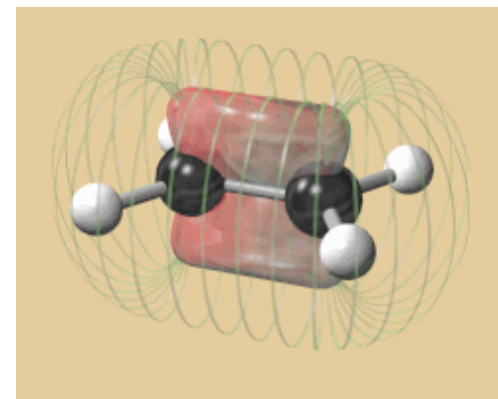


# NMR II

- Chemische Verschiebung
- Chemische Verschiebung für verschiedene Kerne
- Chemische Verschiebung: Beispiel Ethanol
- Berechnung chemischer Verschiebungen: Beispiel Ethanol
- Spin-Spin-Kopplung
- Berechnung der Spin-Spin-Kopplung
- Karplus-Relation



# Chemische Verschiebung

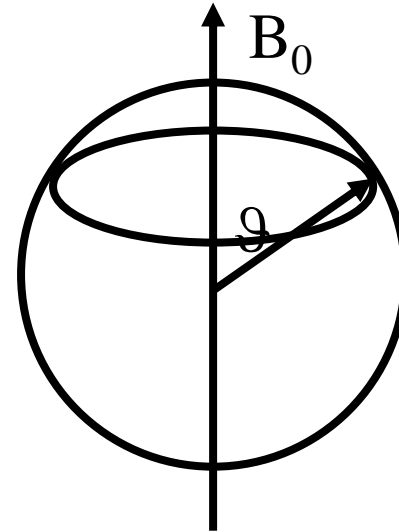
$$B = B_0 + B_{\text{lokal}}$$

a) benachbarte Kerne (magnetische Dipole):

$$B_{\text{lokal}} = \left( \frac{\mu_0}{4\pi} \right) \frac{\mu}{r^3} (3 \cos^2 \vartheta - 1)$$

# Chemische Verschiebung

b) Eigene Elektronenhülle



Bewegungsgleichung eines Elektrons im magnetischen und elektrischen Feld:

$$\nu = \gamma / 2\pi B_0$$

$$g_e = 1 \quad \text{und} \quad \mu_e = \frac{-e\hbar}{2m}$$

# Chemische Verschiebung

$$v = \frac{\mu_e}{\hbar} \frac{1}{2\pi} B_0 = -\frac{e}{4\pi m} B_0$$

$$\mu = \text{Strom} \times \text{Kreisfläche} = e v \times \pi (r \sin \vartheta)^2 = -\frac{e^2 r^2 \sin^2 \vartheta}{4m} B_0$$

$$B_{\text{lokal}} = \left( \frac{\mu_0}{4\pi} \right) \frac{2\mu}{r^3} = -\frac{\mu_0 e^2 \sin^2 \vartheta}{4\pi 2mr} B_0$$

# Chemische Verschiebung

$$B_{\text{lokal}} = -\frac{\mu_0 e^2}{4\pi 3} \sum_i \left( \frac{1}{r_i} \right) B_0 \quad \text{Lamb-Formel}$$

1. Lokales Feld proportional zu  $B_0$
2. Entgegengesetztes Vorzeichen = abschirmend
3. Mehr Elektronen = stärkere Abschirmung
4. größere Kernnähe = stärkere Abschirmung

# Chemische Verschiebung

$$B_{\text{lokal}} \approx -10^{-7} \frac{(10^{-19})^2}{10^{-30}} \frac{1}{10^{-10}} B_0 = 10^{-5} B_0$$

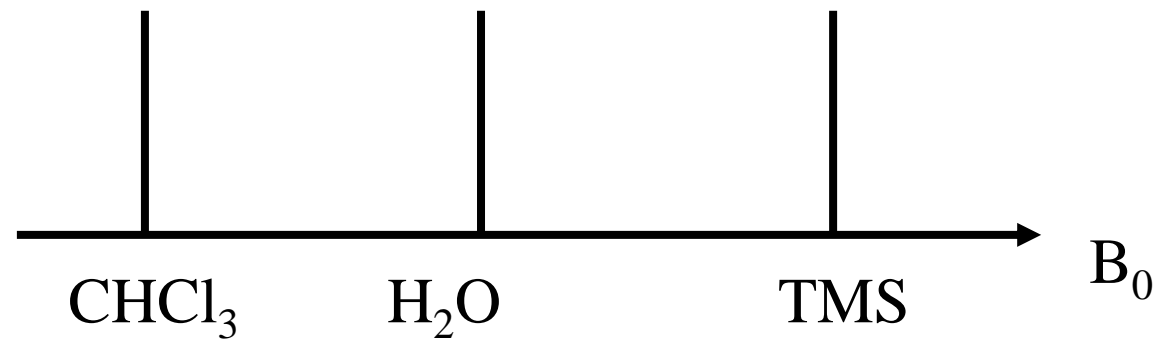
$$B_{\text{lokal}} = -\sigma B_0$$

$$\sigma = -\frac{\mu_0 e^2}{4\pi 3mc^2} \sum_i \left( \frac{1}{r_i} \right)$$

# Chemische Verschiebung

$$B = B_0 + B_{\text{lokal}} = B_0 - \sigma B_0 = B_0(1 - \sigma)$$

$$\nu = \gamma / 2\pi B_0(1 - \sigma)$$



# Chemische Verschiebung

$$\delta = \sigma_{ref} - \sigma$$

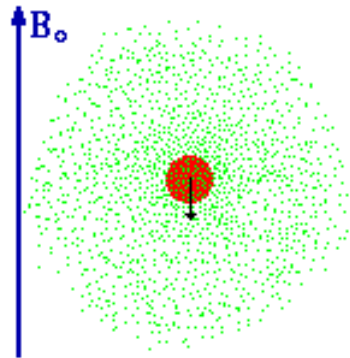
$$\nu = \frac{\gamma}{2\pi} B_0 (1 - \sigma) \rightarrow \frac{2\pi\nu}{\gamma B_0} = 1 - \sigma \rightarrow \sigma = 1 - \frac{2\pi\nu}{\gamma B_0}$$

$$\delta = 1 - \frac{2\pi\nu}{\gamma B_{0ref}} - 1 + \frac{2\pi\nu}{\gamma B_0} = \frac{2\pi\nu}{\gamma} \left( \frac{1}{B_0} - \frac{1}{B_{0ref}} \right) = \frac{2\pi\nu}{\gamma} \frac{B_{0ref} - B_0}{B_{0ref} \cdot B_0} \approx \frac{B_{0ref} - B_0}{B_{0ref}}$$

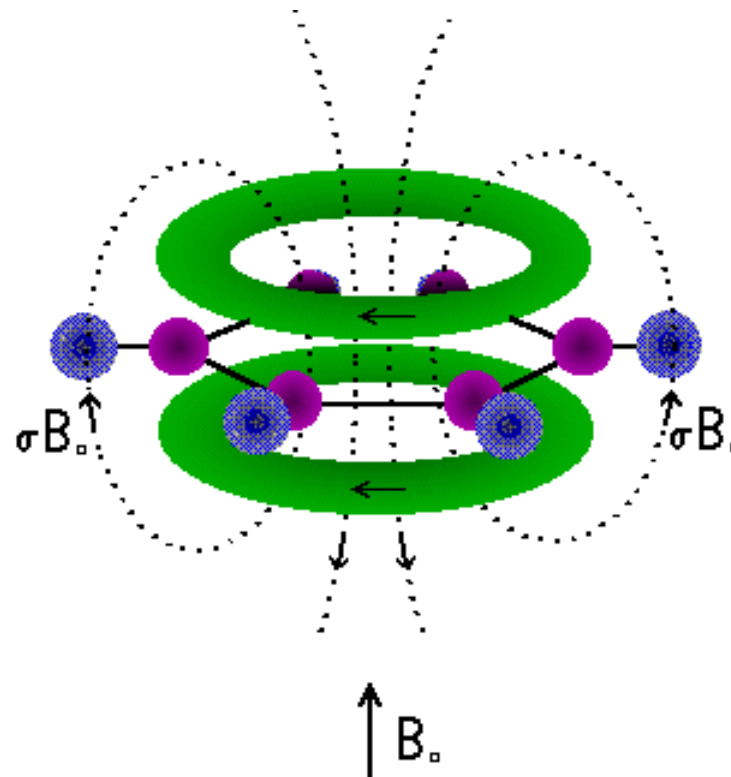
$$\delta = \frac{\nu_{ref} - \nu}{\nu_{ref}} \approx \frac{\nu_{ref} - \nu}{\nu_{Spektrometer}}$$

# Chemische Verschiebung

$$\delta = (\nu - \nu_{\text{ref}}) \times 10^6 / \nu_0$$

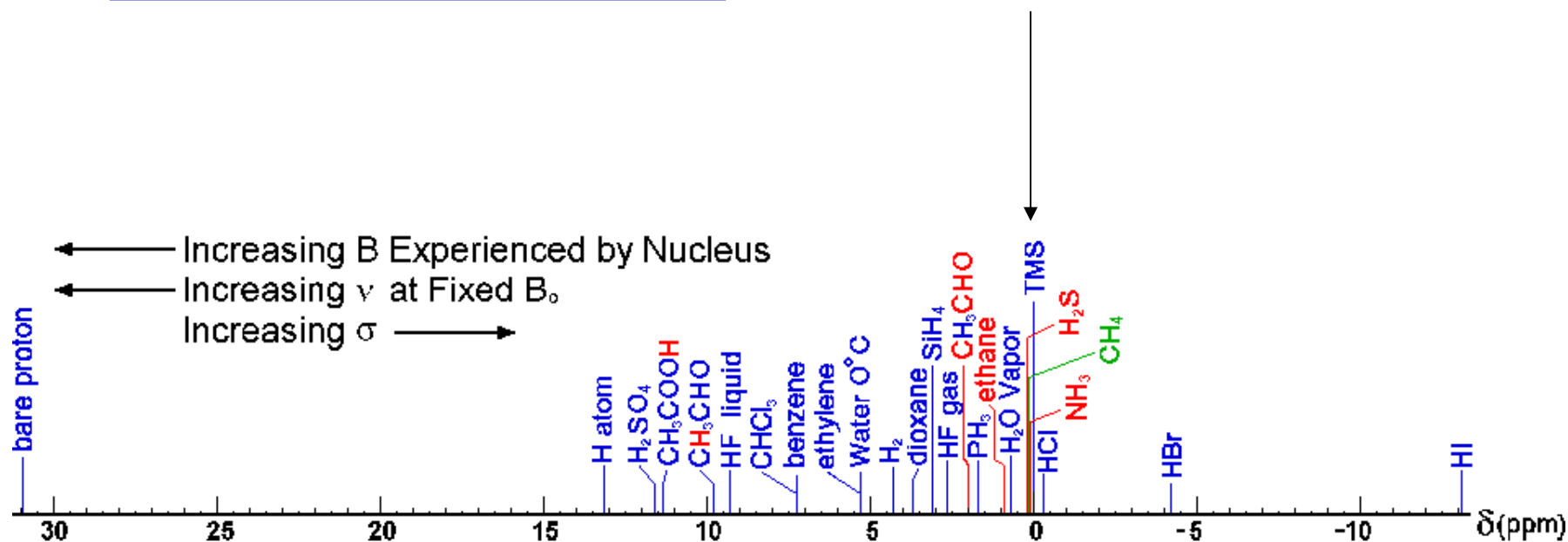
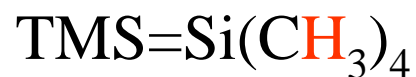


$$B = B_0 (1 - \sigma)$$



# Chemische Verschiebung

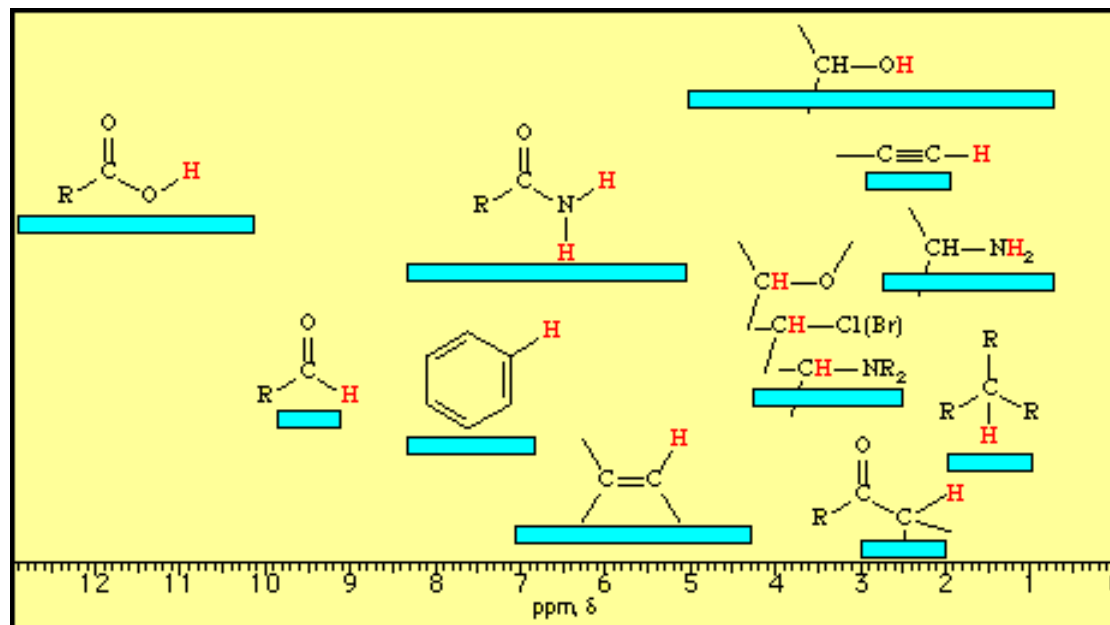
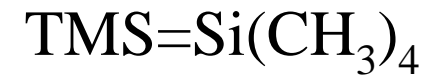
$$\delta = (\nu - \nu_{\text{ref}}) \times 10^6 / \nu_0$$



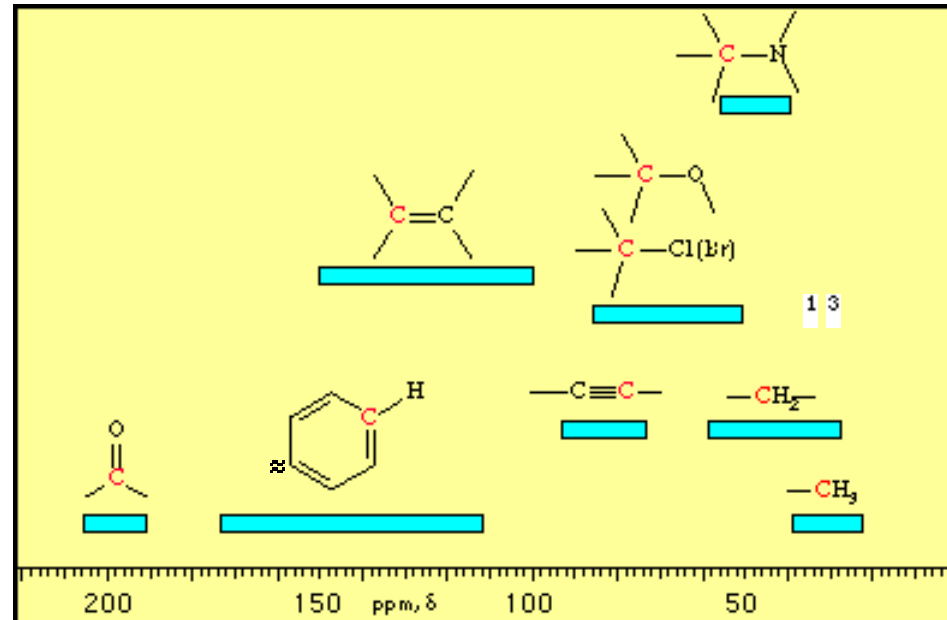
A. Carrington, A.D. McLachlan, *Introduction To Magnetic Resonance*, Chapman and Hall, London, 1967

# Chemische Verschiebung

$$\delta = (v - v_{\text{ref}}) \times 10^6 / v_0$$



# Chemische Verschiebung



- elektronegative Gruppen
- $\pi$ -System von Alkenen, aromatischen Verbindungen
- Carbonyl-Kohlenstoff

# F-19- und C-13 Chemische Verschiebung

<b>Fluorine-19 Environment</b>	<b>Chemical Shift Range (ppm)</b>
UF <sub>6</sub>	-540
FNO	-269
F <sub>2</sub>	-210
bare nucleus	0
C(CF <sub>3</sub> ) <sub>4</sub>	284
CF <sub>3</sub> (COOH)	297
fluorobenzene	333
F <sup>-</sup>	338
BF <sub>3</sub>	345
HF	415

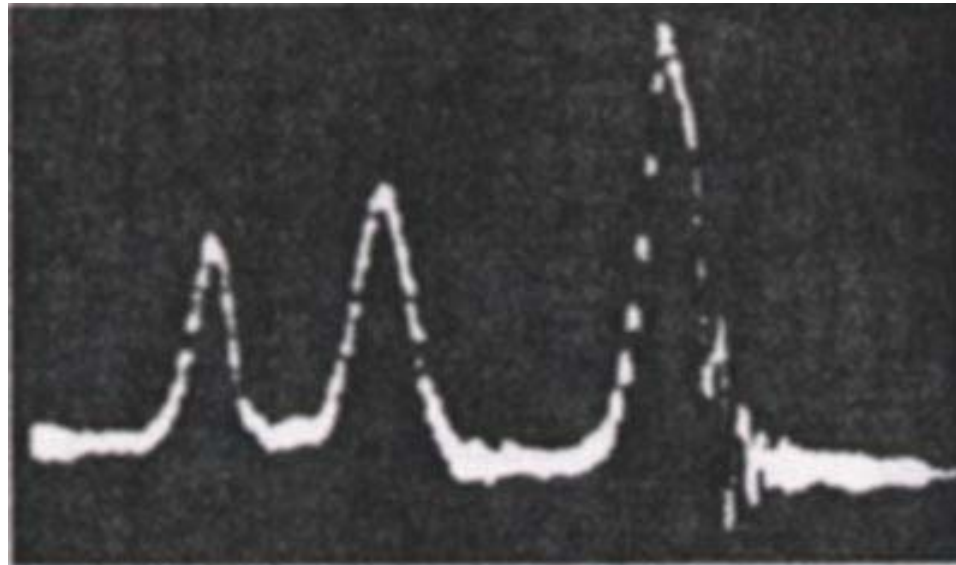
<b>Carbon-13* Environment</b>	<b>Chemical Shift Range (ppm)</b>
(CH <sub>3</sub> ) <sub>2</sub> C*O	-12
CS <sub>2</sub>	0
CH <sub>3</sub> C*OOH	16
C <sub>6</sub> H <sub>6</sub> =	65
CHCl CHCl (cis)	71
CH <sub>3</sub> C*N	73
CCl <sub>4</sub>	97
dioxane	126
C*H <sub>3</sub> CN	196
CHI <sub>3</sub>	332

# N-14- und P-31 Chemische Verschiebung

<b>Nitrogen-14*</b> <b>Environment</b>	<b>Chemical Shift</b> <b>Range (ppm)</b>
NO <sub>2</sub> Na	-355
NO <sub>3</sub> <sup>-</sup> (aqueous)	-115
N <sub>2</sub> (liquid)	-101
pyridine	-93
bare nucleus	0
CH <sub>3</sub> CN	25
CH <sub>3</sub> CONH <sub>2</sub> (aqueous)	152
NH <sub>4</sub> <sup>+</sup> (aqueous)	245
NH <sub>3</sub> (liquid)	266

<b>Phosphorous-31</b> <b>Environment</b>	<b>Chem. Shift</b> <b>Range (ppm)</b>
PBr <sub>3</sub>	-228
(C <sub>2</sub> H <sub>5</sub> O) <sub>3</sub> P	-137
PF <sub>3</sub>	-97
85% phosph. acid	0
PCl <sub>5</sub>	80
PH <sub>3</sub>	238
P <sub>4</sub>	450

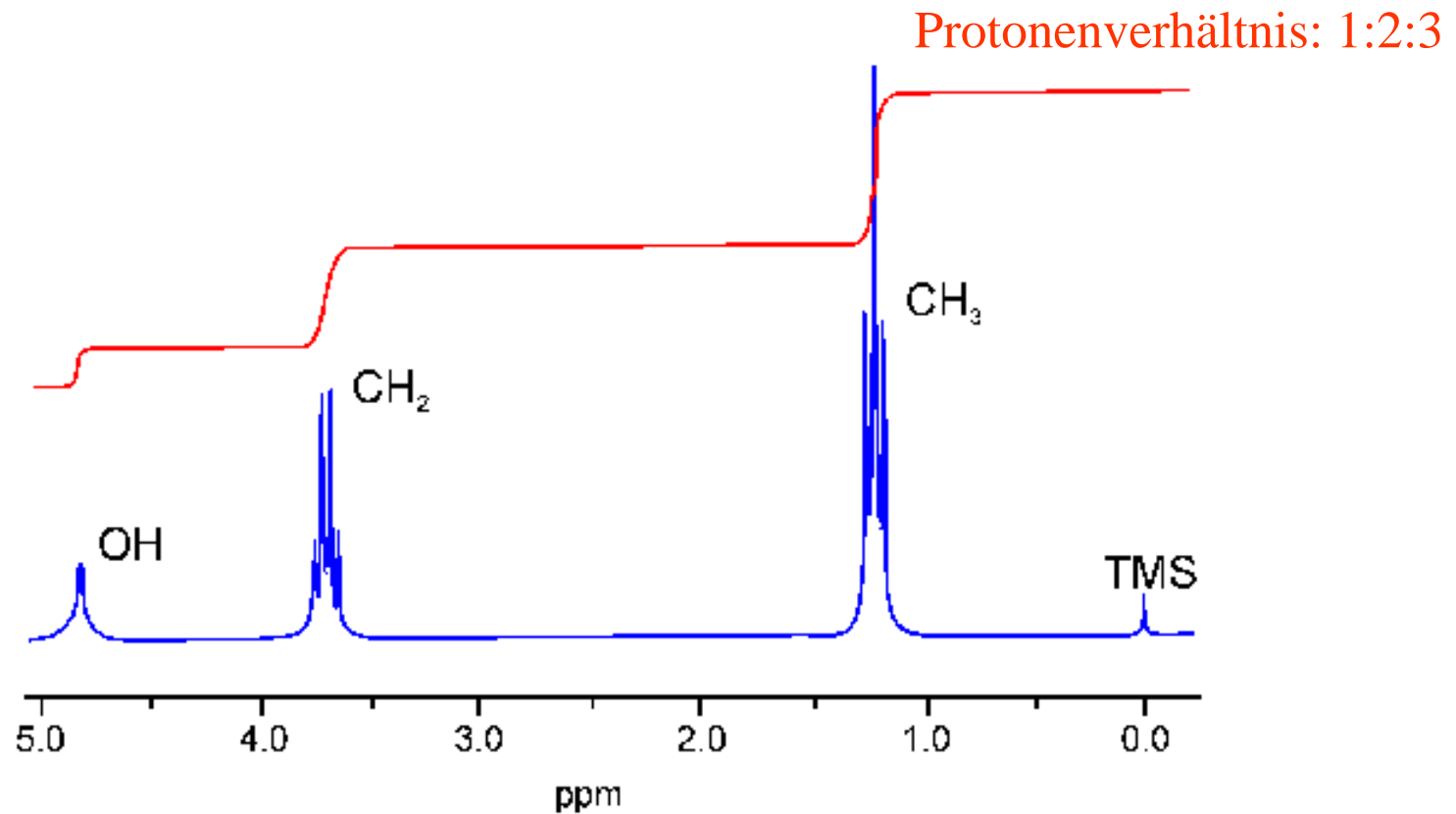
# Chemische Verschiebung: Ethanol



The first NMR spectrum of ethanol, taken at Stanford University in 1951.

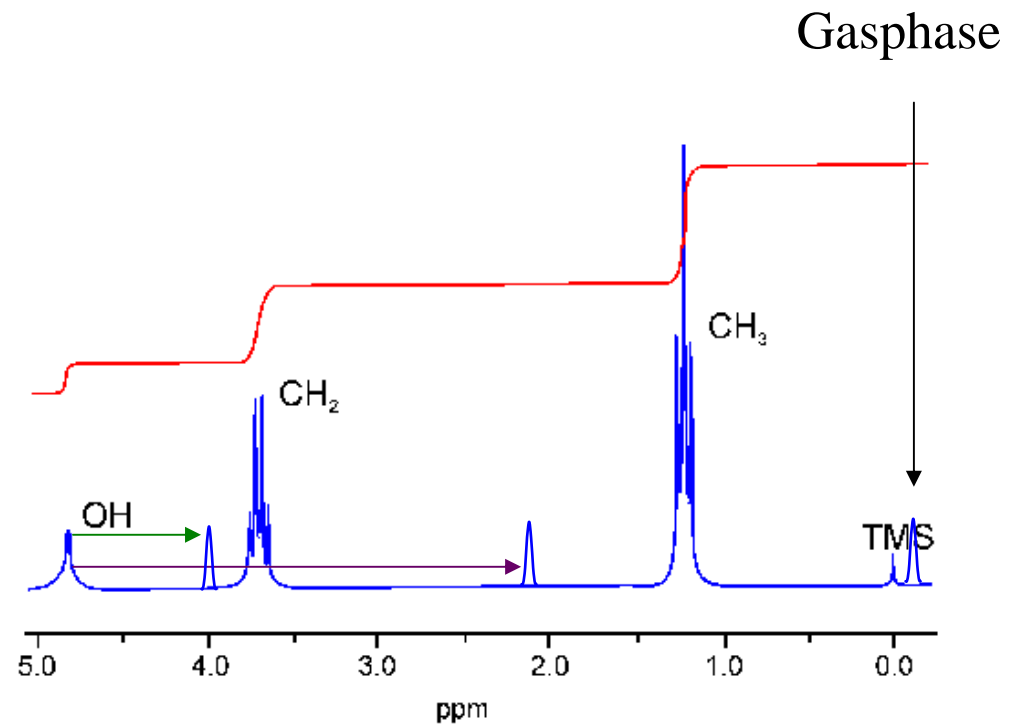
*Courtesy Varian Associates, Inc.*

# Chemische Verschiebung: Ethanol



# Chemische Verschiebung: Ethanol

- Reinheit
- Temperatur
- Lösungsmittel



# Ethanol Monomer

Calculating GIAO nuclear magnetic shielding tensors.

SCF GIAO **Magnetic shielding tensor (ppm):**

1 C Isotropic = 172.8418 Anisotropy = 26.2208

XX= 185.5765 YX= 4.6747 ZX= 0.0000

XY= 11.6289 YY= 176.3202 ZY= 0.0000

XZ= 0.0000 YZ= 0.0000 ZZ= 156.6287

Eigenvalues: 156.6287 171.5744 190.3223

2 C Isotropic = 129.8901 Anisotropy = 61.1341

XX= 154.9325 YX= -27.9942 ZX= 0.0000

XY= -23.3871 YY= 128.6439 ZY= 0.0000

XZ= 0.0000 YZ= 0.0000 ZZ= 106.0940

Eigenvalues: 106.0940 112.9302 170.6462

3 O Isotropic = 289.4129 Anisotropy = 109.5802

XX= 343.4521 YX= 27.8034 ZX= 0.0000

XY= 53.8008 YY= 274.9103 ZY= 0.0000

XZ= 0.0000 YZ= 0.0000 ZZ= 249.8763

Eigenvalues: 249.8763 255.8960 362.4664

4 H Isotropic = 31.5676 Anisotropy = 17.8542

XX= 40.6561 YX= 6.6753 ZX= 0.0000

XY= 5.0013 YY= 31.3583 ZY= 0.0000

XZ= 0.0000 YZ= 0.0000 ZZ= 22.6882

Eigenvalues: 22.6882 28.5441 43.4704

5 H Isotropic = 31.1763 Anisotropy = 8.3637

XX= 36.2128 YX= -2.0366 ZX= 0.0000

XY= -1.9351 YY= 29.4384 ZY= 0.0000

XZ= 0.0000 YZ= 0.0000 ZZ= 27.8776

Eigenvalues: 27.8776 28.8992 36.7520

6 H Isotropic = 30.6497 Anisotropy = 7.2974

XX= 29.0774 YX= 2.1496 ZX= -1.0855

XY= 1.1664 YY= 30.6571 ZY= -3.9012

XZ= -0.6304 YZ= -3.1707 ZZ= 32.2146

Eigenvalues: 27.3820 29.0524 35.5147

7 H Isotropic = 30.6497 Anisotropy = 7.2974

XX= 29.0774 YX= 2.1496 ZX= 1.0855

XY= 1.1664 YY= 30.6571 ZY= 3.9012

XZ= 0.6304 YZ= 3.1707 ZZ= 32.2146

Eigenvalues: 27.3820 29.0524 35.5147

8 H Isotropic = 28.2869 Anisotropy = 6.2100

XX= 28.8501 YX= -1.5301 ZX= 1.4688

XY= -0.9098 YY= 29.3513 ZY= -4.2733

XZ= -0.6740 YZ= -3.2586 ZZ= 26.6592

Eigenvalues: 23.9755 28.4582 32.4269

9 H Isotropic = 28.2869 Anisotropy = 6.2100

XX= 28.8501 YX= -1.5301 ZX= -1.4688

XY= -0.9098 YY= 29.3513 ZY= 4.2733

XZ= 0.6740 YZ= 3.2586 ZZ= 26.6592

Eigenvalues: 23.9755 28.4582 32.4269

# Ethanol Dimer

Calculating GIAO nuclear magnetic shielding tensors.

SCF GIAO Magnetic shielding tensor (ppm):

4 H Isotropic = 31.5676 Anisotropy = 17.8542  
XX= 40.6561 YX= 6.6753 ZX= 0.0000  
XY= 5.0013 YY= 31.3583 ZY= 0.0000  
XZ= 0.0000 YZ= 0.0000 ZZ= 22.6882  
Eigenvalues: 22.6882 28.5441 43.4704

5 H Isotropic = 31.1763 Anisotropy = 8.3637  
XX= 36.2128 YX= -2.0366 ZX= 0.0000  
XY= -1.9351 YY= 29.4384 ZY= 0.0000  
XZ= 0.0000 YZ= 0.0000 ZZ= 27.8776  
Eigenvalues: 27.8776 28.8992 36.7520

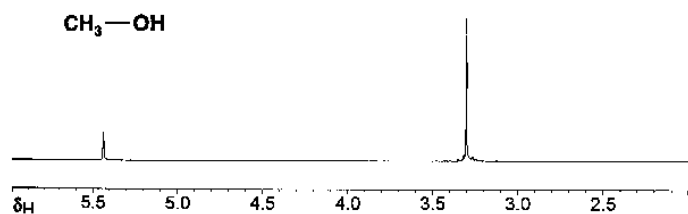
6 H Isotropic = 30.6497 Anisotropy = 7.2974  
XX= 29.0774 YX= 2.1496 ZX= -1.0855  
XY= 1.1664 YY= 30.6571 ZY= -3.9012  
XZ= -0.6304 YZ= -3.1707 ZZ= 32.2146  
Eigenvalues: 27.3820 29.0524 35.5147

7 H Isotropic = 30.6497 Anisotropy = 7.2974  
XX= 29.0774 YX= 2.1496 ZX= 1.0855  
XY= 1.1664 YY= 30.6571 ZY= 3.9012  
XZ= 0.6304 YZ= 3.1707 ZZ= 32.2146  
Eigenvalues: 27.3820 29.0524 35.5147

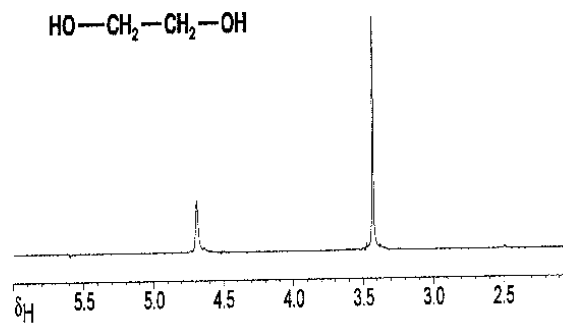
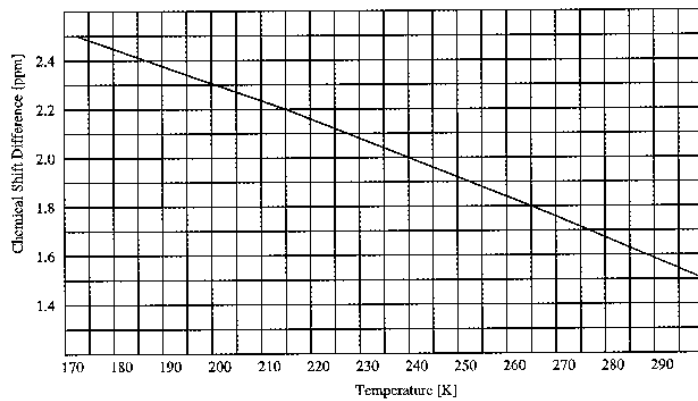
8 H Isotropic = 28.2869 Anisotropy = 6.2100  
XX= 28.8501 YX= -1.5301 ZX= 1.4688  
XY= -0.9098 YY= 29.3513 ZY= -4.2733  
XZ= -0.6740 YZ= -3.2586 ZZ= 26.6592  
Eigenvalues: 23.9755 28.4582 32.4269

9 H Isotropic = 28.2869 Anisotropy = 6.2100  
XX= 28.8501 YX= -1.5301 ZX= -1.4688  
XY= -0.9098 YY= 29.3513 ZY= 4.2733  
XZ= 0.6740 YZ= 3.2586 ZZ= 26.6592  
Eigenvalues: 23.9755 28.4582 32.4269

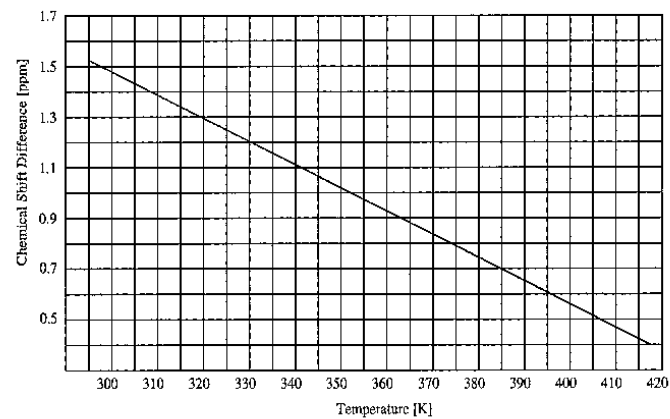
# NMR-Thermometer



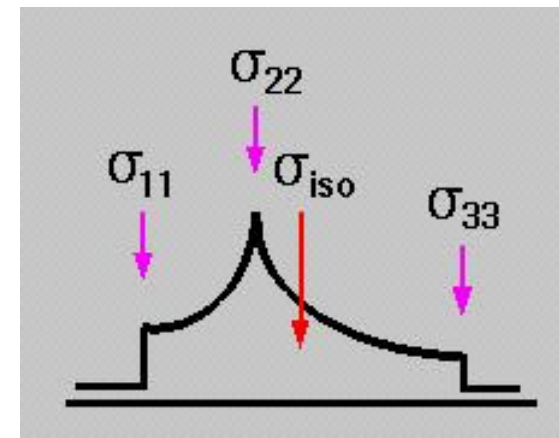
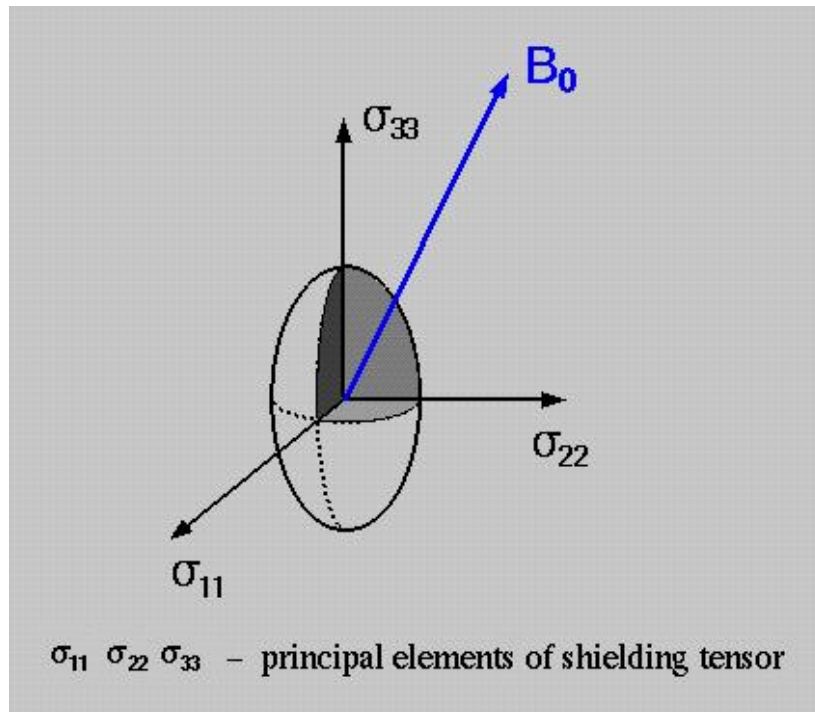
Calibration Curve for 4% Methanol in  $[\text{D}_4]$ Methanol



Calibration Curve for 1,2-Ethandiol in  $[\text{D}_6]$ DMSO

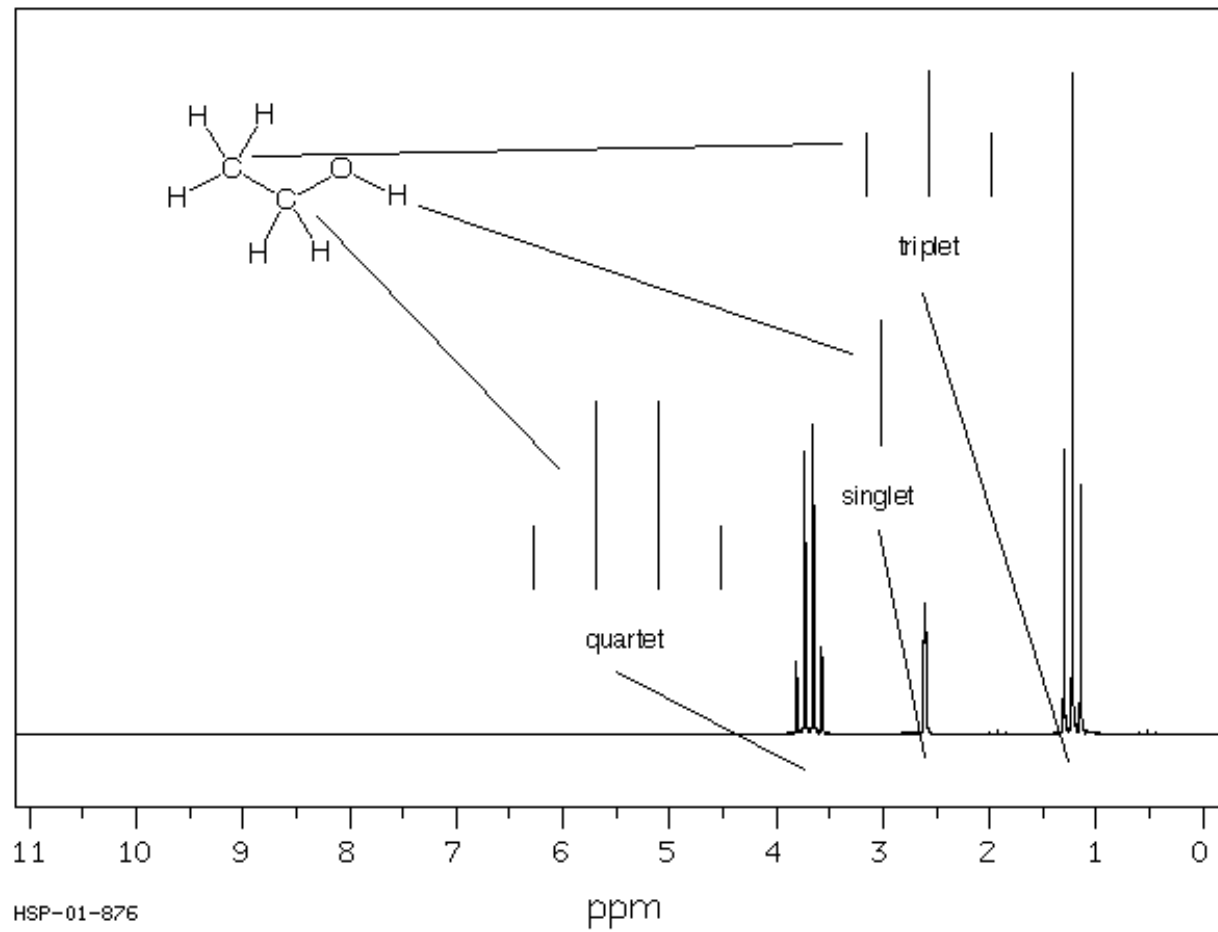


# NMR-Festkörper: CSA

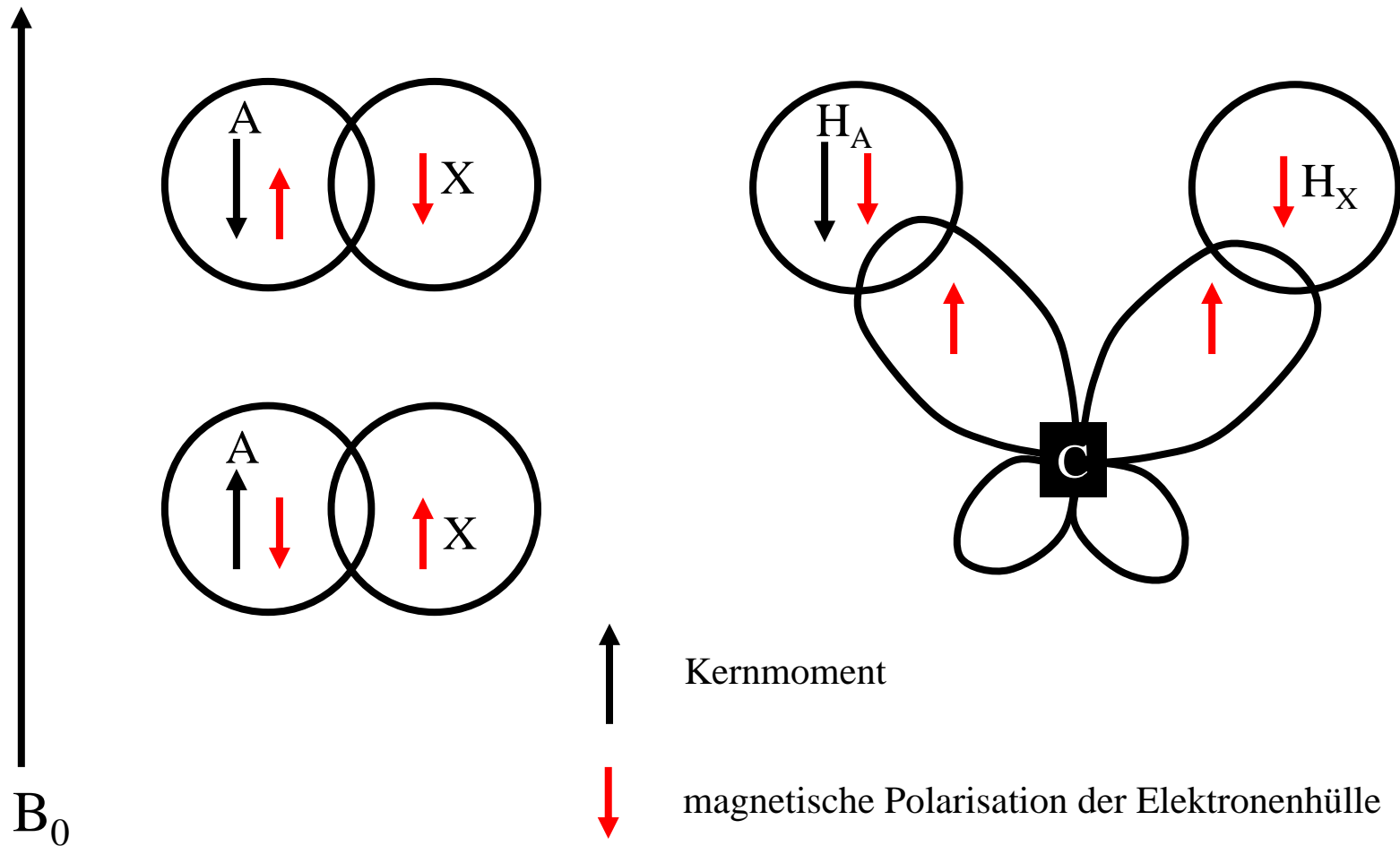


$$\sigma_{iso} = (\sigma_{11} + \sigma_{22} + \sigma_{33}) / 3$$

# Spin-Spin-Kopplung: Ethanol



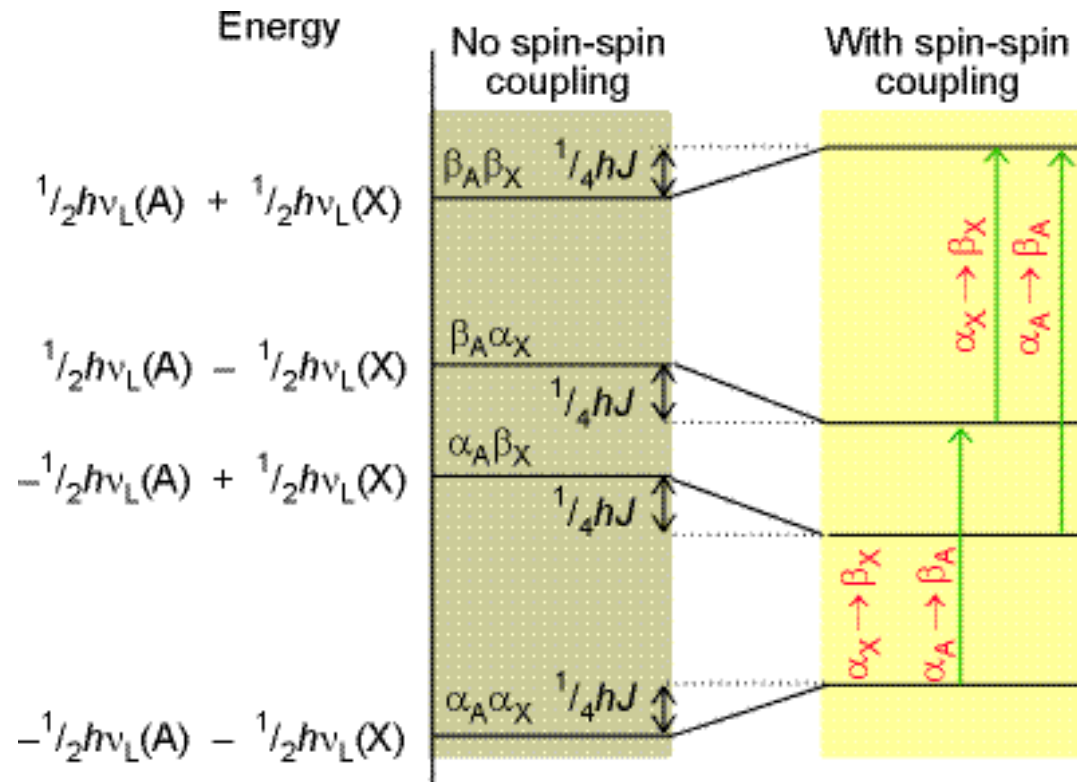
# Spin-Spin-Kopplung: J-Kopplung



# J-Kopplung

$$E = J_{AX} \mathbf{I}(A) \mathbf{I}(X)$$

↓  
skalare  
Kopplungskonstante



# J-Kopplung

$$E(\text{Hz}) = \sum_i \nu_i m_I(i) + \sum_{i < j} \sum J_{ij} m_I(i) m_I(j)$$

$$(1) \quad E_1 = \frac{1}{2} \nu_A + \frac{1}{2} \nu_X + \frac{1}{4} J_{AX}$$

$$(2) \quad E_2 = \frac{1}{2} \nu_A - \frac{1}{2} \nu_X - \frac{1}{4} J_{AX}$$

$$(3) \quad E_3 = -\frac{1}{2} \nu_A + \frac{1}{2} \nu_X - \frac{1}{4} J_{AX}$$

$$(4) \quad E_4 = -\frac{1}{2} \nu_A - \frac{1}{2} \nu_X + \frac{1}{4} J_{AX}$$

# J-Kopplung

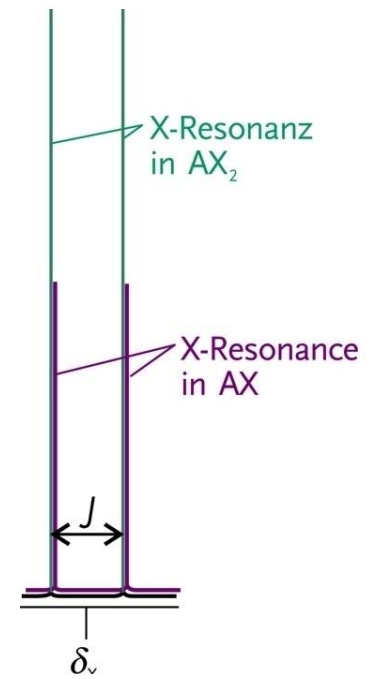
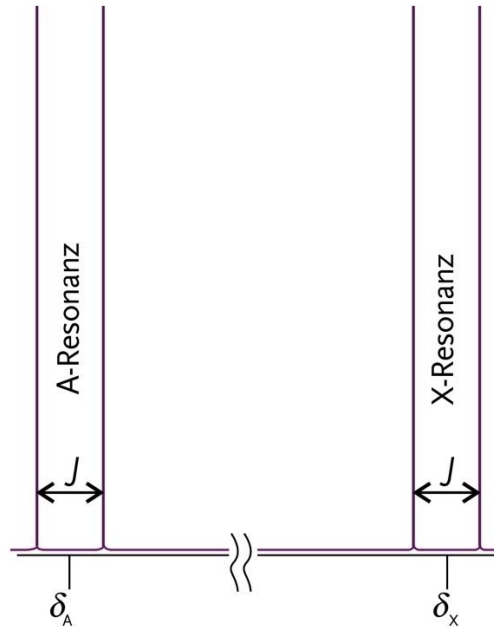
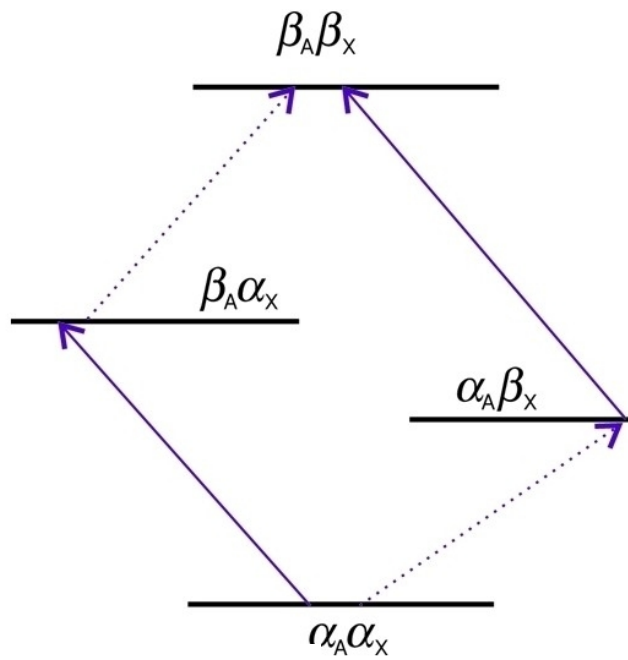
$$(3) \rightarrow (1) \quad E_1 - E_3 = \nu_A + \frac{1}{2} J_{AX}$$

$$(4) \rightarrow (2) \quad E_2 - E_4 = \nu_A - \frac{1}{2} J_{AX}$$

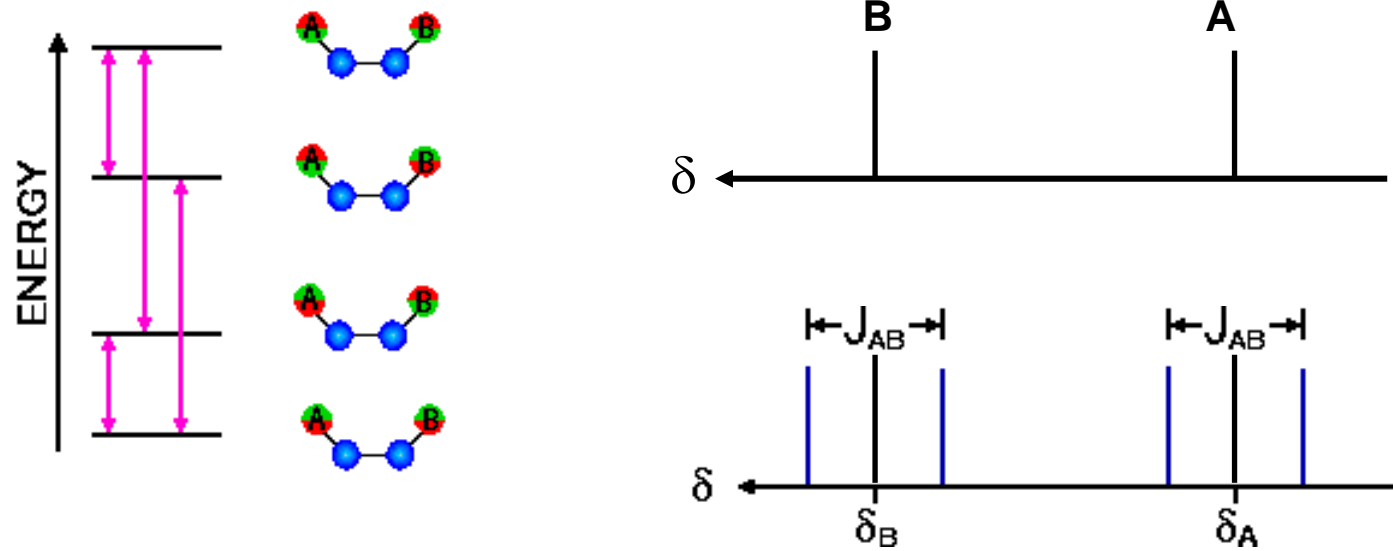
$$(2) \rightarrow (1) \quad E_1 - E_2 = \nu_X + \frac{1}{2} J_{AX}$$

$$(4) \rightarrow (3) \quad E_4 - E_3 = \nu_X - \frac{1}{2} J_{AX}$$

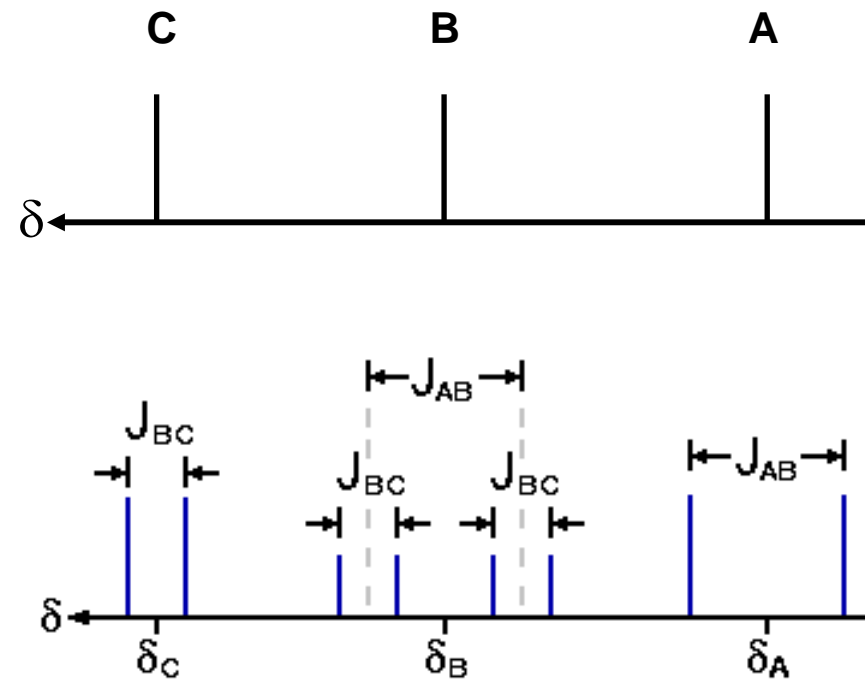
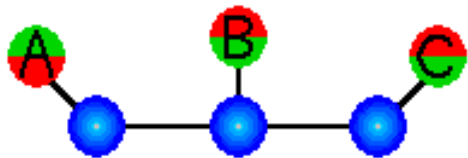
# J-Kopplung



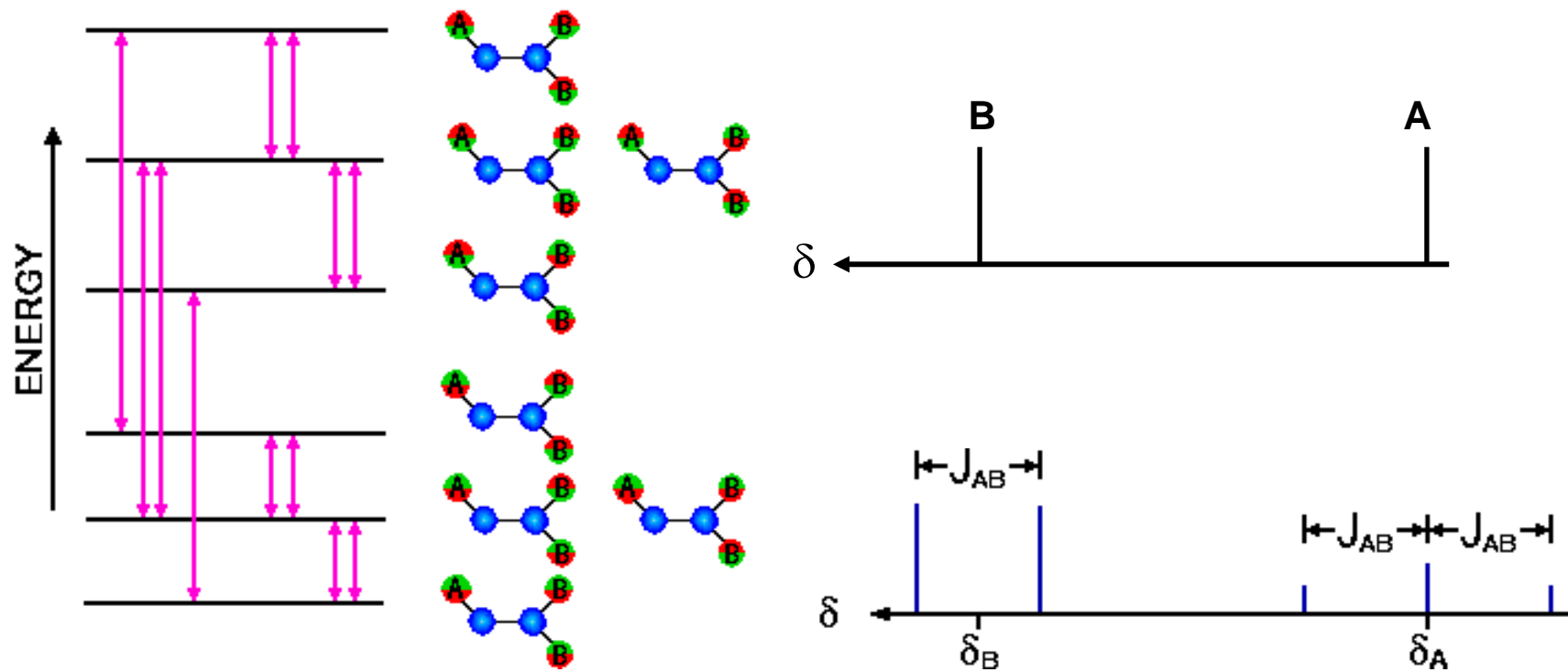
# J-Kopplung: System A+B Spins 1/2



# J-Kopplung: System A+B+C Spins 1/2



# J-Kopplung: System A + 2B Spins 1/2



# J-Kopplung: Linienintensitäten

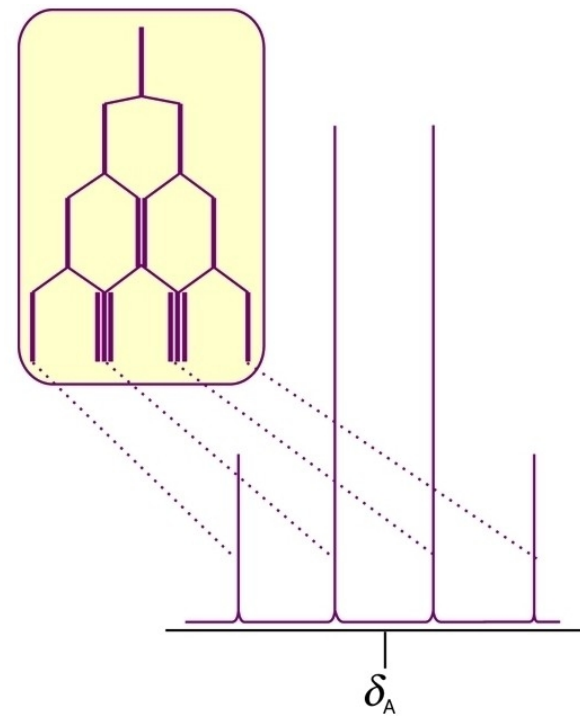
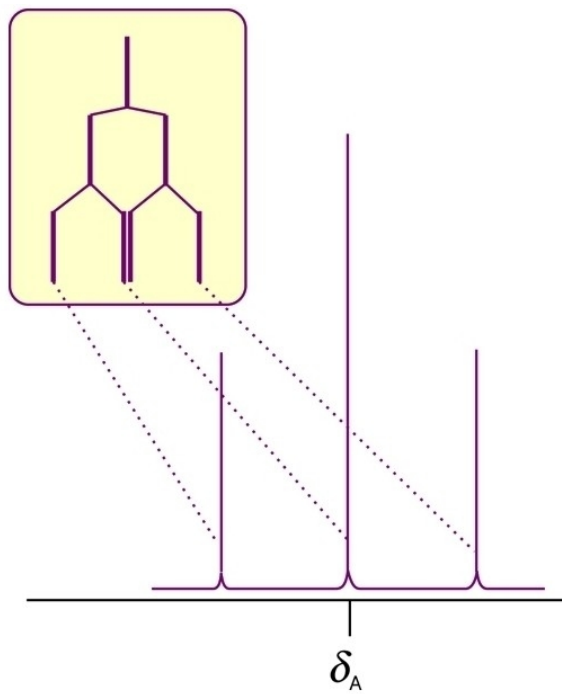
Pascalsches Dreieck

Konfiguration	Peak-Verhältnis
A	1
AB	1:1
AB <sub>2</sub>	1:2:1
AB <sub>3</sub>	1:3:3:1
AB <sub>4</sub>	1:4:6:4:1
AB <sub>5</sub>	1:5:10:10:5:1
AB <sub>6</sub>	1:6:15:20:15:6:1

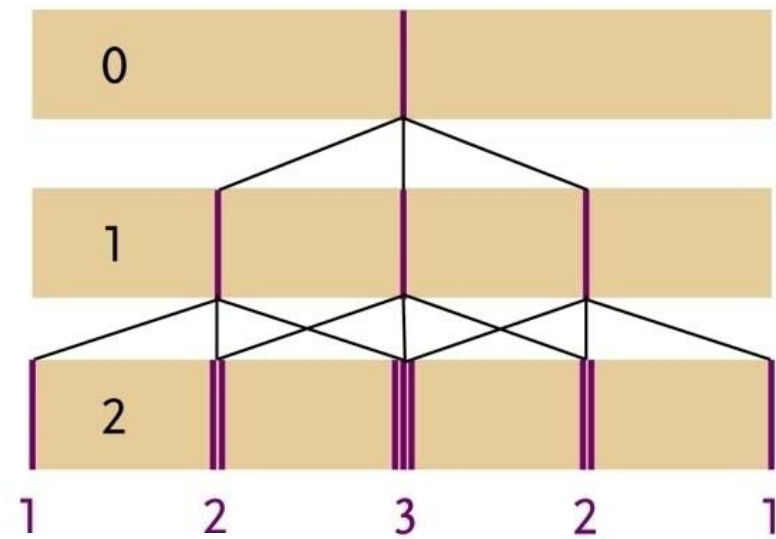
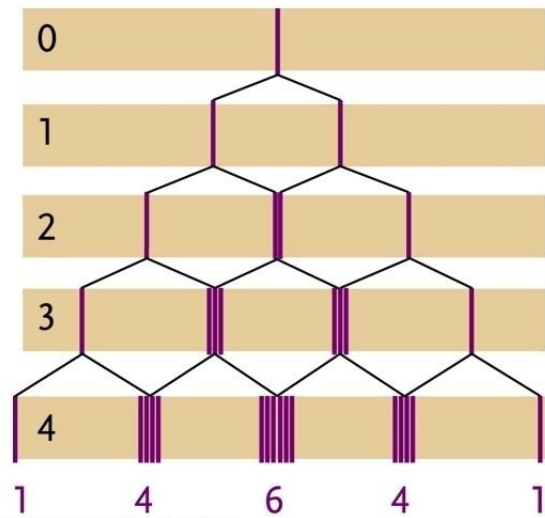
Binomial-Koeffizienten:

$$1 : \frac{n}{1} : \frac{n(n-1)}{2 \cdot 1} : \frac{n(n-1)(n-2)}{3 \cdot 2 \cdot 1} \dots$$

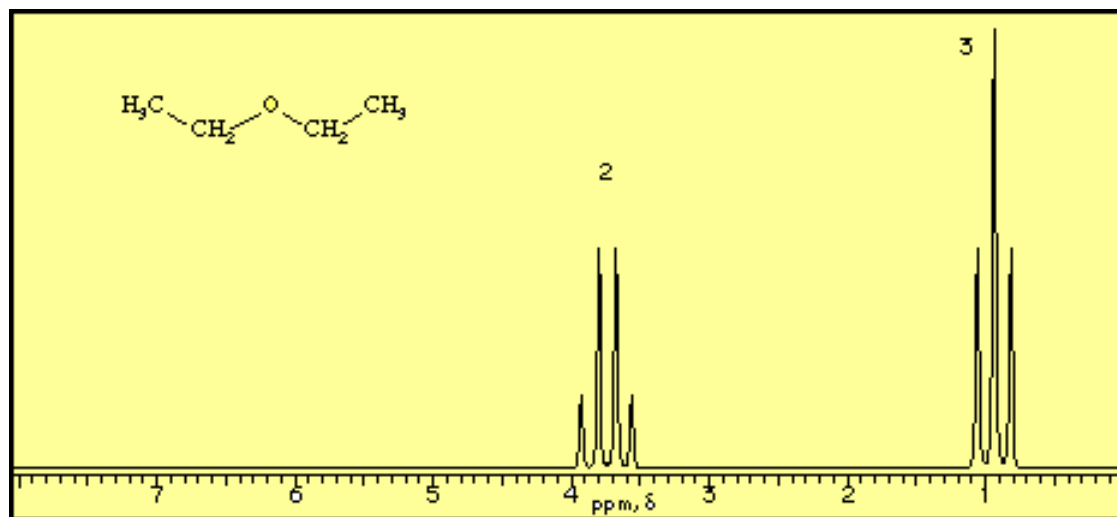
# J-Kopplung



# J-Kopplung

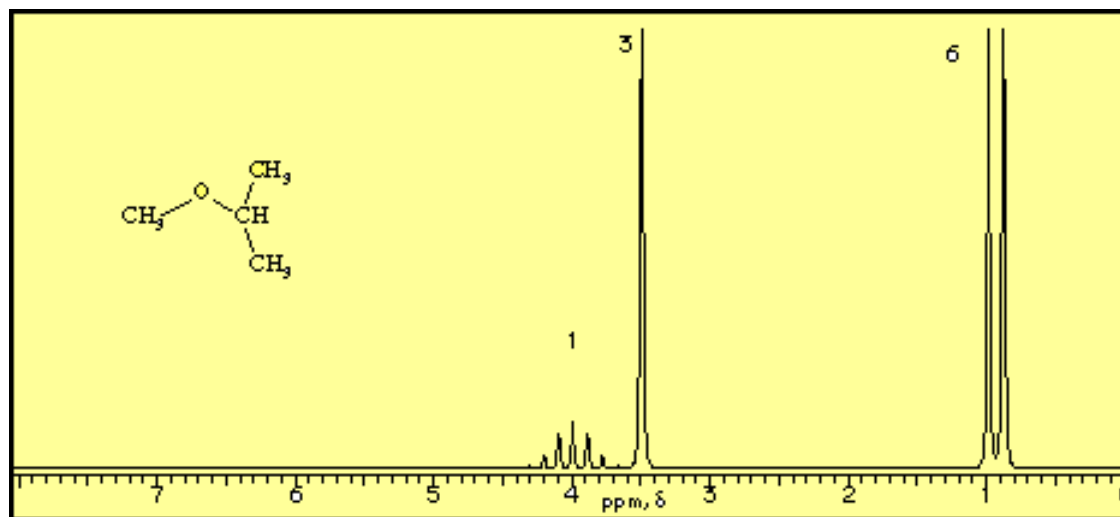


# J-Kopplung



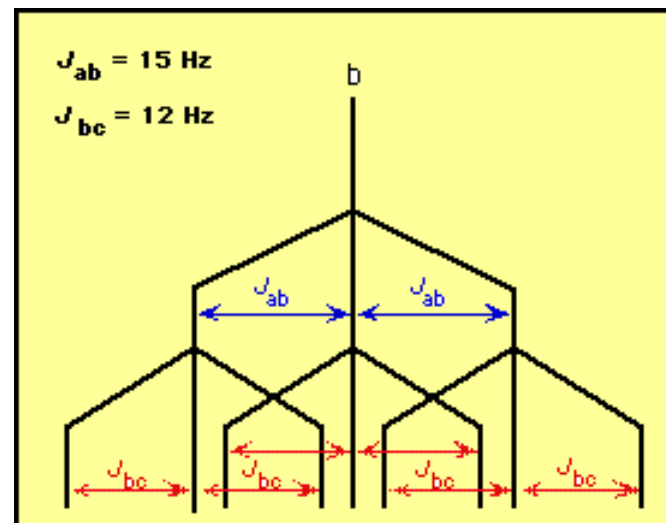
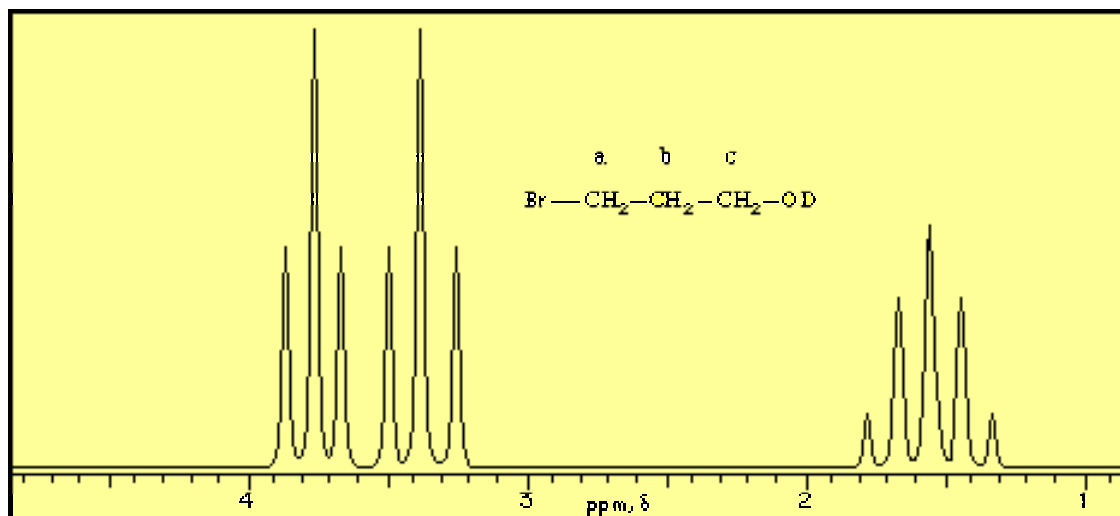
diethyl ether,  $\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3$

# J-Kopplung

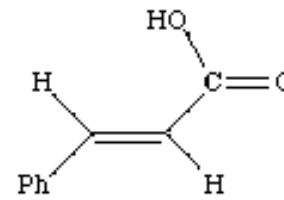
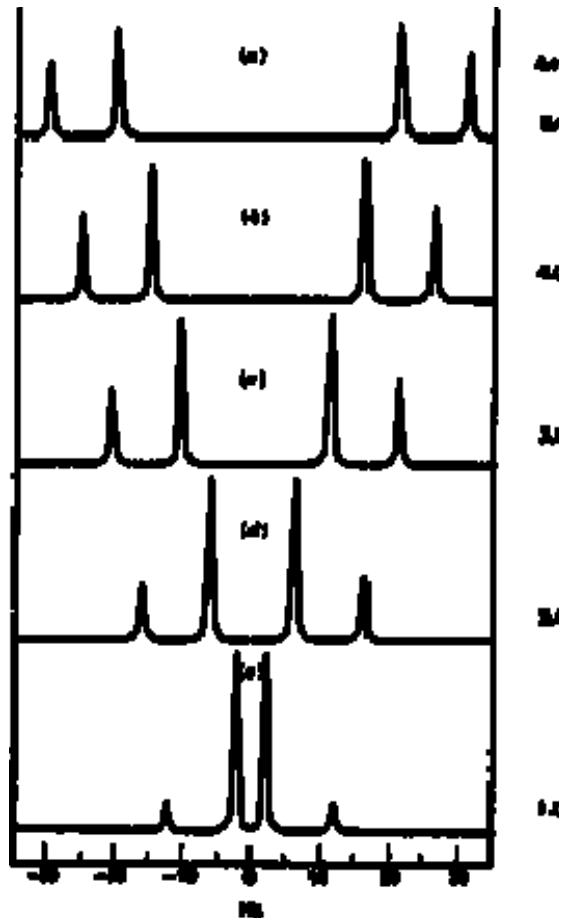


methyl isopropyl ether ( $\text{CH}_3\text{-CH}(\text{CH}_3)_2$ )

# J-Kopplung

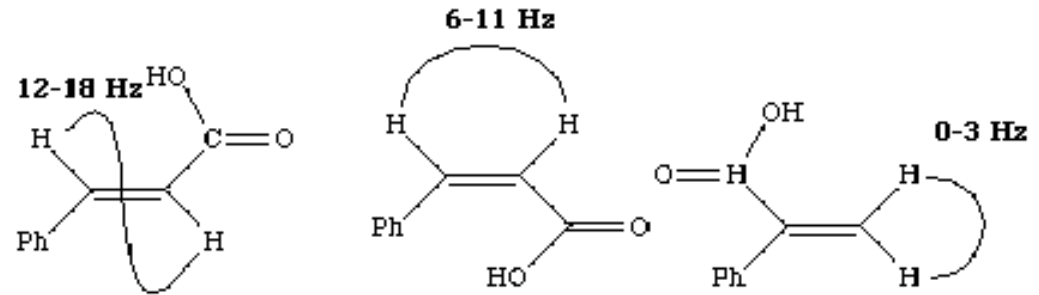


# J-Kopplung

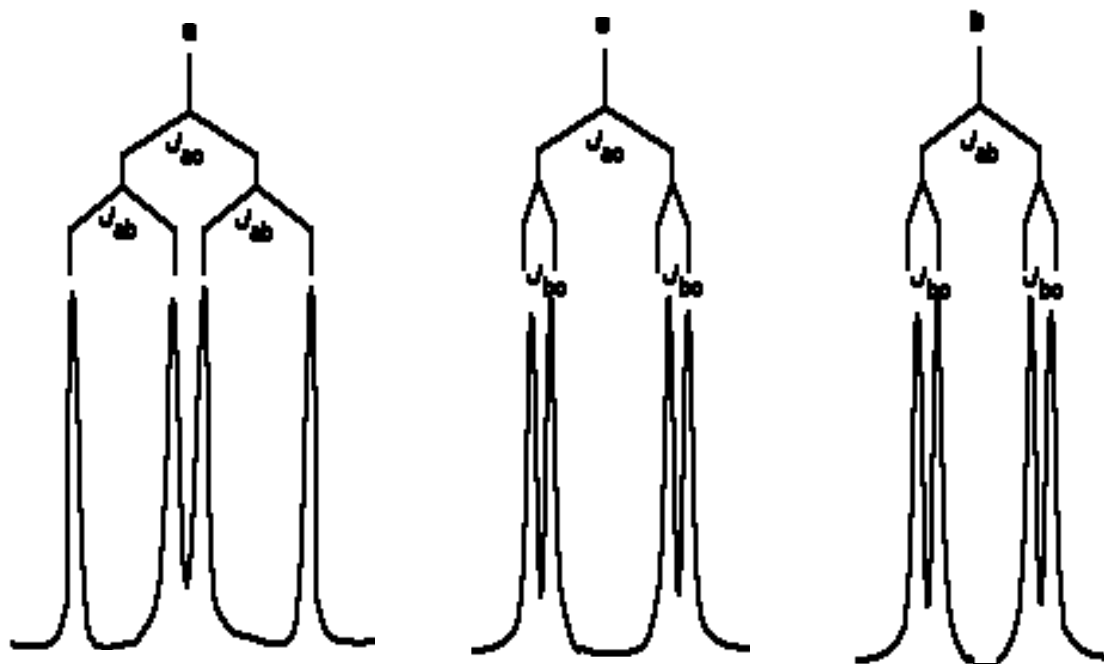


*trans*-3-phenyl propenoic acid

$\omega_0=60, 100, 300, 600$  und  $1000$  MHz

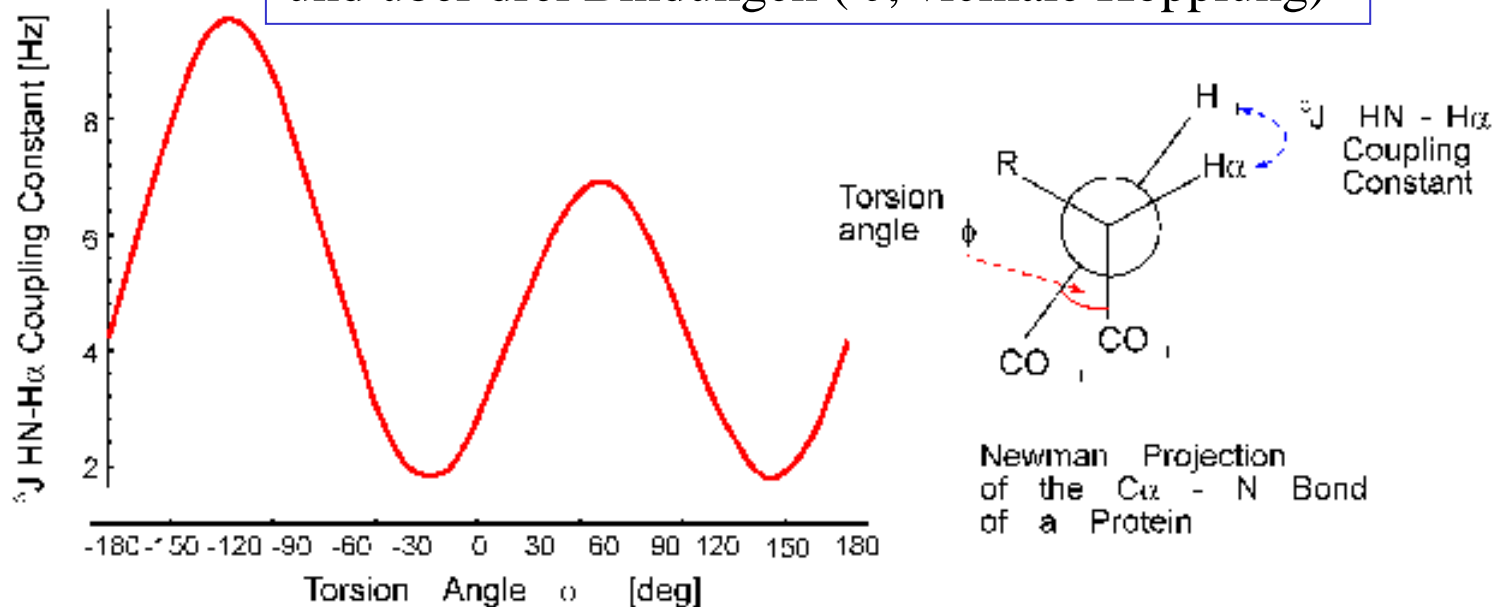


# J-Kopplung



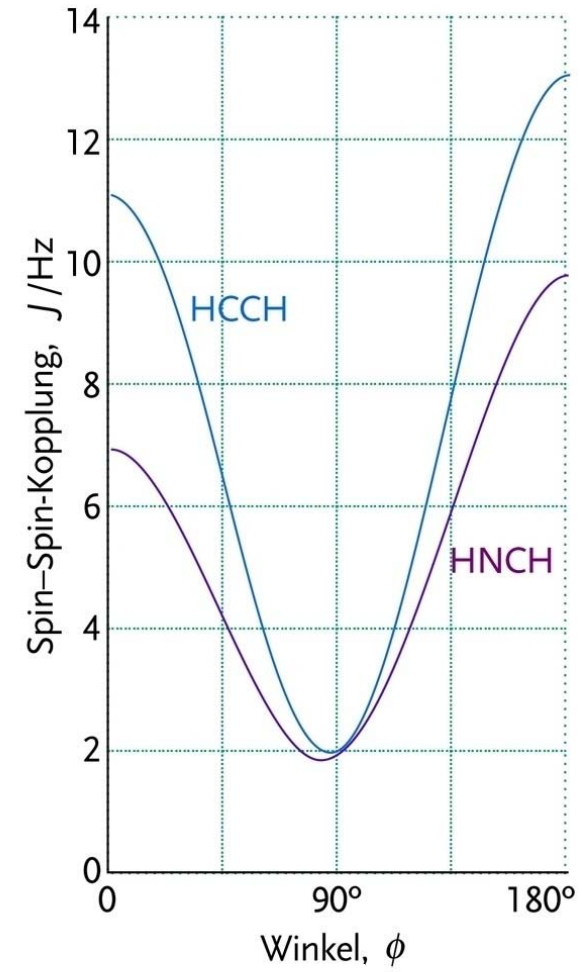
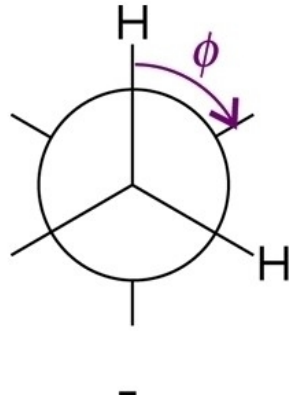
# Karplus-Relation

Über eine Bindung ( $^1J$ ),  
über zwei Bindungen ( $^2J$ , geminale Kopplung)  
und über drei Bindungen ( $^3J$ , vicinale Kopplung)



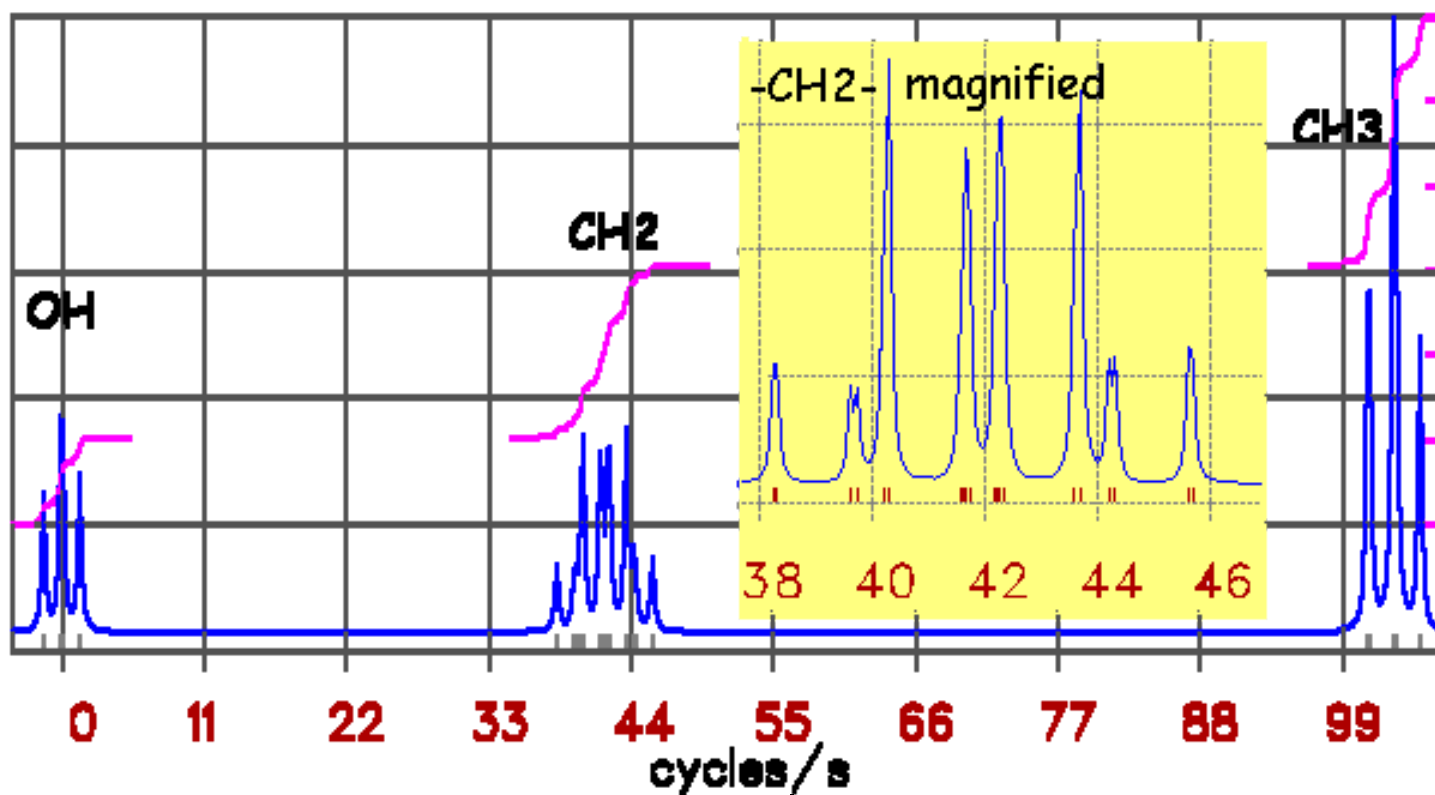
$$J(\phi) = A * \cos^2(\phi - 60) - B * \cos(\phi - 60) + C$$

# Karplus-Relation

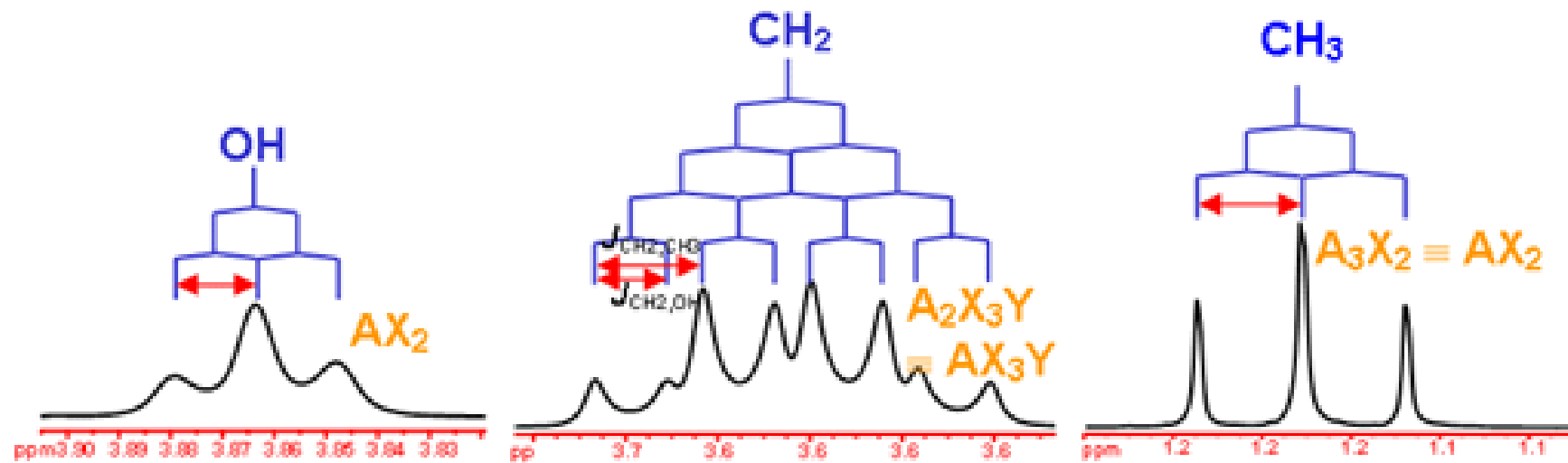


# ‘Dry Ethanol’

## NMR-Spectrum of ‘Dry Ethanol’



# Chemische Verschiebung: Ethanol



# Spin-Spin-Kopplung: Ethanol

Total nuclear spin-spin coupling J (Hz):

	1	2	3	4	5				
1	0.000000D+00								
2	0.461375D+02	0.000000D+00							
3	-0.940207D+01	0.166717D+02	0.000000D+00						
4	0.861734D+01	-0.101183D+01	-0.648852D+02	0.000000D+00					
5	0.121006D+03	0.280775D+01	-0.122382D+02	0.260490D+01	0.000000D+00				
6	0.127948D+03	-0.419774D+01	-0.141571D+01	-0.116199D+01	-0.153431D+02				
7	0.127948D+03	-0.419774D+01	-0.141571D+01	-0.116199D+01	-0.153431D+02				
8	-0.833506D+00	0.139279D+03	-0.325211D+01	0.392778D+00	0.149879D+01				
9	-0.833506D+00	0.139279D+03	-0.325211D+01	0.392778D+00	0.149879D+01				
	6	7	8	9					
6	0.000000D+00								
7	-0.143862D+02	0.000000D+00							
8	0.116439D+02	0.430160D+01	0.000000D+00						
9	0.430160D+01	0.116439D+02	-0.872699D+01	0.000000D+00					

# Spin-Spin-Kopplung: Methanol

Total nuclear spin-spin coupling J (Hz):

	1	2	3	4	5
1	0.000000D+00				
2	0.178828D+02	0.000000D+00			
3	0.140164D+03	-0.136081D+02	0.000000D+00		
4	0.134339D+03	-0.299792D+01	-0.139327D+02	0.000000D+00	
5	0.134339D+03	-0.299792D+01	-0.139327D+02	-0.889219D+01	0.000000D+00
6	-0.159330D+01	-0.637339D+02	0.128428D+02	0.498275D+00	0.498275D+00
6					
6	0.000000D+00				