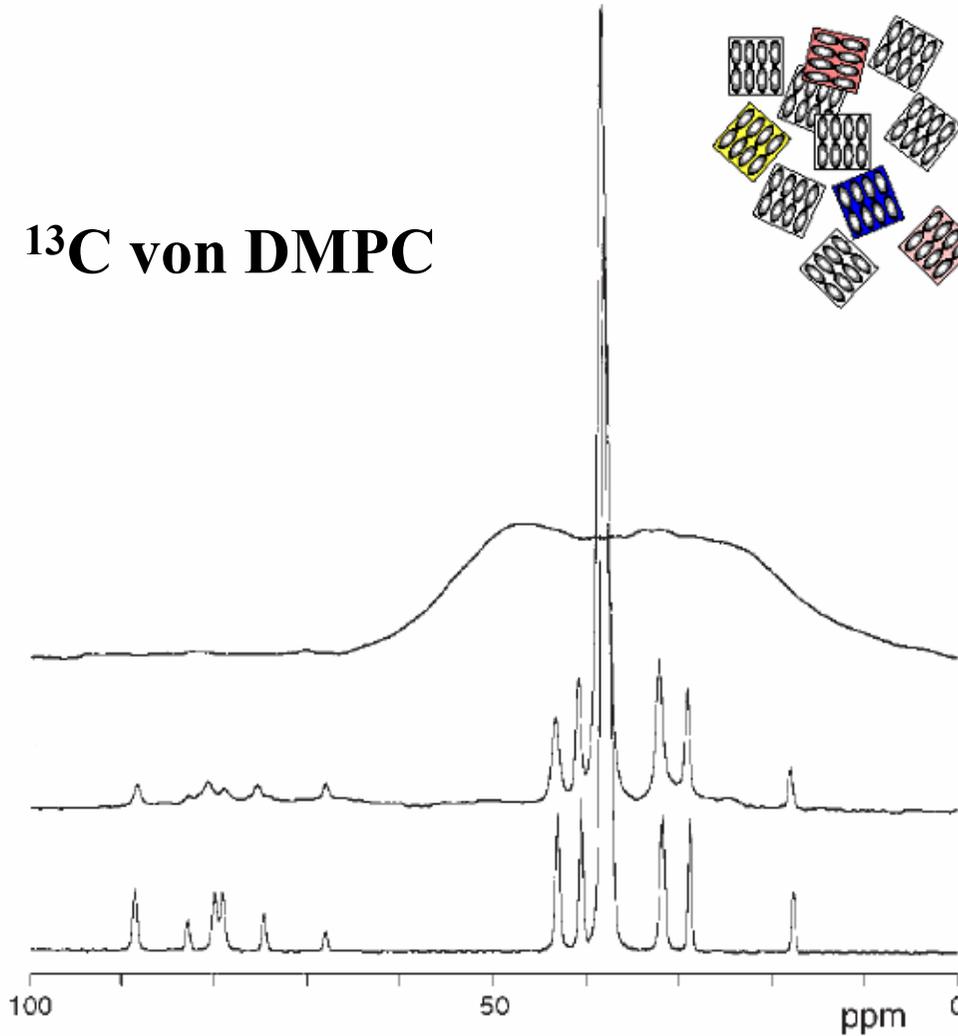


Auflösungserhöhung durch  
**MAS**: Rotation um den  
magischen Winkel

**NMR an Festkörpern hat breite Spektren zur Folge**



# $^{13}\text{C}$ von DMPC

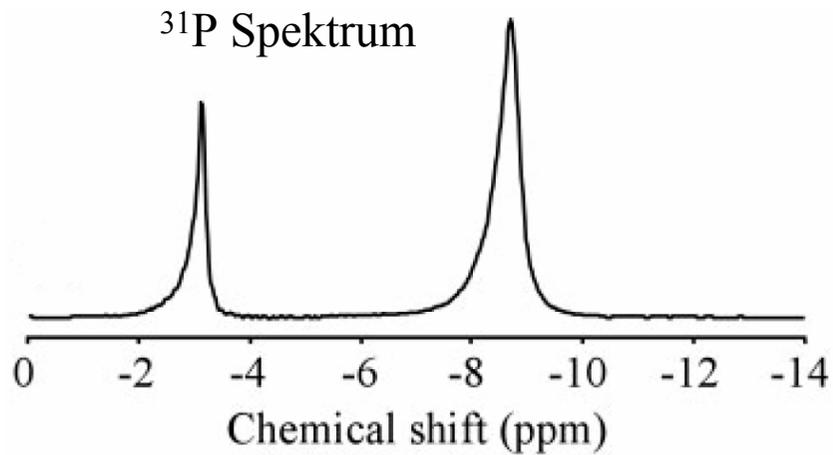
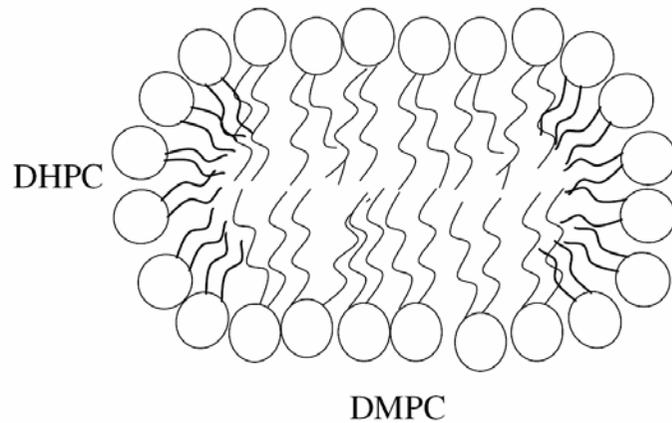


- statisch

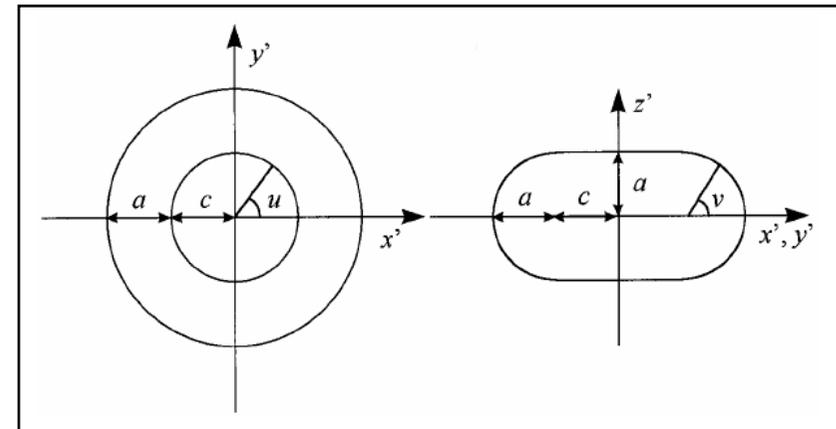
- MAS 6 kHz

- hydratisierte Dispersion

## Tricks zur Auflösungserhöhung



## Modell von Bizellen

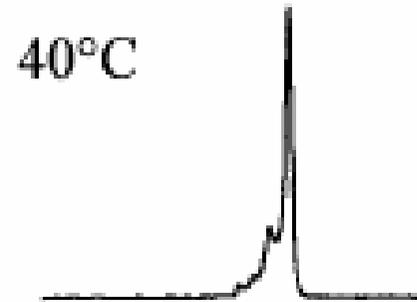
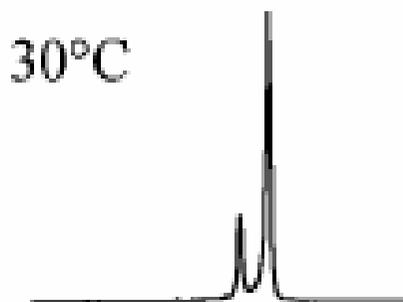
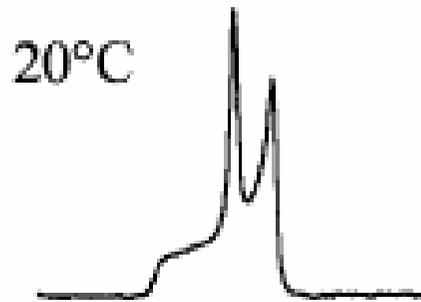
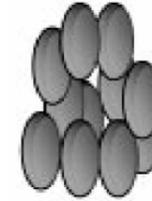


## Asymmetrieparameter

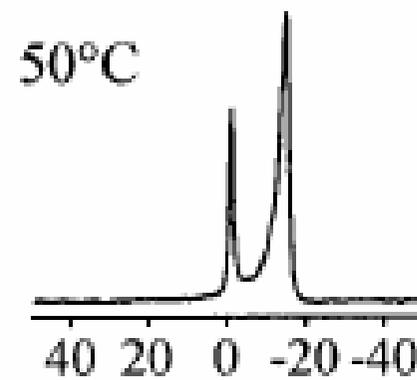
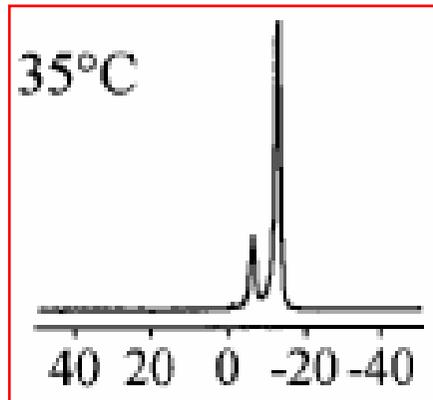
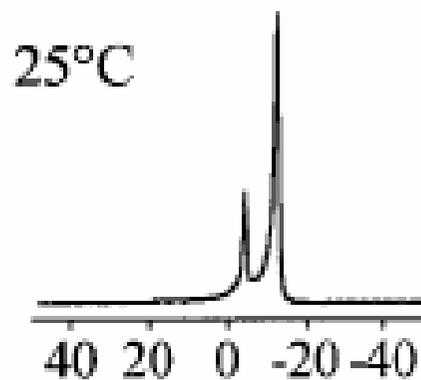
$$r = \frac{a}{c}$$



<sup>31</sup>P DMPC/DHPC (3:1)

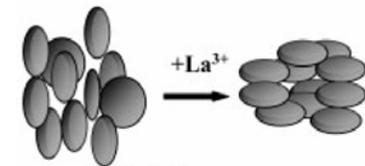


- Statisch
- hydratisierte Dispersion
- **Selbsterorientierung**



Chemical shift (ppm)

beste Selbsterorientierung



Tricks zur Auflösungserhöhung



## $^1\text{H}$ DMPC/DHPC (3:1)

50 mg Lipid

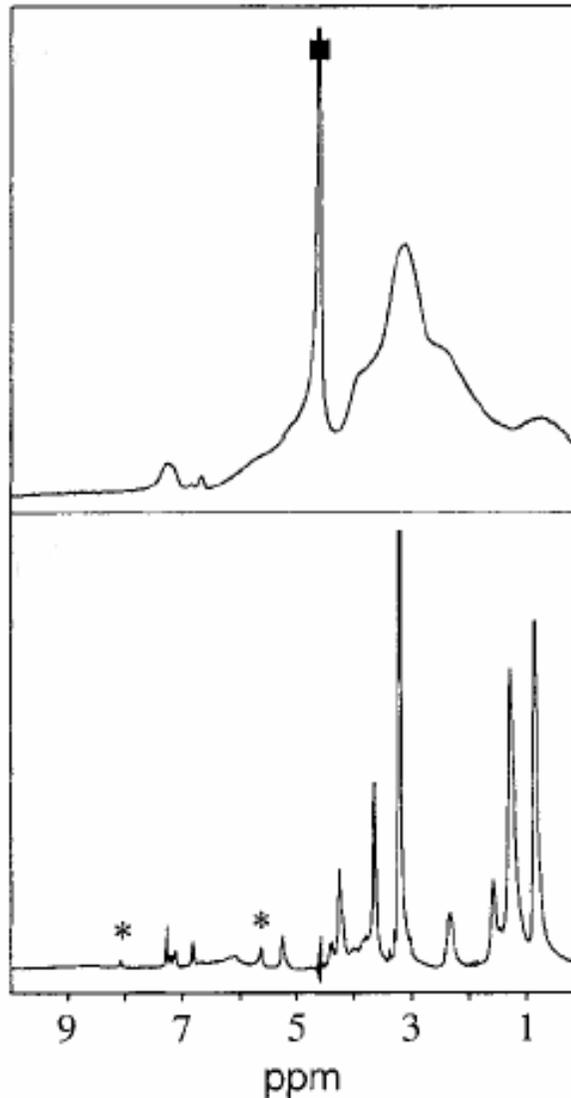
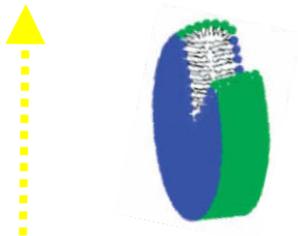
140  $\mu\text{l}$   $\text{D}_2\text{O}$  mit

70 mM  $\text{NaPO}_3$

30 mM KCl

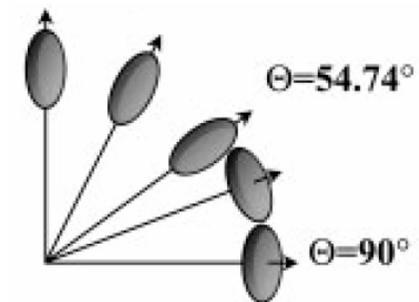
pD 7

305.5 K



- statisch
- hydratisierte Dispersion
- Selbstorientierung

- MAS: 980 Hz
- hydratisierte Dispersion
- Selbstorientierung

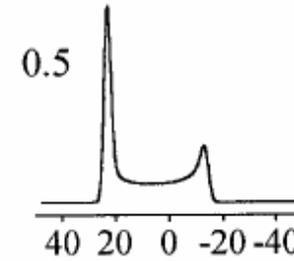
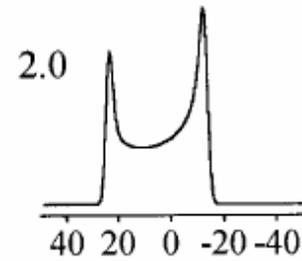
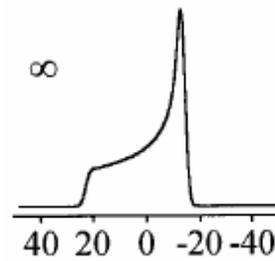


Tricks zur Auflösungserhöhung

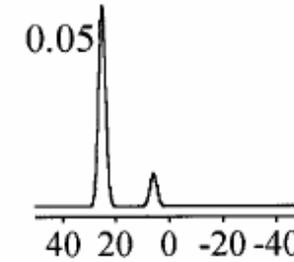
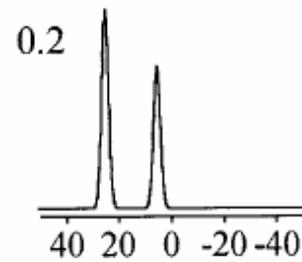
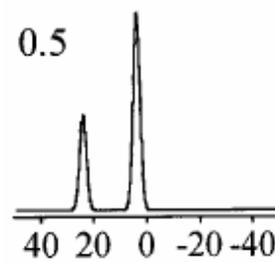
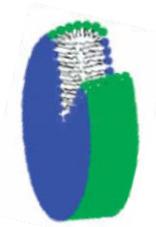


Simulationen

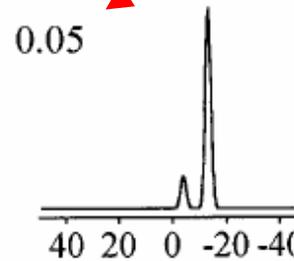
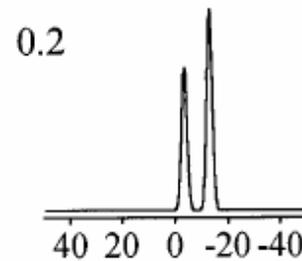
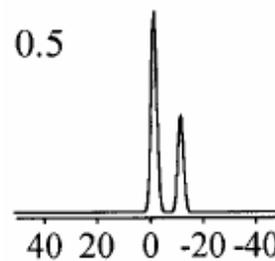
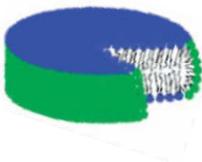
statisch



Chemical shift (ppm)

axiale Rotation  
laterale Diffusion

Chemical shift (ppm)



Chemical shift (ppm)

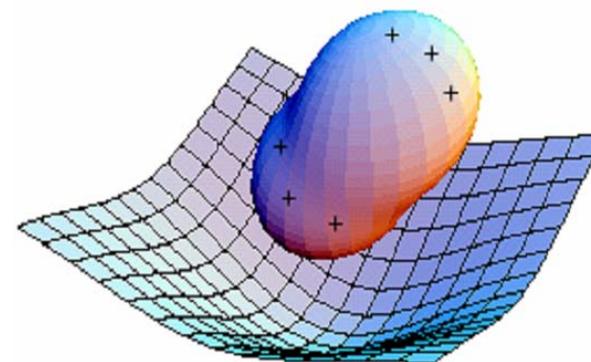
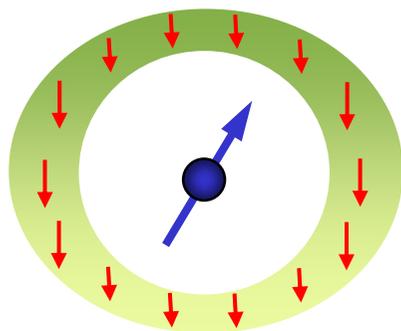
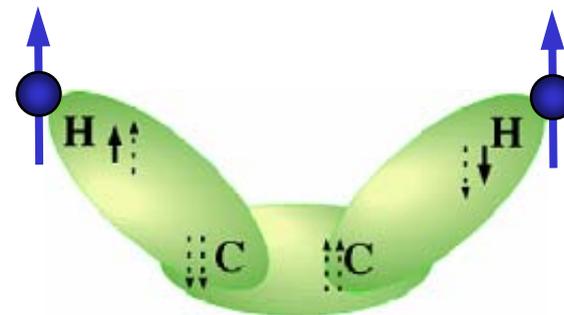
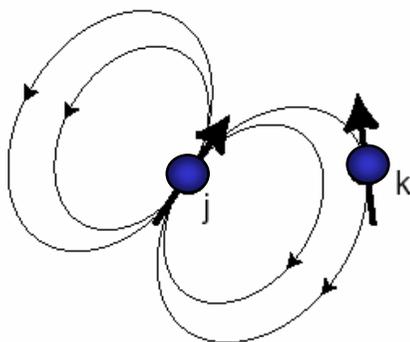
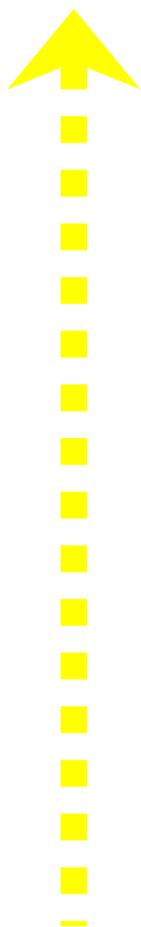
$$r = \frac{a}{c}$$

## Bewegungsprozesse in $^{31}\text{P}$ -Spektren von Bizellen



# Strukturaufklärung

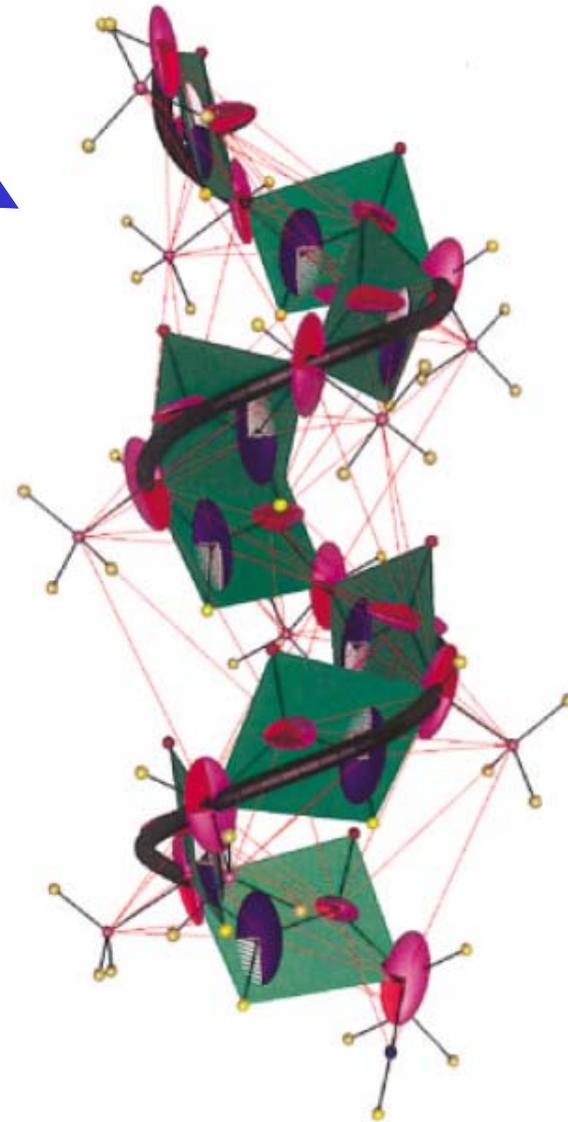
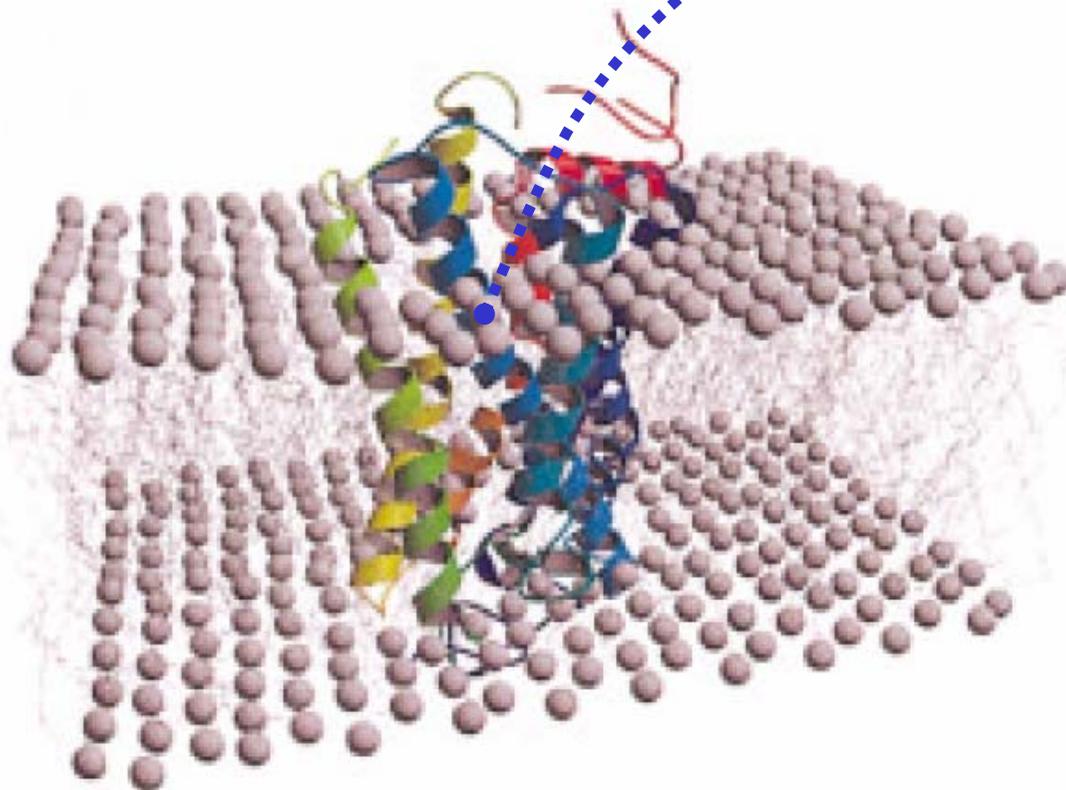
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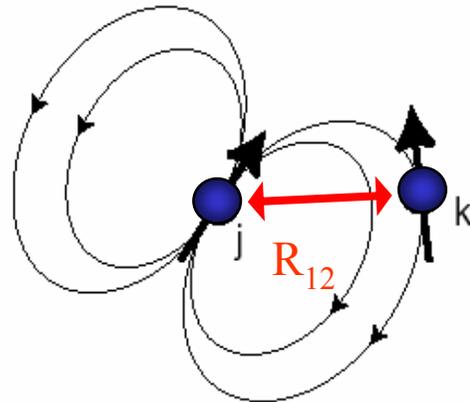
## Der kleine Zoo der NMR-Wechselwirkungen



Rhodopsin ( $\alpha$ -Helix)  
PDB-Eintrag: 1F88

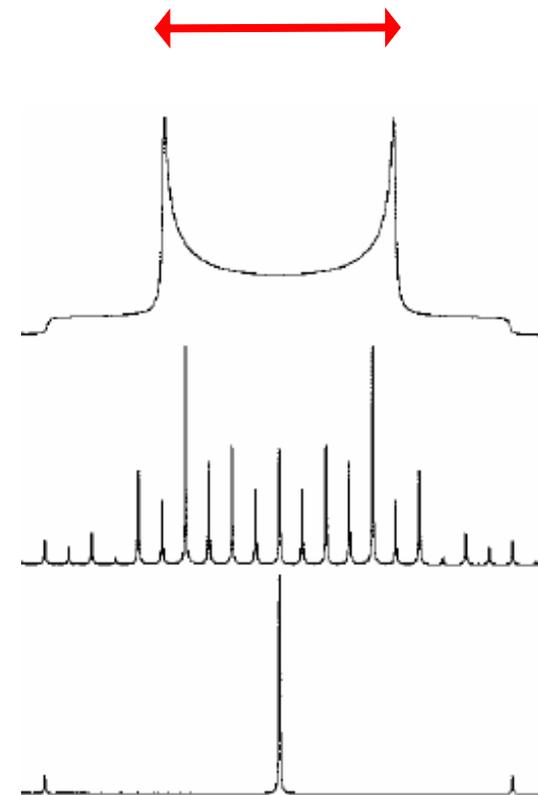


**NMR-Parameter-Repräsentation für Strukturaufklärung**



$$D_{12} = \hbar \frac{\mu_0}{4\pi} \frac{\gamma_1 \gamma_2}{R_{12}^3}$$

„Heteros“:  $D$   
„Homos“:  $3/2 D$

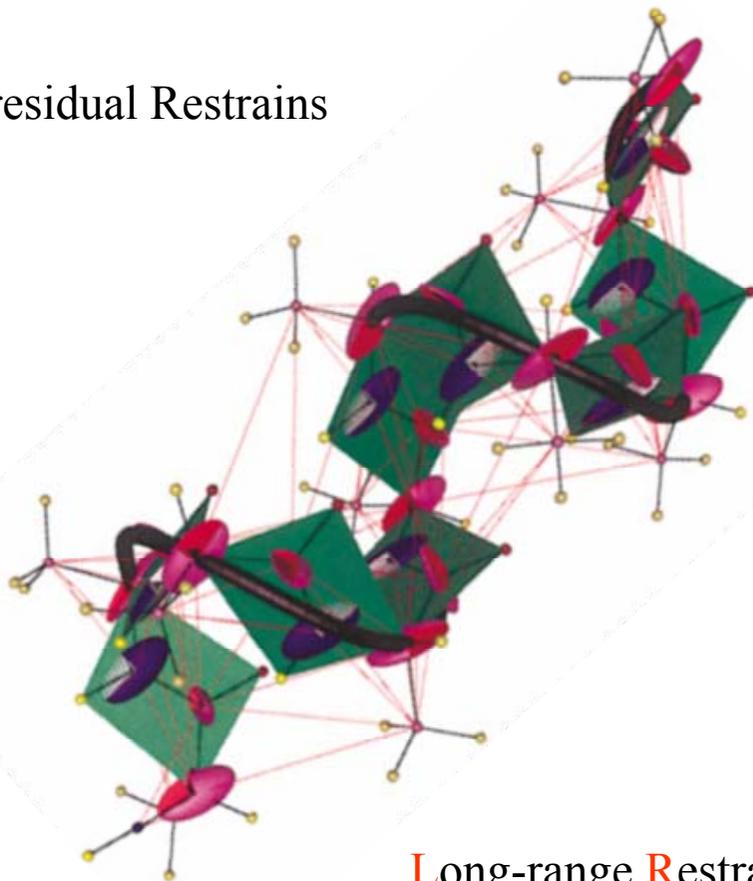


Der wichtigste Parameter: dipolare Kopplung



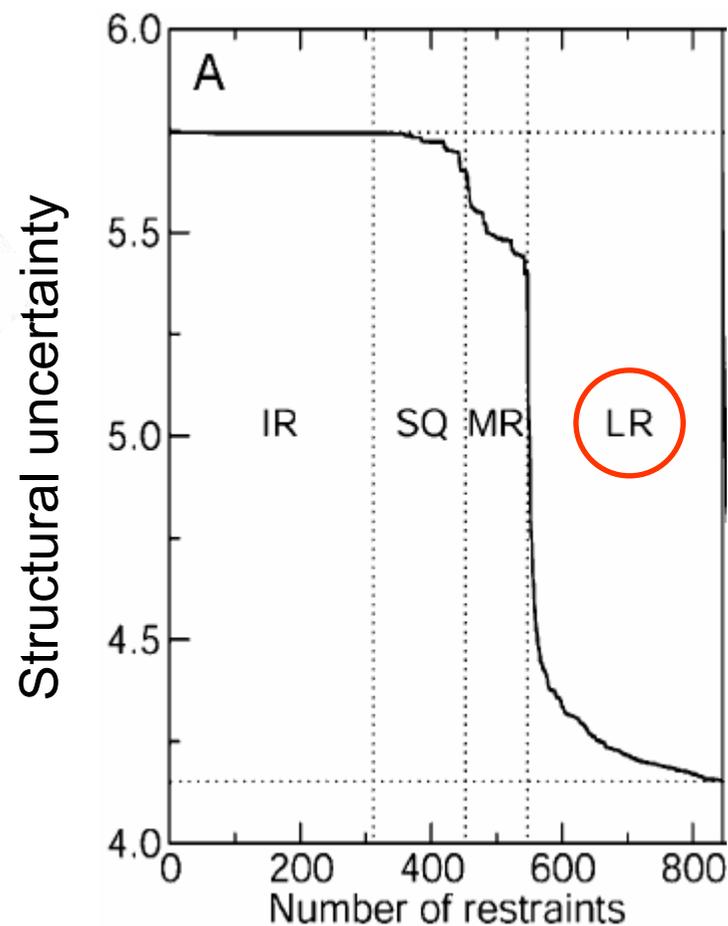
## Medium-range Restraints

Intraresidual Restraints

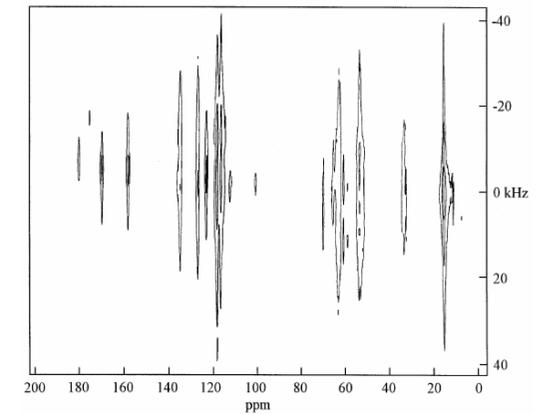
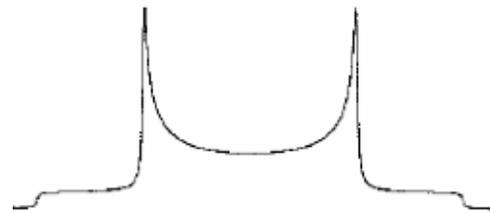
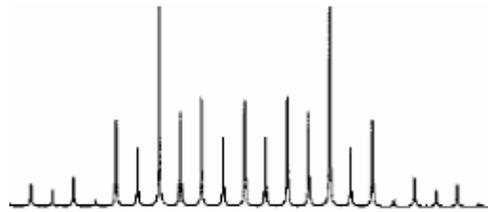


Long-range Restraints

Sequential Restraints



Welche dipolaren Kopplungen sind für eine Strukturaufklärung wichtig?



statisches Experiment  
1D-MAS-Experiment

SLF

$R^2$

REDOR

C7

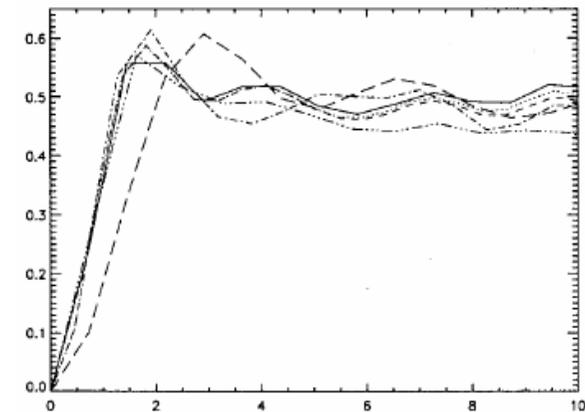
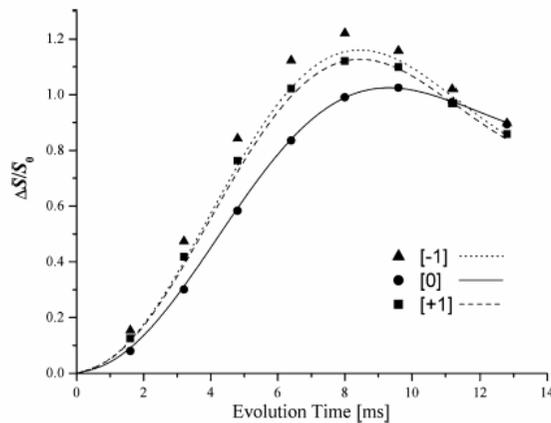
Post-C7

BABA

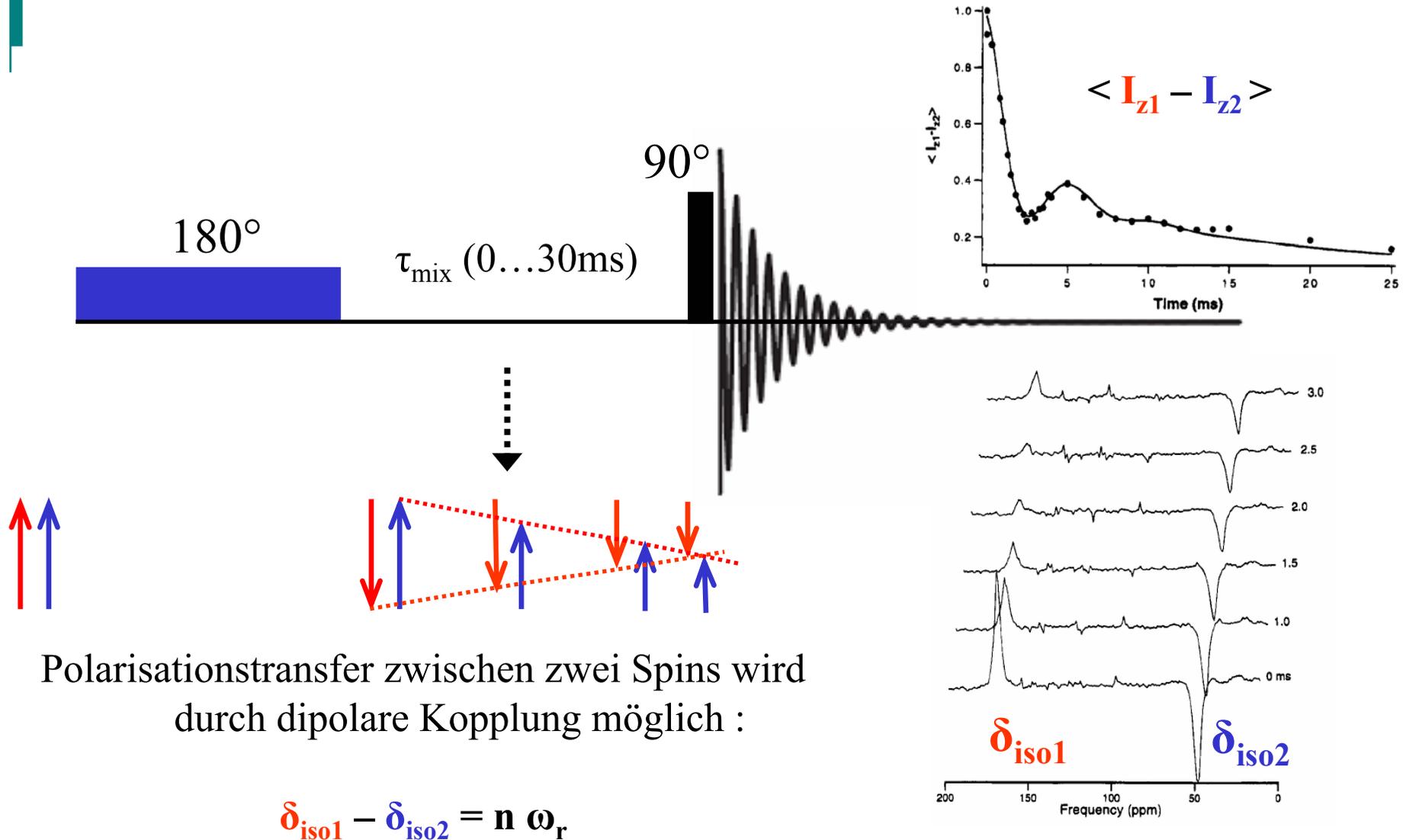
RFDR

PDSD

...



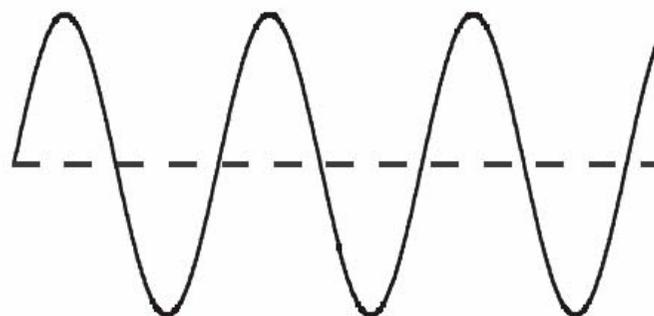
Zoo von Experimenten zur Bestimmung der dipolaren Kopplung



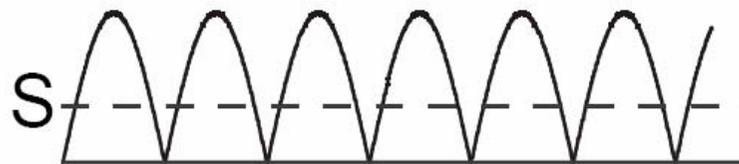
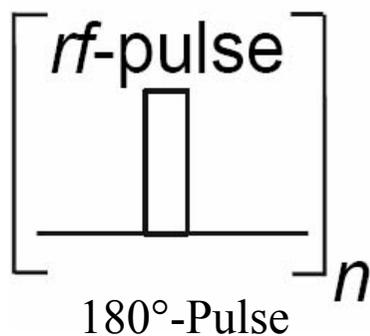
## R<sup>2</sup>: Rotational Resonance



MAS



$$\omega_{\text{dip}}(t) = 0$$



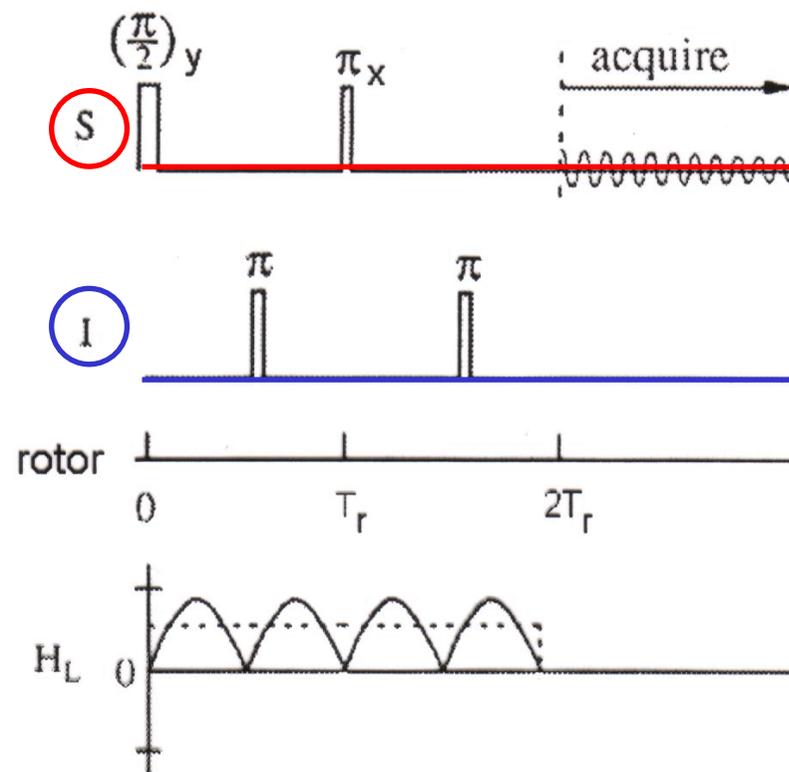
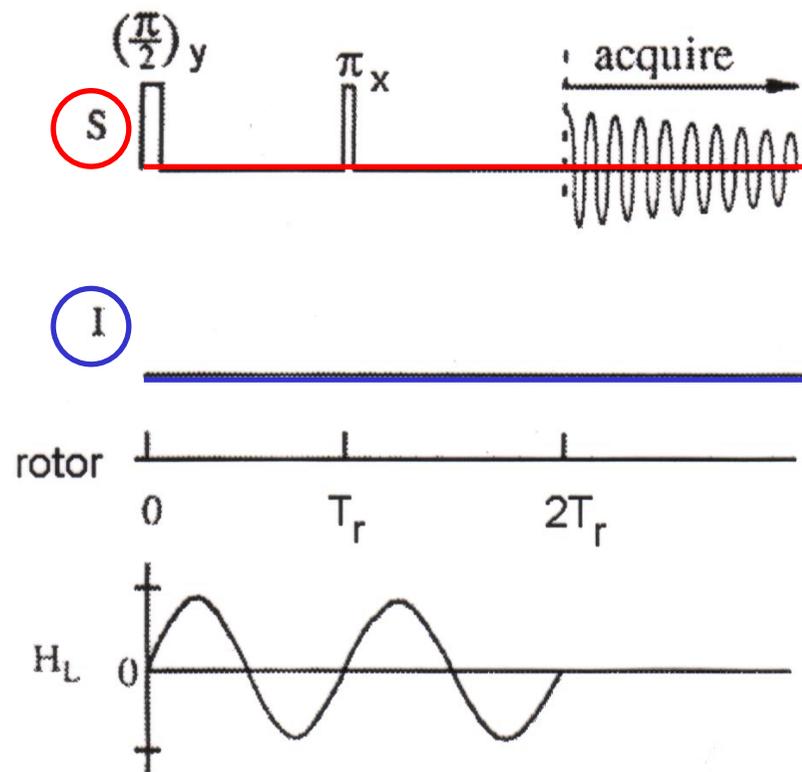
$$\omega_{\text{dip}}(t) \neq 0$$

## Rotational-Echo double Resonance (REDOR)



$Signal_{CS}$

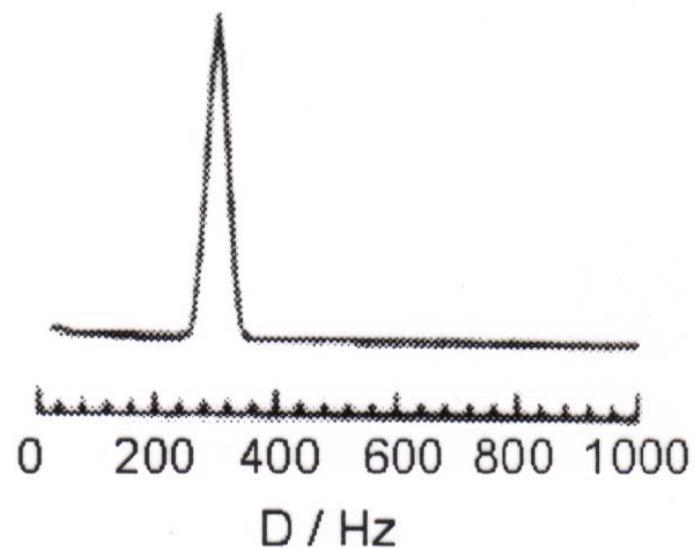
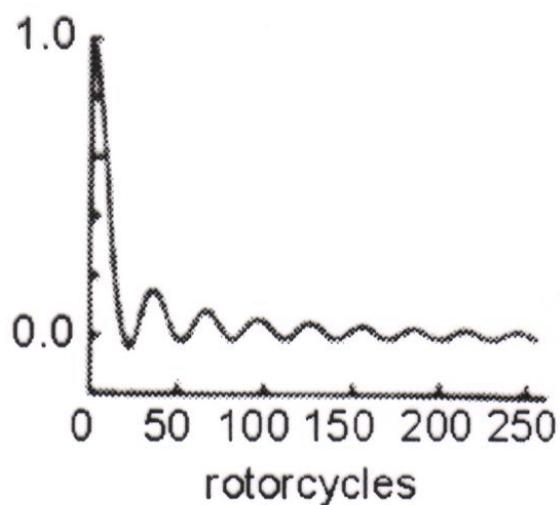
$Signal_{CS} \cdot Signal_{IS}$



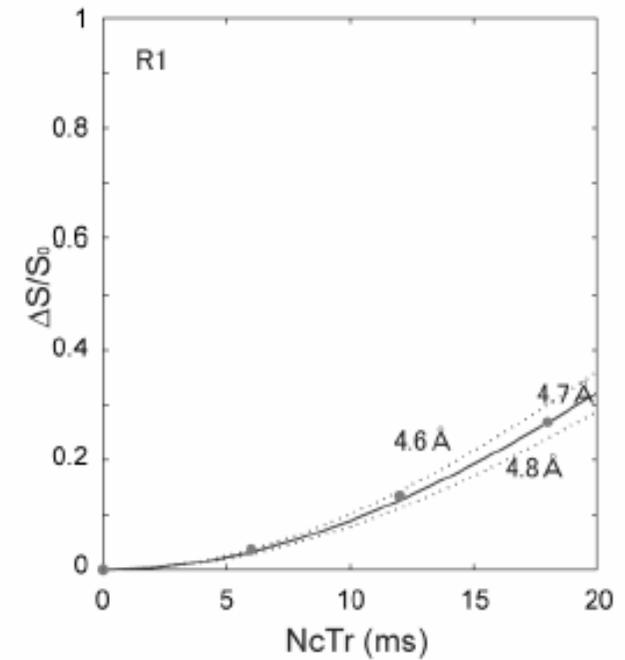
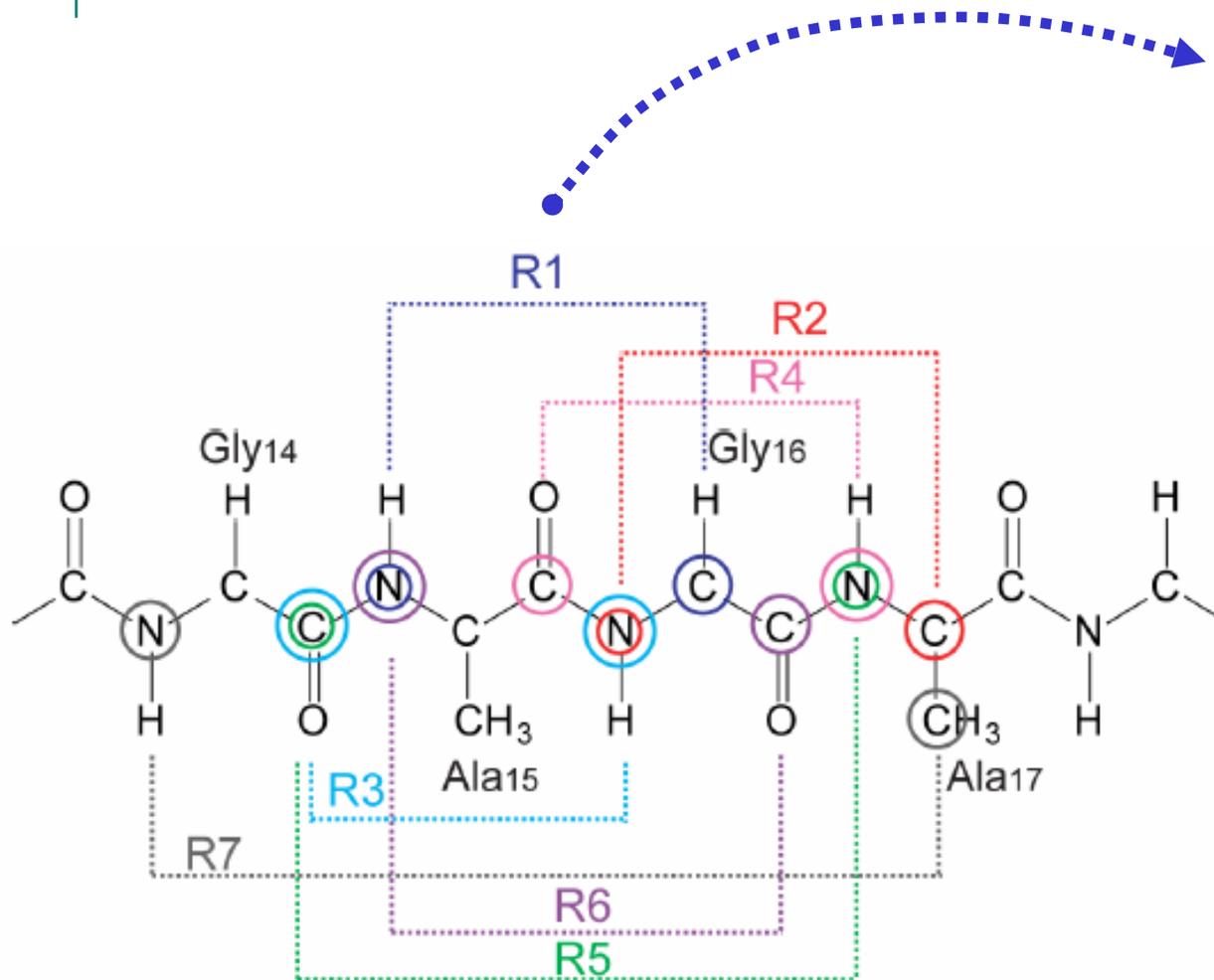
**Rotational-Echo double Resonance (REDOR)**



$$\frac{\text{Signal}_{CS} - \text{Signal}_{CS} \cdot \text{Signal}_{IS}}{\text{Signal}_{CS}} = 1 - \text{Signal}_{IS}$$



## REDOR-Signal und REDOR-Transformation

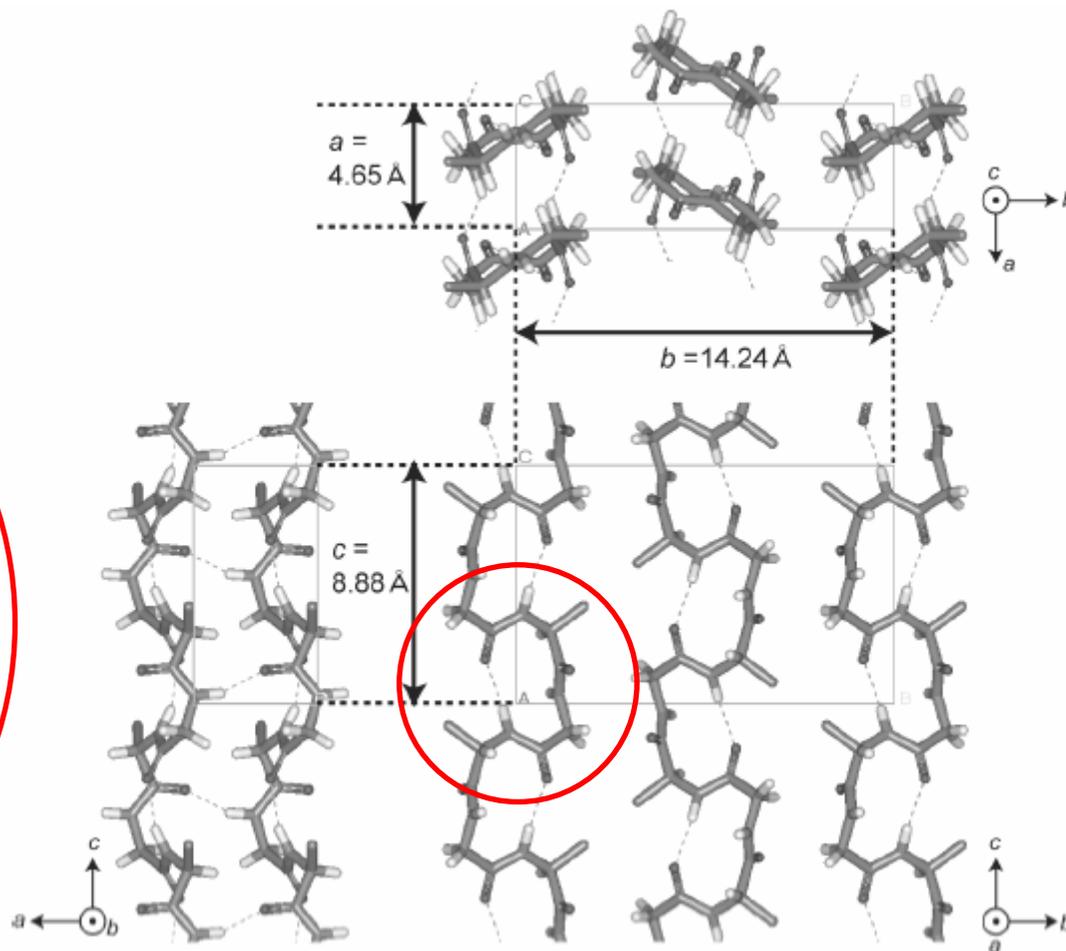
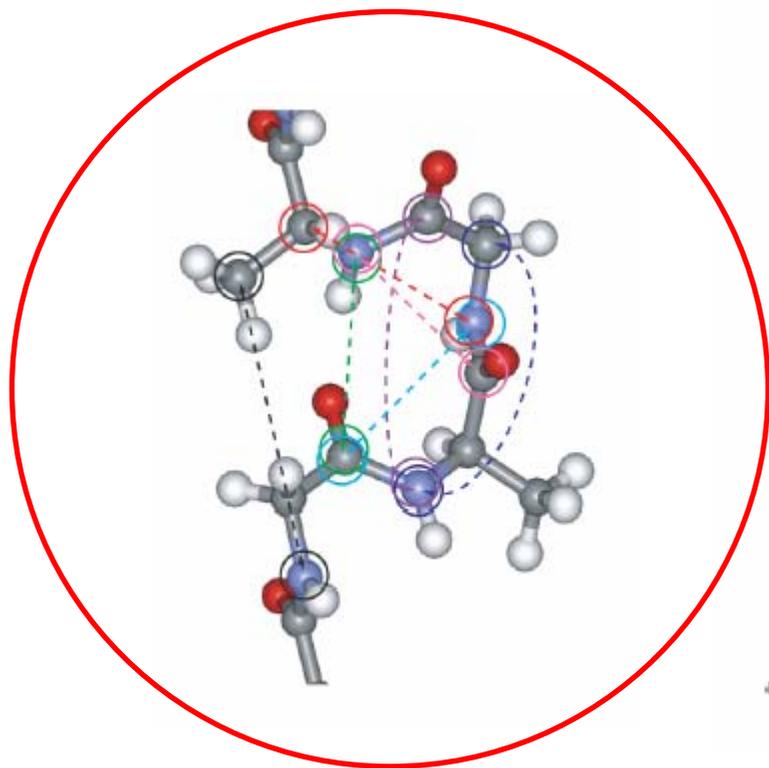


REDOR-Kurve (C-N)

## REDOR an Seide I Fibroin



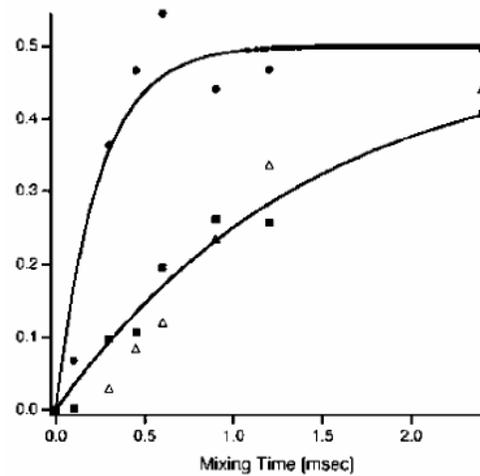
REDOR-Abstände (C-N)



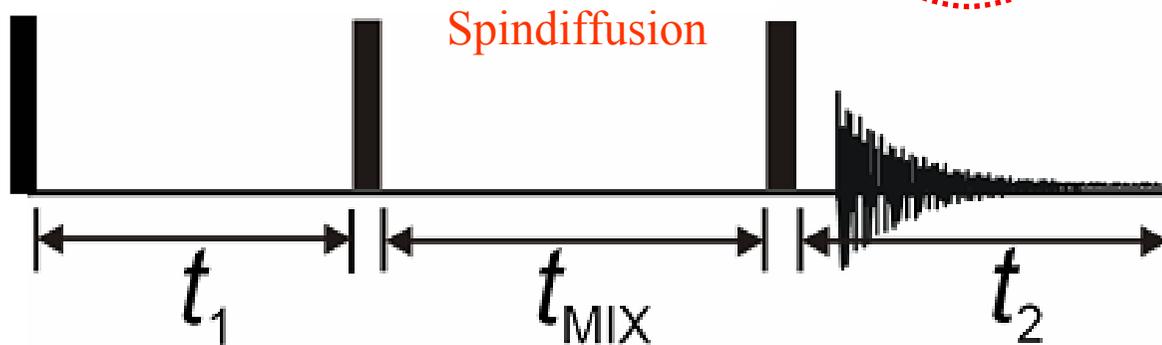
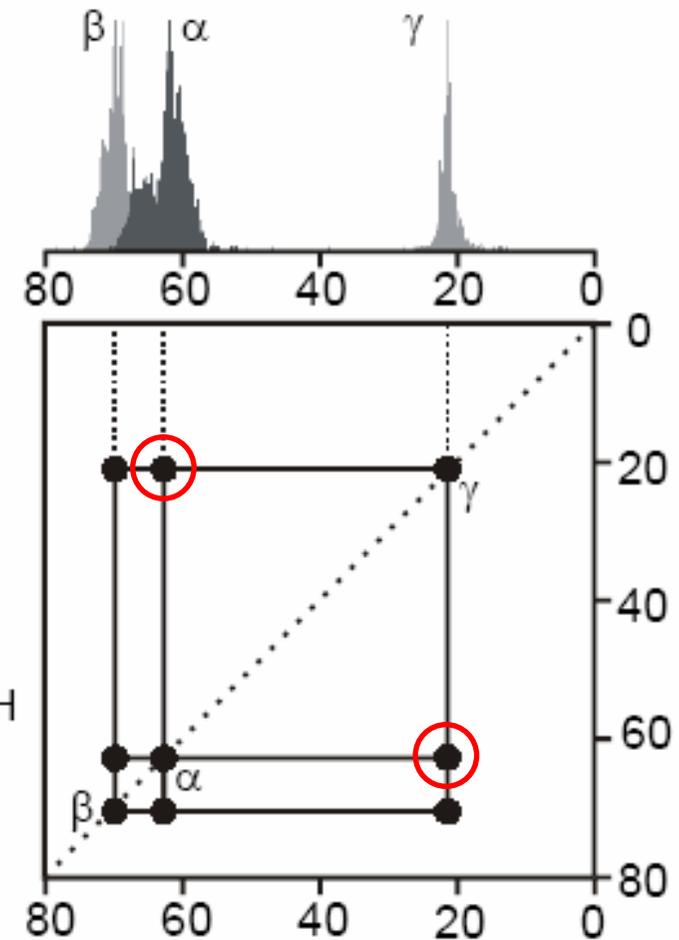
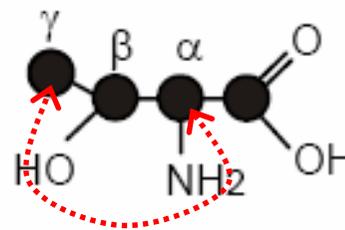
## REDOR an Seide I Fibroin



## Aufbaukurven des Magnetisierungstransfers



threonine

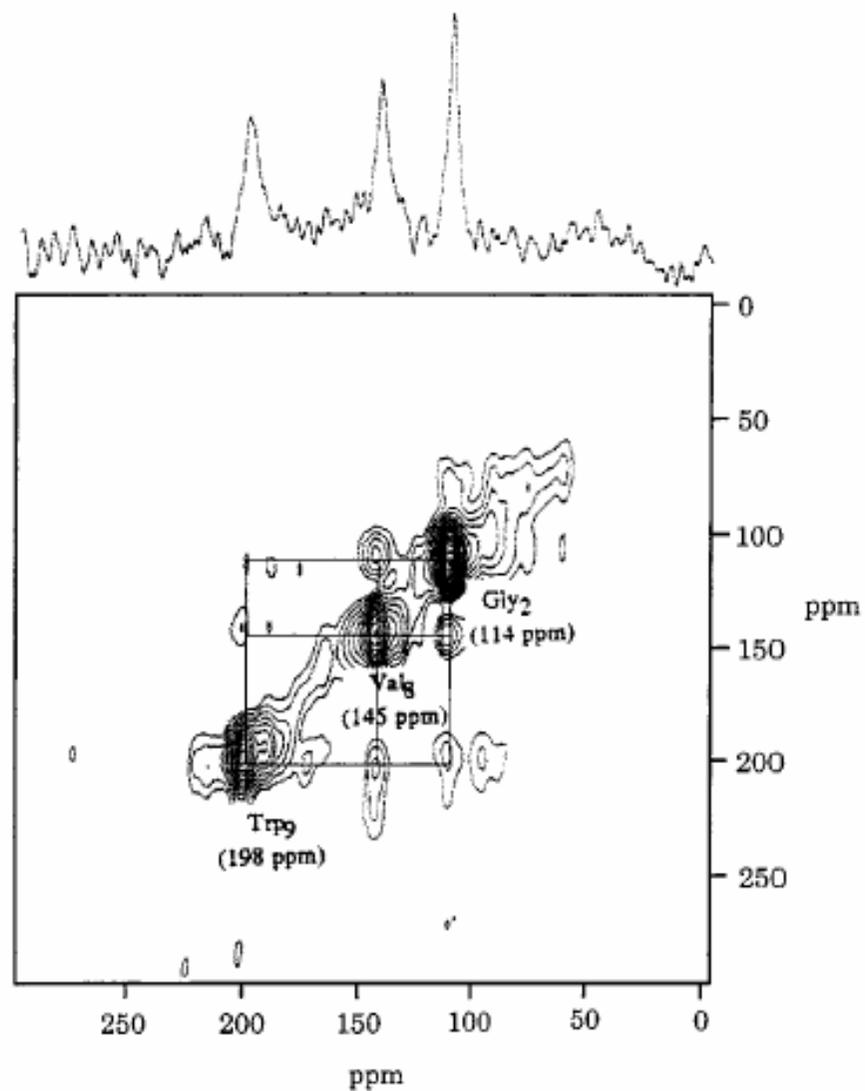


## Proton Driven Spin Diffusion (PDSD)

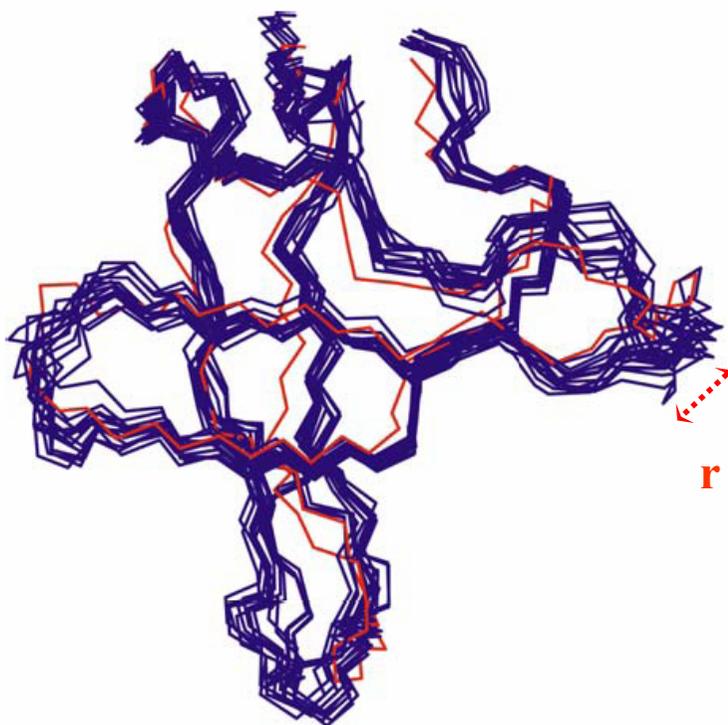


Spindiffusion zwischen den  
Windungen der  $\beta$ -Helix von

$^{15}\text{N}$ -Gly<sub>2</sub>  
 $^{15}\text{N}$ -Val<sub>8</sub>  
 $^{15}\text{N}$ -Trp<sub>9</sub>

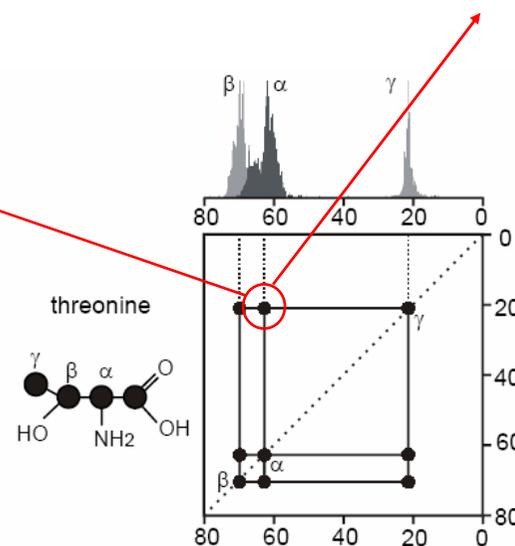


**PDSD an  $^{15}\text{N}$ -GA**



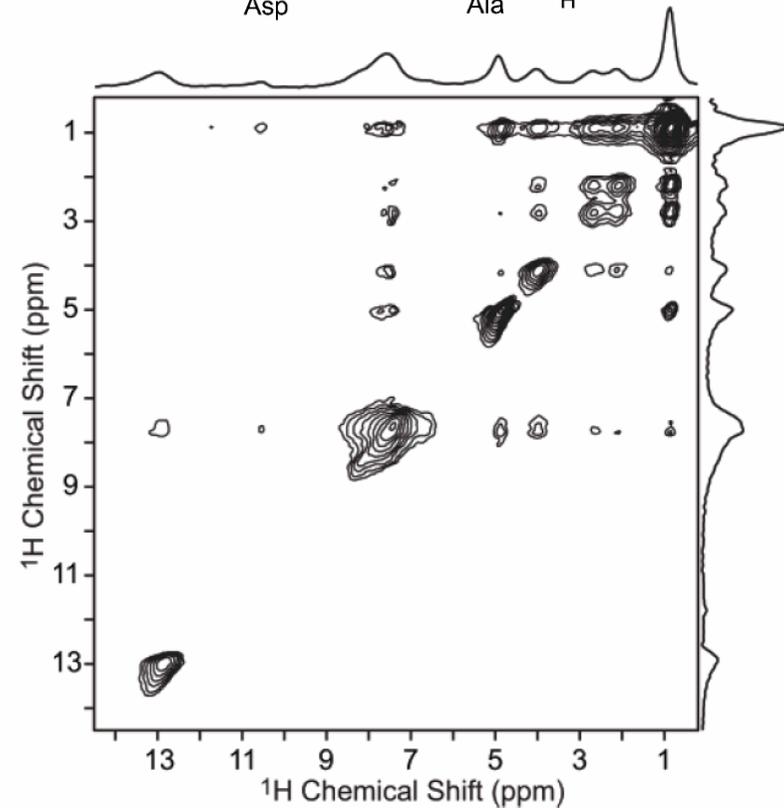
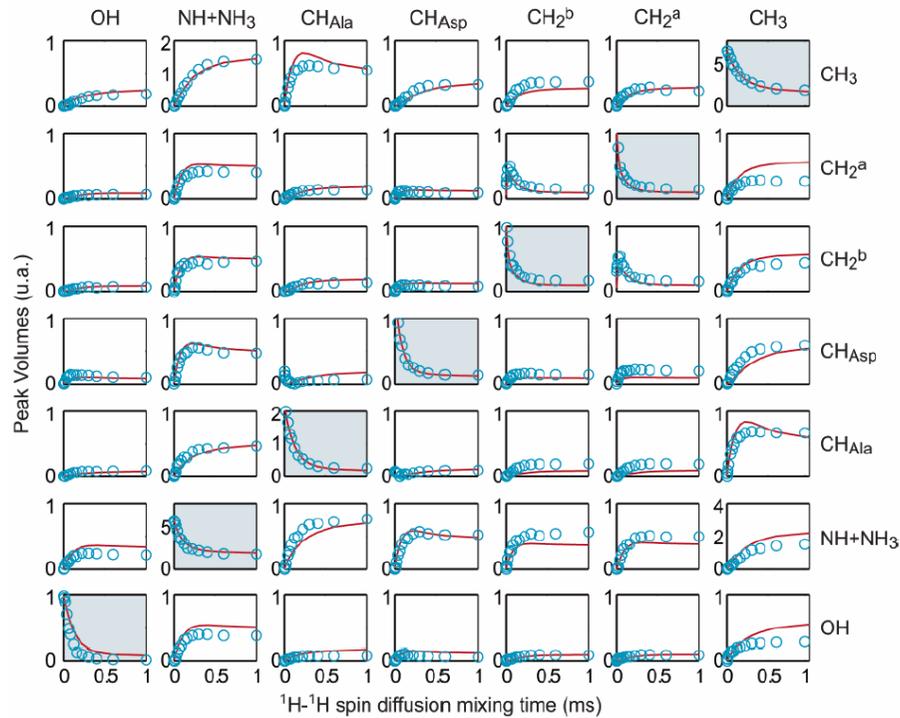
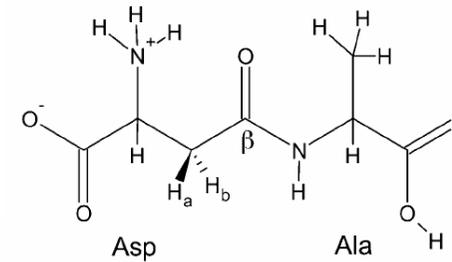
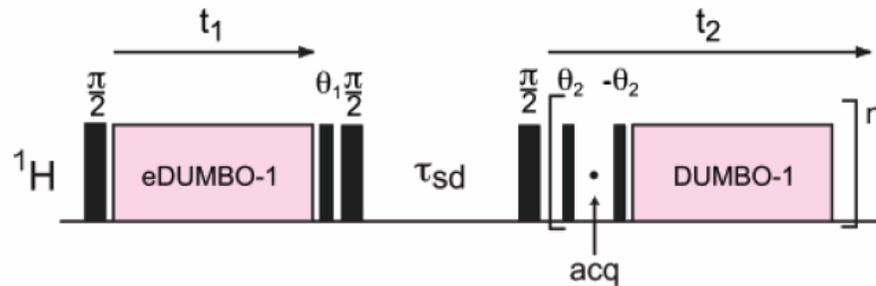
Automatische Signalzuordnung  
und Strukturbestimmung.

Bei Kreuzsignalen:  $2.5\text{\AA} < r < 6.5\text{\AA}$

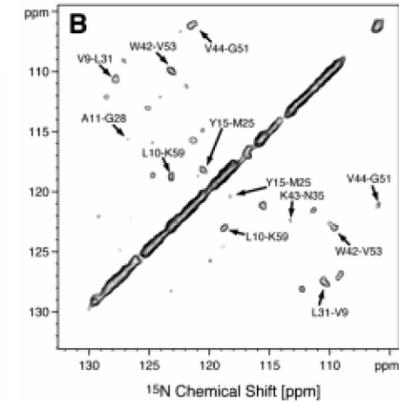
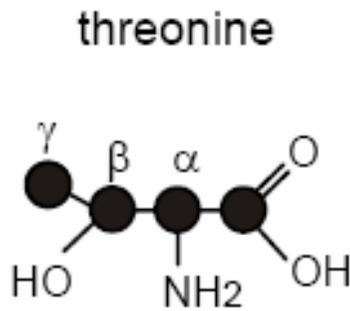
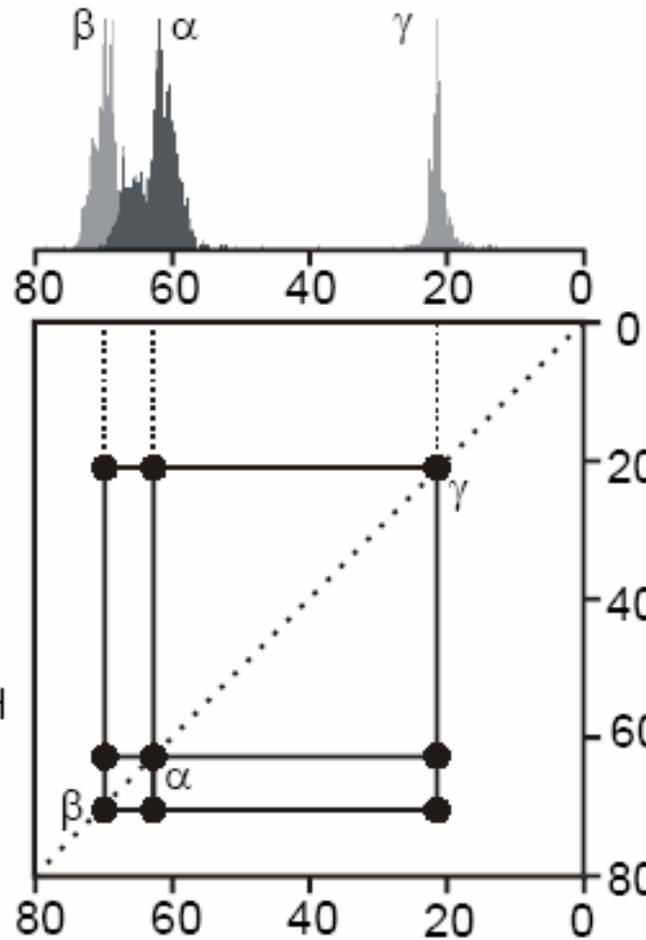
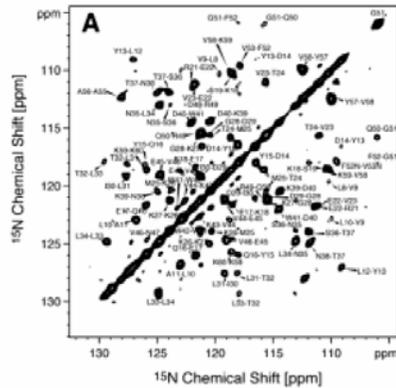




mikrokristallines  $\beta$ -L-aspartyl-L-alanine

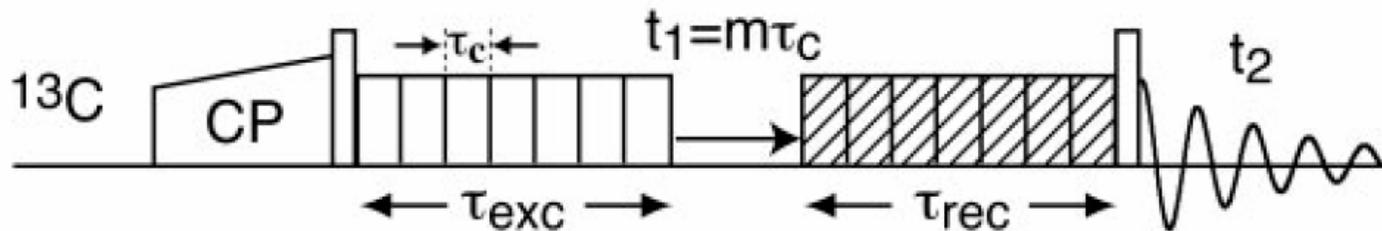
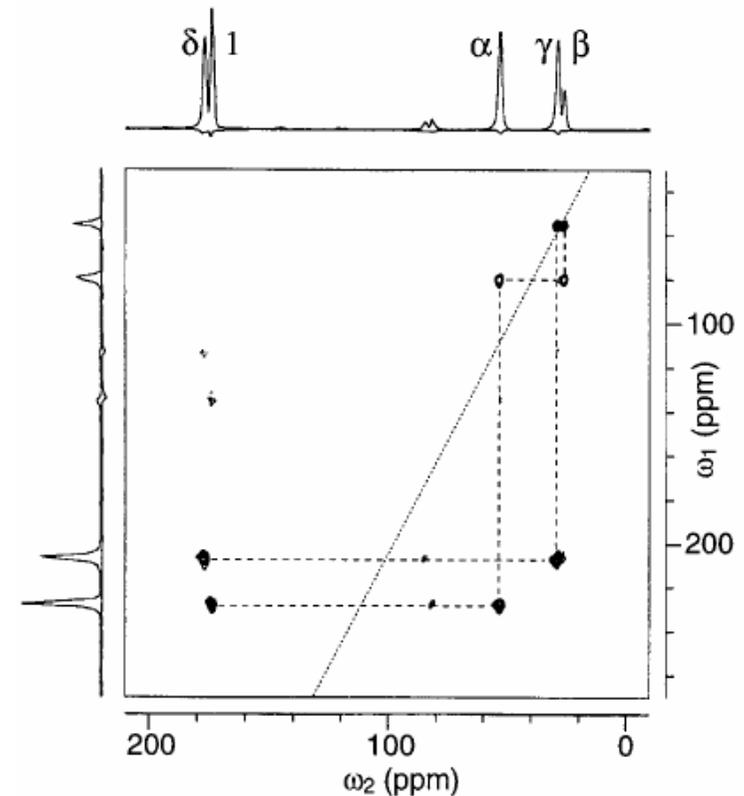
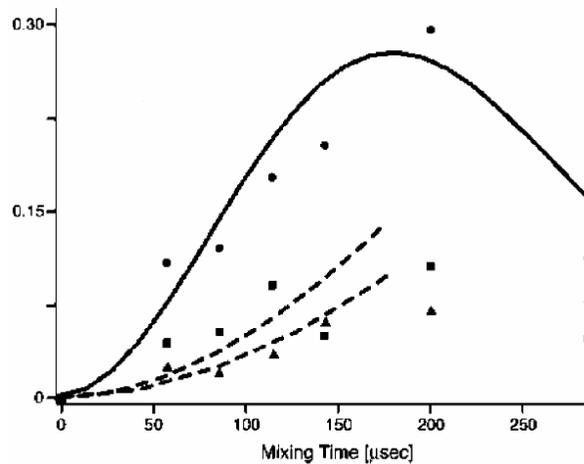


## $^1\text{H}$ - $^1\text{H}$ -Spindiffusion





## Aufbaukurven des Magnetisierungstransfers



## C7-Doppelquanten-INADEQUAT



$$H_{II} = \hbar \cdot \omega_D \cdot \{ A + B + C + D + E + F \}$$

$$A = + (1 - 3 \cos^2\theta) I_{1z} I_{2z}$$

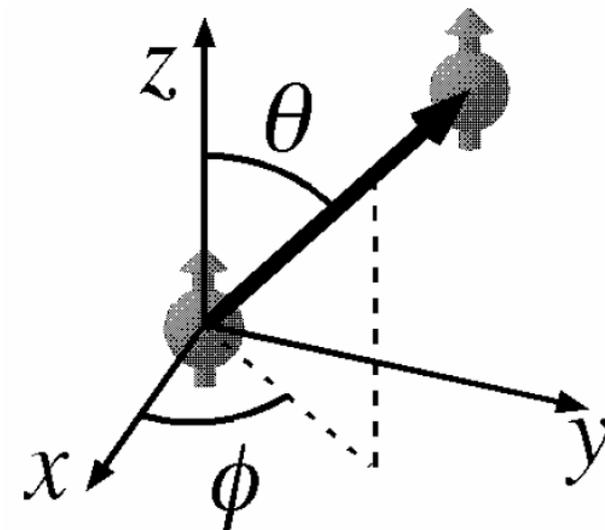
$$B = -\frac{1}{4}(1 - 3 \cos^2\theta) (I_{1+} I_{2-} + I_{1-} I_{2+})$$

$$C = -\frac{3}{2} \sin\theta \cos\theta e^{-i\phi} (I_{1z} I_{2+} + I_{1+} I_{2z})$$

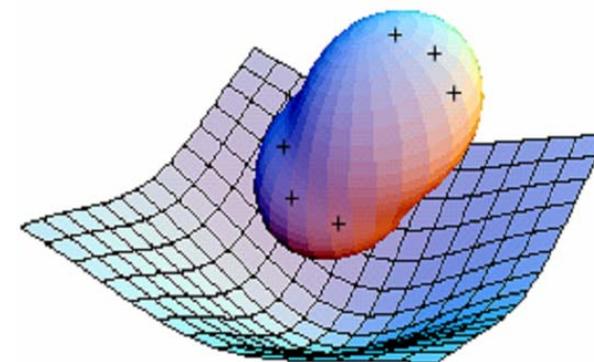
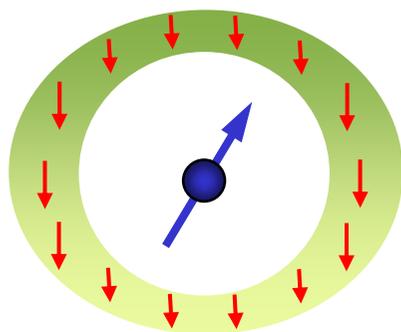
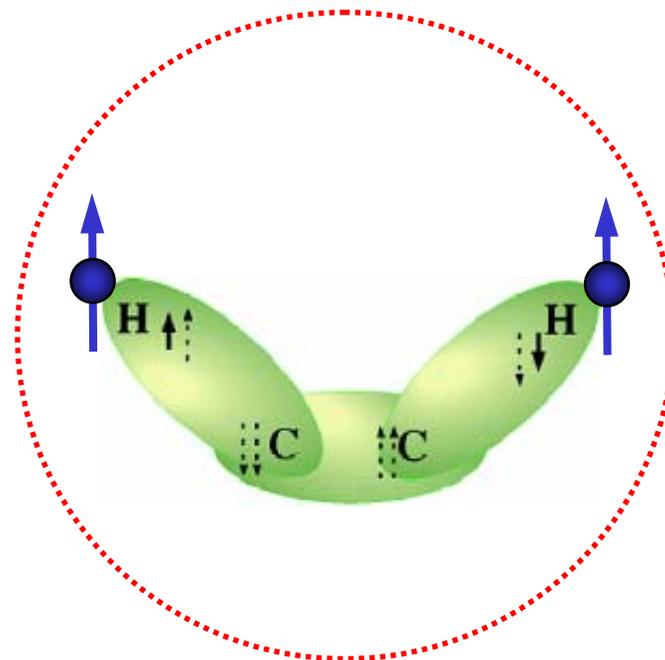
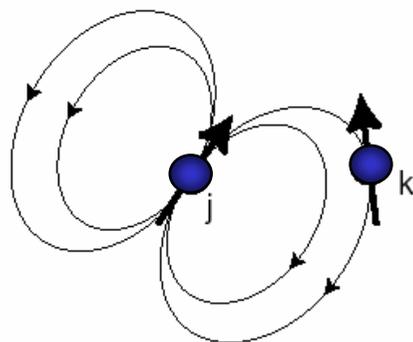
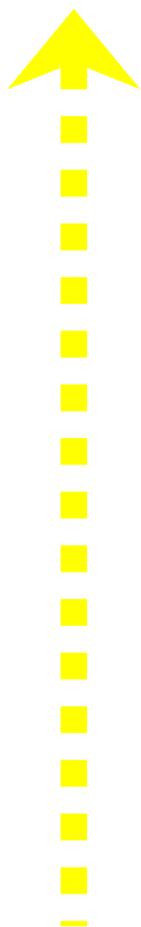
$$D = -\frac{3}{2} \sin\theta \cos\theta e^{i\phi} (I_{1z} I_{2-} + I_{1-} I_{2z})$$

$$E = -\frac{3}{4} \sin^2\theta e^{-2i\phi} \quad I_{1+} I_{2+}$$

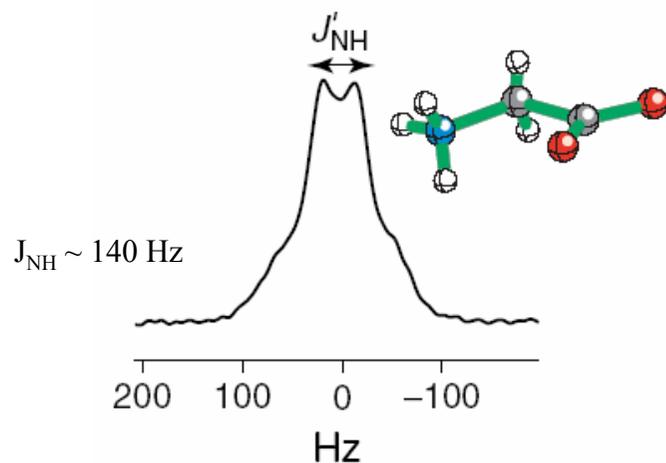
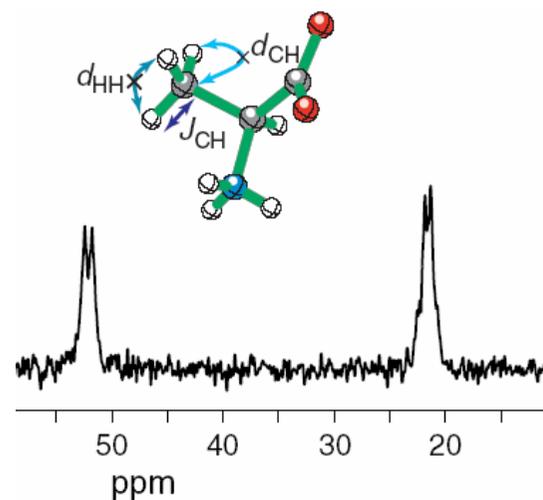
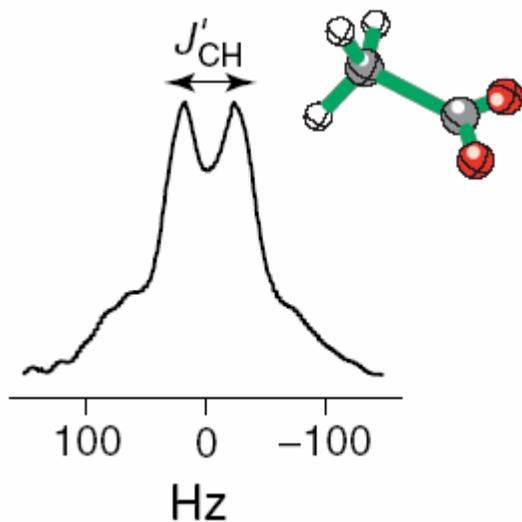
$$F = -\frac{3}{4} \sin^2\theta e^{2i\phi} \quad I_{1-} I_{2-}$$



Was sind Doppelquanten?

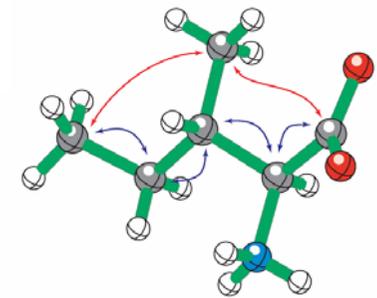
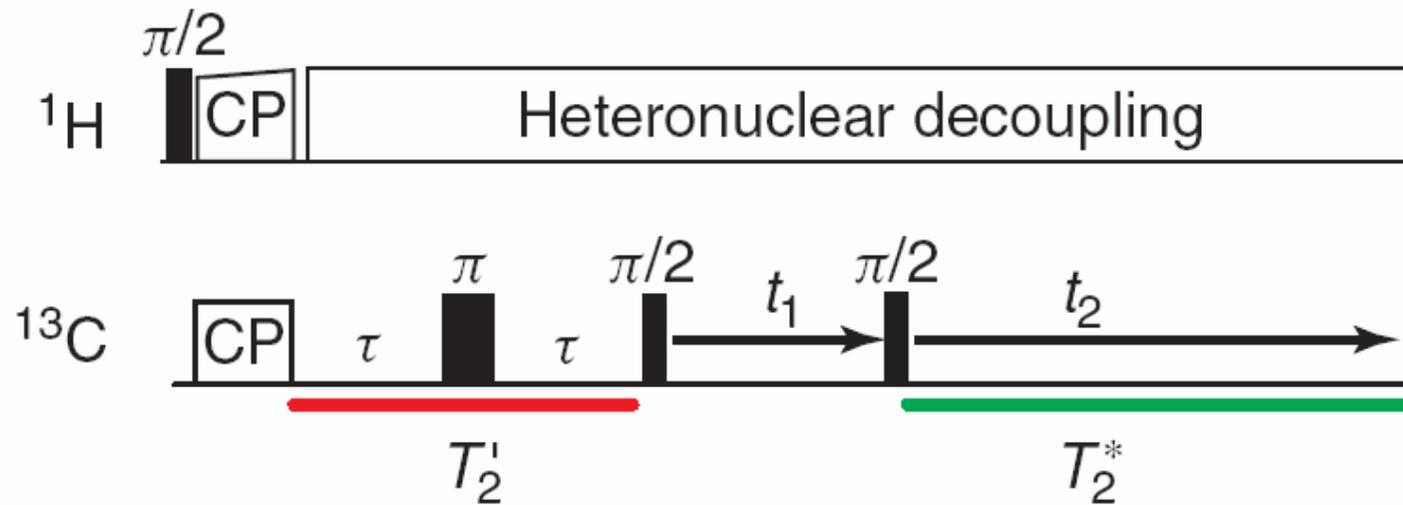


## Der kleine Zoo der NMR-Wechselwirkungen



**J-Kopplungsspektren unter MAS und  
homonuklearer Protonenkopplung  
(Skalierung mit  $1/\sqrt{3}$ )**

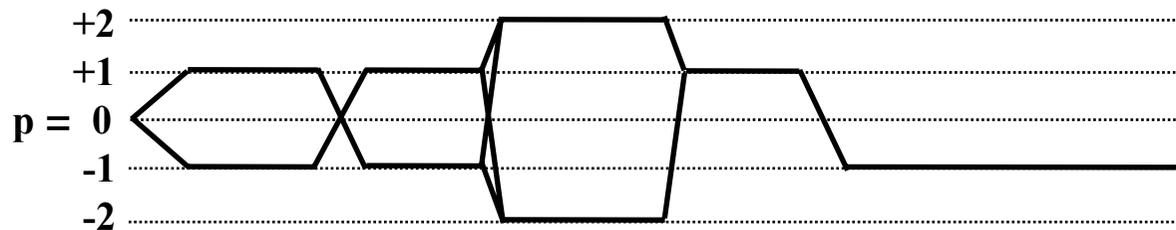
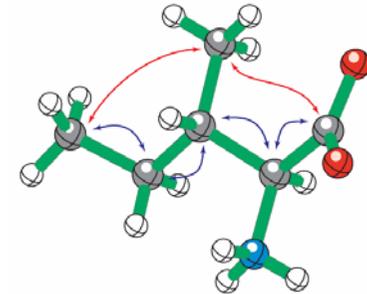
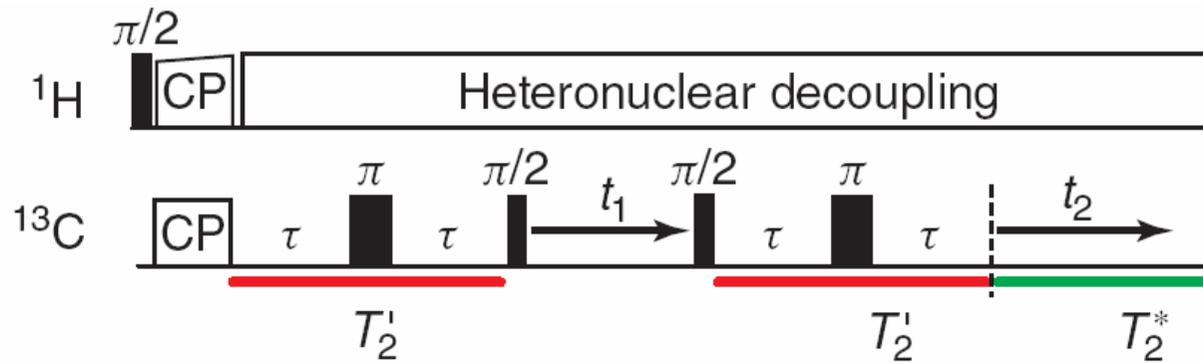
## 1D-Spektren zur J-Kopplung



Rotorsynchrones Echo für die  
homonukleare skallare Kopplung

$$\tau = \frac{1}{4 J_{CC}} = n \tau_r$$

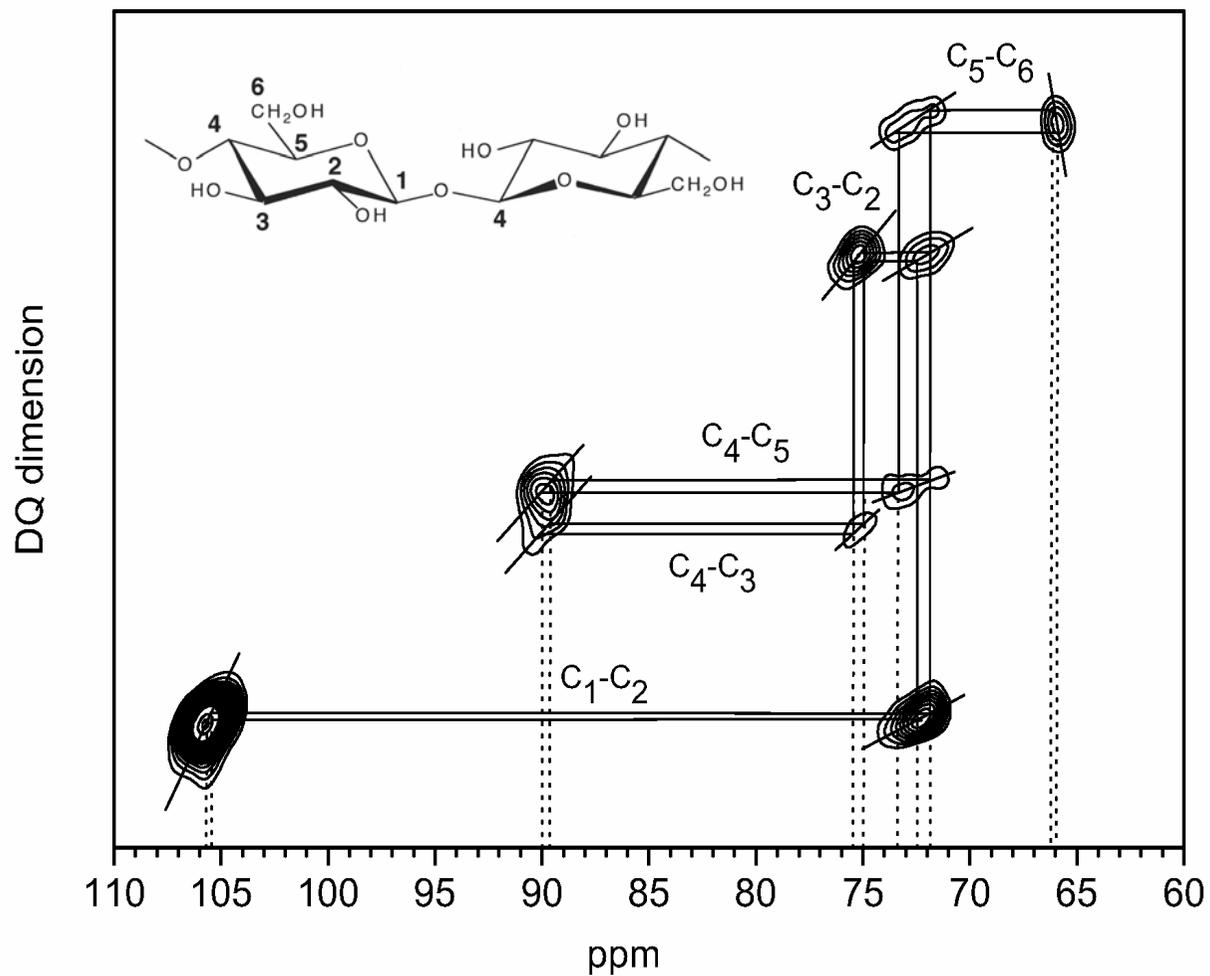
## Korrelationsexperiment mittels J-Kopplung



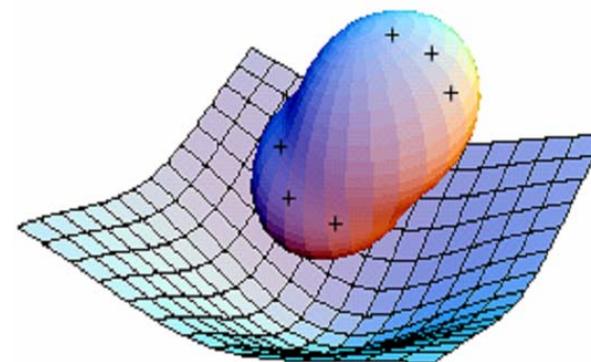
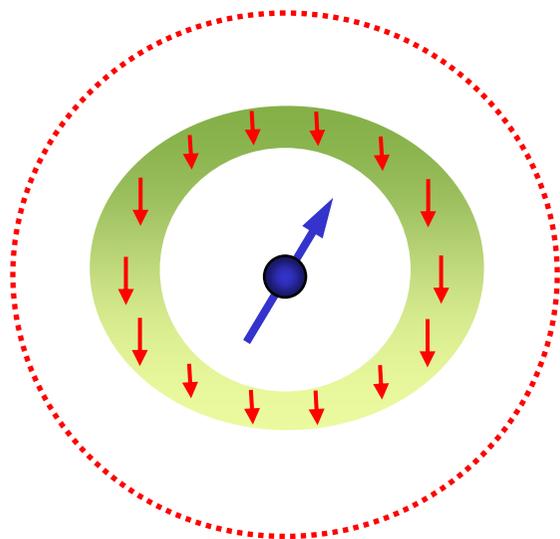
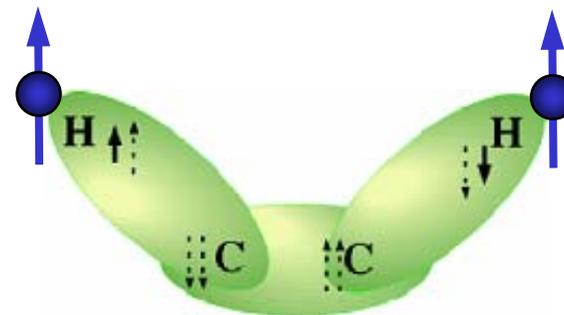
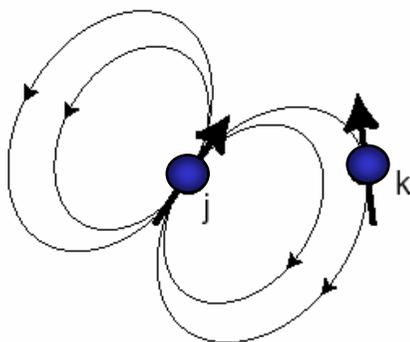
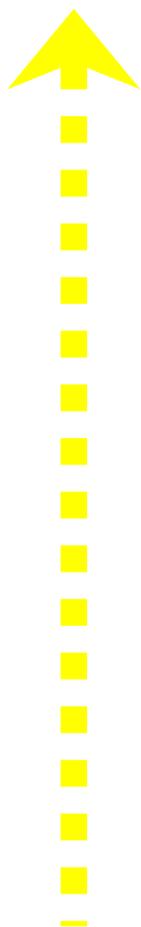
Rotorsynchrones Refokussieren der  
homonuklearen skalaren Kopplung.

$$\tau = \frac{1}{4 J_{CC}} = n \tau_r$$

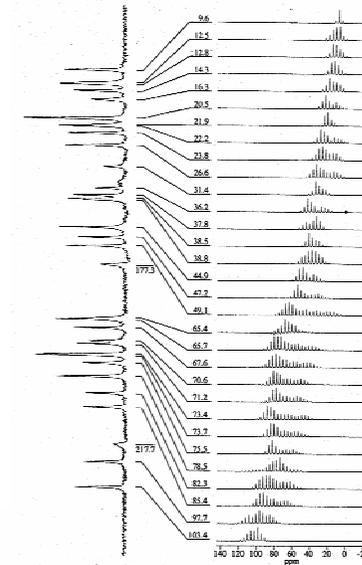
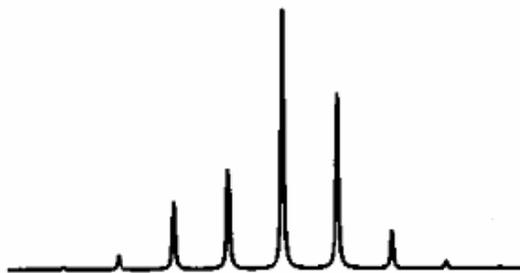
refocused INADEQUATE



refocused-INADEQUATE an Cellulose



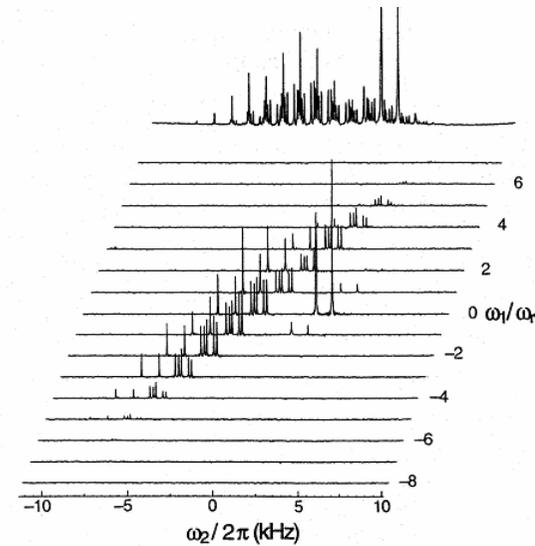
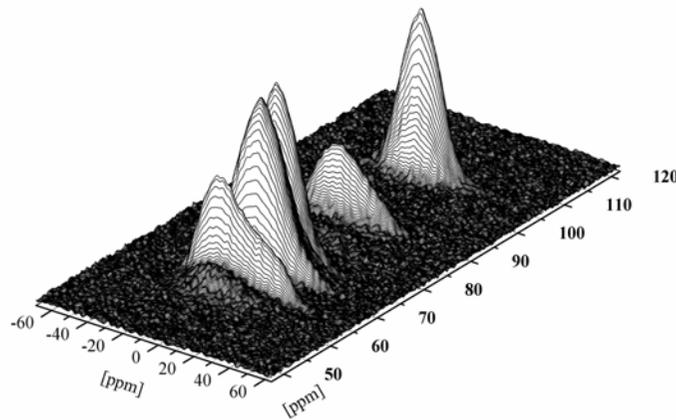
## Der kleine Zoo der NMR-Wechselwirkungen



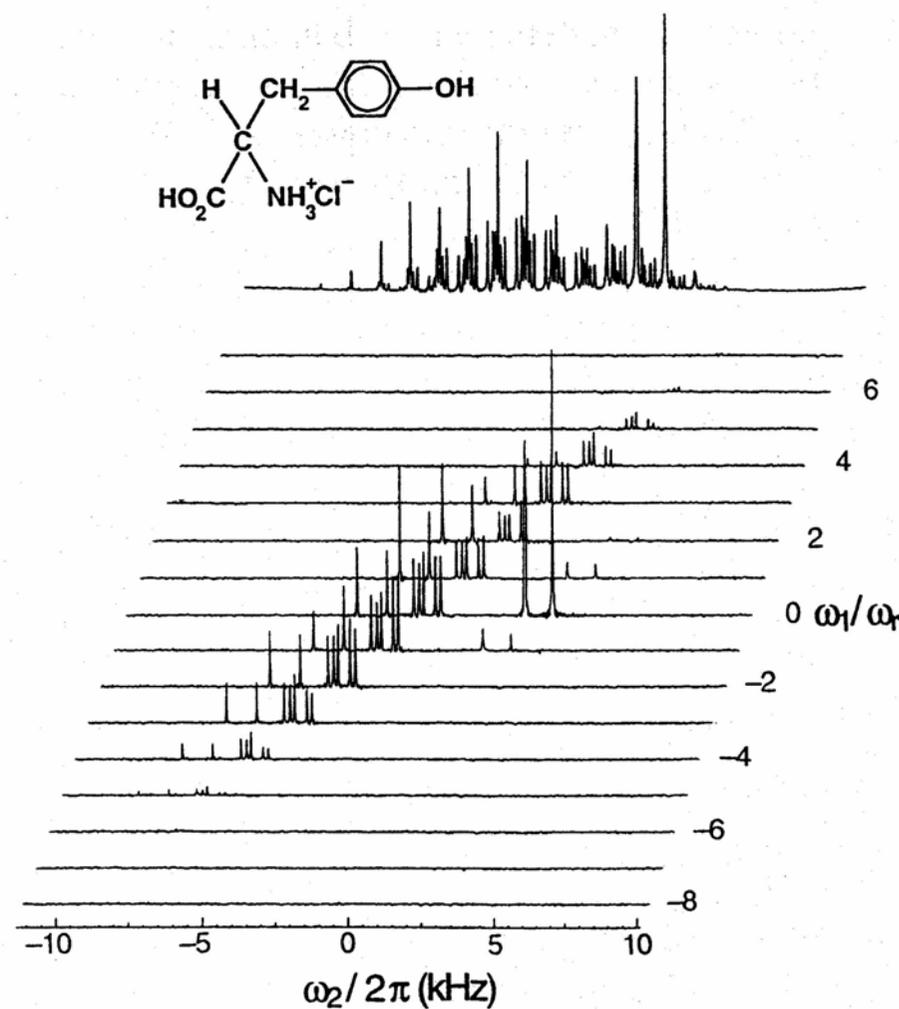
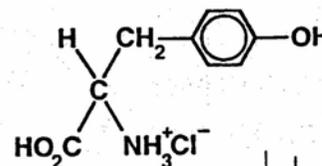
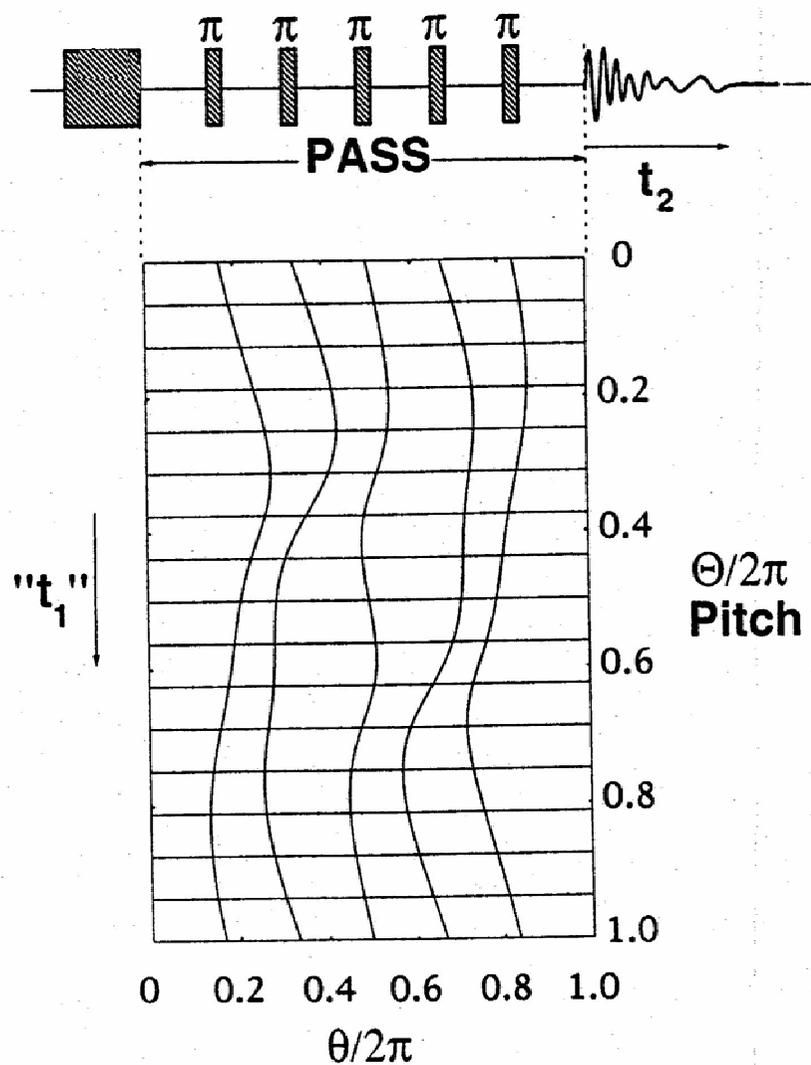
statisches Experiment  
1D-MAS-Experiment

TOSS  
PASS  
MAT  
RAI  
SUPER  
ROCSA

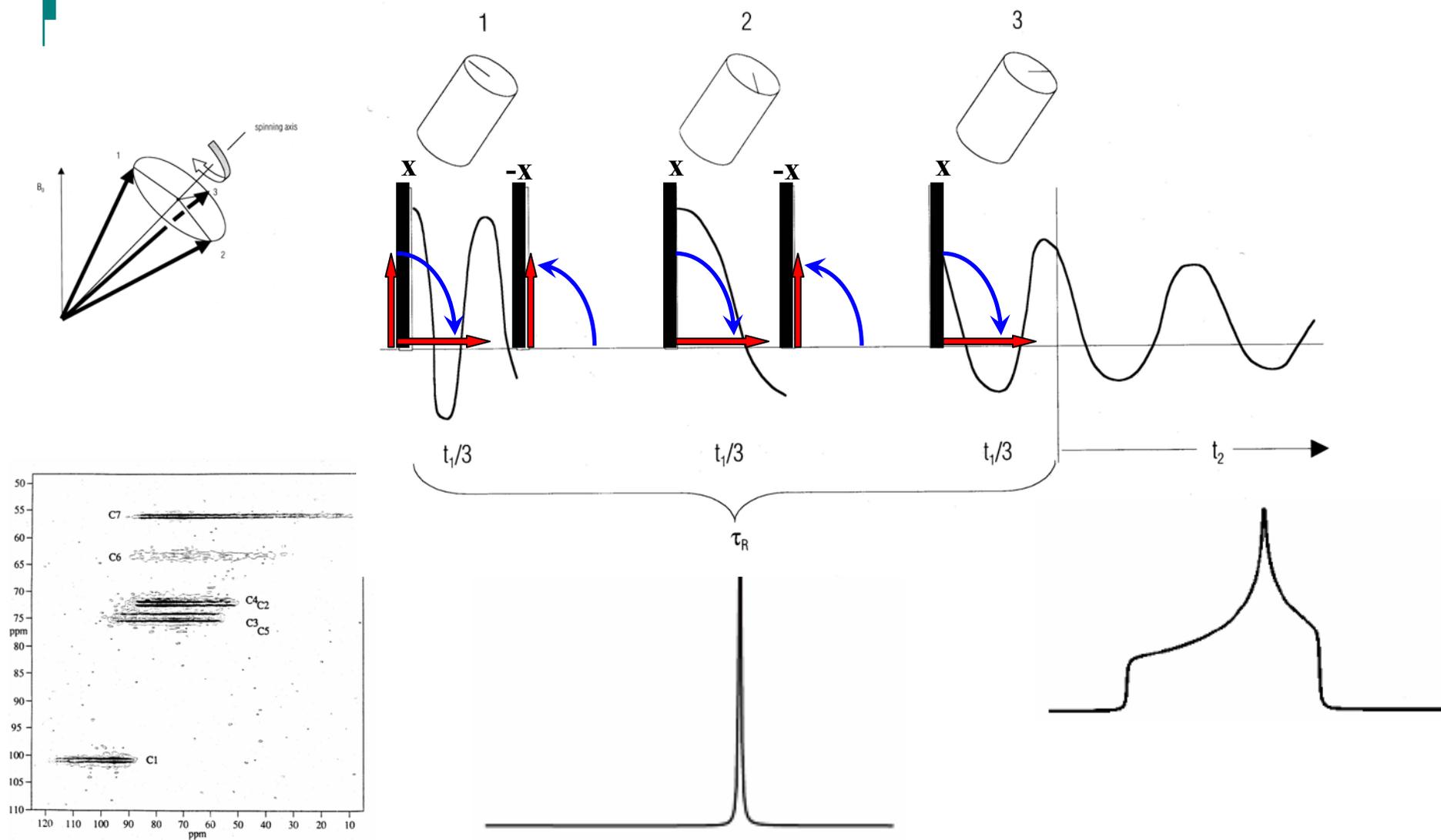
....



## Zoo von Experimenten zur Bestimmung der chemischen Verschiebung



## PASS: Phase Adjusted Spinning Sidebands



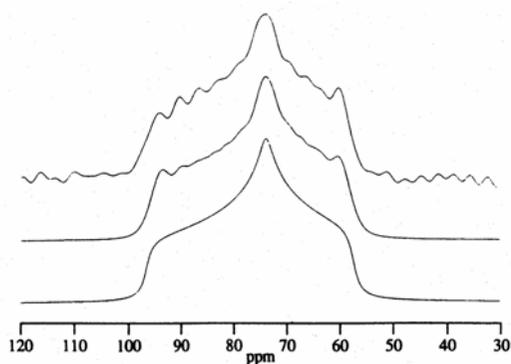
## MAT: Magic Angle Turning



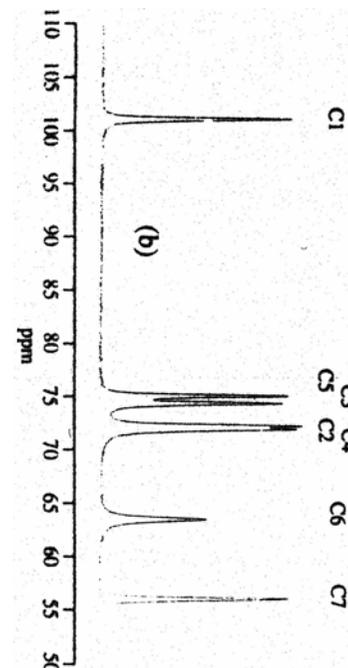
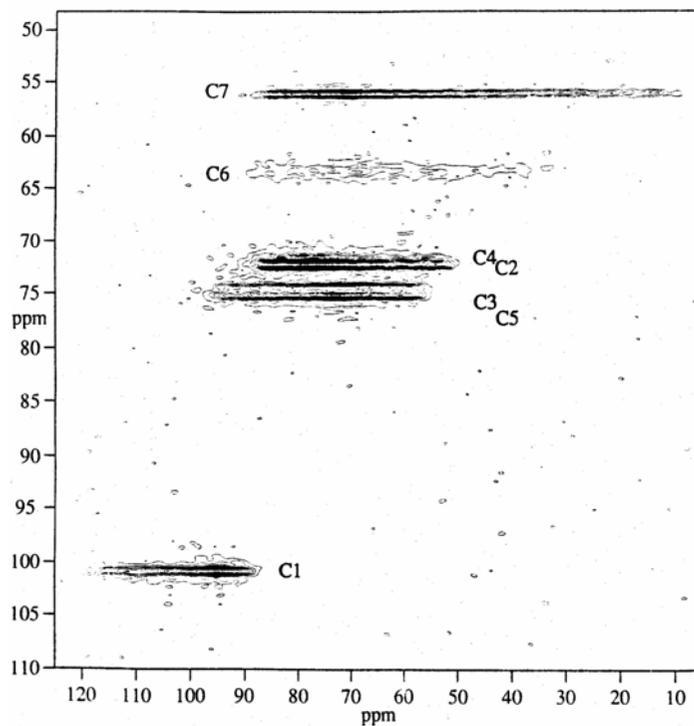
Slice

MAT-Simulation

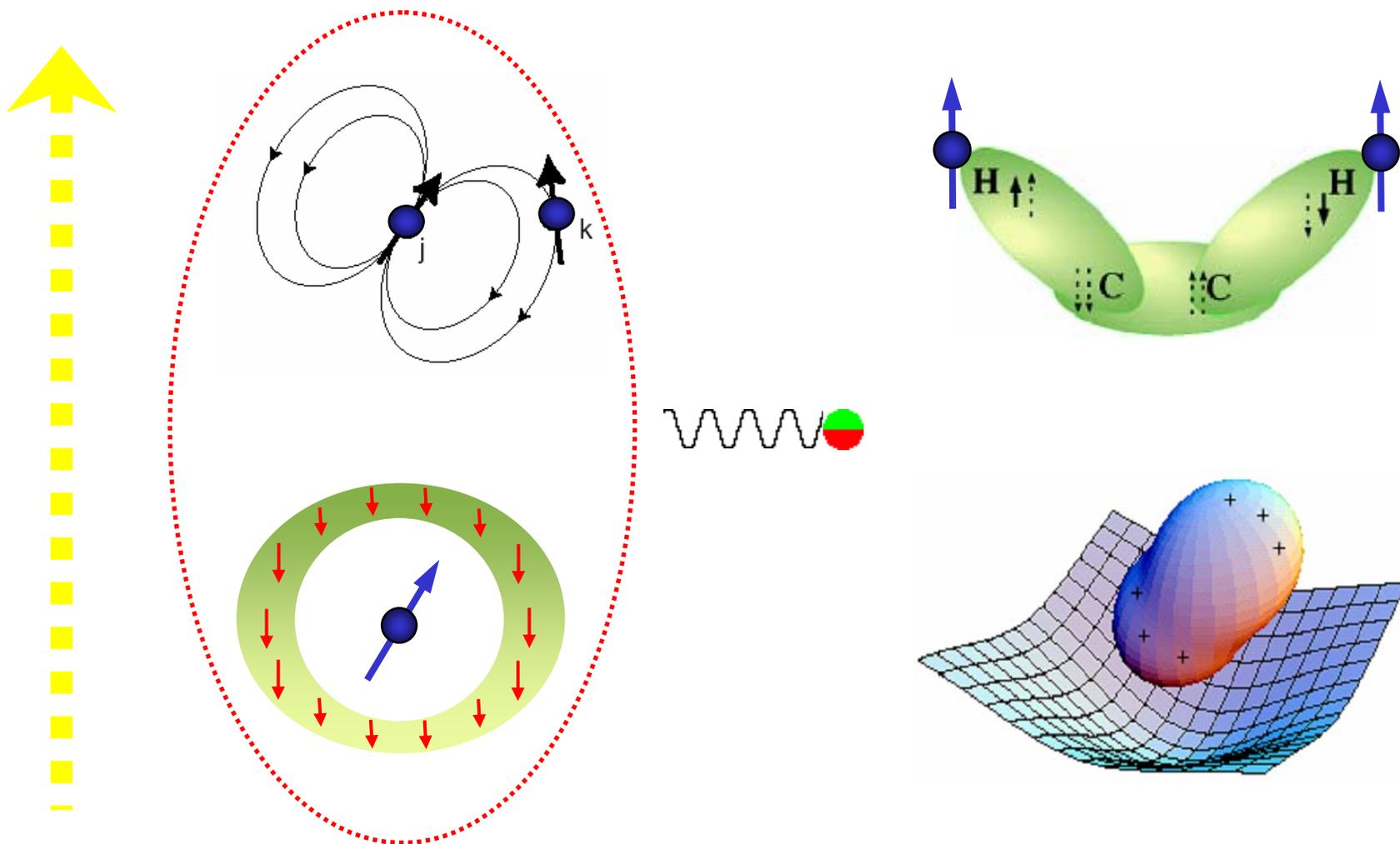
Pulversimulation



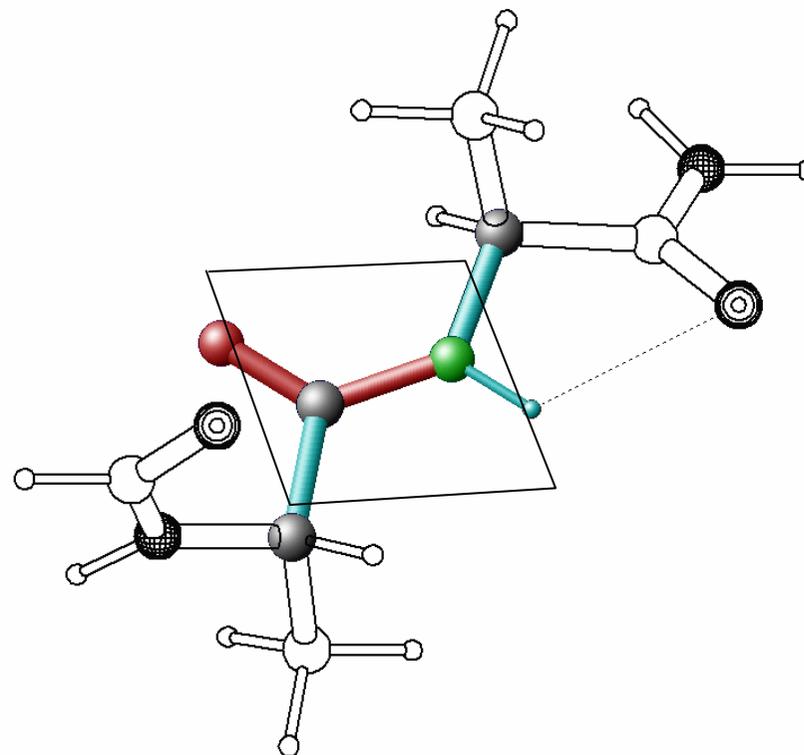
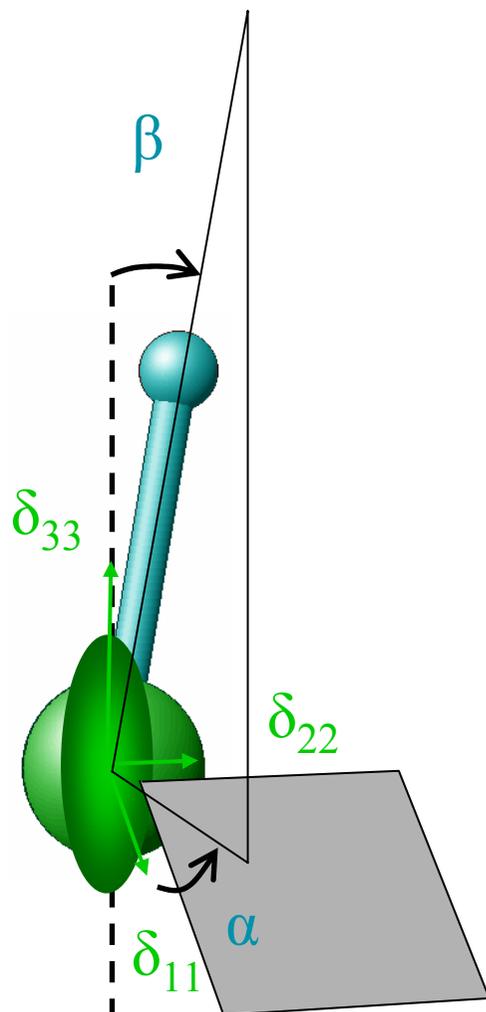
Methyl- $\alpha$ -D-glucopyranoside



**MAT: Magic Angle Turning**



## Der kleine Zoo der NMR-Wechselwirkungen

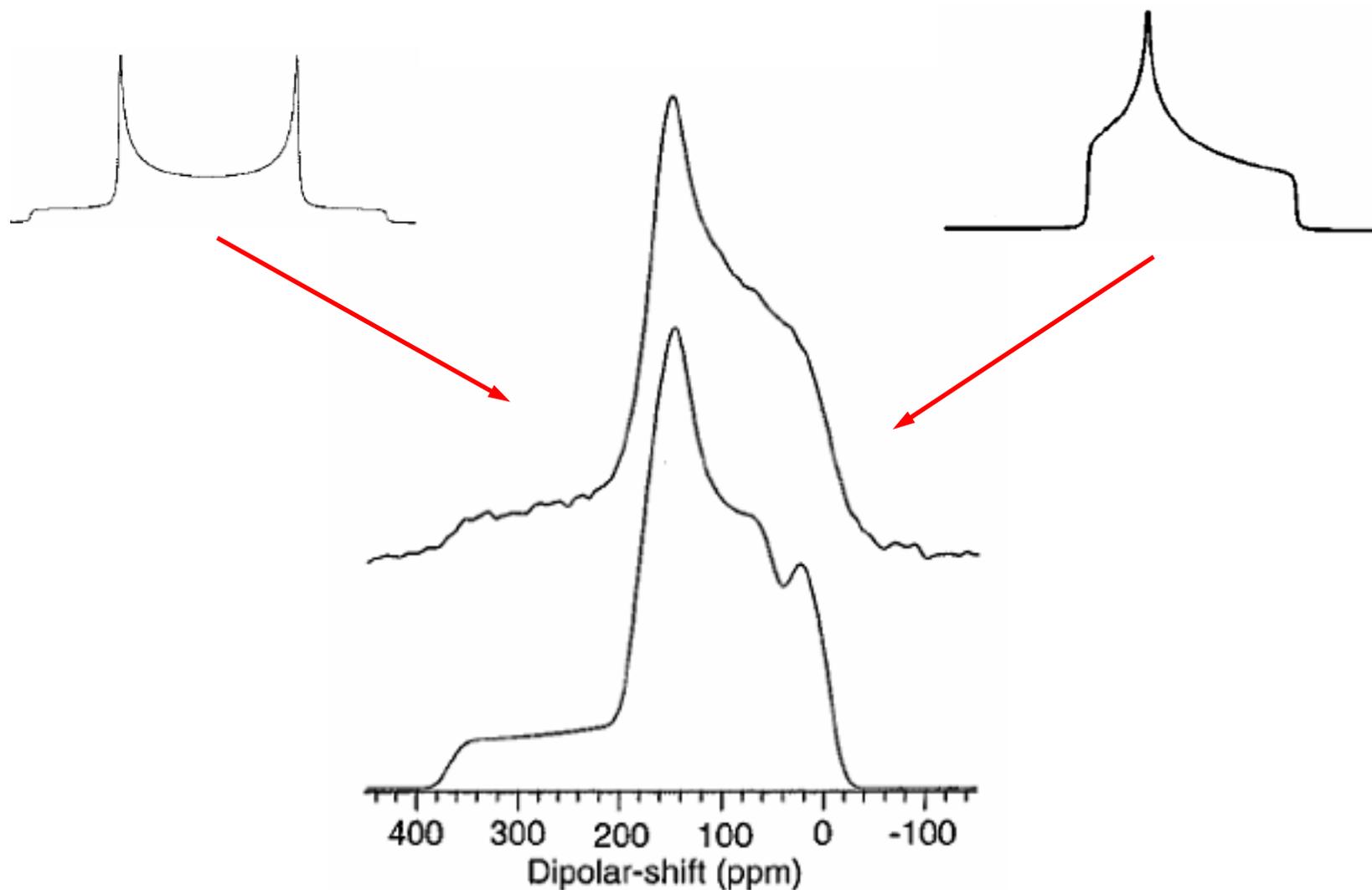


**$^{15}\text{N}$ -amide :**

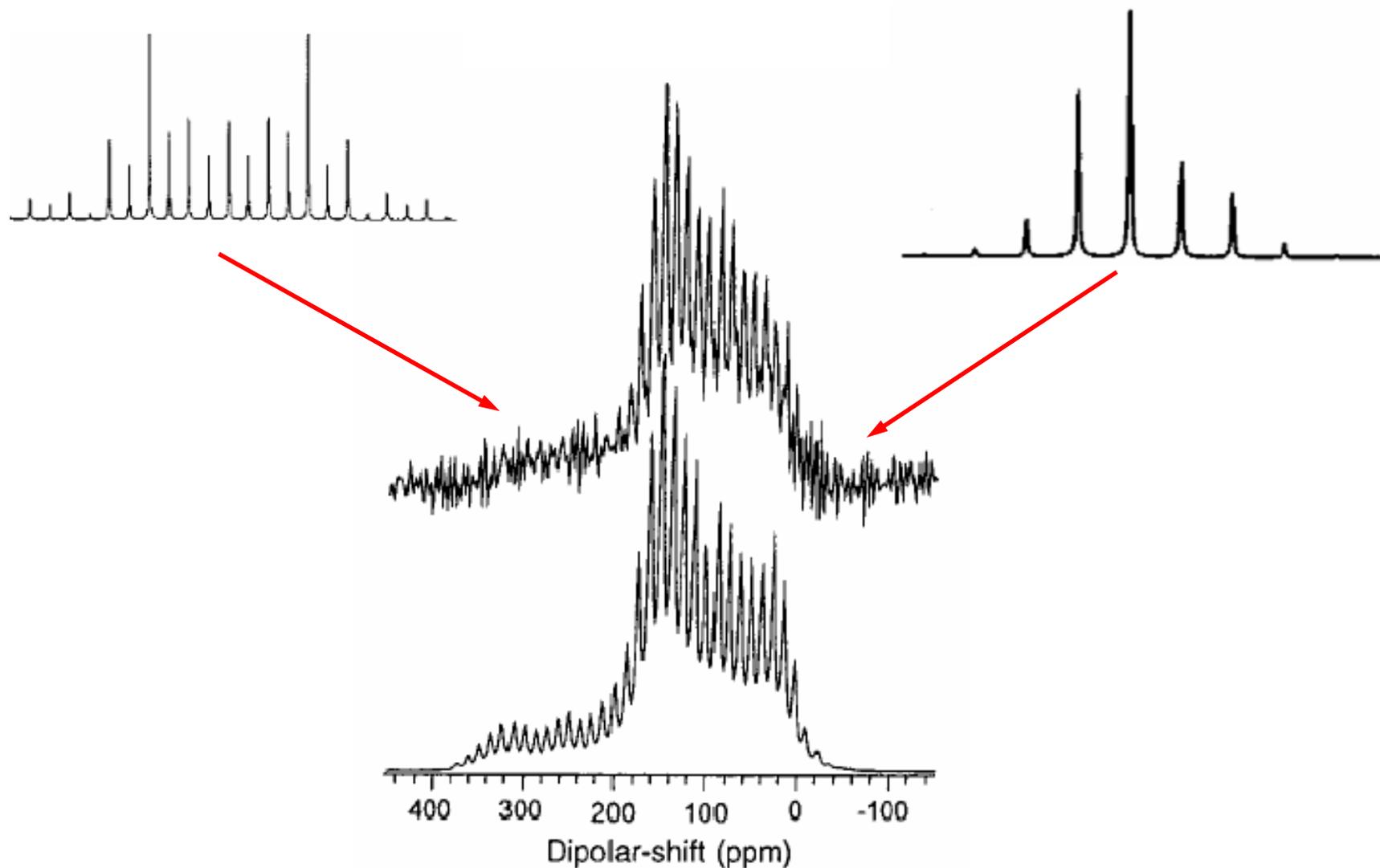
$$\delta_{11}=64\text{ppm}, \delta_{22}=77\text{ppm}, \delta_{33}=217\text{ppm}$$

$$\alpha=0^\circ, \beta=17^\circ$$

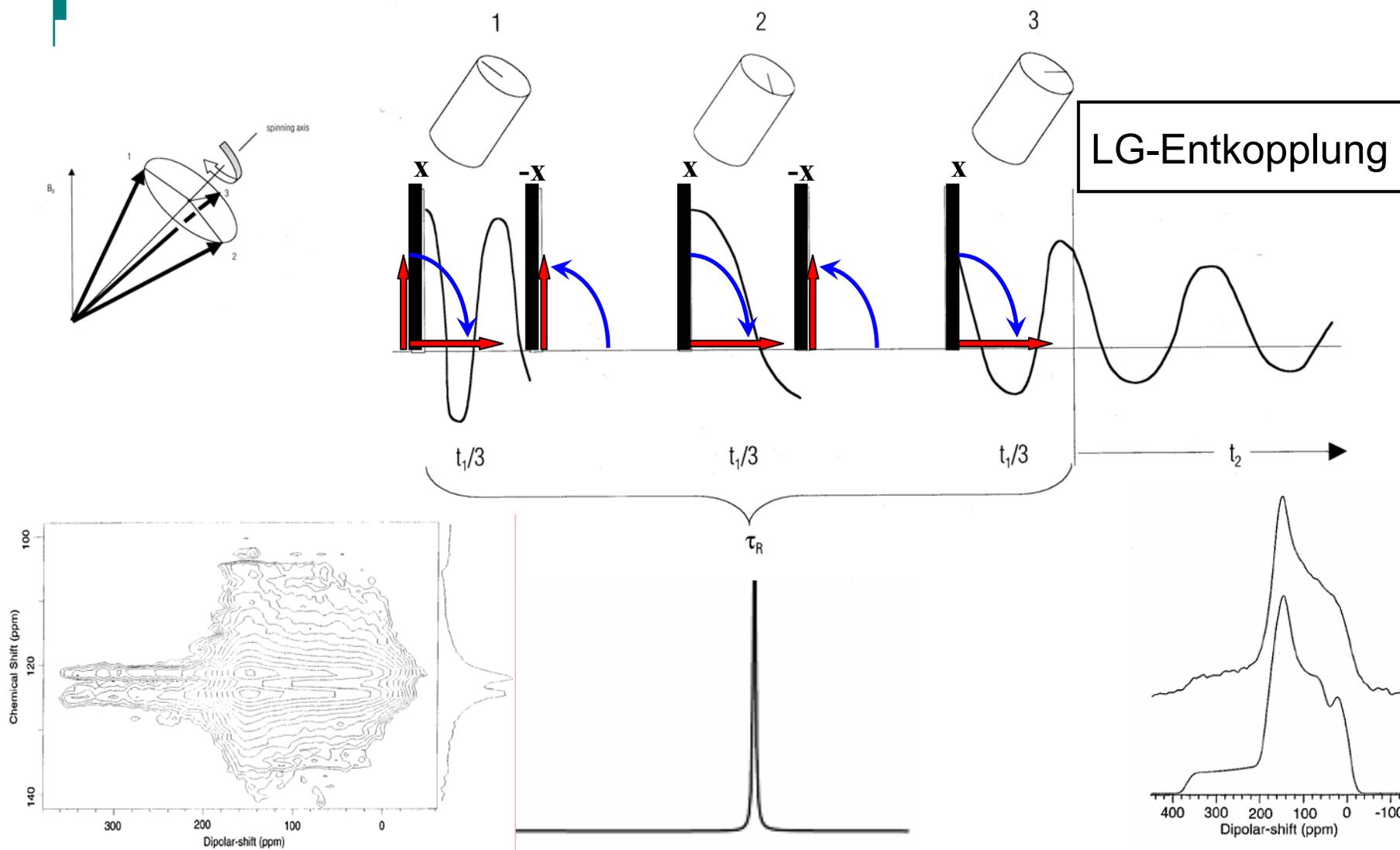
**NMR-Parameter und deren Lage zueinander**



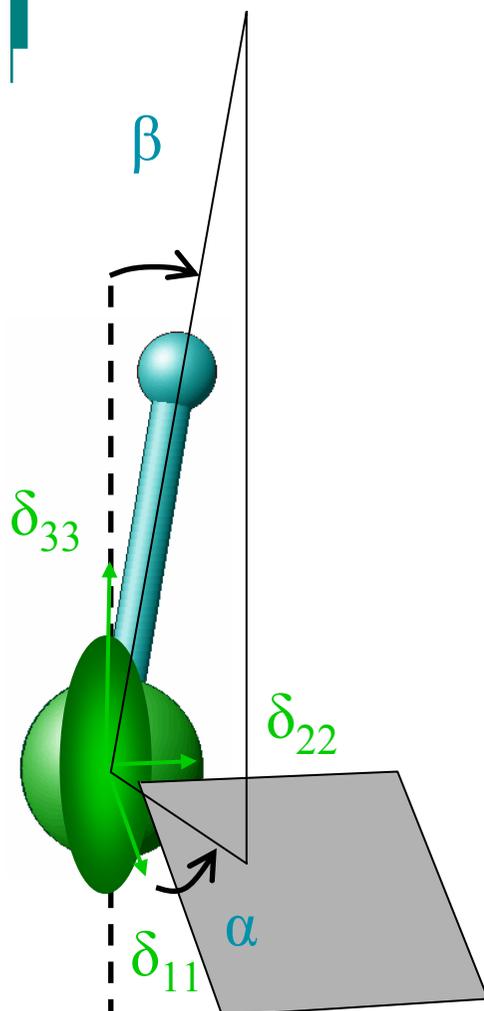
## Statisches Experiment



## 1D-MAS-Experiment

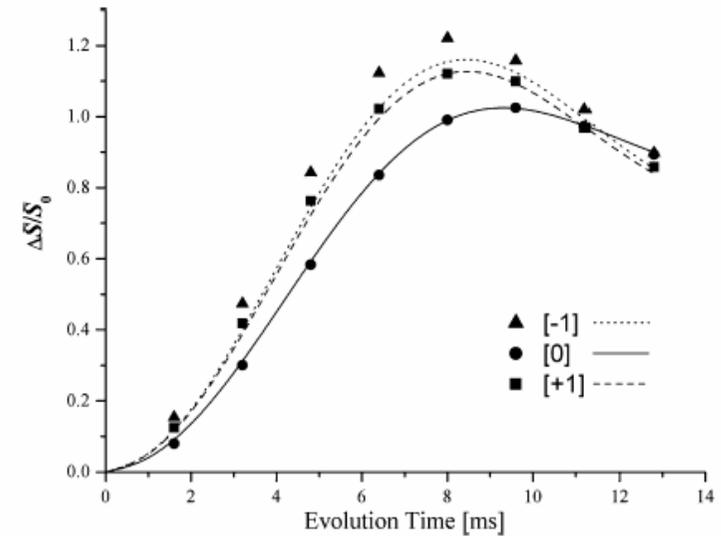
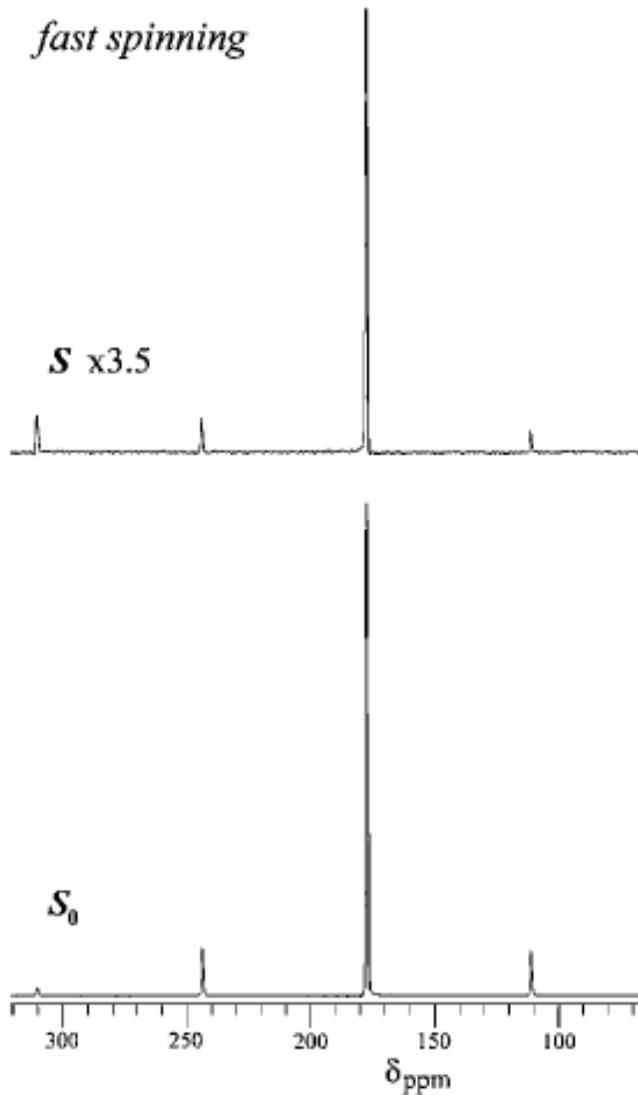


# MADMAT: Magic Angle Decoupling Magic Angle Turning



sample	$\sigma_{11N}$	$\sigma_{22N}$	$\sigma_{33N}$	$\sigma_{iso}$	$\beta_N$ (°)	$\alpha_N$ (°)
NAVL: <sup>d</sup> 200-Hz MAS	58.7	93.7	232.8	128.4	18 ± 2	36 ± 11
500-Hz MAS	58.7	93.7	232.8	128.4	17 ± 3	41 ± 11
gramicidin A <sup>e</sup>						
D-Leu <sup>4</sup> (dry)	53.6	84.6	219.6	119.6	14.5	0
D-Leu <sup>4</sup> (hydrated and at 143 K)	62.3	84.3	234.6	127.6	14.5	0
D-Leu <sup>10</sup> (dry)	58.6	88.6	224.6	123.9	14.5	0
D-Leu <sup>12</sup> (dry)	58.6	86.6	216.6	120.6	14.5	0
D-Leu <sup>12</sup> (hydrated and at 276 K)	63.6	89.6	215.6	122.9	14.5	0
D-Leu <sup>12</sup> (hydrated and Na <sup>+</sup> at 276 K)	65.6	89.6	217.6	124.3	14.5	0
D-Leu <sup>14</sup> (dry)	55.6	81.6	218.6	118.6	14.5	0
Leu <sup>14</sup> (hydrated and at 143K)	64.6	84.6	228.6	125.6	14.5	0
sample	$\sigma_{11N}$	$\sigma_{22N}$	$\sigma_{33N}$	$\sigma_{iso}^b$	$\beta_N$ (°)	$\alpha_N$ (°)
NAV <sup>e</sup>	59.6	80.5	235.3	125.5	21 ± 2	20 ± 15
	57.5	81.0	227.0	121.1	—	—
	59.6	80.0	238.0	125.5	19 ± 2	0
	59.1	84.1	228.1	123.8	—	—
	—	—	—	—	—	-25
NAVL: <sup>f</sup> 200-Hz MAS	60.2	87.1	230.1	125.7	20 ± 2	34 ± 12
500-Hz MAS	60.2	87.1	230.1	125.7	19 ± 2	44 ± 13
Val <sup>26</sup> in ubiquitin	—	—	—	123.6	—	—
gramicidine A <sup>g</sup>						
Val <sup>1</sup>	59.6	83.6	233.6	125.6	13.6 ± 2	28 ± 5
Val <sup>6</sup>	57.6	82.6	222.6	119.6	14.5 ± 2	0 ± 5
Val <sup>7</sup>	57.6	80.6	223.6	120.6	15.5	0
Val <sup>8</sup> (dry)	48.6	75.6	221.6	115.6	14.5	0
Val <sup>8</sup> (hydrated and at 143 K)	58.6	81.6	224.6	121.6	14.5 ± 2	0 ± 10

## Beispiele



L-[1- $^{13}\text{C}$ ,  $^{15}\text{N}$ ]alanine

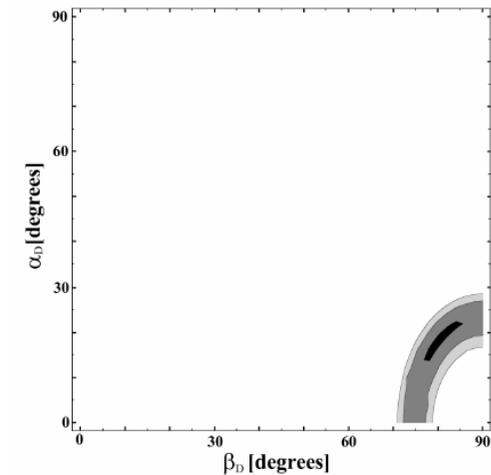
$$\omega_r = 5000 \text{ Hz}$$

$$\delta = 5265 \text{ Hz}$$

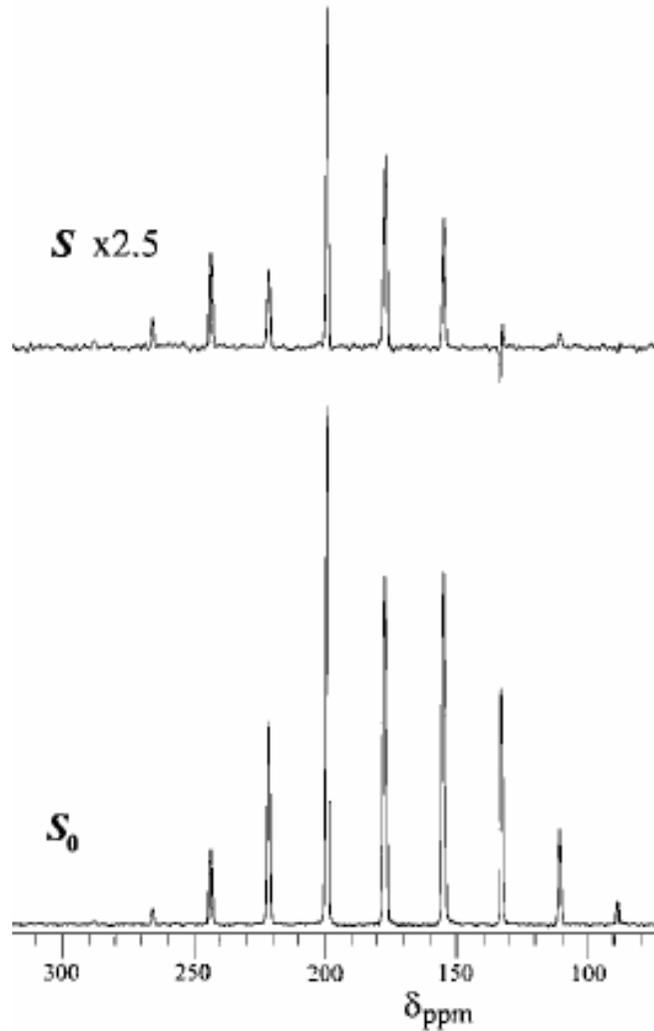
$$\eta = 0.79$$

$$\alpha_D = 27^\circ$$

$$\beta_D = 80^\circ$$



**CSA-DD-Lagebestimmung aus REDOR-Seitenbändern**



L-[1-<sup>13</sup>C, <sup>15</sup>N]alanine

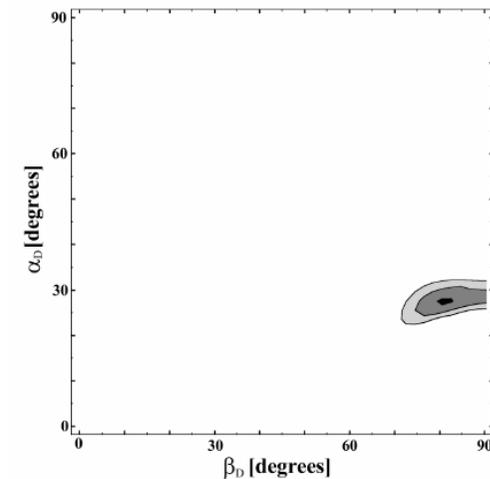
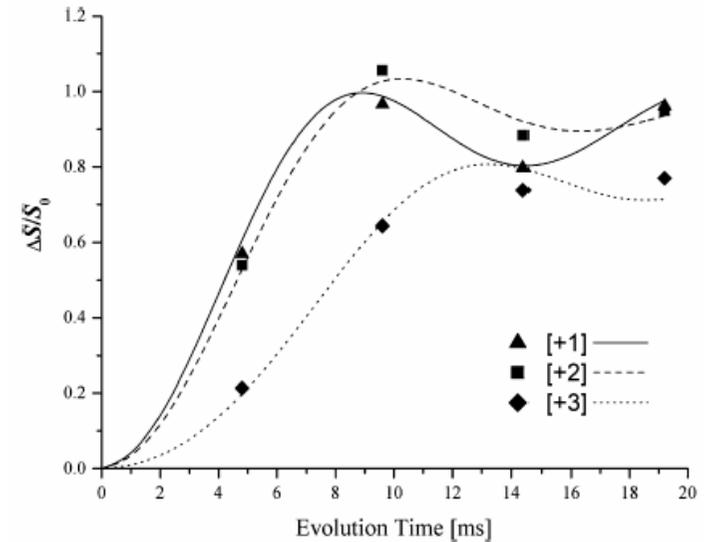
$$\omega_r = 1667 \text{ Hz}$$

$$\delta = 5265 \text{ Hz}$$

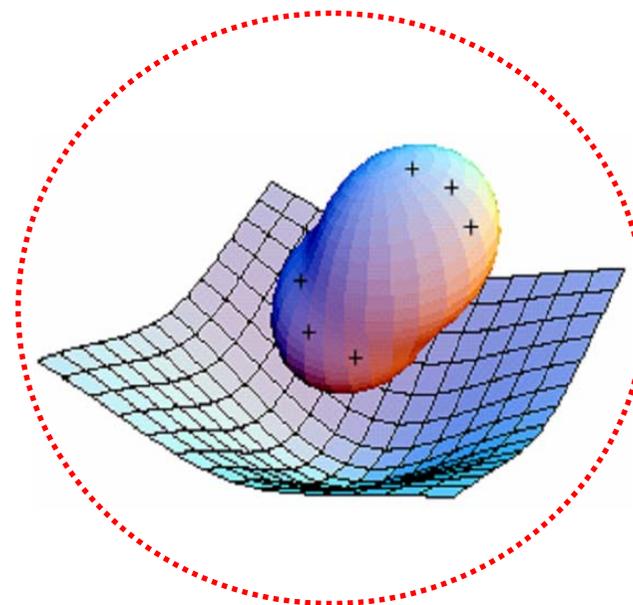
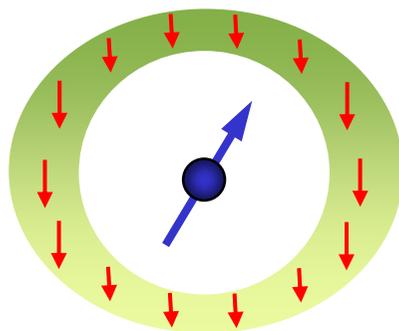
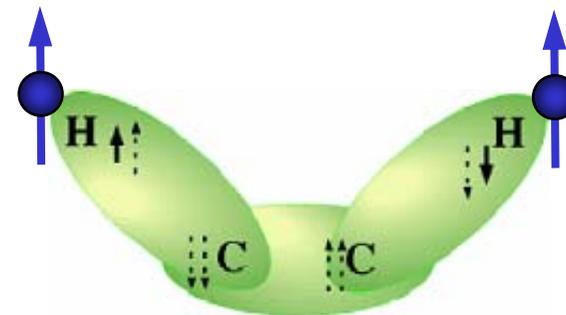
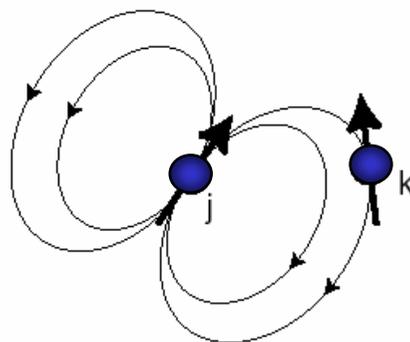
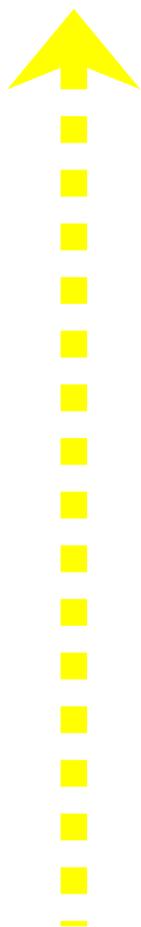
$$\eta = 0.79$$

$$\alpha_D = 27^\circ$$

$$\beta_D = 80^\circ$$



CSA-DD-Lagebestimmung aus REDOR-Seitenbändern

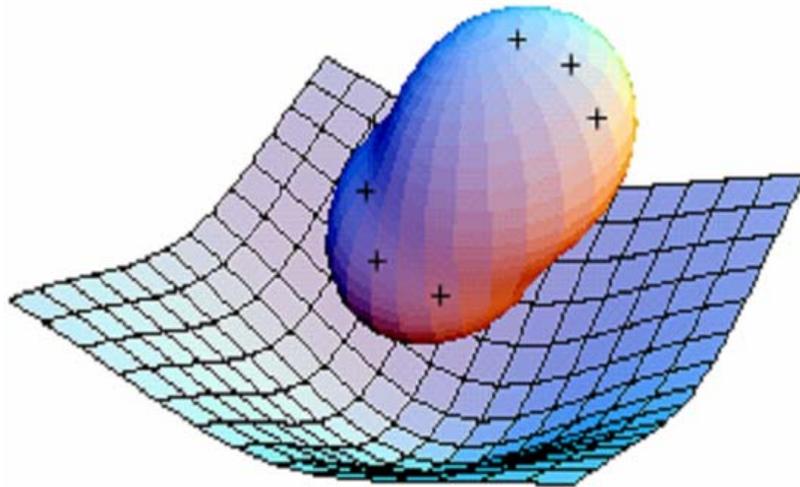


## Der kleine Zoo der NMR-Wechselwirkungen



Quadrupolmoment:

$$Q \approx \frac{4}{5} Z R \Delta R$$



elektrischer Feldgradienten der Elektronenverteilung

$^2\text{D}$	$^{14}\text{N}$	$^{17}\text{O}$
0.286 fm <sup>2</sup>	2.044 fm <sup>2</sup>	-2.56 fm <sup>2</sup>

$^2\text{D}$ :

$$Z = 2$$

$$R = 2.1 \text{ fm}$$

$$\Delta R = 4\% R$$

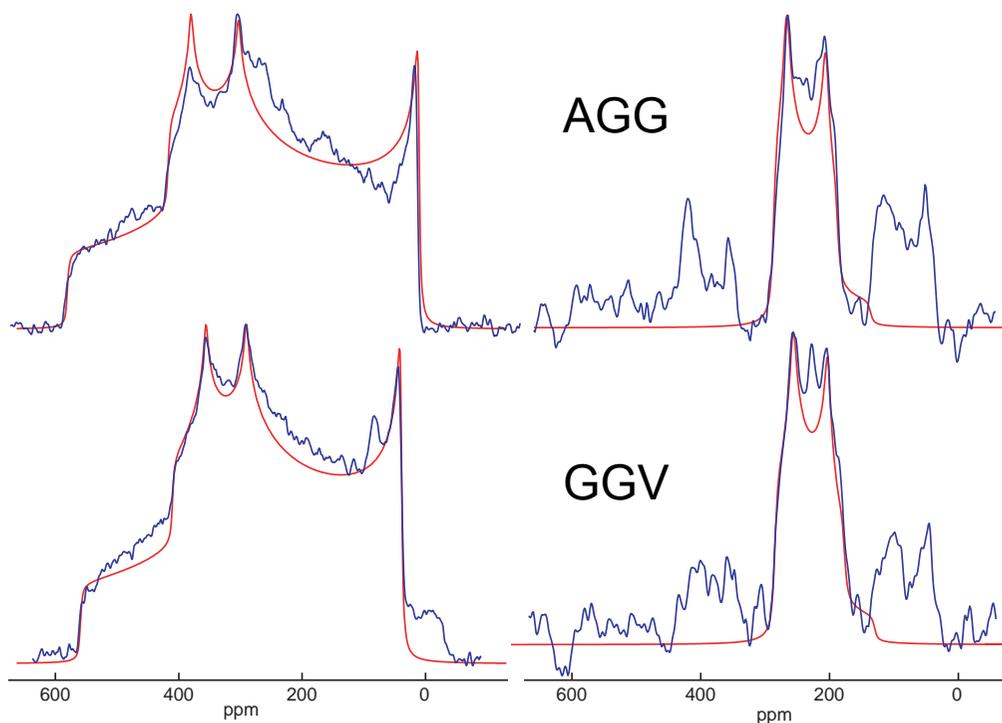
(96% s-Wellenfunktion:  $l=0$ )

4% d-Wellenfunktion:  $l=2$ )



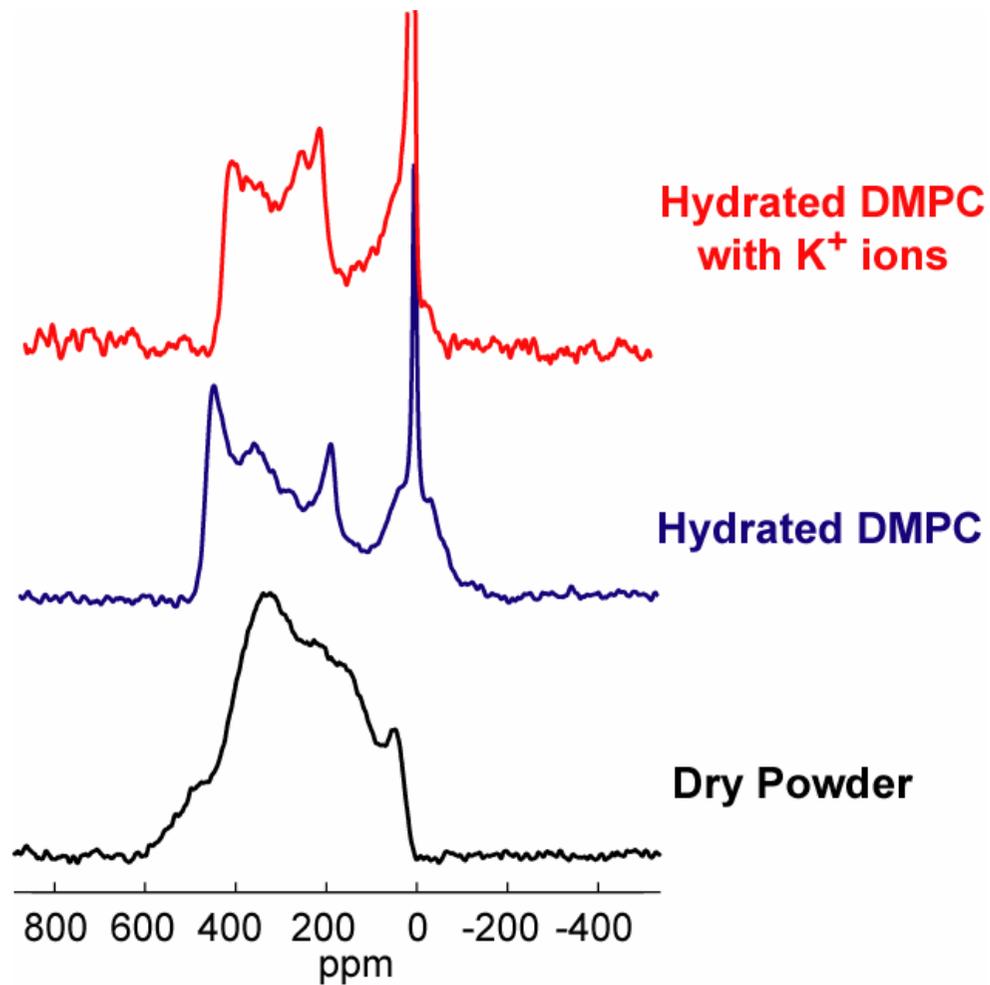
Statische Spektren  
bei 900 MHz

MAS-Spektren  
bei 600 MHz



	AGG	GGV
$\chi$ (MHz)	$8.5 \pm 0.1$	$8.5 \pm 0.1$
$\eta$	$0.22 \pm 0.05$	$0.22 \pm 0.05$
$\delta_{11}$ (ppm)	$541 \pm 10$	$514 \pm 10$
$\delta_{22}$ (ppm)	$397 \pm 10$	$390 \pm 10$
$\delta_{33}$ (ppm)	$-45 \pm 10$	$-24 \pm 10$
$\delta_{iso}$ (ppm)	$297 \pm 10$	$293 \pm 10$
$\alpha$	$73 \pm 2^\circ$	$74 \pm 2^\circ$
$\beta$	$90 \pm 3^\circ$	$90 \pm 3^\circ$
$\gamma$	$5 \pm 10^\circ$	$0 \pm 10^\circ$

**$^{17}\text{O}$  Untersuchung an kleinen Peptiden**

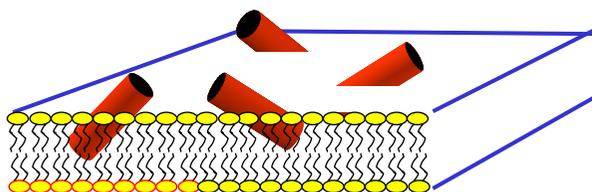


$^{17}\text{O}$  Untersuchung an  $\text{Leu}_{10}\text{-}^{17}\text{O}$  GA



## Festkörper NMR

### 3. NMR an orientierten Proben





$$n = \frac{1}{2} \frac{m N_0}{(N_{\text{Glas}} - 1) MW} \frac{A_{\text{lipid}}}{A_{\text{Glas}}}$$

### Beispiel:

50 Glasplättchen

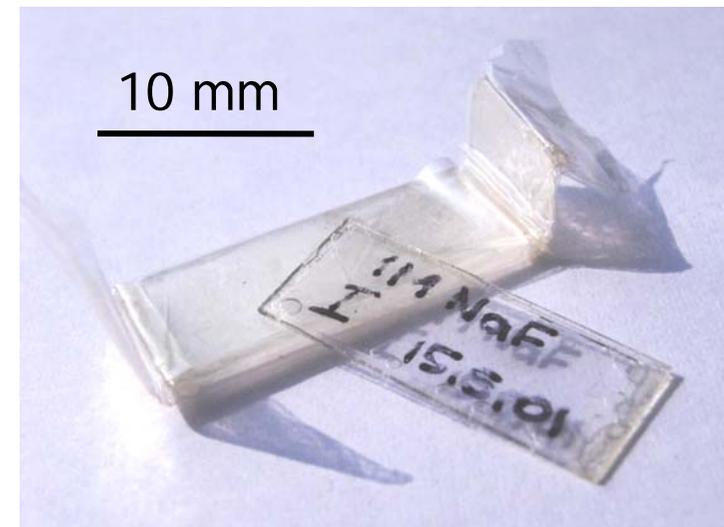
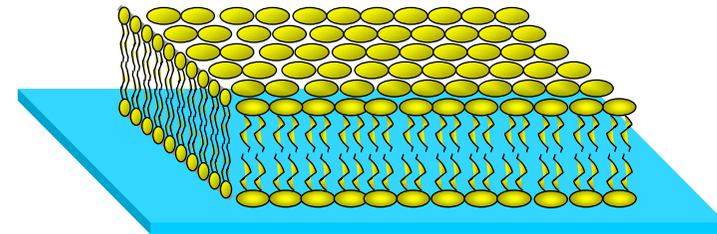
$N_0 = 6.0 \cdot 10^{23} / \text{mol}$

$A_{\text{Glas}} = 8 \times 19 \times 0.07 \text{ mm}^2 = 152 \text{ mm}^2$

DMPC ( $m = 30 \text{ mg}$ ):  $MW = 678 \text{ g/mol}$

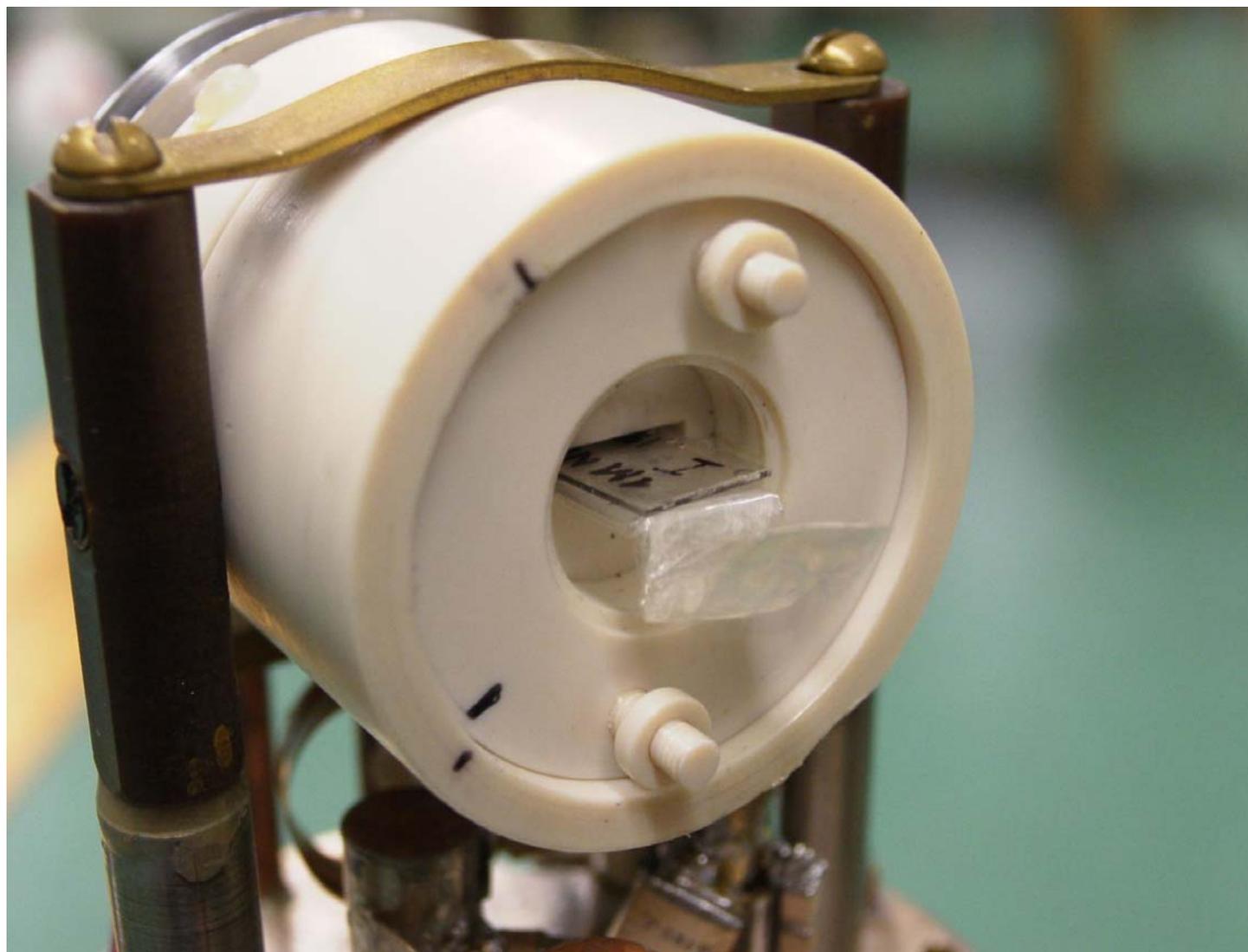
$A_{\text{Lipid}} = 60 \text{ \AA}^2$

$\implies \quad \mathbf{n = 1070}$

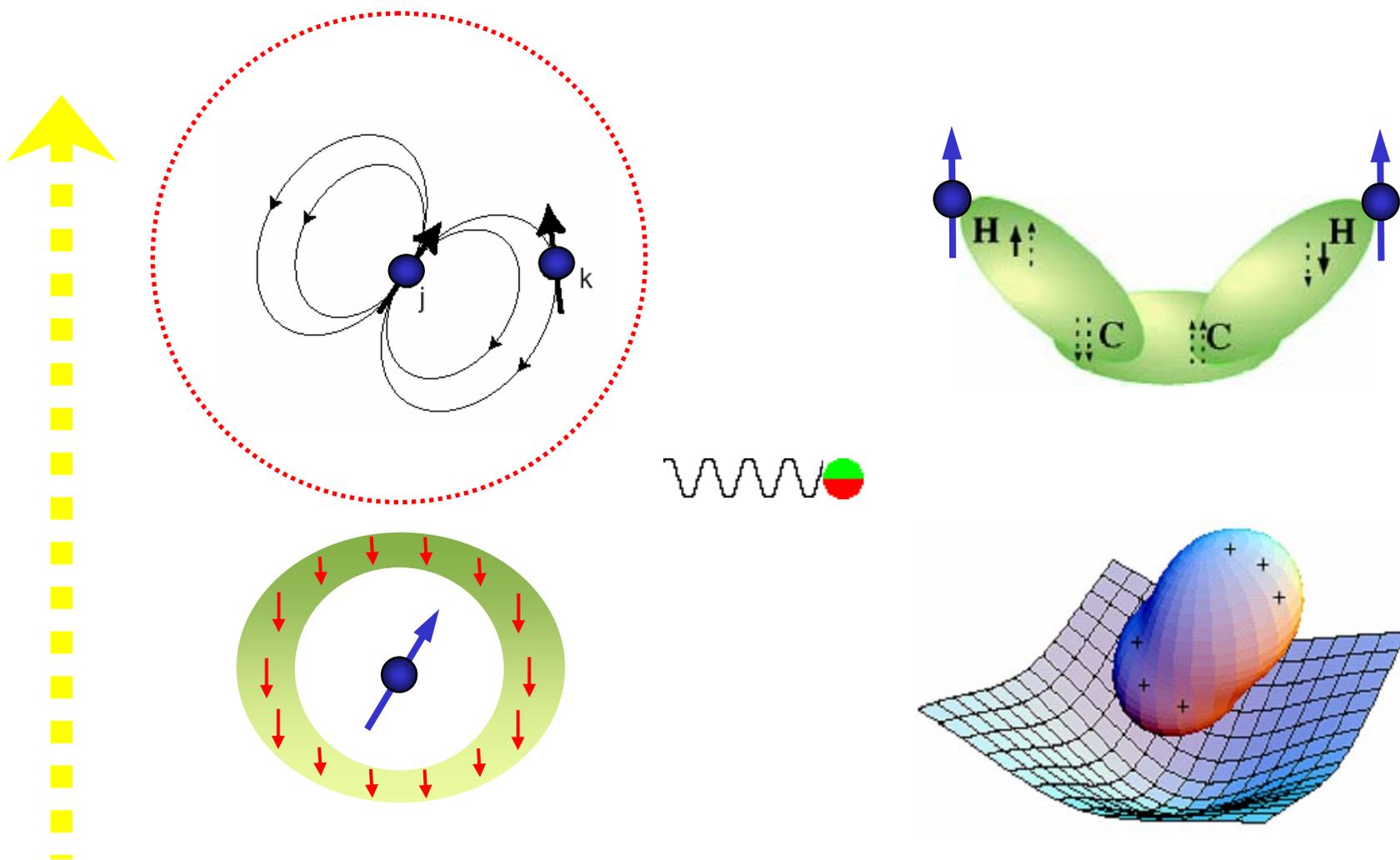


Tipp: - wiederholte Hydratisierung/Dehydratisierung verbessert Orientierung  
- es helfen auch Phasenübergänge (kurzzeitiges Einfrieren und Auftauen)

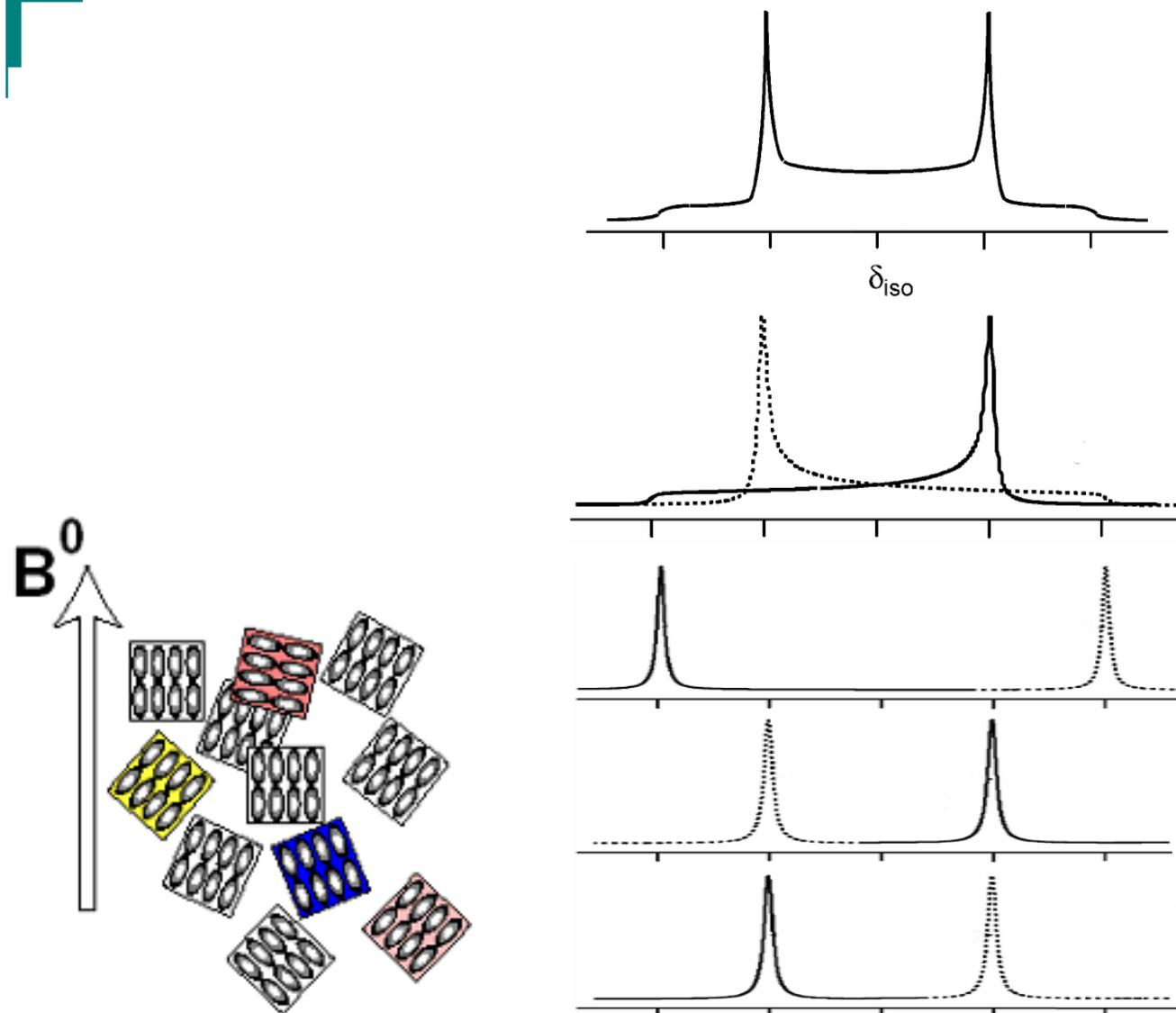
**Wieviele Bilayer sind nach der Hydratisierung zwischen den Glasplättchen?**



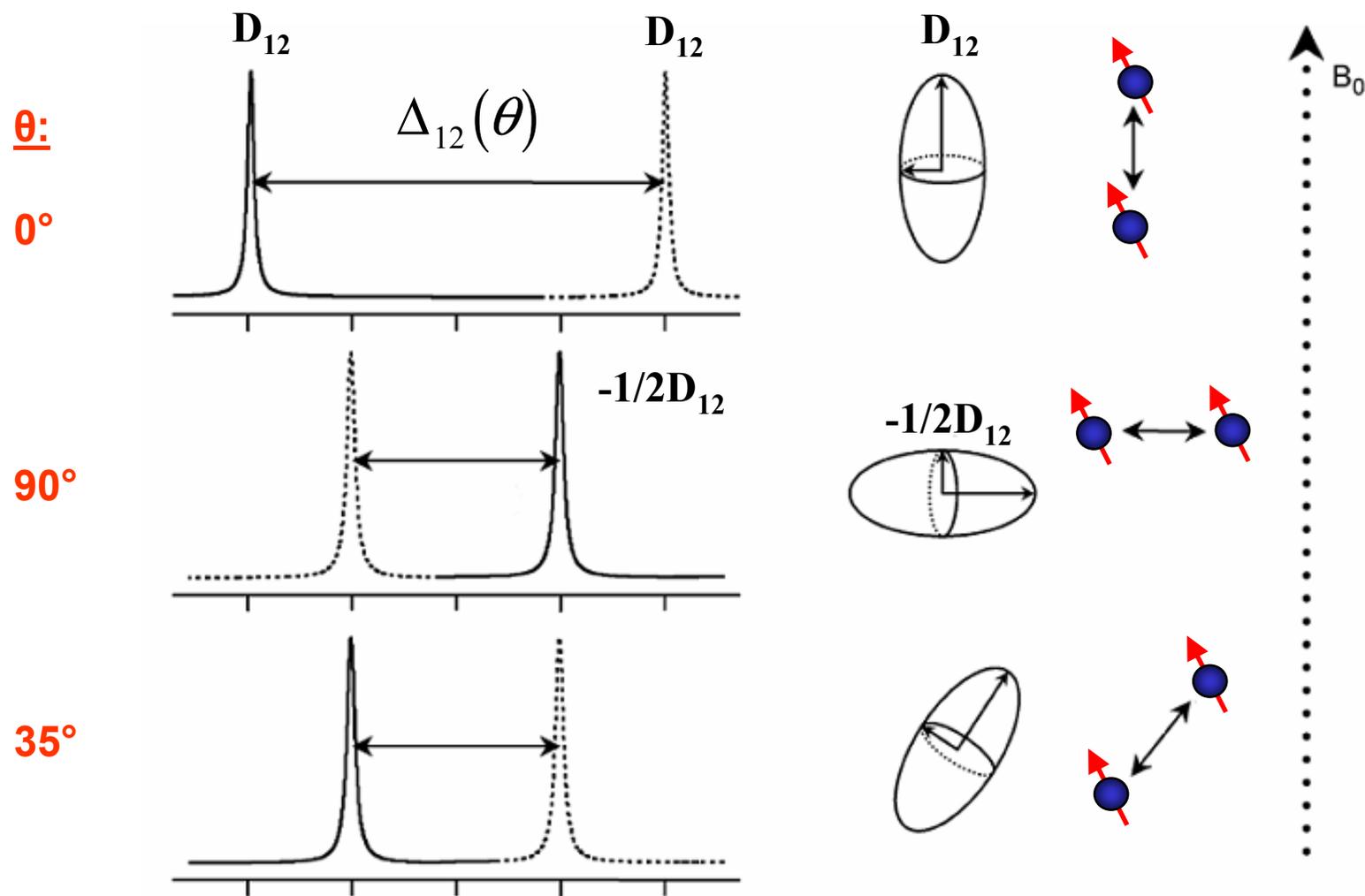
**Makroskopische Orientierung zum äußeren Magnetfeld**



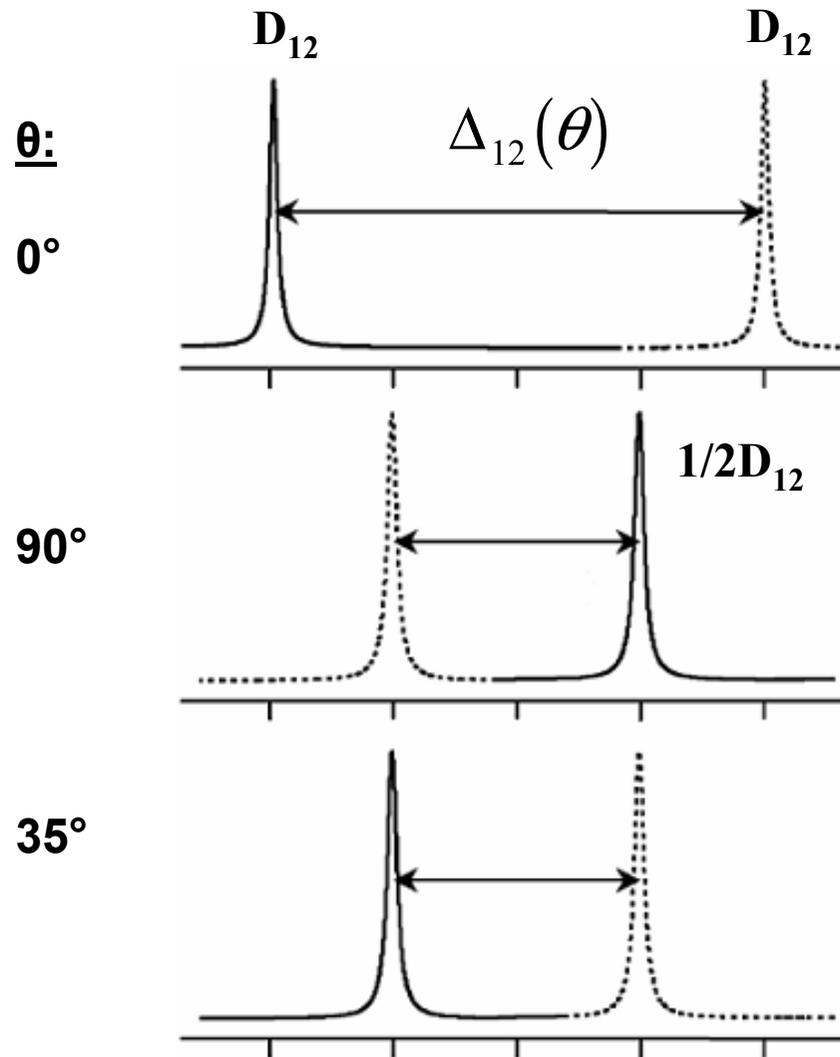
## Der kleine Zoo der NMR-Wechselwirkungen



## Pulverspektrum dipolar gekoppelter Kerne



## Spektren orientierter dipolar gekoppelter Kerne



Ordnungsparameter

$$\Delta_{12} = D_{12} \frac{1}{2} (3 \cos^2 \theta - 1) S_{zz}$$

$$D_{12} = \hbar \frac{\mu_0}{4\pi} \frac{\gamma_1 \gamma_2}{R_{12}^3} \begin{cases} 1 & \text{„Heteros“} \\ \frac{3}{2} & \text{„Homos“} \end{cases}$$

Spektren zweier orientierter dipolar gekoppelter Kerne



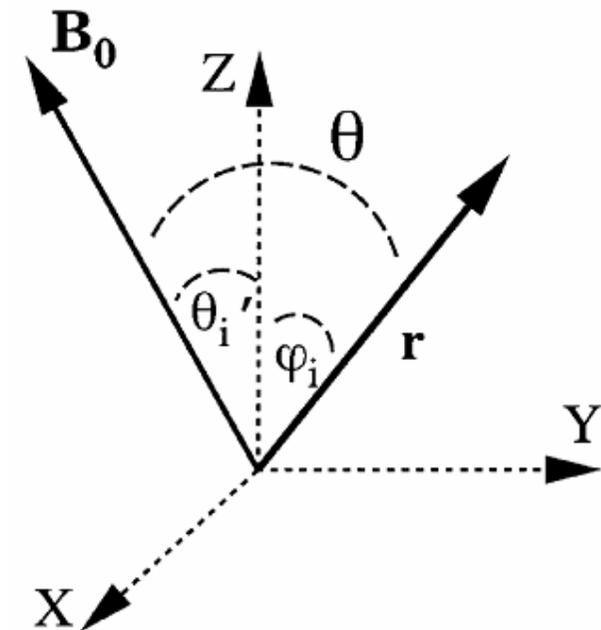
$$\Delta_{12} = D_{12} \frac{1}{2} \langle (3 \cos^2 \theta - 1) \rangle$$

$$\sum_{i,j} S_{ij} \cos \varphi_i \cos \varphi_j$$



Ordnungsmatrix:

$$S_{ij} = \left\langle \frac{3 \cos^2 \theta'_i \cos^2 \theta'_j - \delta_{ij}}{2} \right\rangle$$

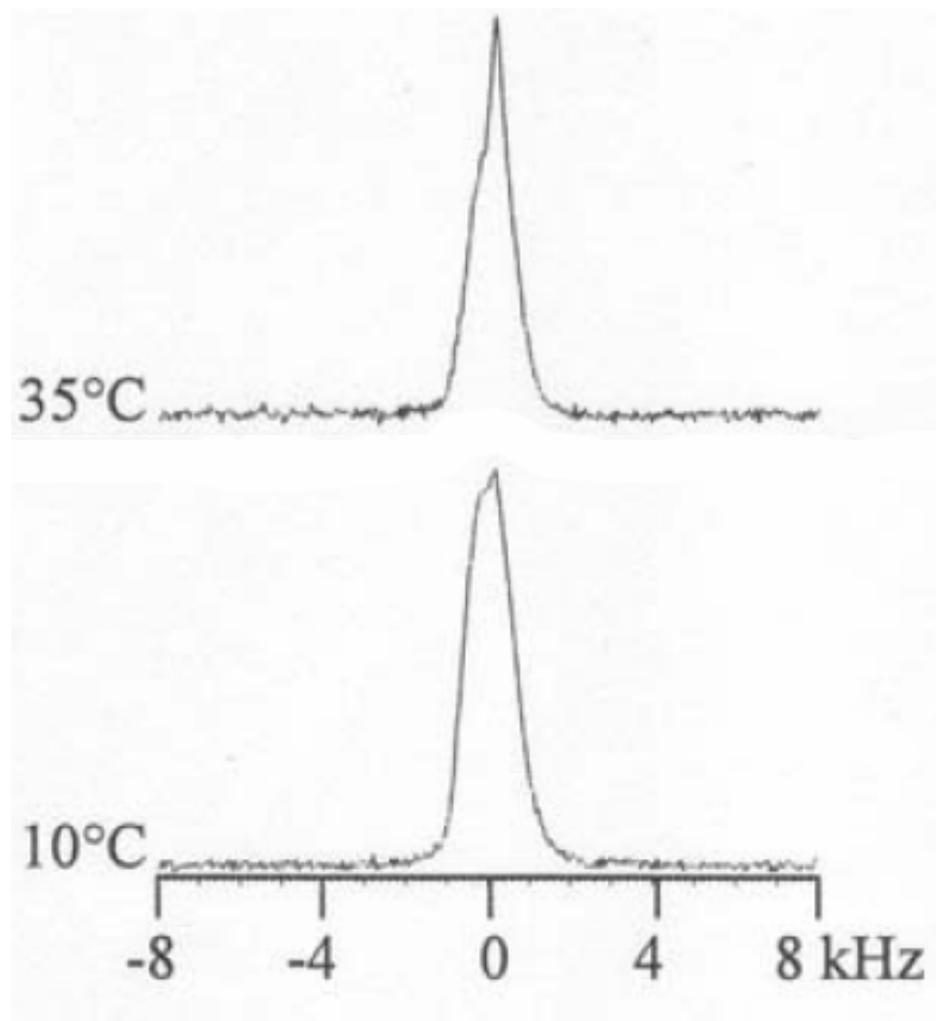
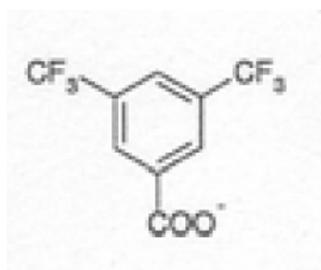


$$\Delta_{12} = D_{12} \left[ S_{zz} \frac{3 \cos^2 \phi_{12}^z - 1}{2} + (S_{xx} - S_{yy}) \frac{\cos^2 \phi_{12}^x - \cos^2 \phi_{12}^y}{2} + 2S_{xz} \cos \phi_{12}^x \cos \phi_{12}^z \right]$$

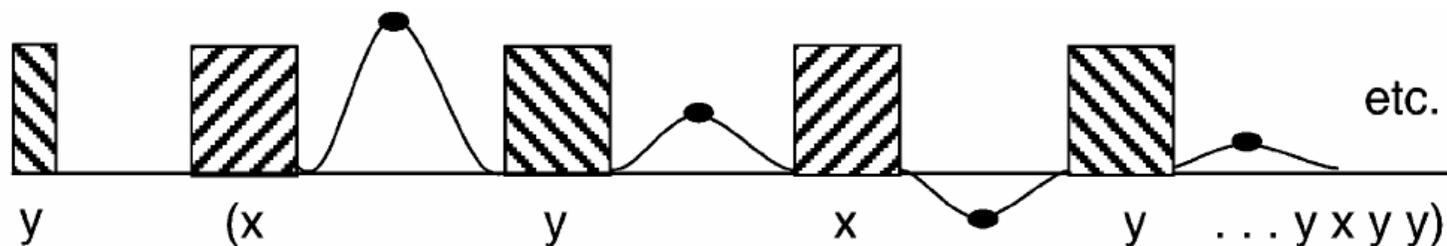
Der Ordnungsparameter S „ist eine Ordnungsmatrix“.



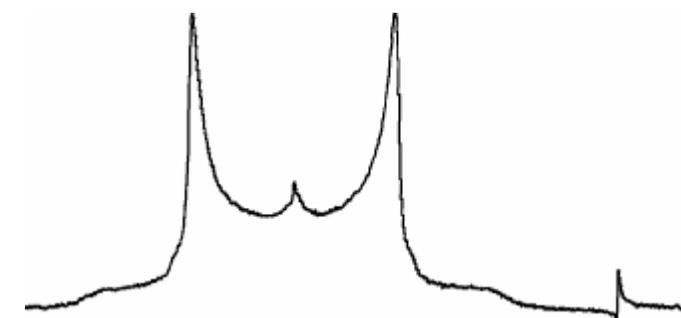
kompliziertes 6-Spinsystem



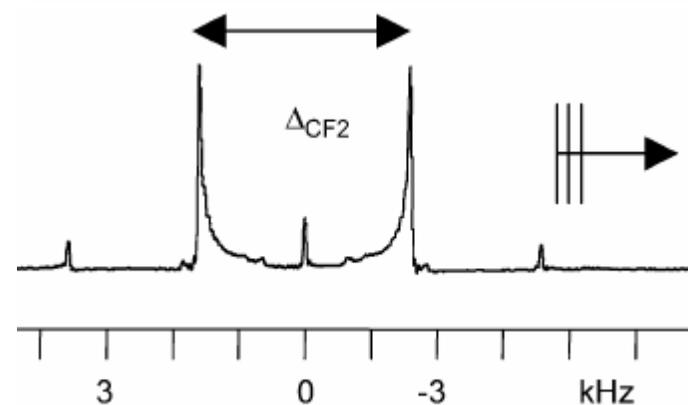
**Einpulsexperimente geben ungenügend Information.**



Pulverspektrum



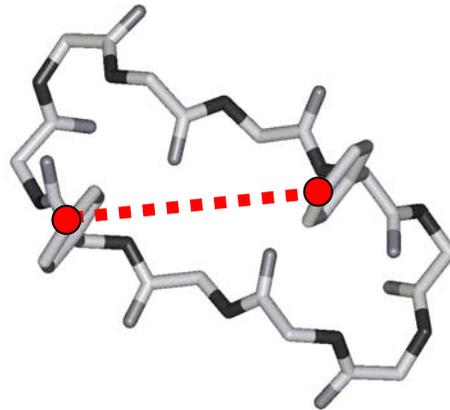
0° orientierte Probe



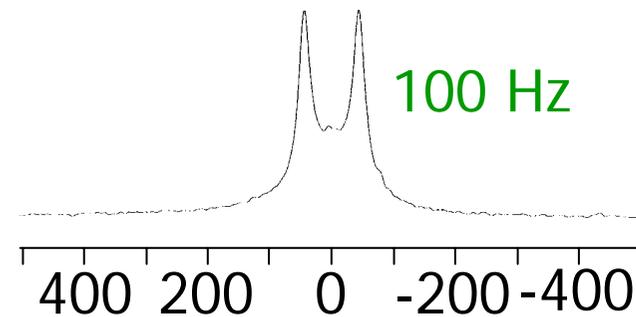
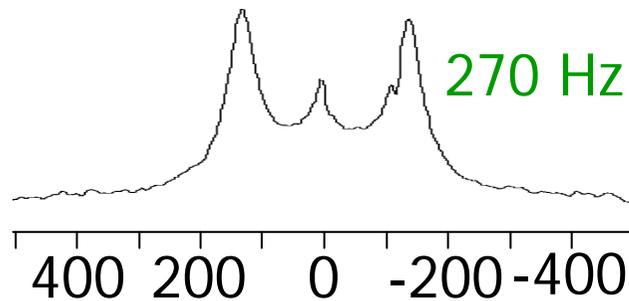
**CPMG (Carr, Purcell, Meiboom, Gill) an CF<sub>3</sub>-Phenylglycine**



$^{19}\text{F}$ - $^{19}\text{F}$   
distance

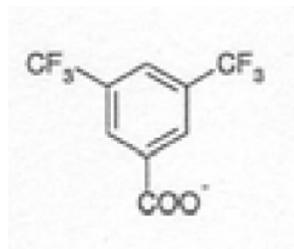
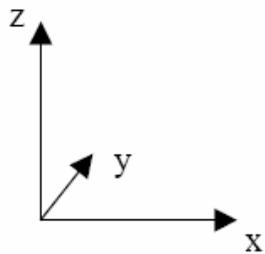


dipolar  
coupling



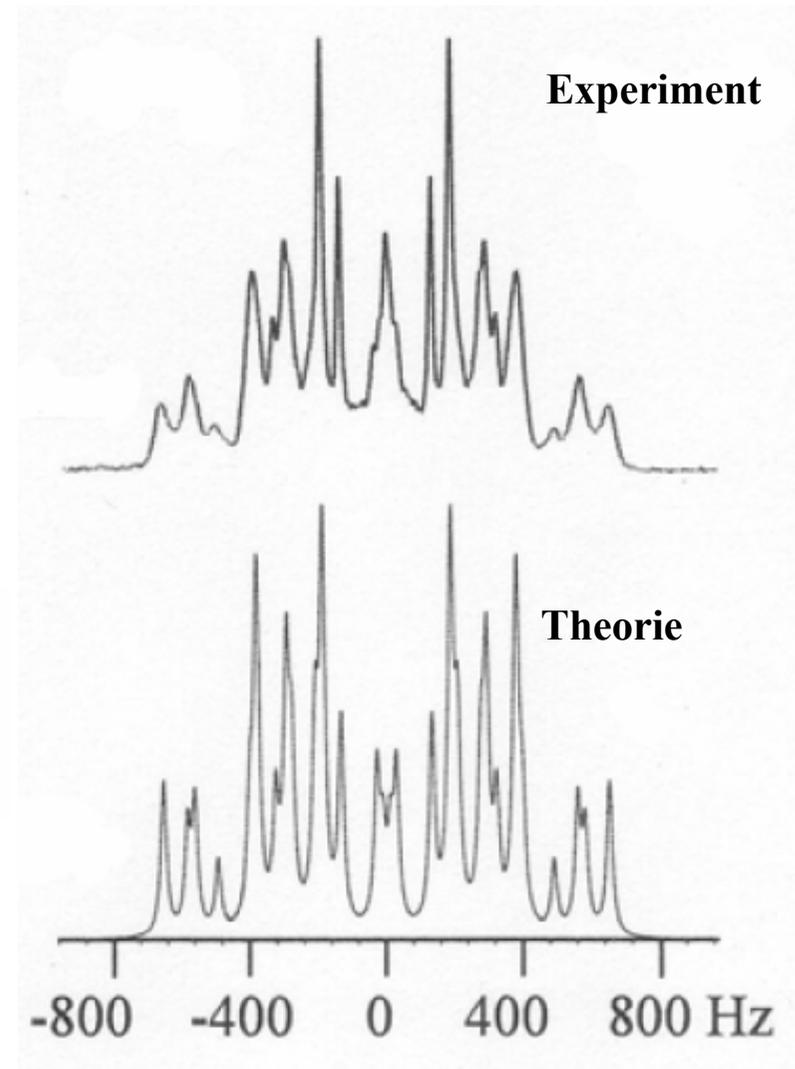
Leu3/8  $\rightarrow$  4F-Phg: 6 Å  
(wild type 7.3 Å)

Val5/10  $\rightarrow$  4F-Phg: 8 Å  
(wild type 8.2 Å)

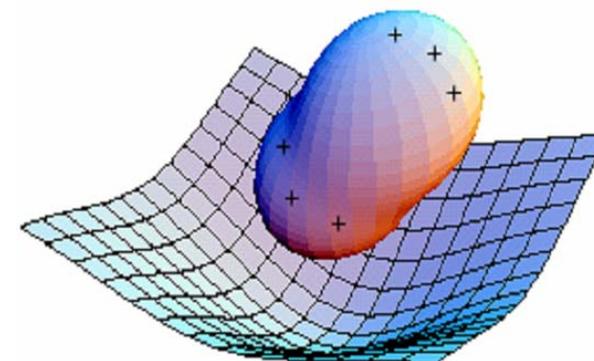
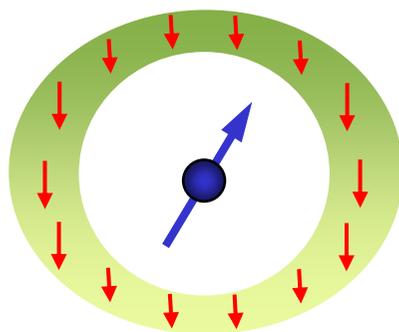
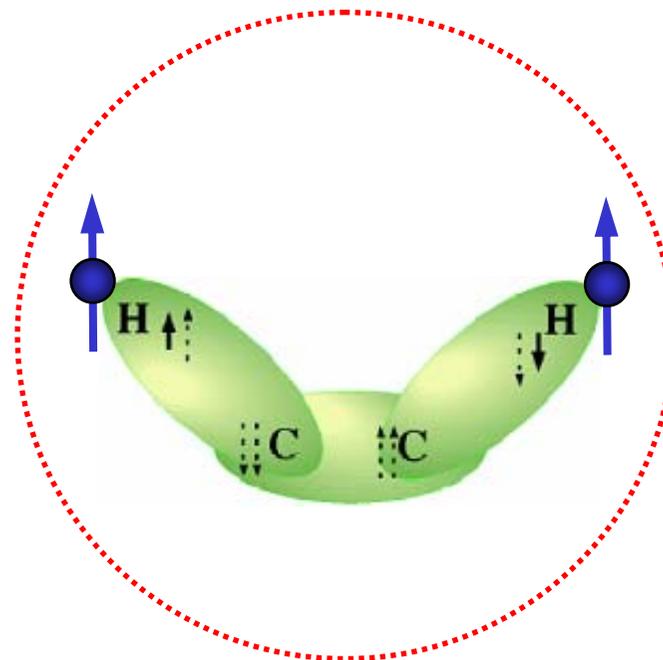
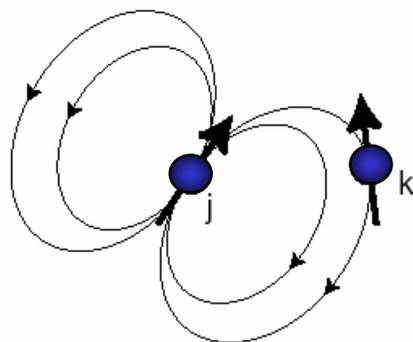
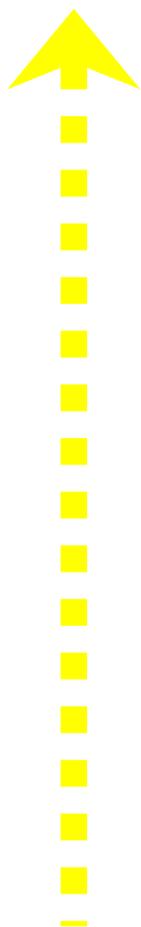


system	$\underline{D}_{11}$ [Hz]	$\underline{D}_{22}$ [Hz]	$\underline{D}_{12}$ [Hz]	$\underline{S}_{zz}$	$\underline{S}_{xx}-\underline{S}_{yy}$	$\underline{S}_{xx}$	$\underline{S}_{yy}$	$\underline{S}_{xz}$
BA-F <sub>6</sub>	124	124	-89	0.1356	0.022	-0.0570	-0.0786	./.
	-124	-124	89	-0.1356	-0.022	0.0570	0.0786	./.

$$\Delta_{12} = D_{12} \left[ S_{zz} \frac{3 \cos^2 \phi_{12}^z - 1}{2} + (S_{xx} - S_{yy}) \frac{\cos^2 \phi_{12}^x - \cos^2 \phi_{12}^y}{2} + 2 S_{xz} \cos \phi_{12}^x \cos \phi_{12}^z \right]$$



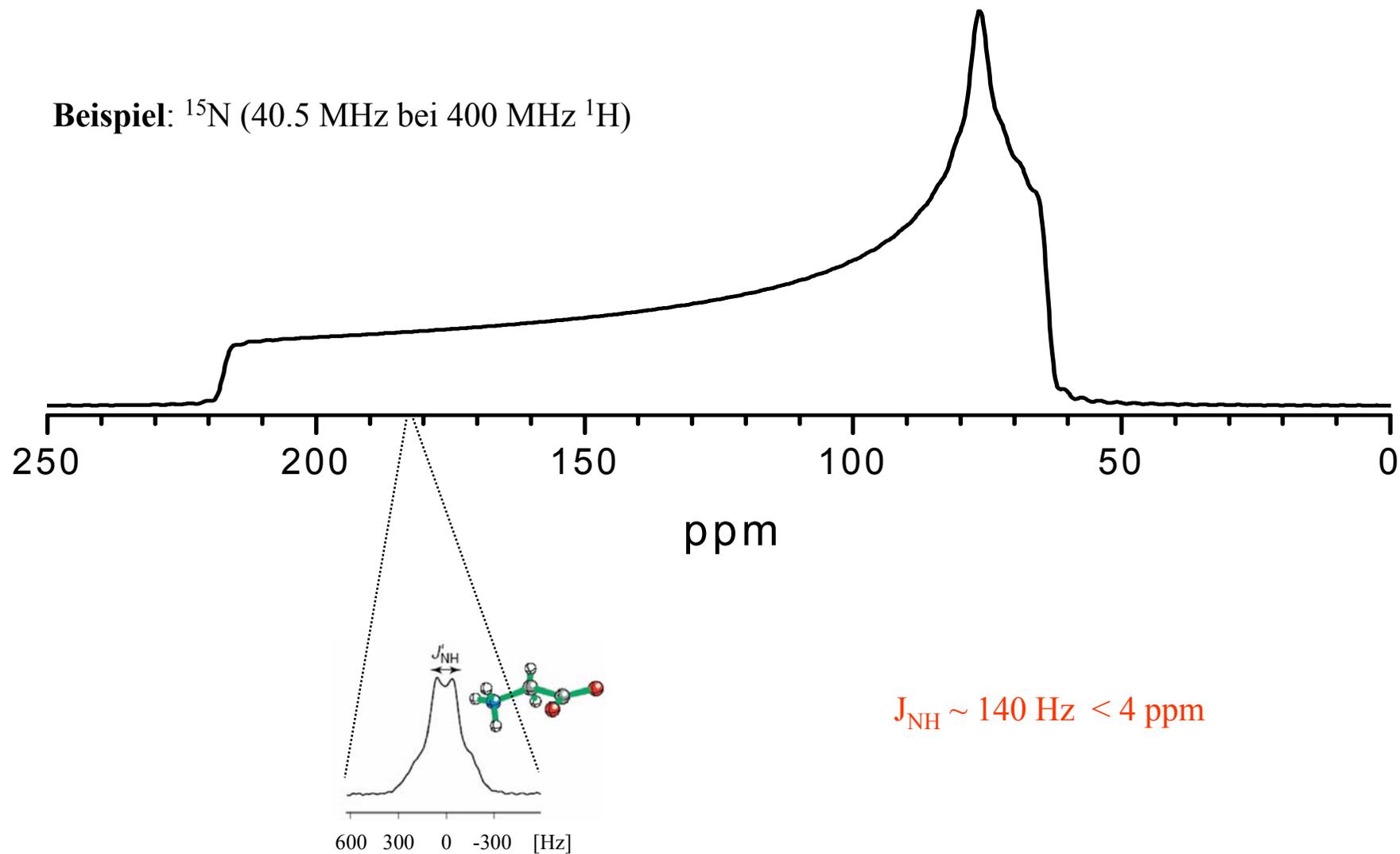
## CPMG an BA-F<sub>6</sub>



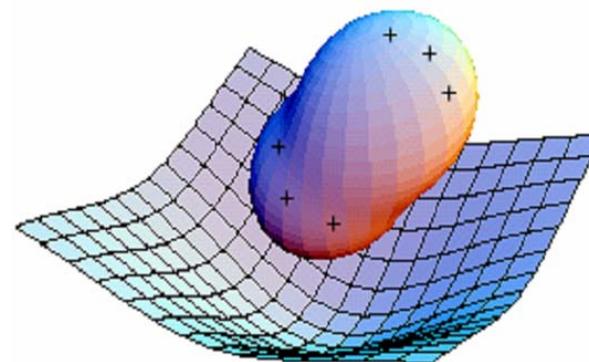
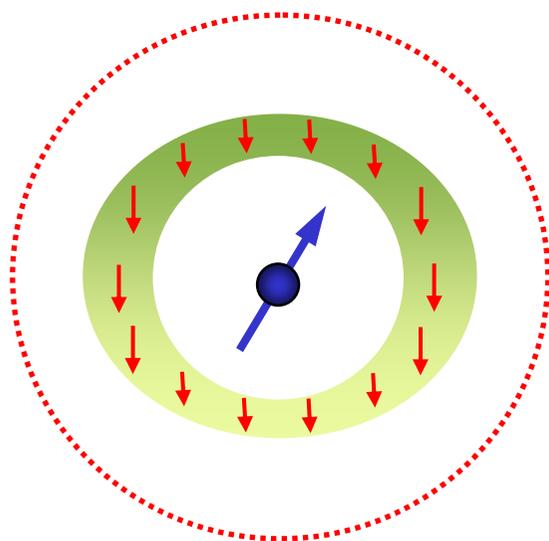
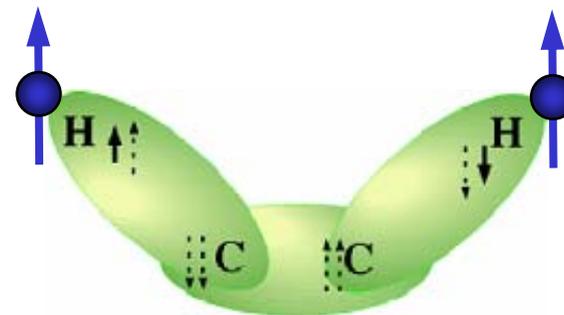
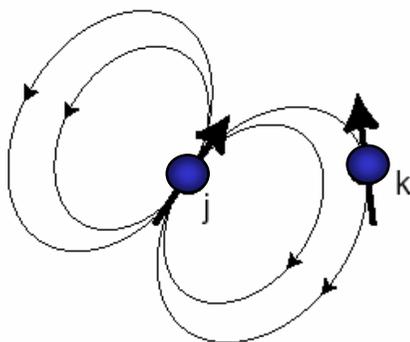
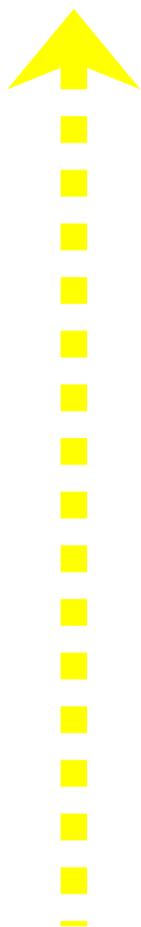
## Der kleine Zoo der NMR-Wechselwirkungen



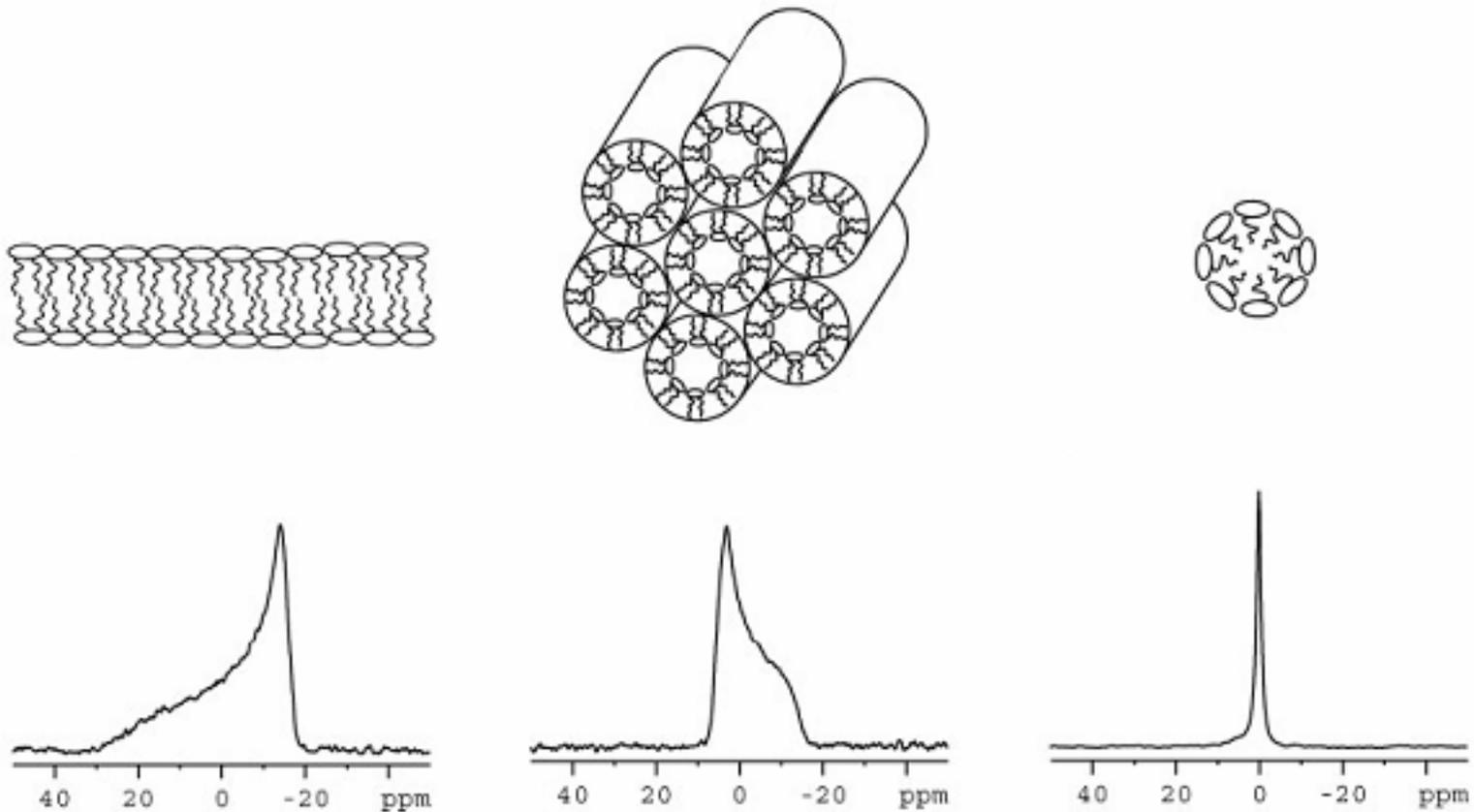
Beispiel:  $^{15}\text{N}$  (40.5 MHz bei 400 MHz  $^1\text{H}$ )



**J-Kopplung als Feinaufspaltung (bisher unbeachtet)**



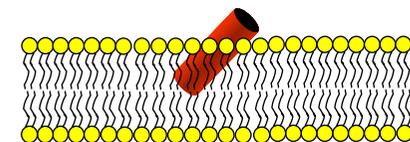
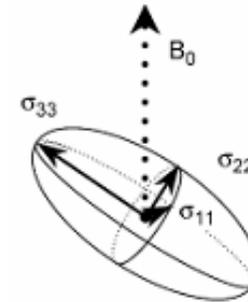
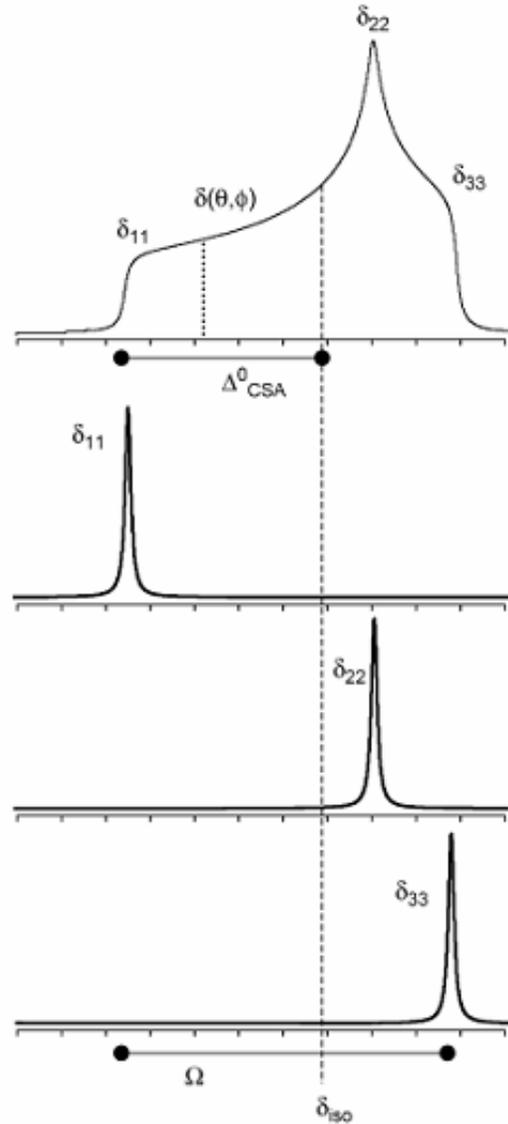
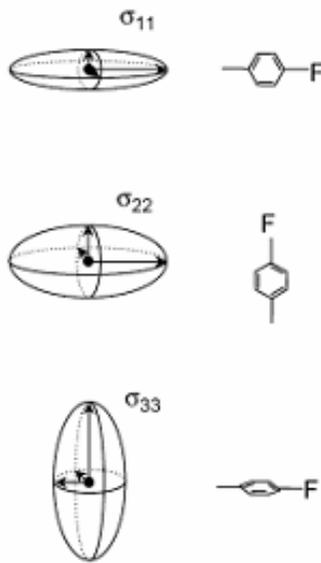
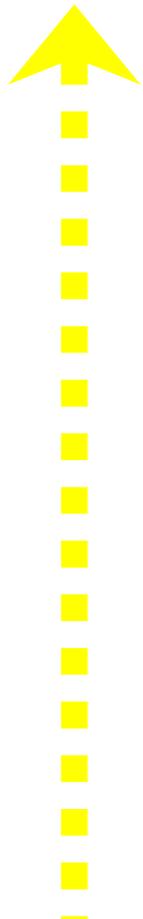
## Der kleine Zoo der NMR-Wechselwirkungen



laminare Bilayer

hexagonale Phase

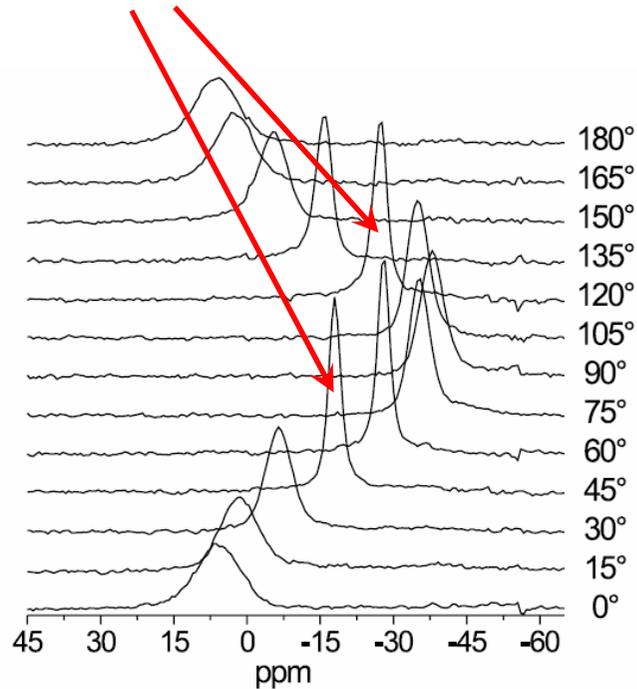
Mizellen



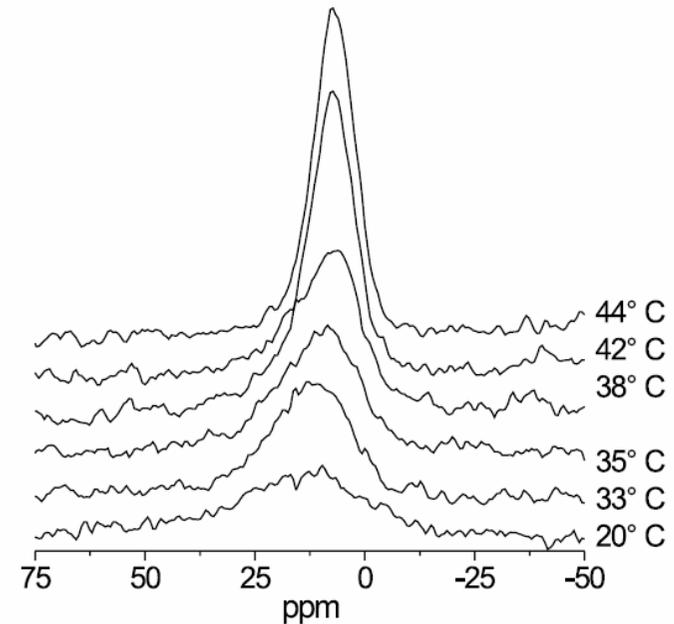
## Orientierungsabhängige CSA-Spektren



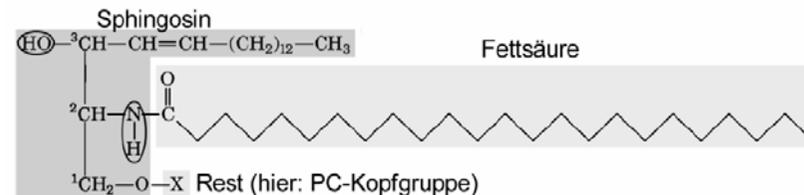
Kopfgruppe rotiert um den magischer Winkel



Variation des Winkels  $\theta$  von 0-180°



0°-Orientierung beim Phasenübergang



**$^{31}\text{P}$ -Spektren von EYSM (egg yolk sphingomyelin)**



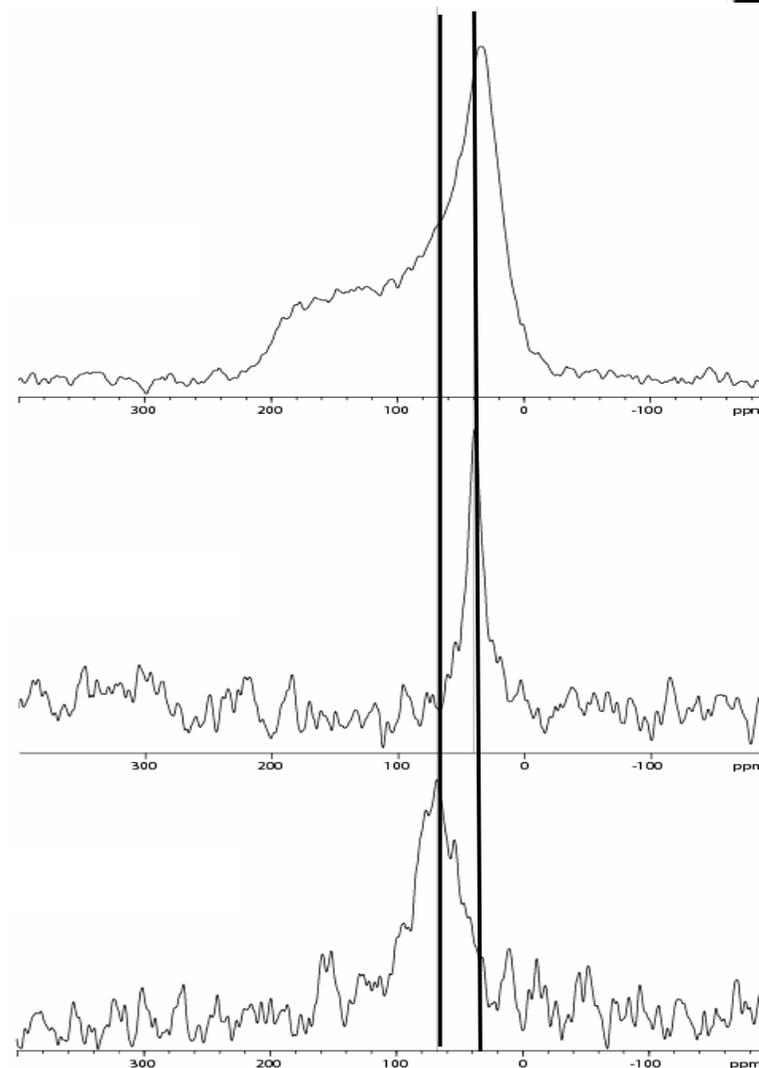
Pulverspektrum

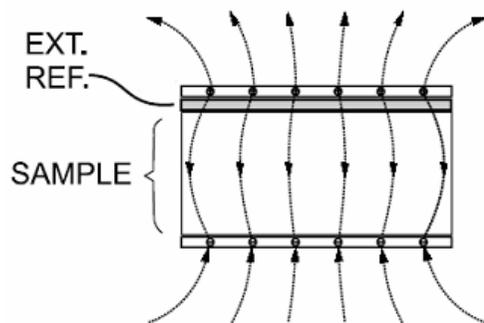
Niedrige Konzentration (1:200):

40 ppm entspricht 90°-Lage

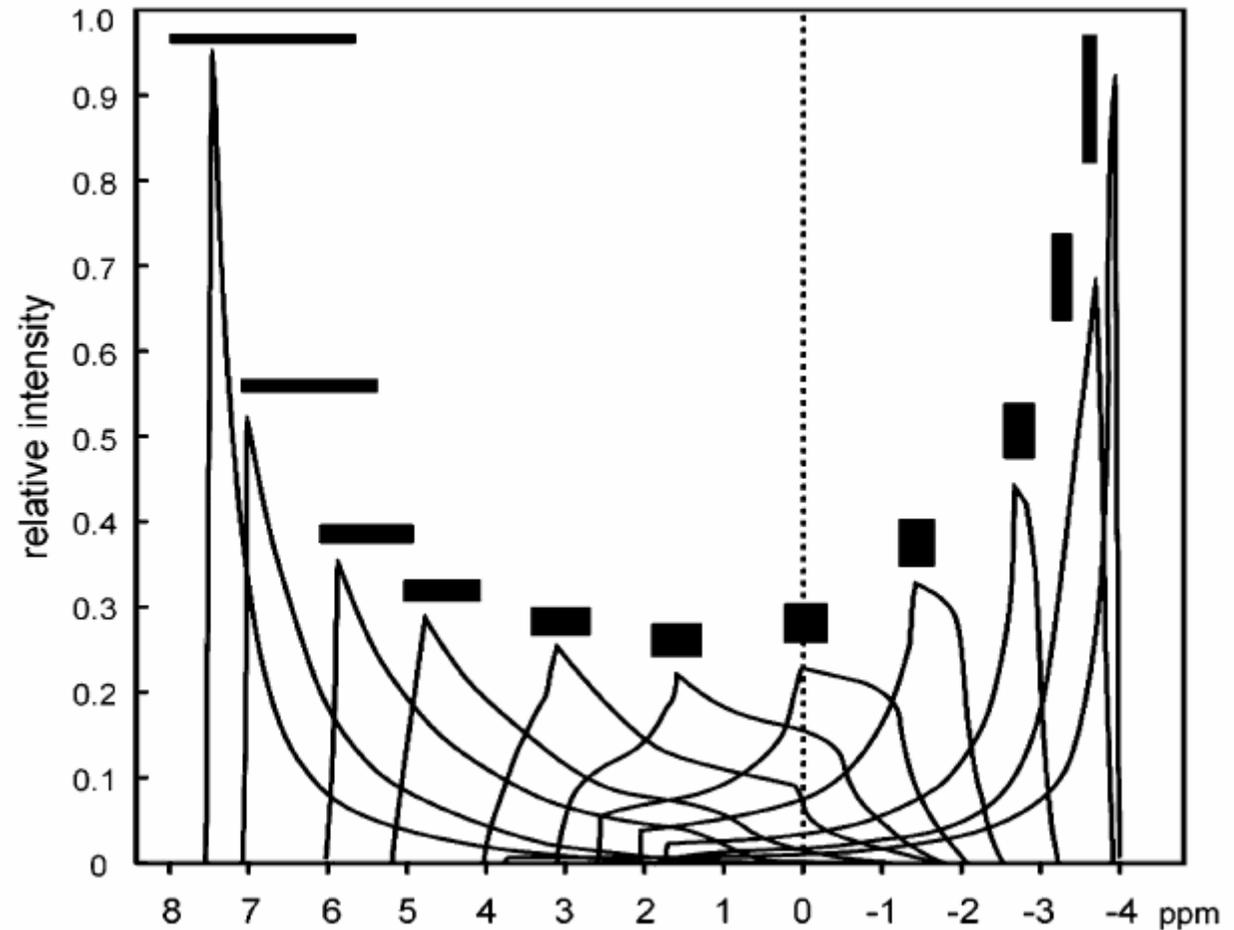
Hohe Konzentration (1:50):

68 ppm entspricht 60-80°-Lage

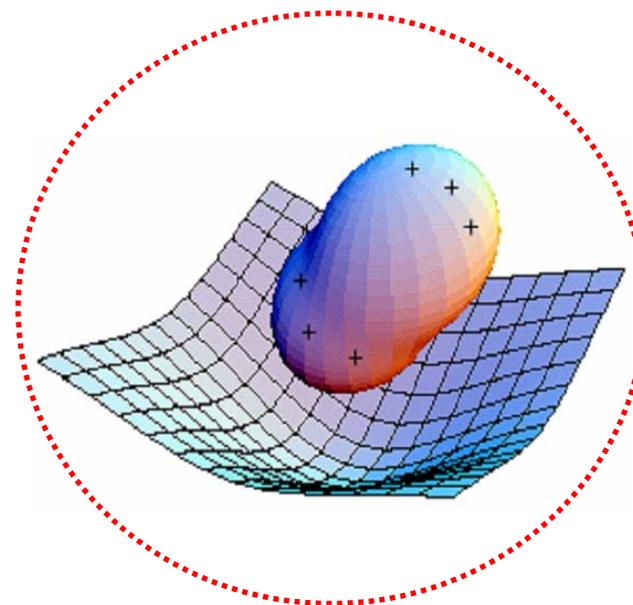
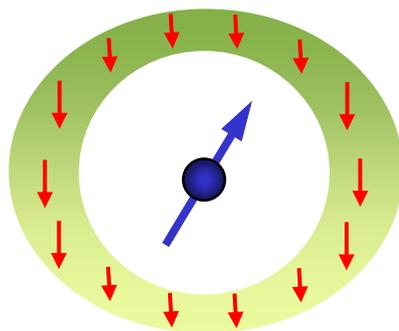
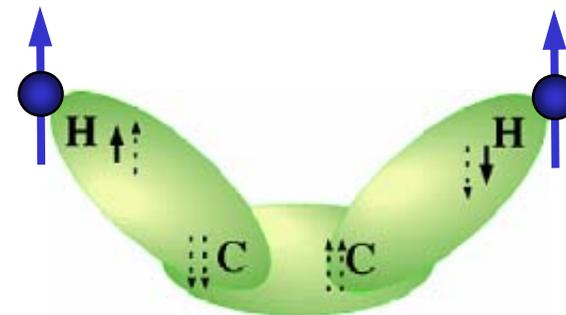
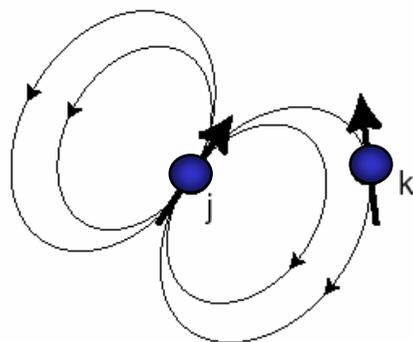
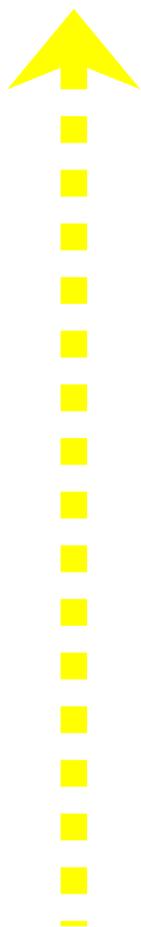




Korrekte Referenzierung  
ist notwendig!



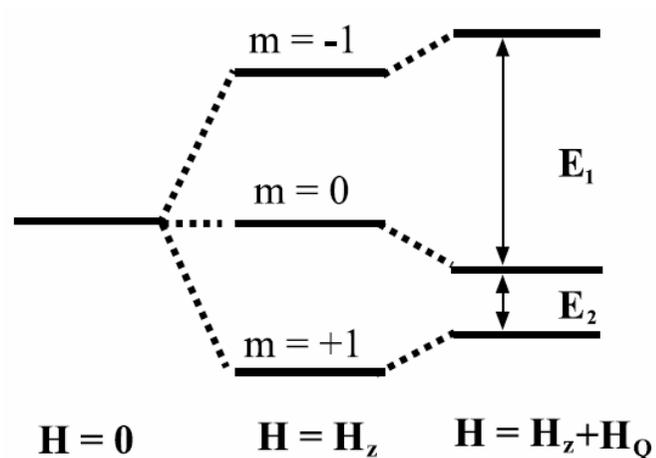
Suszeptibilitätsverschiebung in Abhängigkeit von der Probengeometrie



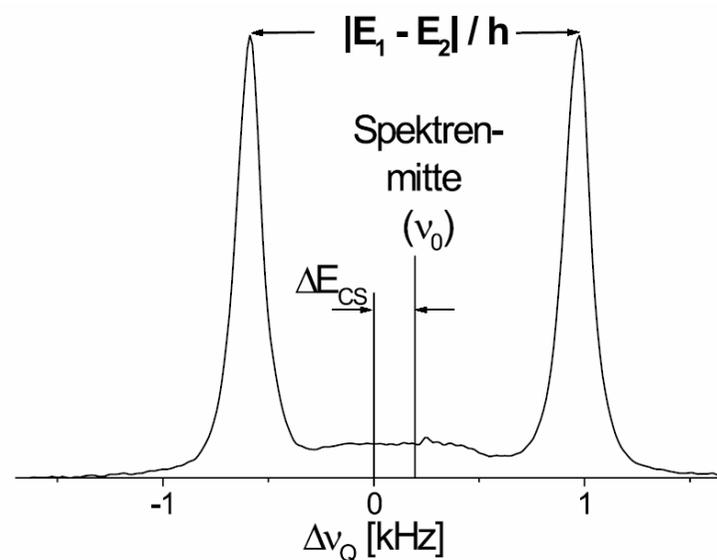
## Der kleine Zoo der NMR-Wechselwirkungen



### Niveauschema



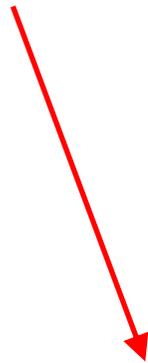
### NMR-Spektrum



$$\Delta\nu_Q = \frac{3}{2} \chi \frac{(3 \cos^2 \theta - 1)}{2} \left( S_{33} - \frac{\eta}{3} (S_{11} - S_{22}) \right)$$



$$\Delta\nu_Q = \frac{3}{2} \chi \frac{(3 \cos^2 \theta - 1)}{2} \left( S_{33} + \frac{\eta}{3} (S_{11} - S_{22}) \right)$$



$$\chi = \frac{e^2 q Q}{\hbar}$$

$$S_{33} = \frac{1}{2} \langle 3 \cos^2 \beta - 1 \rangle$$

$$S_{11} - S_{22} = \langle \sin^2 \beta \cos 2\alpha \rangle$$

C-D	O-D	N-D...O
170 kHz	220 kHz	(253-572/R <sup>3</sup> ) kHz

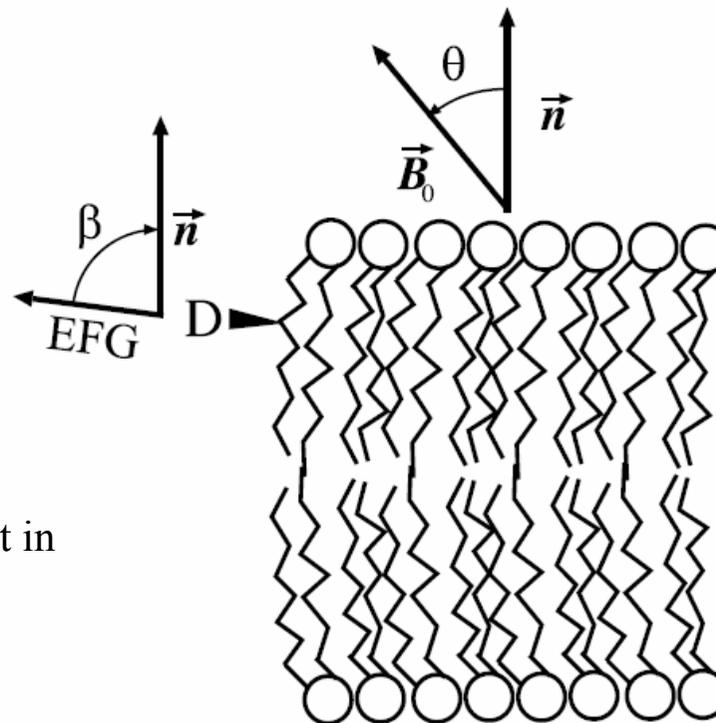


### Spektrale Frequenz

$$\Delta\nu_Q = \frac{3}{2} \chi \frac{1}{2} (3 \cos^2 \theta - 1) S_{33}$$

### Ordnungsparameter

$$S_{33} = \frac{1}{2} \langle 3 \cos^2 \beta - 1 \rangle$$

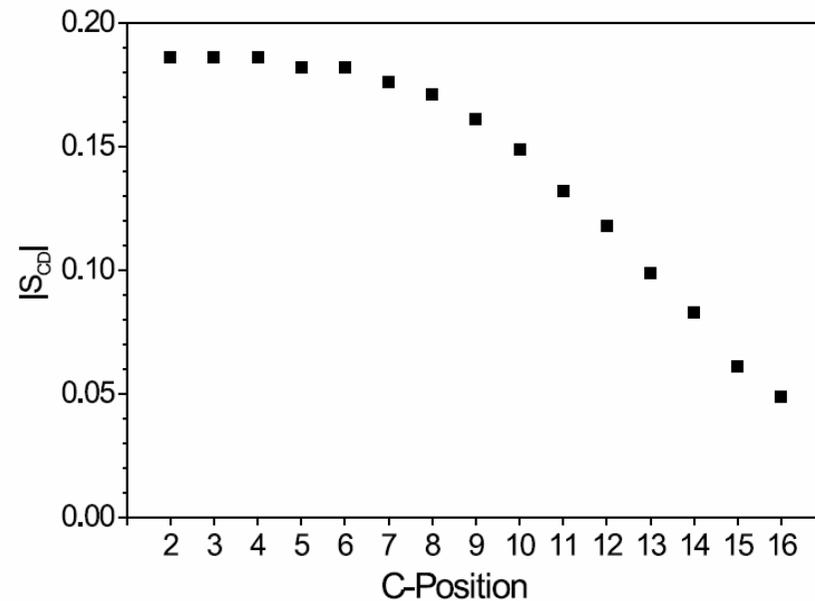
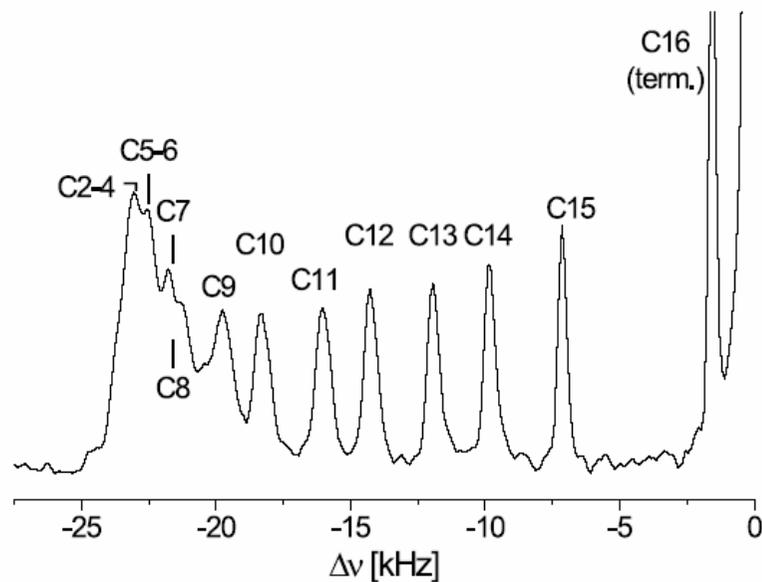


Elektrischer Feldgradient ist in  
Bindungsrichtung: C-D  
(oft reicht  $\eta \approx 0$ )



$^2\text{D}$ -Spektrenhälfte einer vollhydratisierten  
POPC-Membran ( $0^\circ$ -Orientierung,  $n_w=28.6$ ,  $42^\circ\text{C}$ )

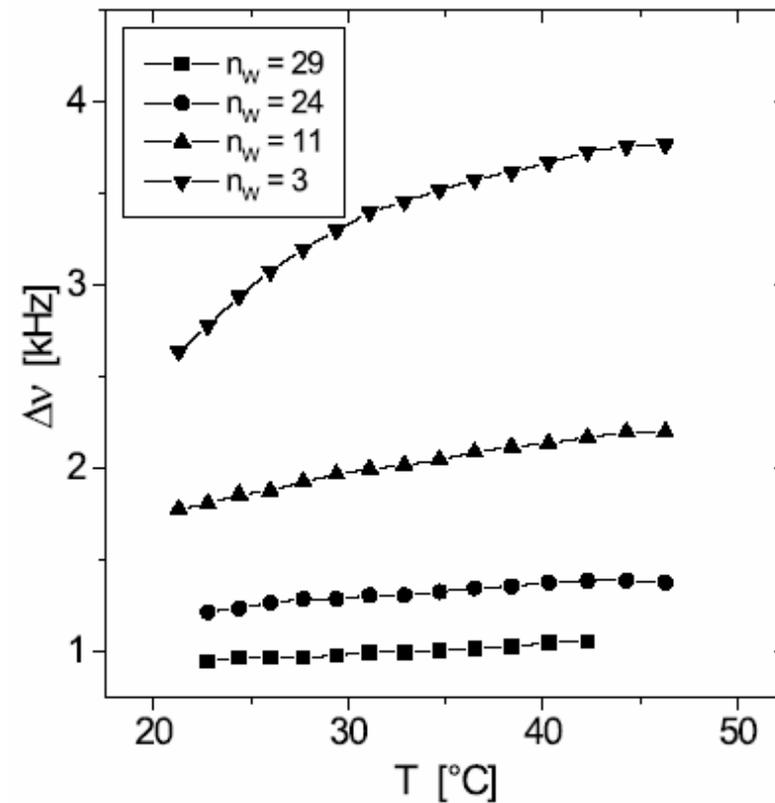
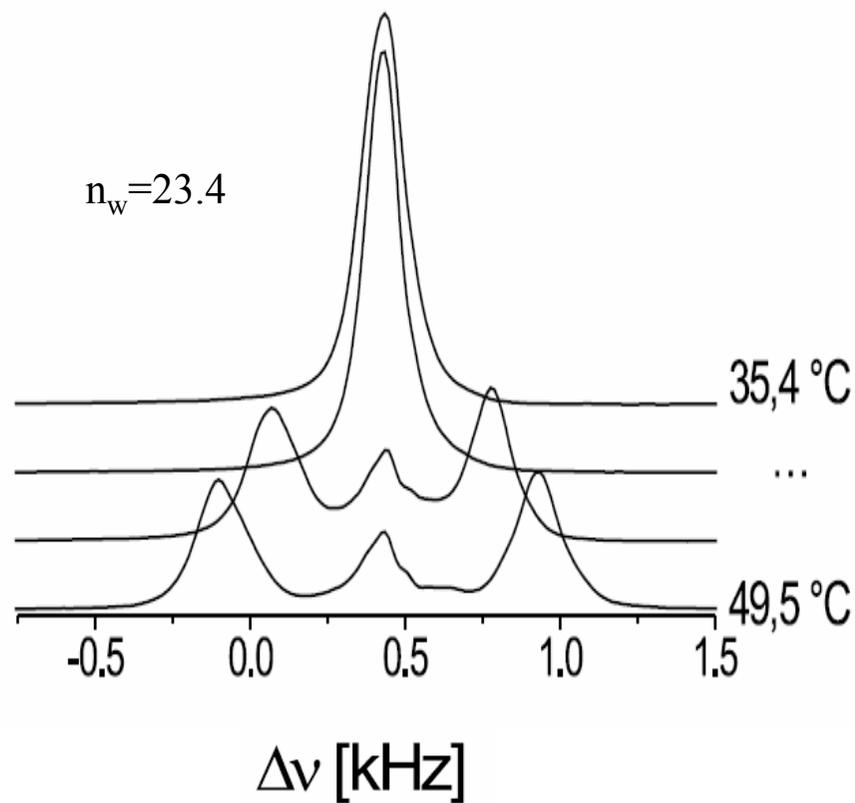
Ordnungsparameter



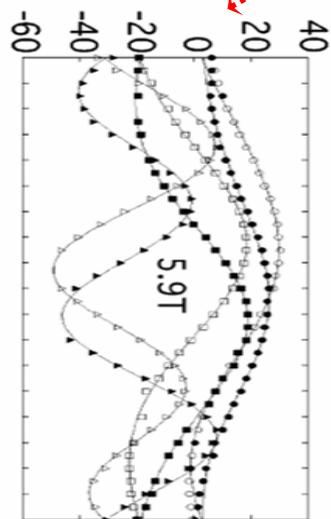
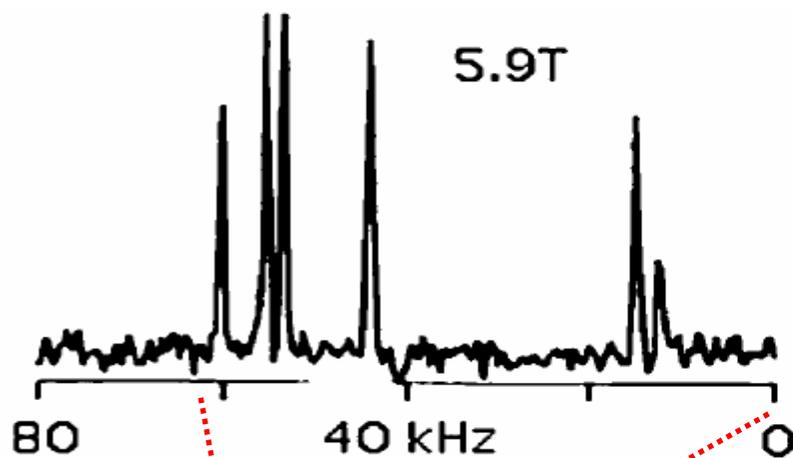
**Kettendeutertes POPC**



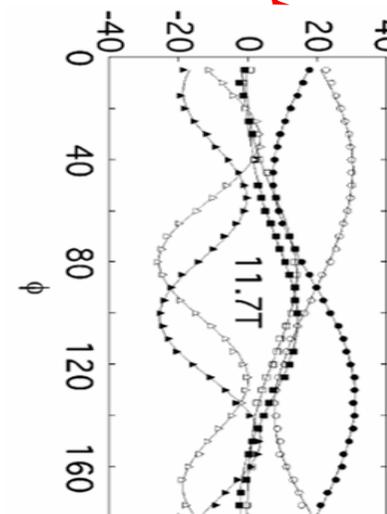
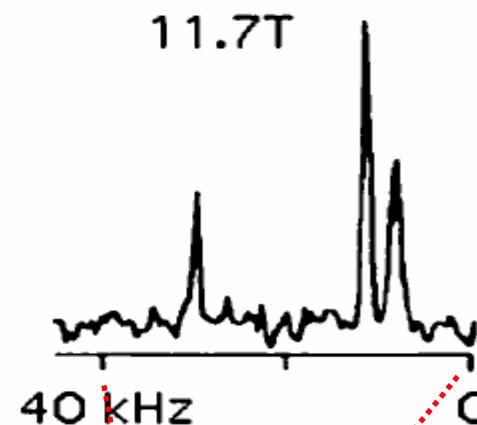
D<sub>2</sub>O-Spektren von orientiertem POPC in Abhängigkeit von der Temperatur und Hydratisierung.



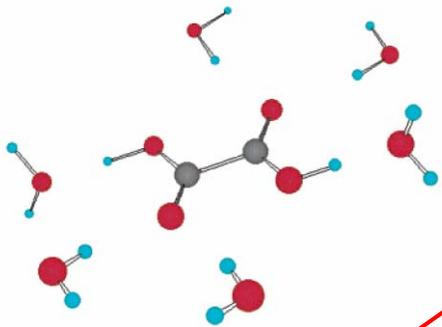
**Kann sich Wasser orientieren?**



Drehung um die  
drei Achsen der  
Kristalleinheitszelle  
( $a^*$ ,  $b$ ,  $c$ )



## Einkristallmessungen an $^{17}\text{O}$ $\alpha$ -oxalic acid dihydrate

Table 2.  $^{17}\text{O}$  CS Tensors for  $\alpha$ -Oxalic Acid Dihydrate<sup>a</sup>

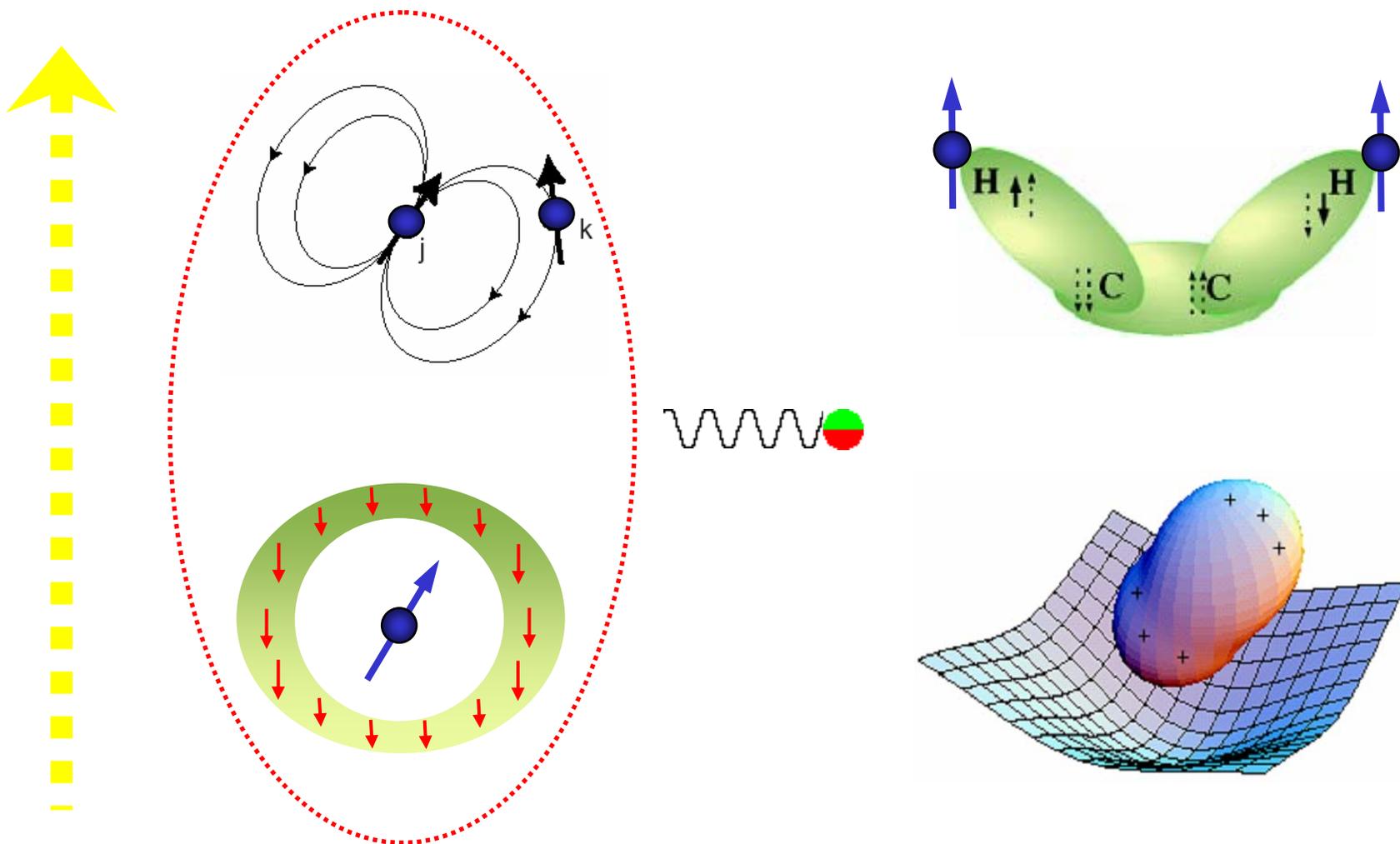
	$\delta_{11}$	$\delta_{22}$	$\delta_{33}$	$x$	$y$	$z$
C=O	476(18)	413(11)	14(13)	plane	orthog	C=O
$a^*$	-0.844(0.051)	-0.235(0.114)	0.464(0.029)	-0.523	-0.114	0.847
$b$	0.345(0.059)	0.402(0.043)	0.845(0.012)	-0.851	0.013	-0.521
$c$	0.386(0.116)	-0.874(0.063)	0.263(0.016)	0.049	-0.993	-0.104
COH	351(4)	142(3)	55(4)	plane	orthog	COH
$a^*$	-0.480(0.011)	-0.755(0.019)	0.446(0.029)	-0.523	-0.611	-0.594
$b$	0.458(0.010)	0.218(0.035)	0.861(0.009)	-0.851	0.414	0.324
$c$	0.748(0.008)	-0.617(0.014)	-0.241(0.030)	0.049	0.675	-0.737

Eigenvektoren im Kristallsystem

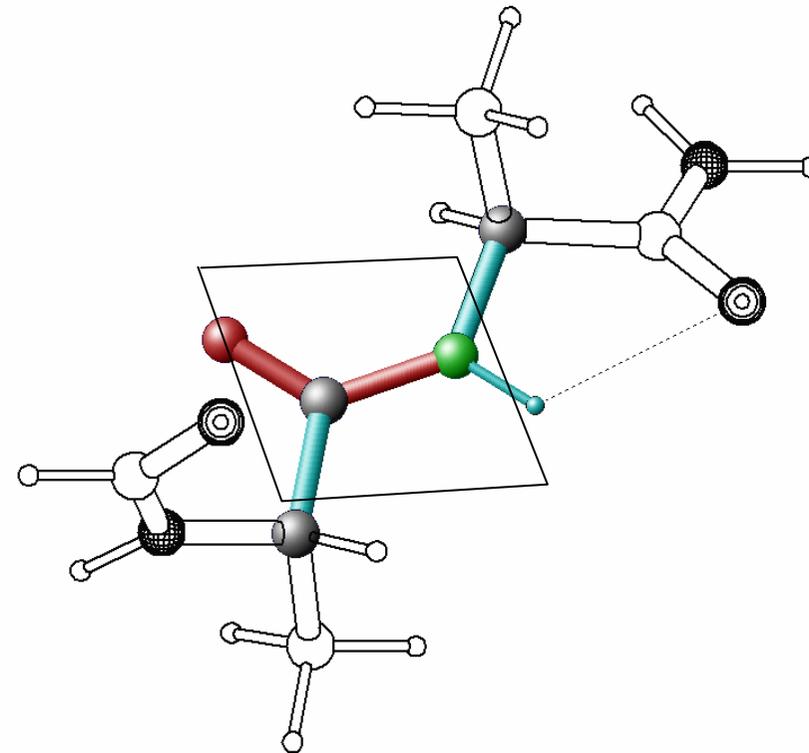
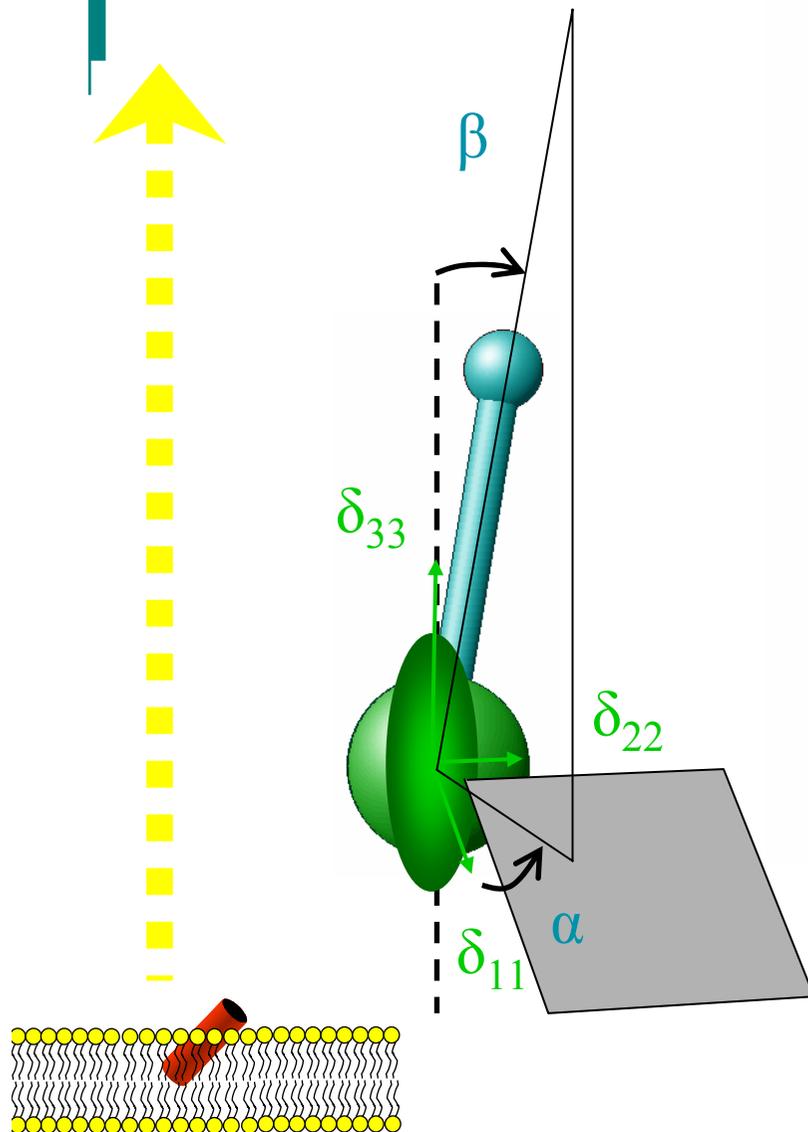
Table 1.  $^{17}\text{O}$  QC Tensors ( $\chi$ ) for  $\alpha$ -Oxalic Acid Dihydrate<sup>a</sup>

	$\chi_{xx}$	$\chi_{yy}$	$\chi_{zz}$	$x$	$y$	$z$
C=O	-3.88(0.19)	-4.49(0.22)	8.30(0.23)	plane	orthog	C=O
$a^*$	0.211(0.234)	0.839(0.059)	0.439(0.006)	-0.523	-0.114	0.847
$b$	0.932(0.068)	-0.242(0.260)	0.015(0.006)	-0.851	0.013	-0.521
$c$	-0.119(0.114)	-0.405(0.037)	0.898(0.006)	0.049	-0.993	-0.104
COH	2.80(0.23)	3.88(0.25)	-6.68(0.08)	plane	orthog	COH
$a^*$	-0.432(0.184)	0.588(0.024)	0.658(0.005)	-0.523	-0.611	-0.594
$b$	0.848(0.058)	0.437(0.235)	0.177(0.008)	-0.851	0.414	0.324
$c$	0.183(0.153)	-0.635(0.069)	0.732(0.005)	0.049	0.675	-0.737

Einkristallmessungen an  $^{17}\text{O}$   $\alpha$ -oxalic acid dihydrate



## Der kleine Zoo der NMR-Wechselwirkungen

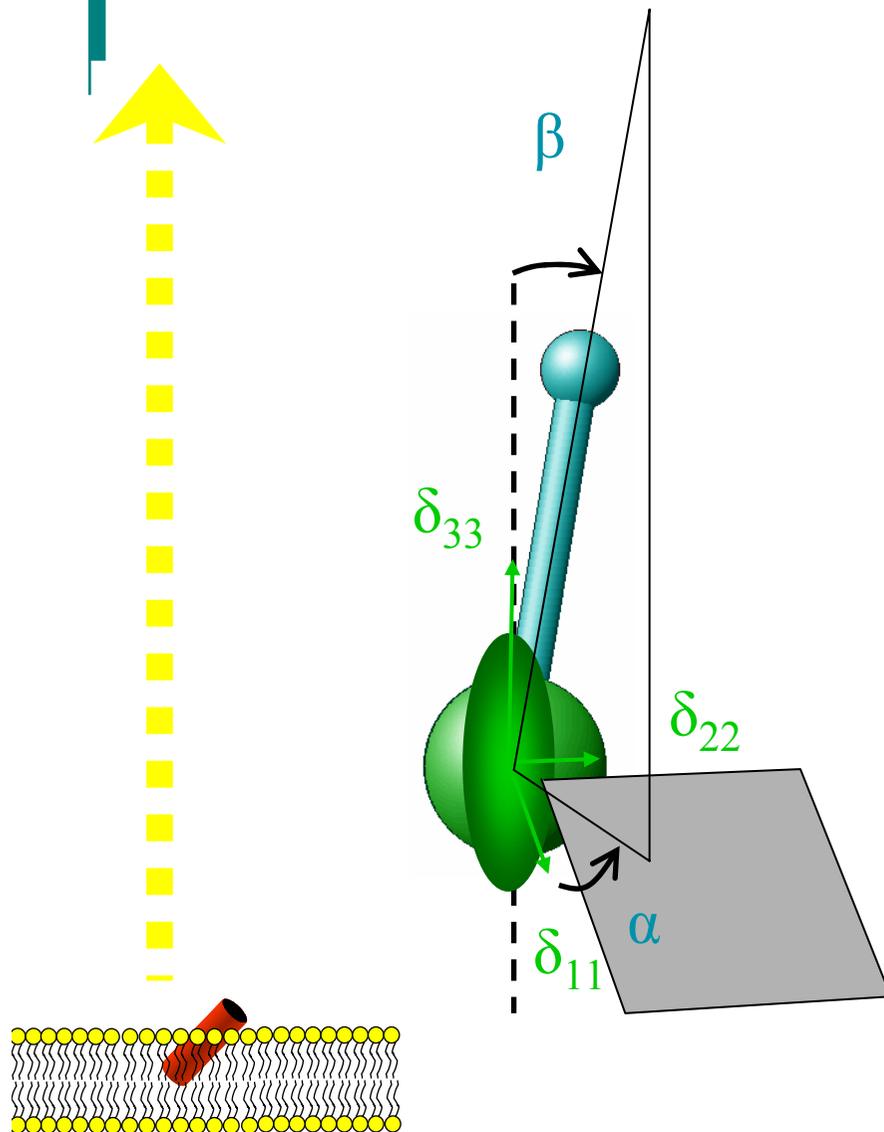


$^{15}\text{N}$ - amide :

$$\delta_{11}=64\text{ppm}, \delta_{22}=77\text{ppm}, \delta_{33}=217\text{ppm}$$

$$\alpha=0^\circ, \beta=17^\circ$$

**NMR-Parameter und deren globale Lage zueinander**

 **$^{15}\text{N}$ - amide :**

$$\delta_{11}=64\text{ppm}, \delta_{22}=77\text{ppm}, \delta_{33}=217\text{ppm}$$

$$\alpha=0^\circ, \beta=17^\circ$$

 **$^{15}\text{N}_\pi$ -His:**

$$\delta_{11}=77\text{ppm}, \delta_{22}=203\text{ppm}, \delta_{33}=260\text{ppm}$$

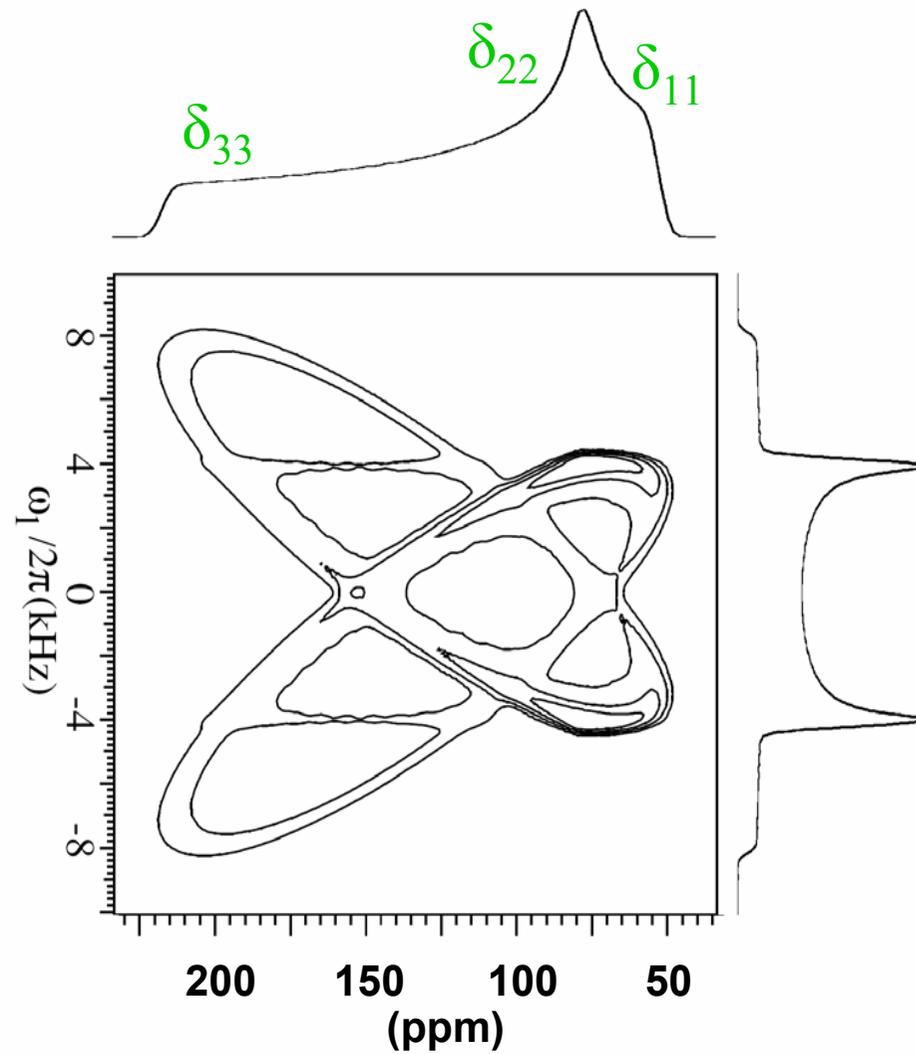
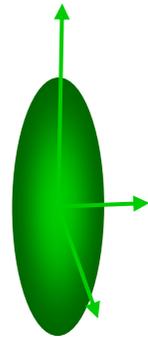
$$\alpha=0 \pm 30^\circ, \beta=5 \pm 3^\circ$$

 **$^{15}\text{N}_{\epsilon 1}$ -Trp:**

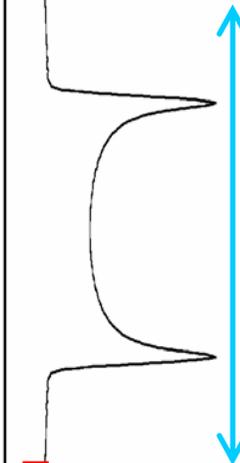
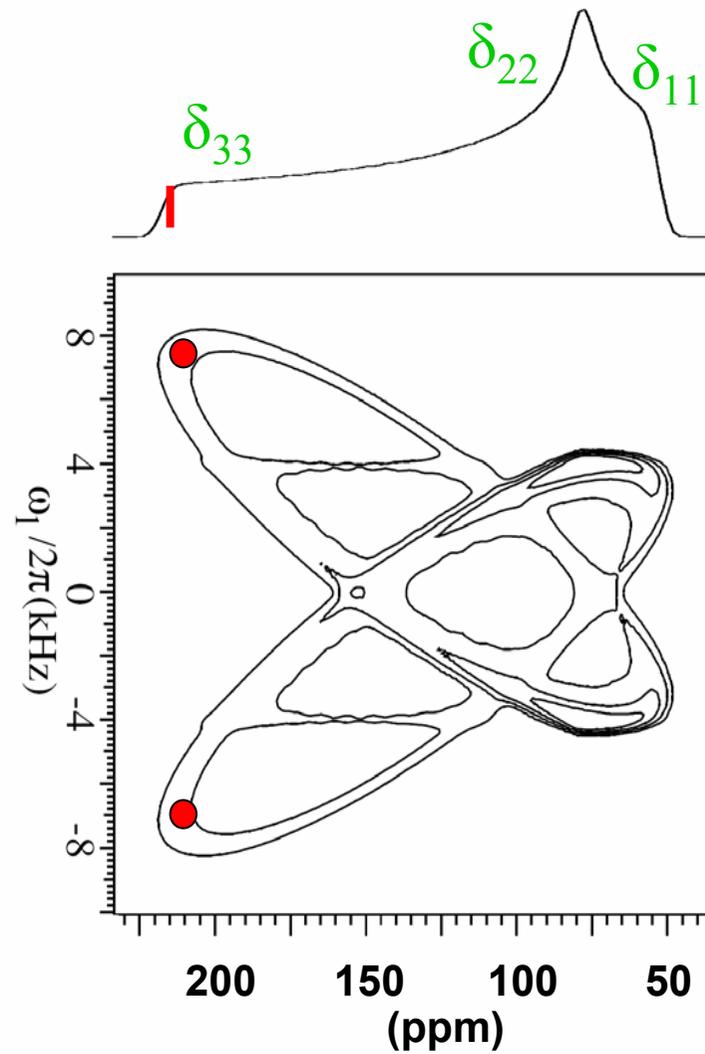
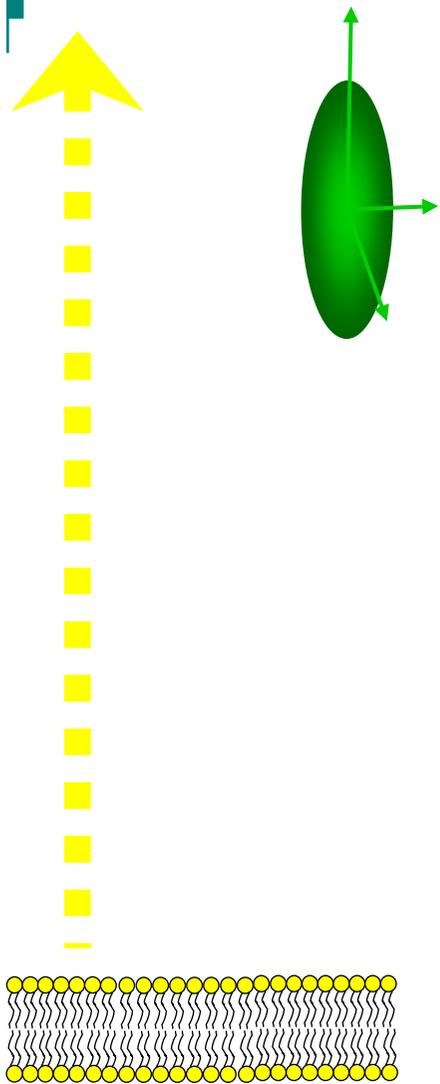
$$\delta_{11}=61\text{ppm}, \delta_{22}=130\text{ppm}, \delta_{33}=181\text{ppm}$$

$$\alpha=0 \pm 30^\circ, \beta=5 \pm 3^\circ$$

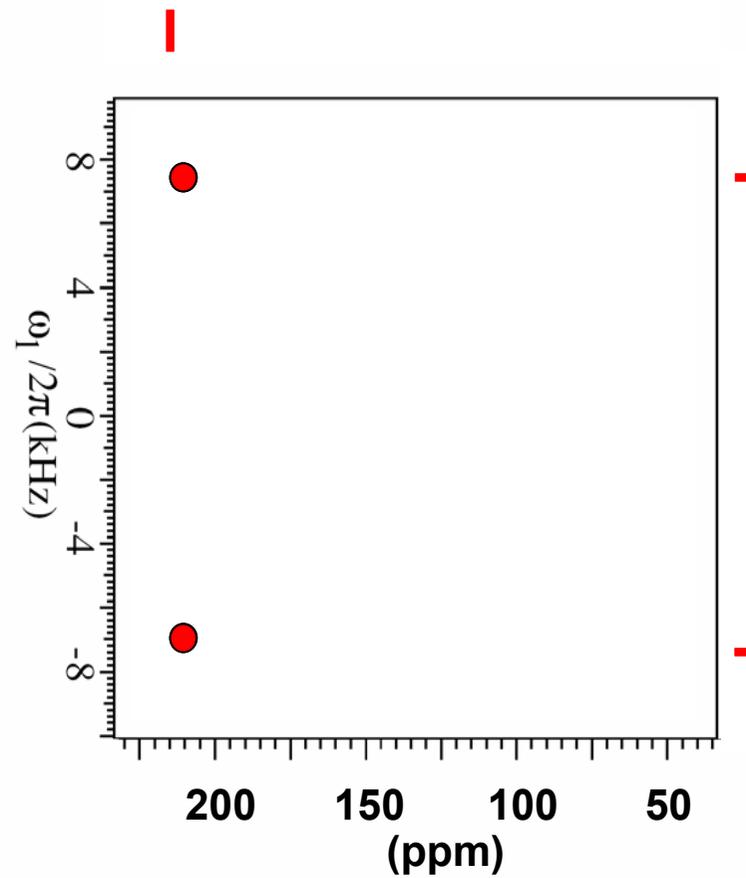
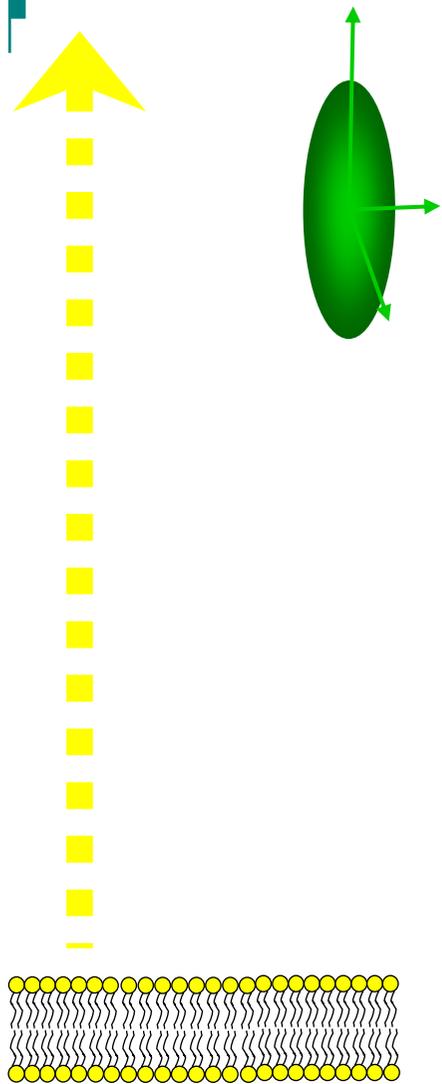
**NMR-Parameter und deren globale Lage zueinander**



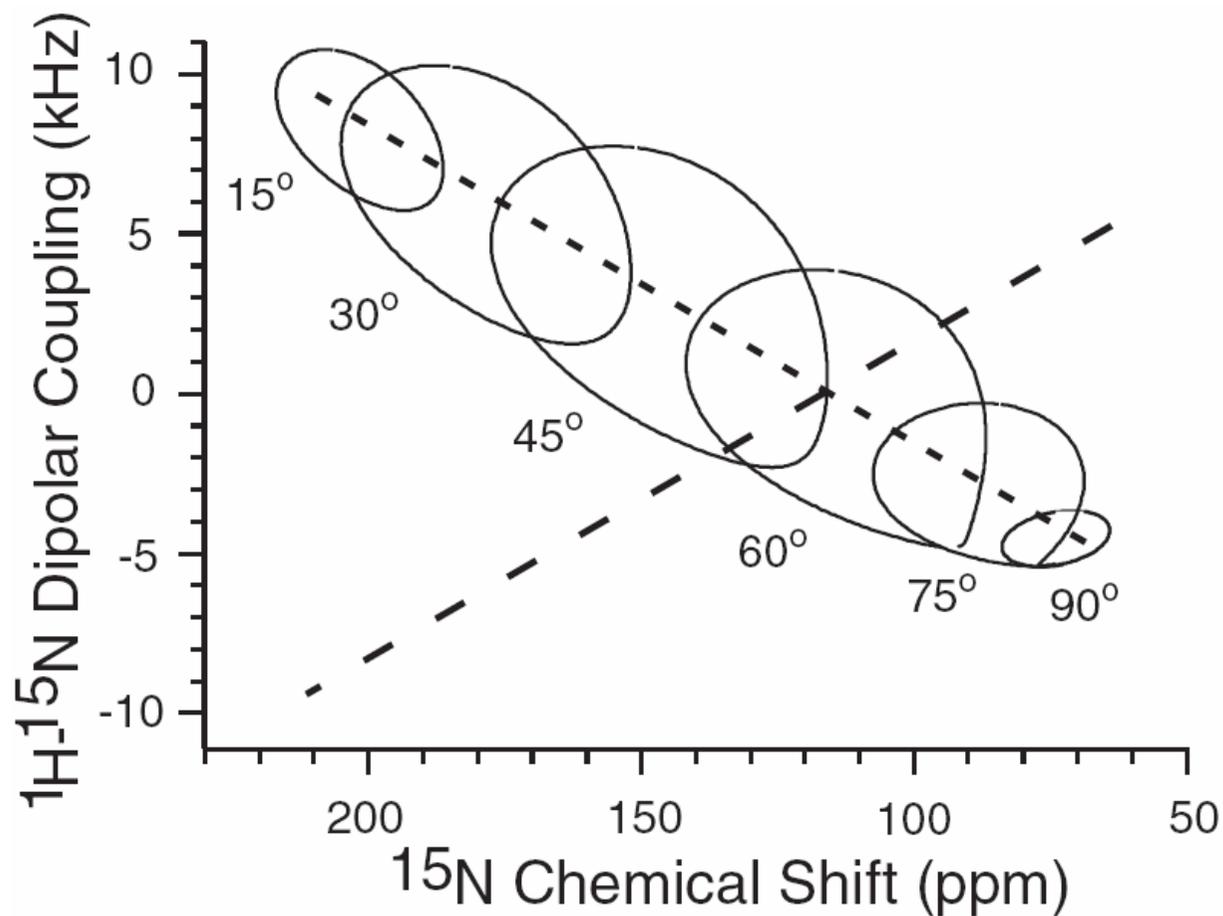
## PISEMA-Spektrum



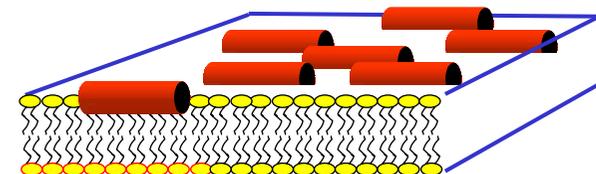
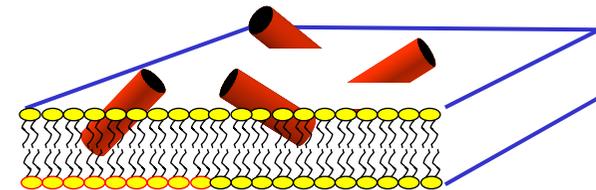
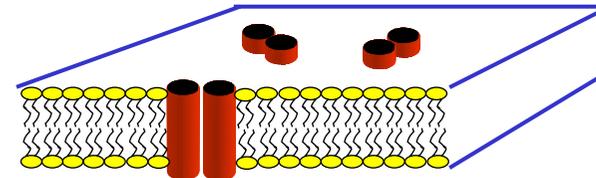
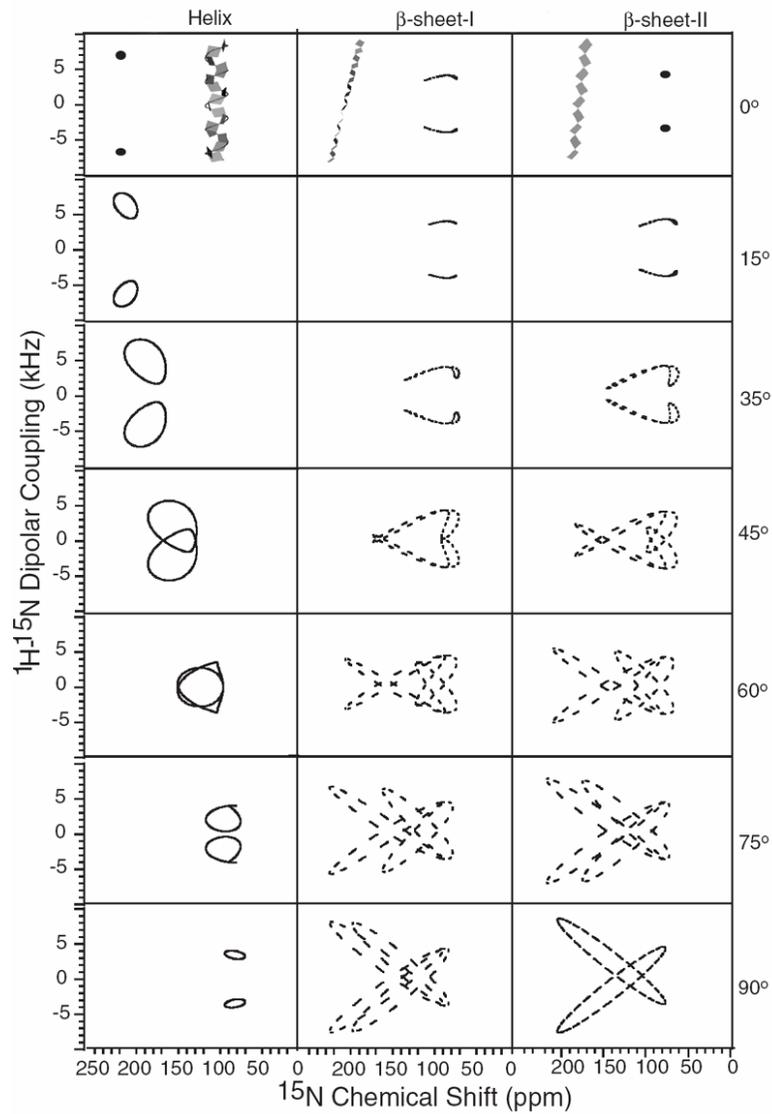
## PISEMA-Spektrum

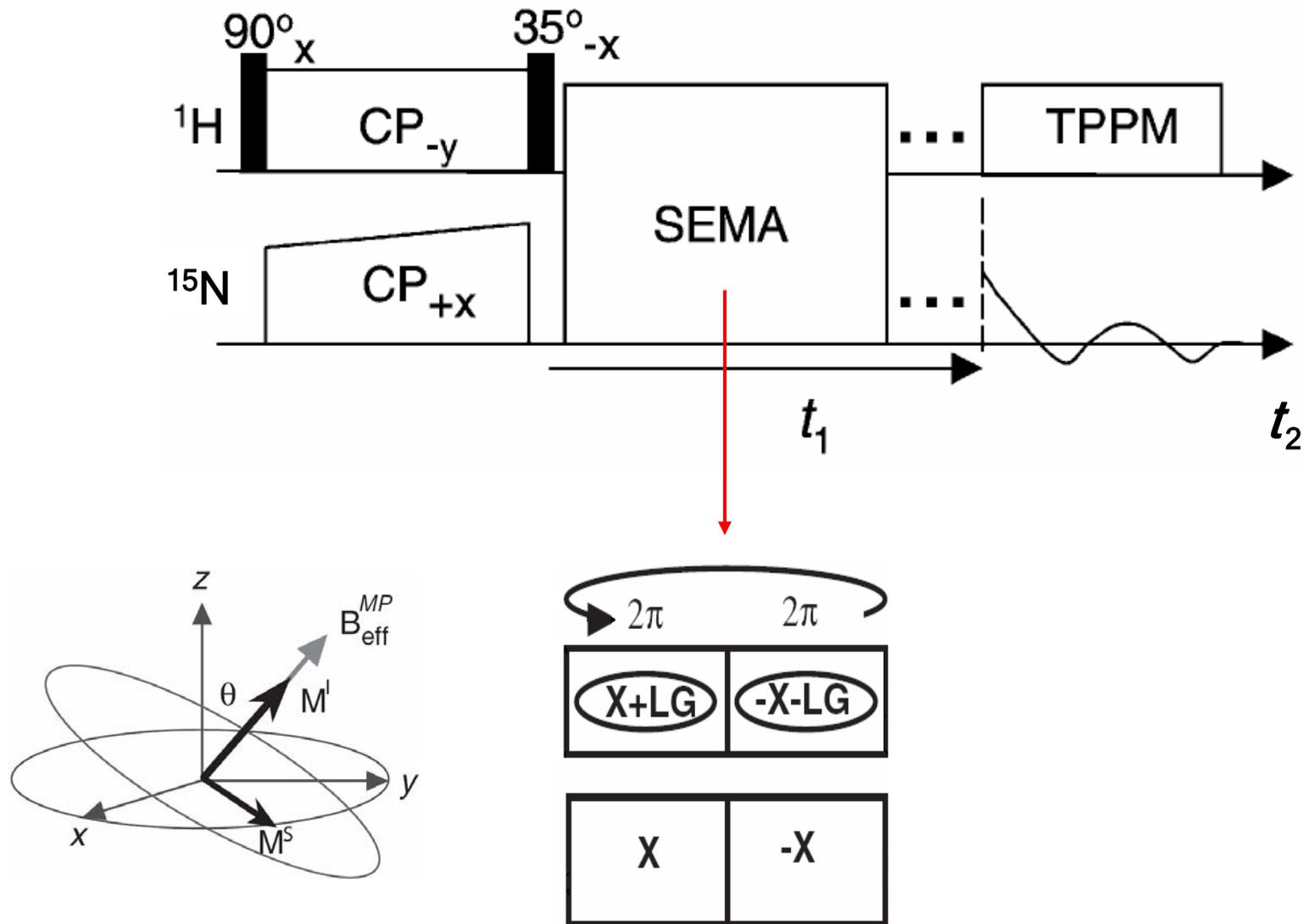


PISEMA-Spektrum

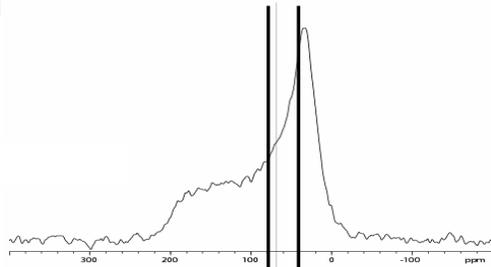


Polarity Index Slant Angle Wheel





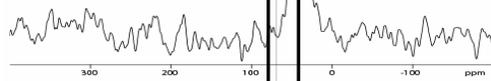
**PISEMA (Polarization Inversion Spine Exchange at the Magic Angle)**



Pulverspektrum

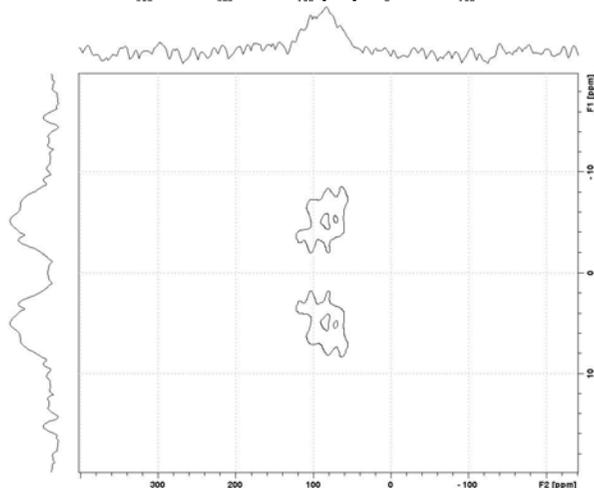
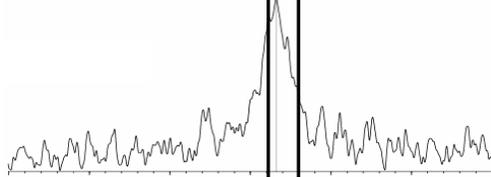
niedrige Konzentration (1:200):

40 ppm entspricht 90°-Orientierung

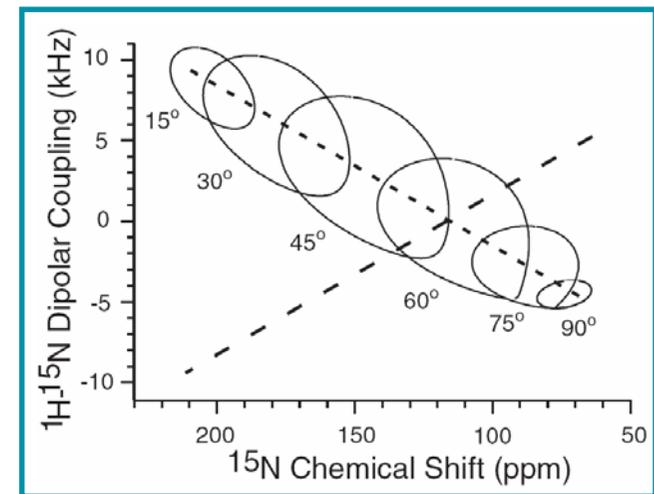


hohe Konzentration (1:50):

68 ppm entspricht 60-80°-Orientierung



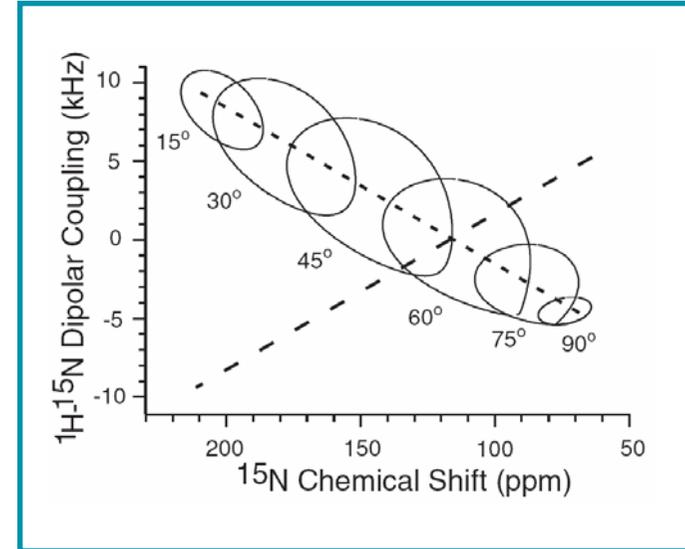
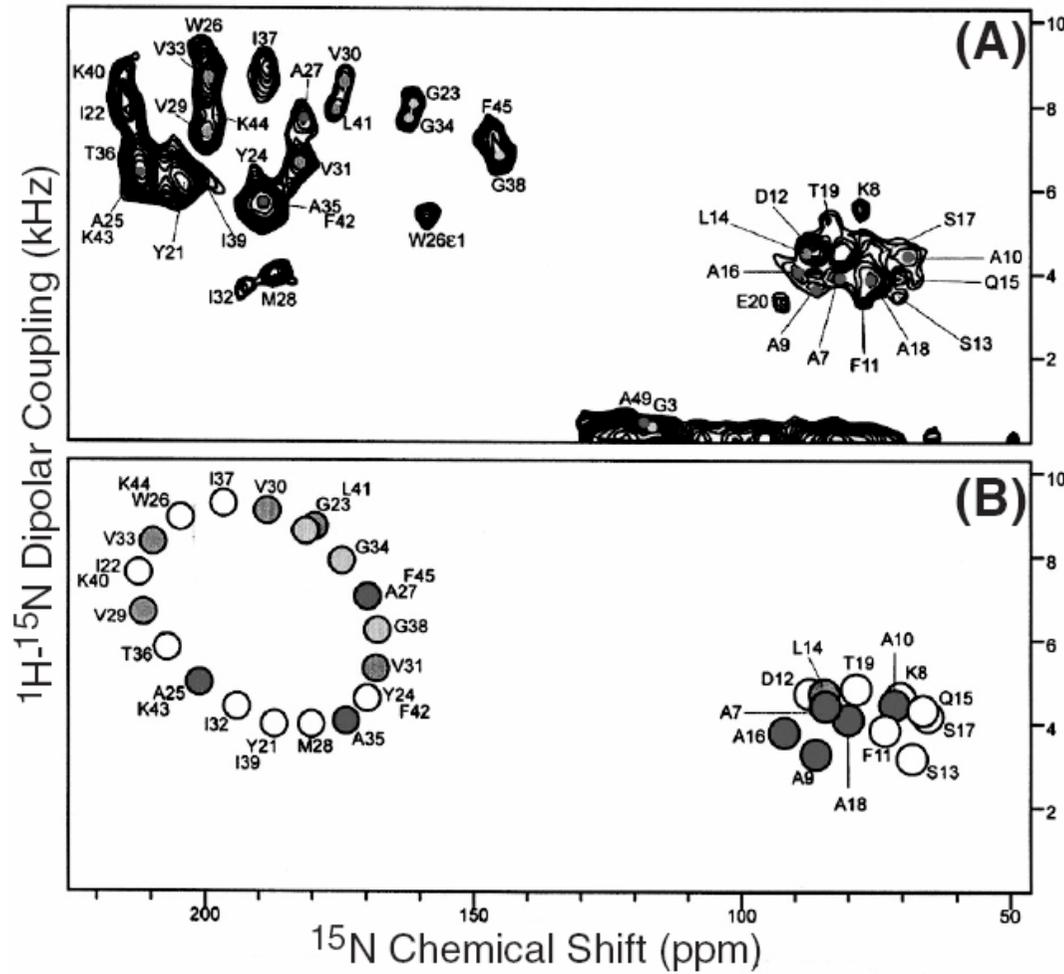
PISEMA (1:50)



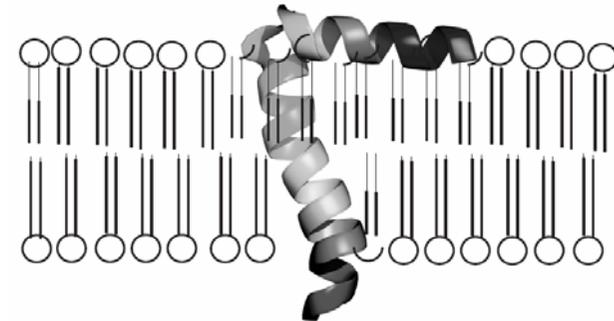
PISEMA von PGLa

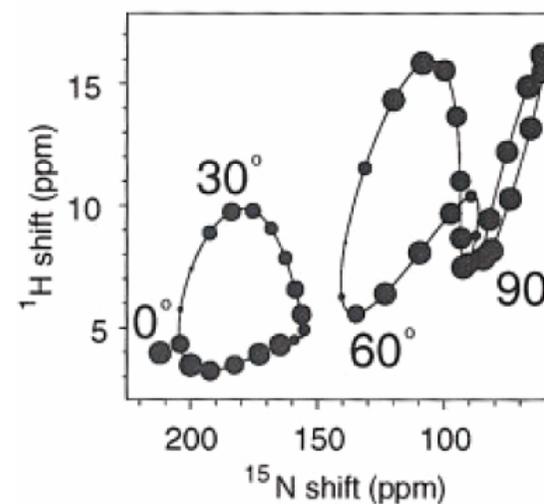
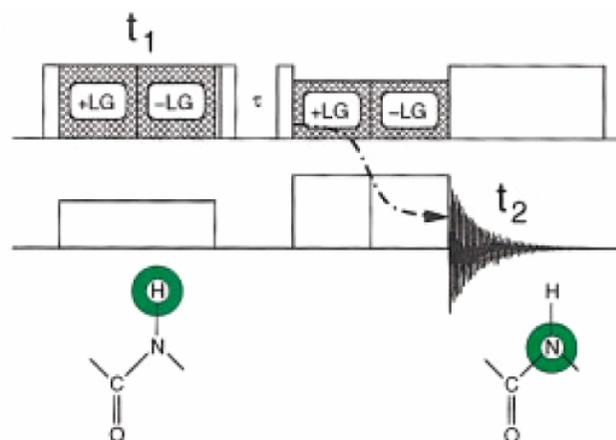
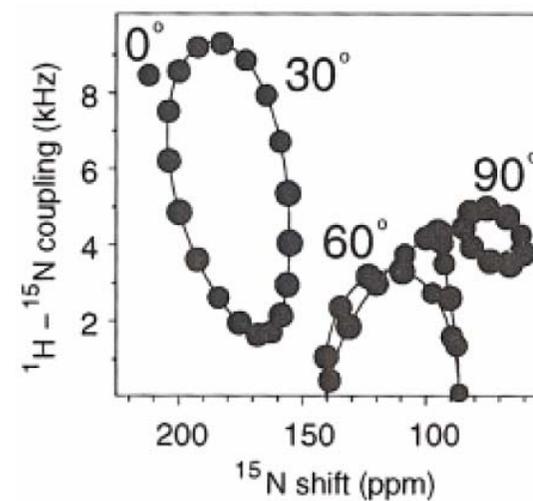
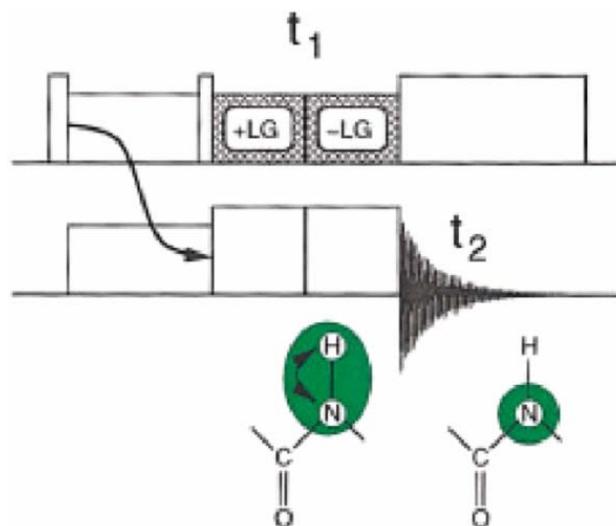


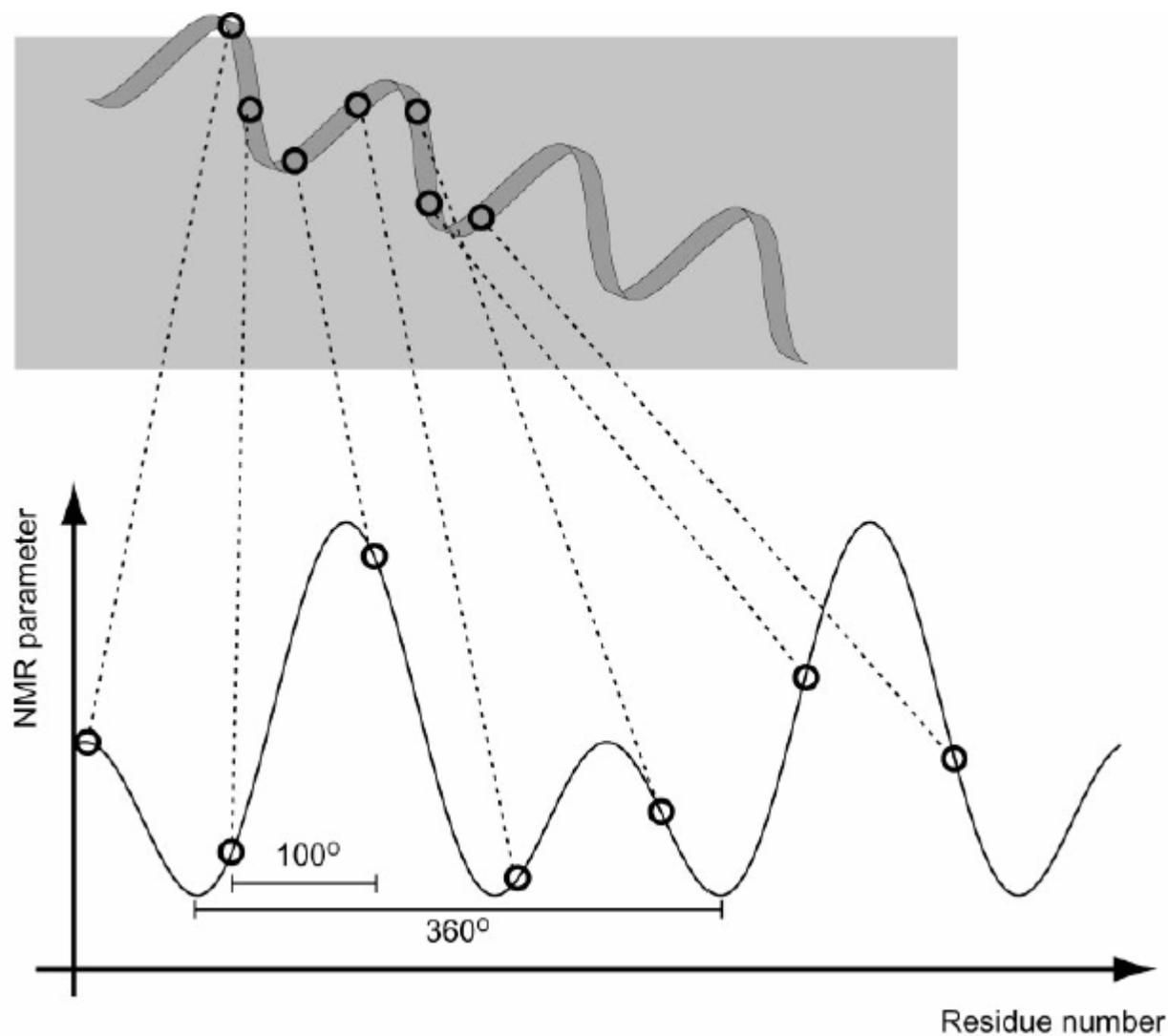
AEGDD PAKAA FDSLQ ASATÉ YIGYA WAMVV VIVGA TIGIK LFKKF TSKAS  
IP TM



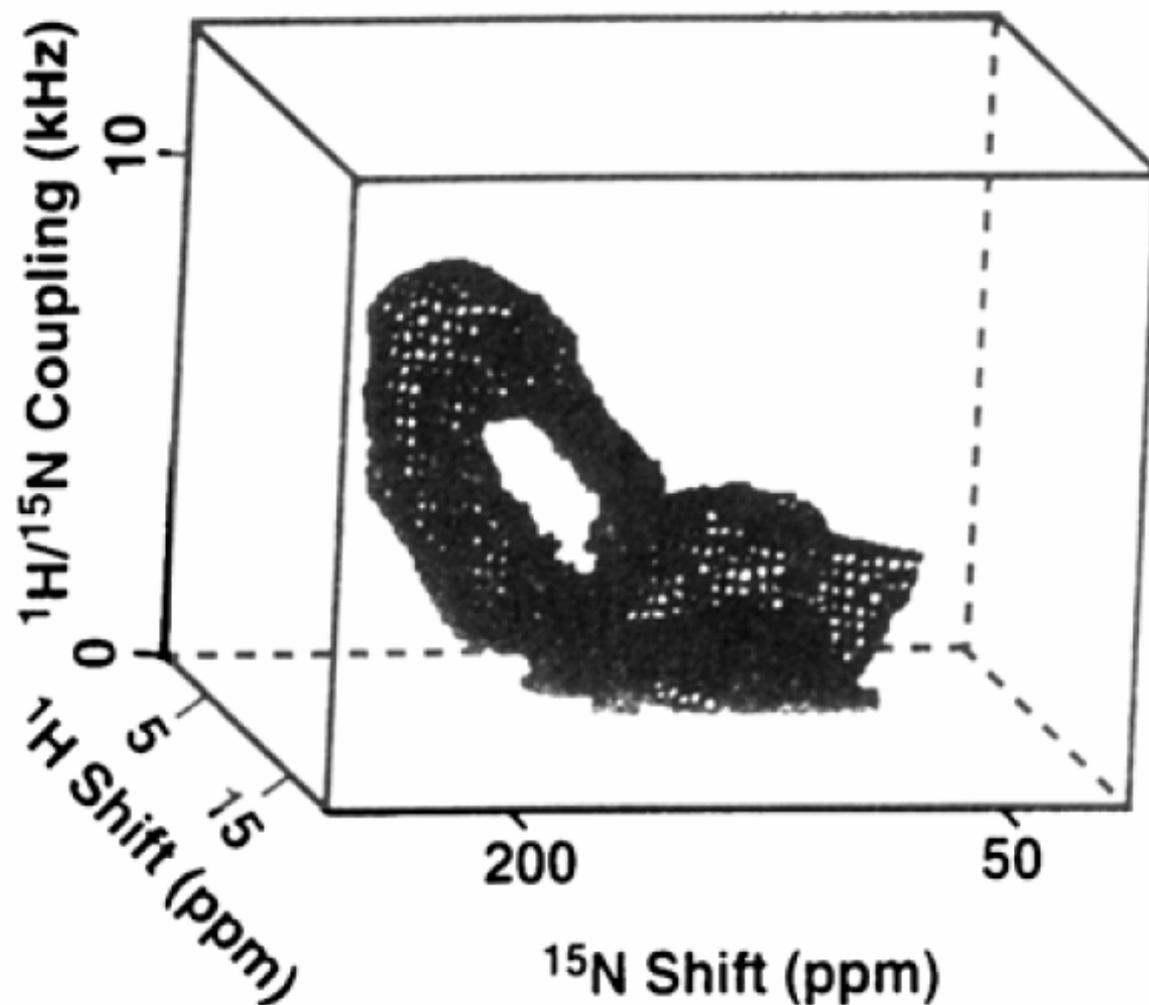
Helices with tilts:  
87° and 30°



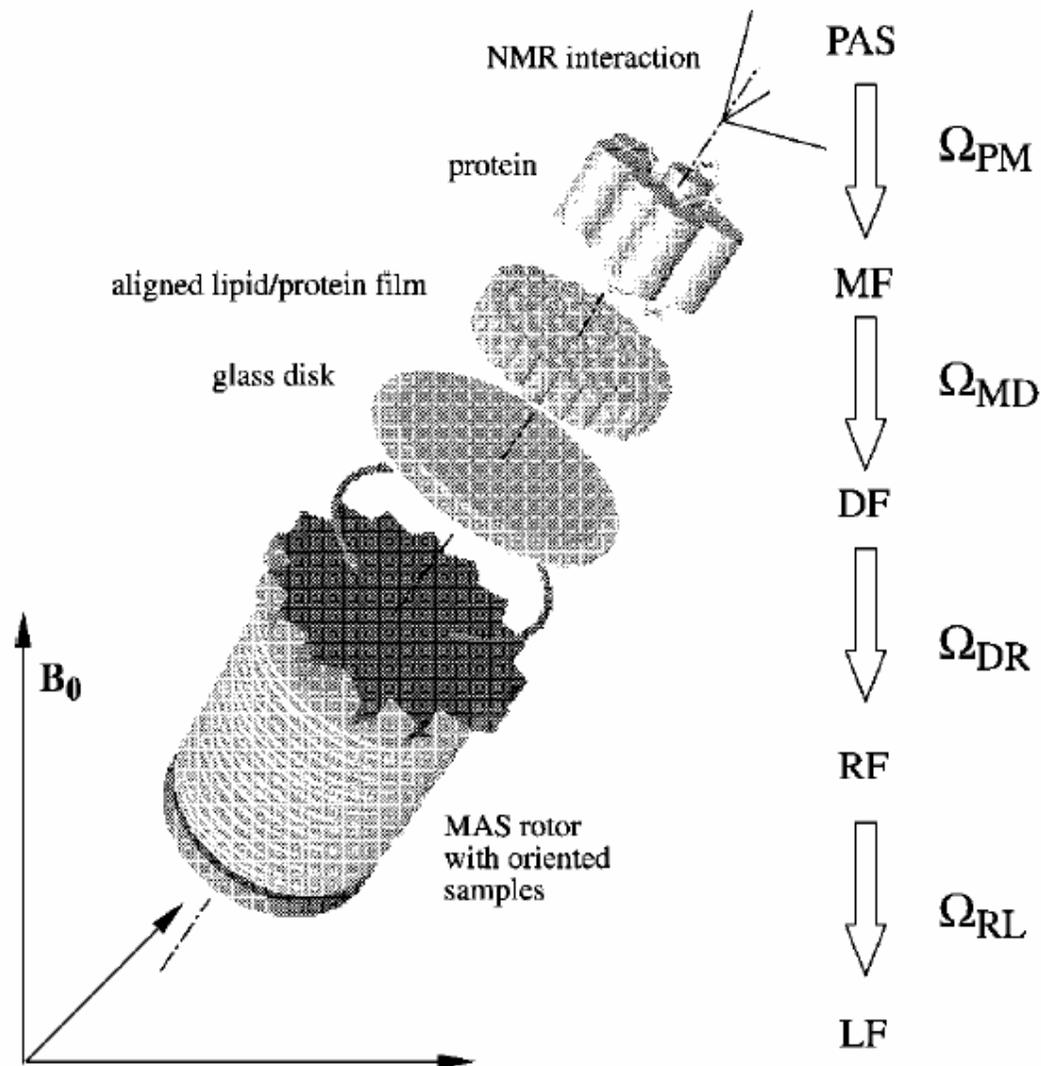




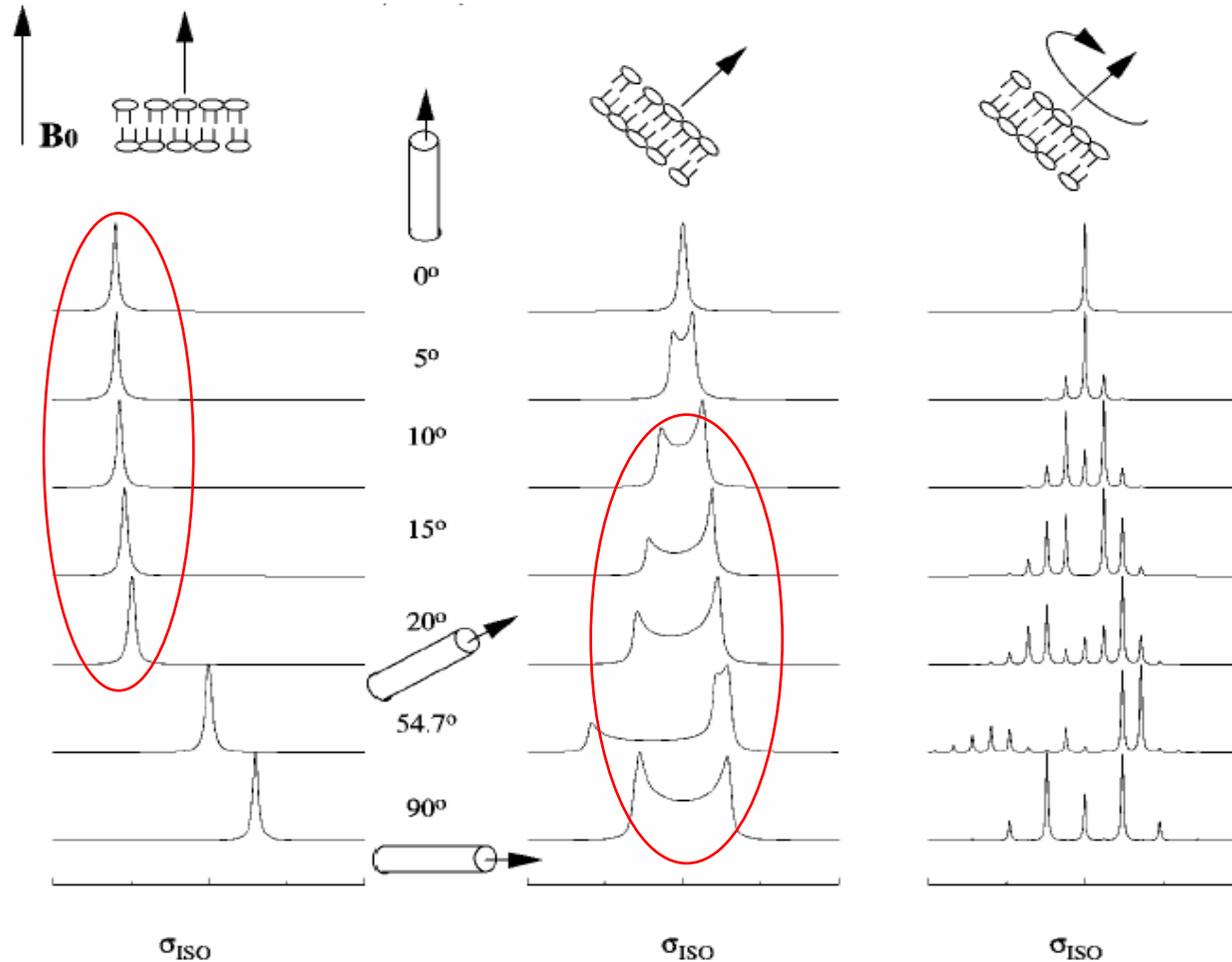
## Helikale Wellen



Eine helikale „3D-Welle“



## Rotation orientierter Proben (MAOSS)



- geringe  
Winkelauflösung  
- gute Sensitivität

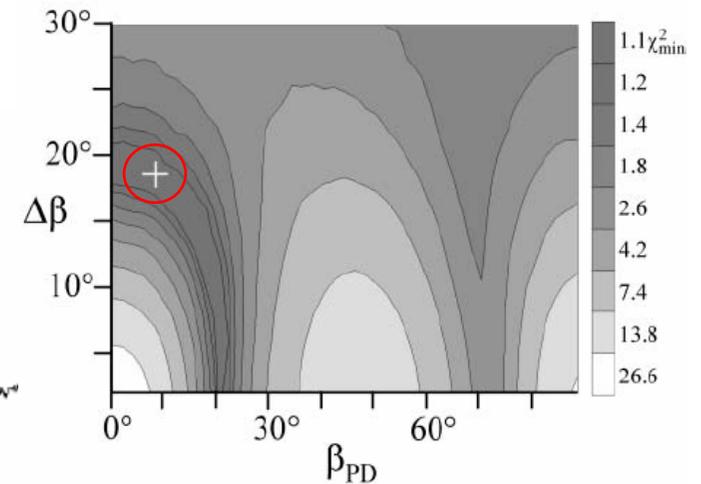
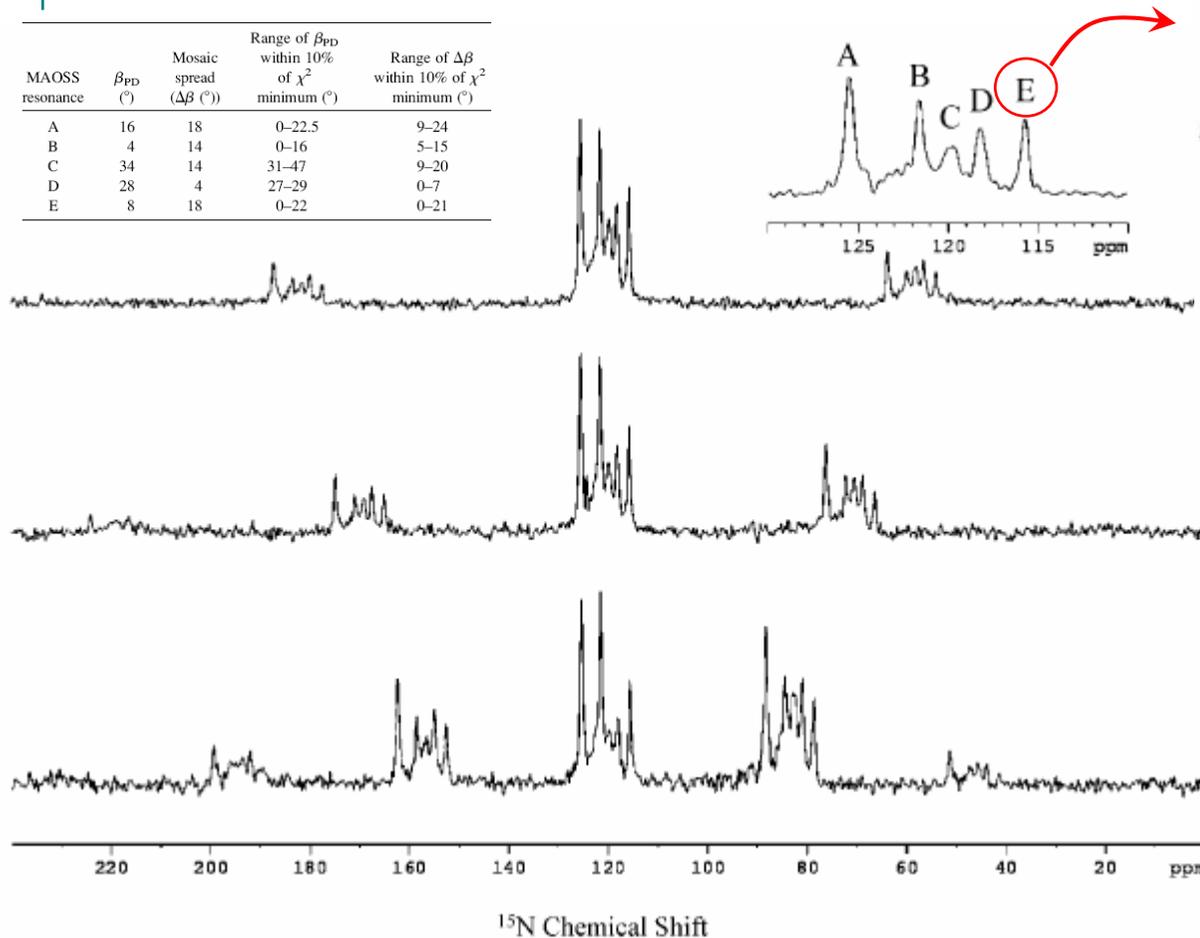
- hohe  
Winkelauflösung  
- schlechte  
Sensitivität

- hohe  
Winkelauflösung  
- gute Sensitivität

## Rotation orientierter Proben ( $^{15}\text{N}$ -MAOSS)



MAOSS resonance	$\beta_{PD}$ (°)	Mosaic spread ( $\Delta\beta$ (°))	Range of $\beta_{PD}$ within 10% of $\chi^2$ minimum (°)	Range of $\Delta\beta$ within 10% of $\chi^2$ minimum (°)
A	16	18	0–22.5	9–24
B	4	14	0–16	5–15
C	34	14	31–47	9–20
D	28	4	27–29	0–7
E	8	18	0–22	0–21

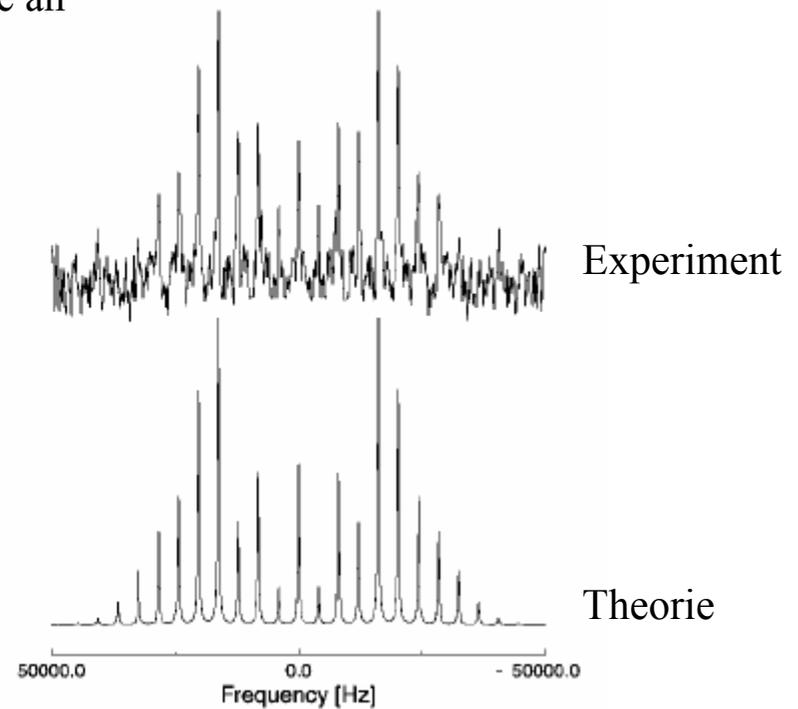
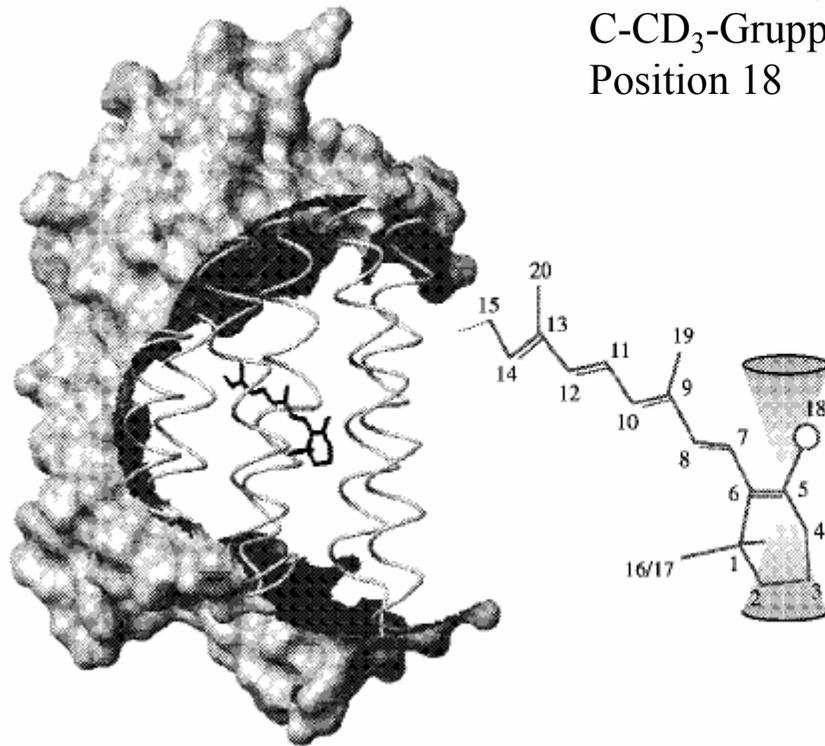


Bestimmung des  
Orientierungswinkels  
 $\beta_{PD}=8^\circ$  aus den  
Seitenbändern unter  
Berücksichtigung der  
Mosaikverschmierung  
 $\Delta\beta_{PD}=18^\circ$



Untersuchung der  
C-CD<sub>3</sub>-Gruppe an  
Position 18

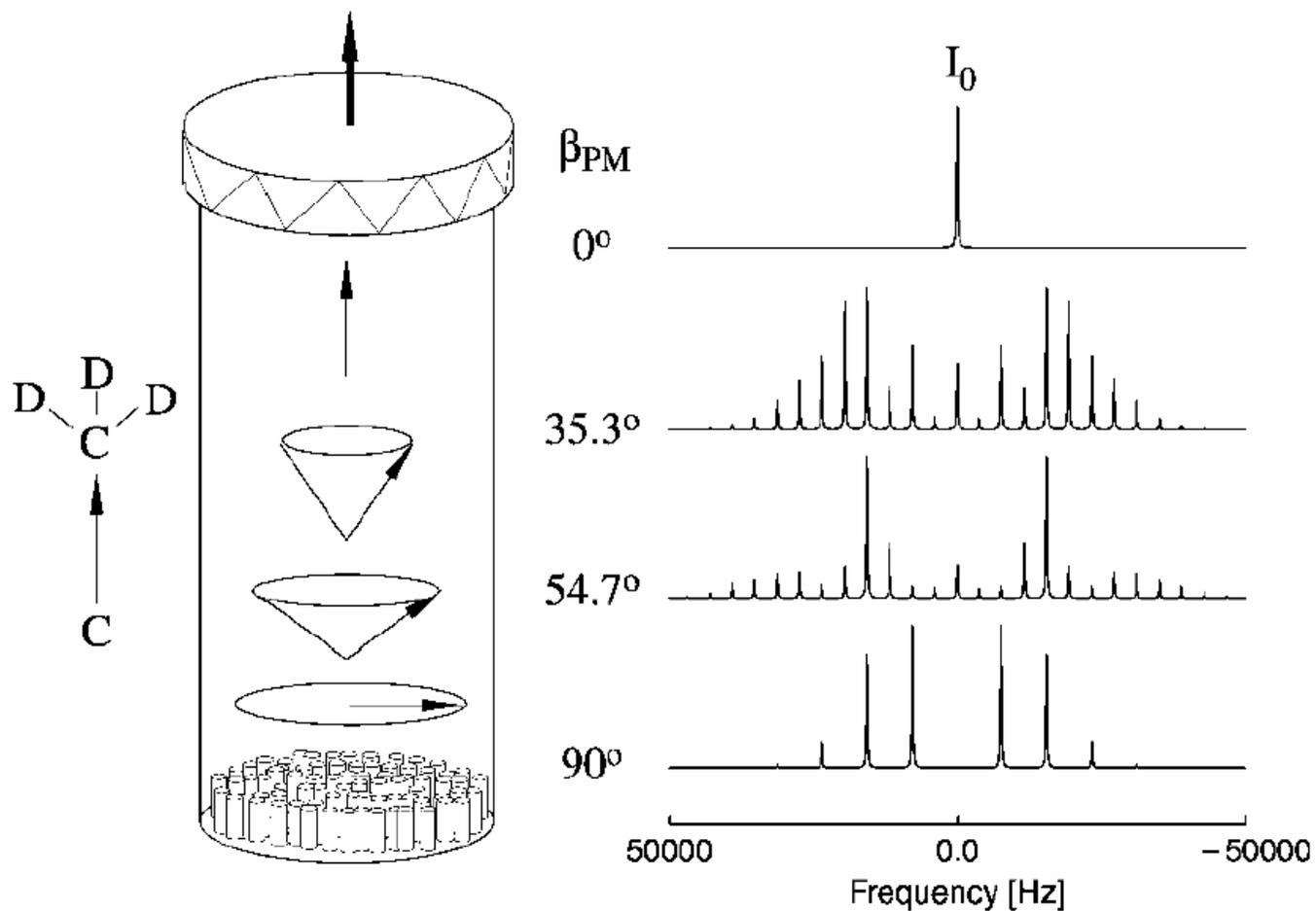
4 kHz MAS  
210 K



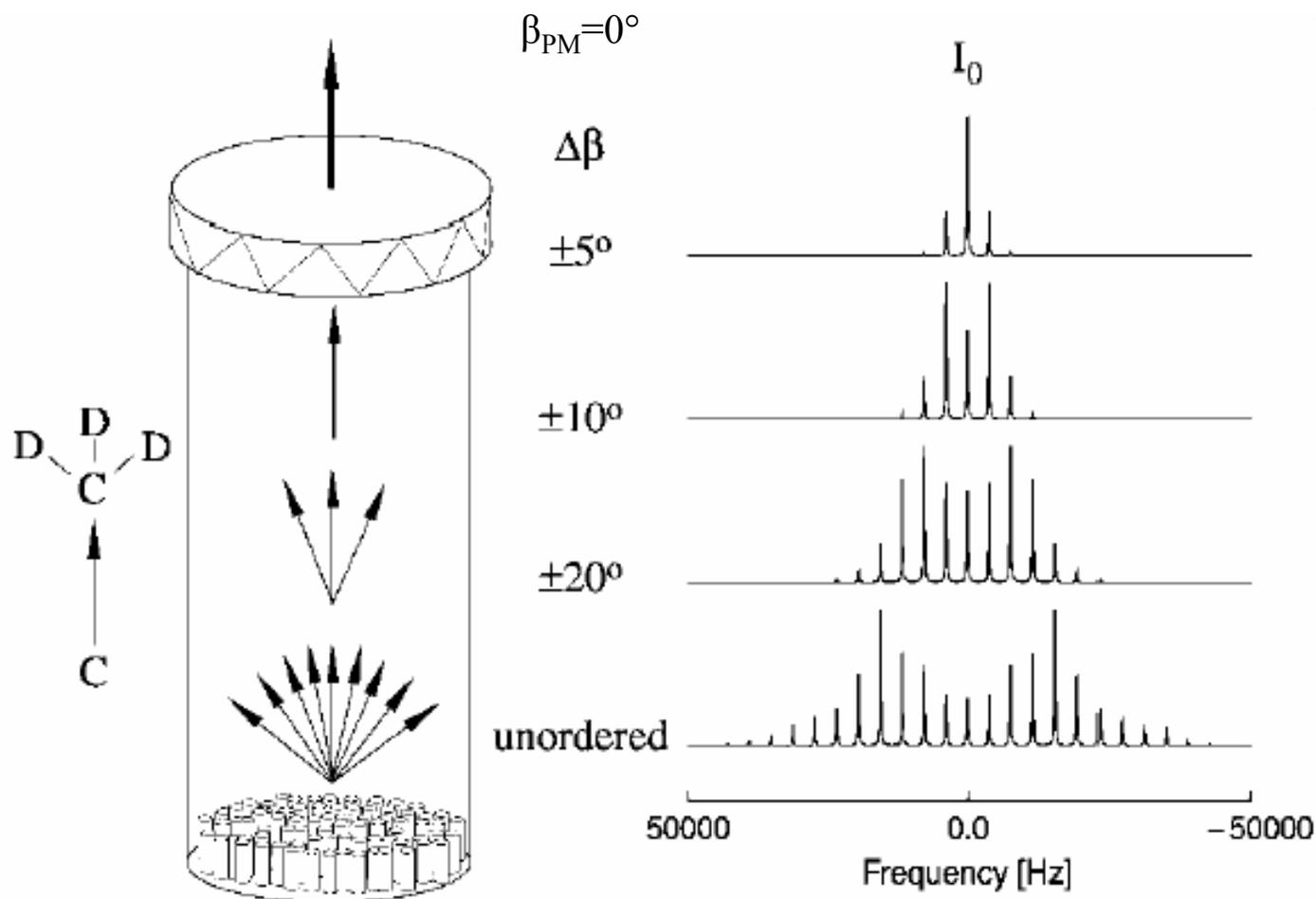
In jedem Seitenband steckt die Orientierungsinformation:

Grundzustand:  $\beta_{PM}=37^\circ$  (tilt)

**<sup>2</sup>H-MAOSS am Retinalligand von Bakteriorhodopsin**



## $^2\text{H}$ -Winkelabhängigkeit



Mosaikverschmierung:  $\Delta\beta$

