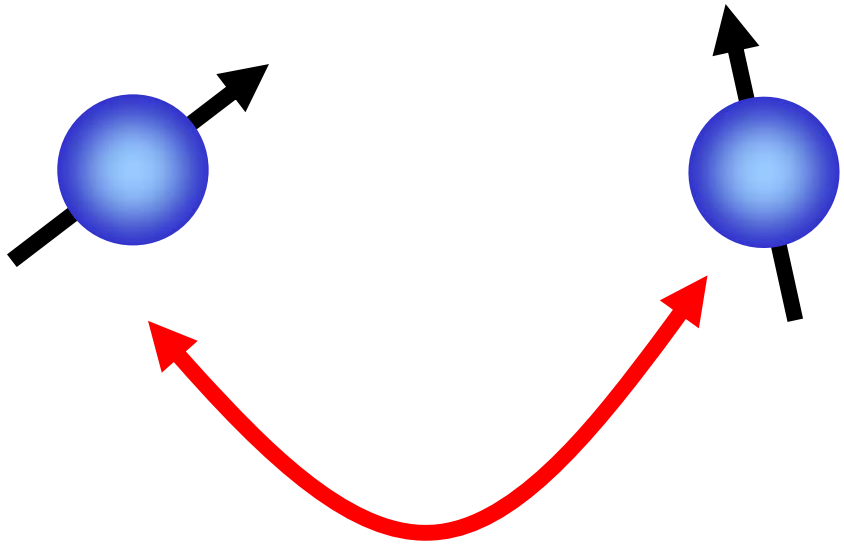
Relaxationsmechanismen

1. Dipol-Dipol-Wechselwirkung (DD)
2. Quadrupolare Wechselwirkung (Q)
3. Anisotropie der chemischen Verschiebung (CSA)
4. Skalare Kopplung (SC)
5. Spin-Rotation-Wechselwirkung (SR)

$$\frac{1}{T_1} = \frac{1}{T_1^{DD}} + \frac{1}{T_1^{Q}} + \frac{1}{T_1^{CSA}} + \frac{1}{T_1^{SC}} + \frac{1}{T_1^{SR}}$$

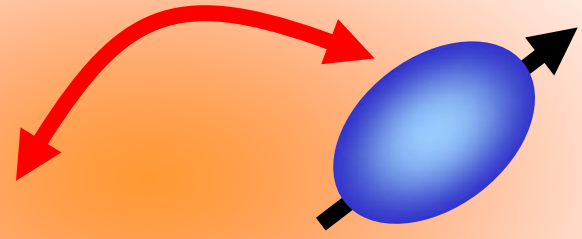
Relaxationsmechanismen

1. Dipol-Dipol-Wechselwirkung (DD)



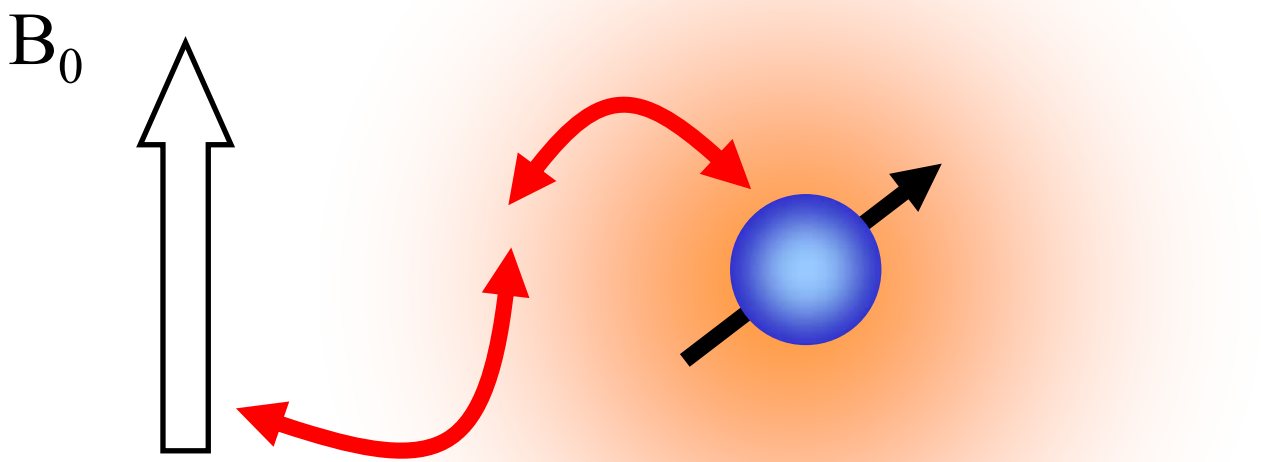
Relaxationsmechanismen

2. Quadrupolare Wechselwirkung (Q)



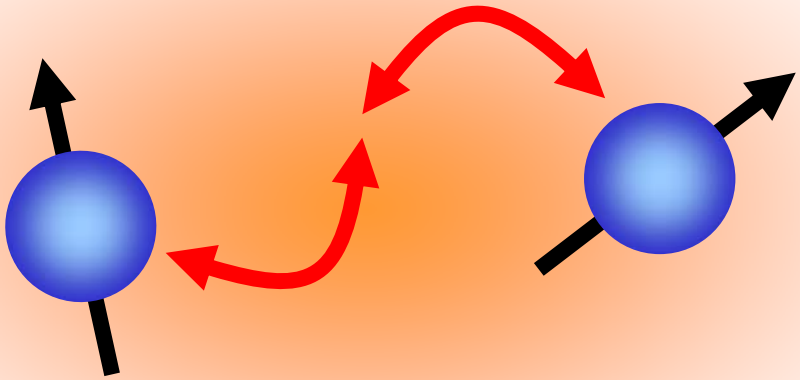
Relaxationsmechanismen

3. Anisotropie der chemischen Verschiebung (CSA)



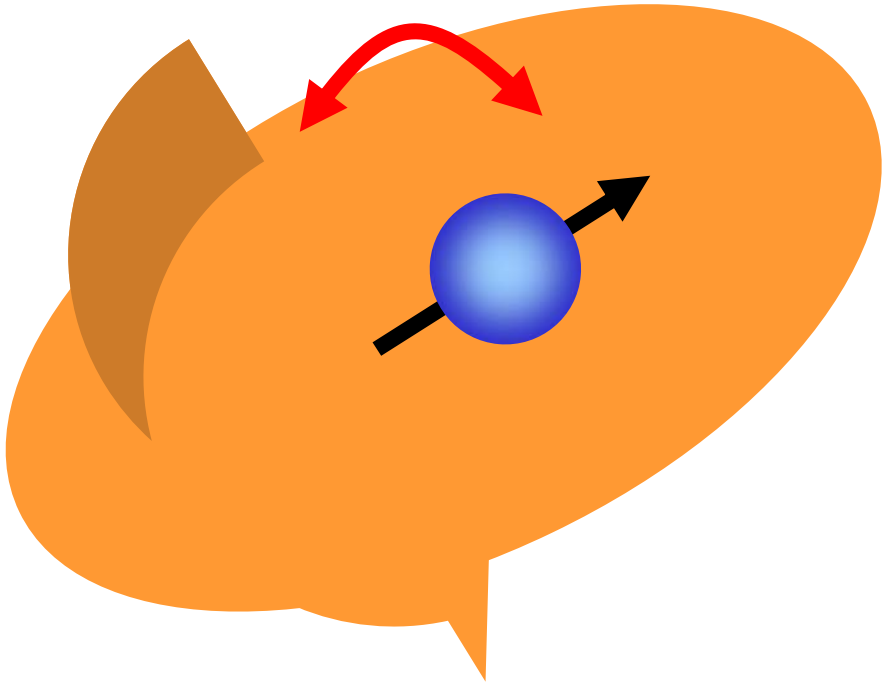
Relaxationsmechanismen

4. Skalare Kopplung (SC)

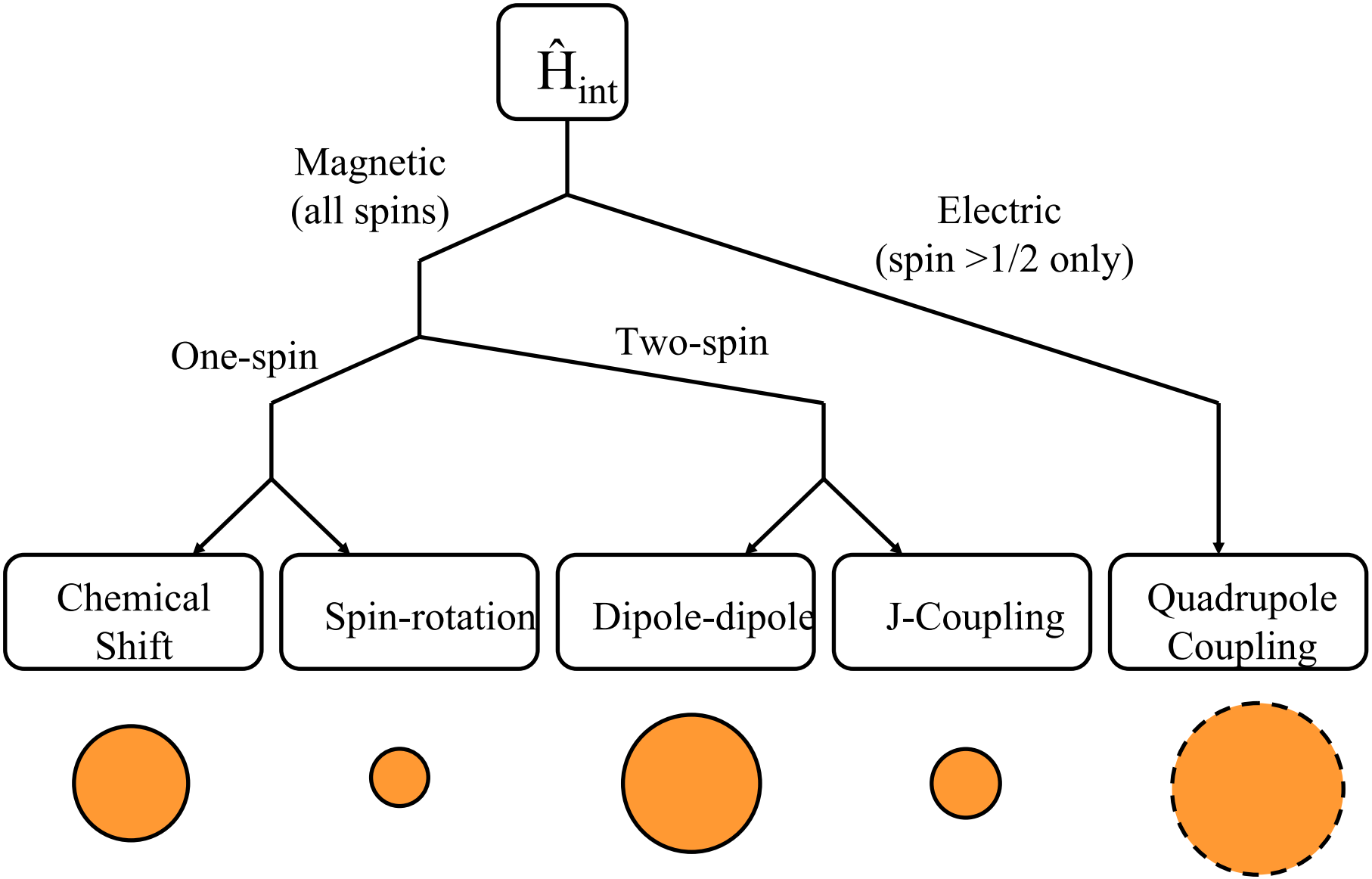


Relaxationsmechanismen

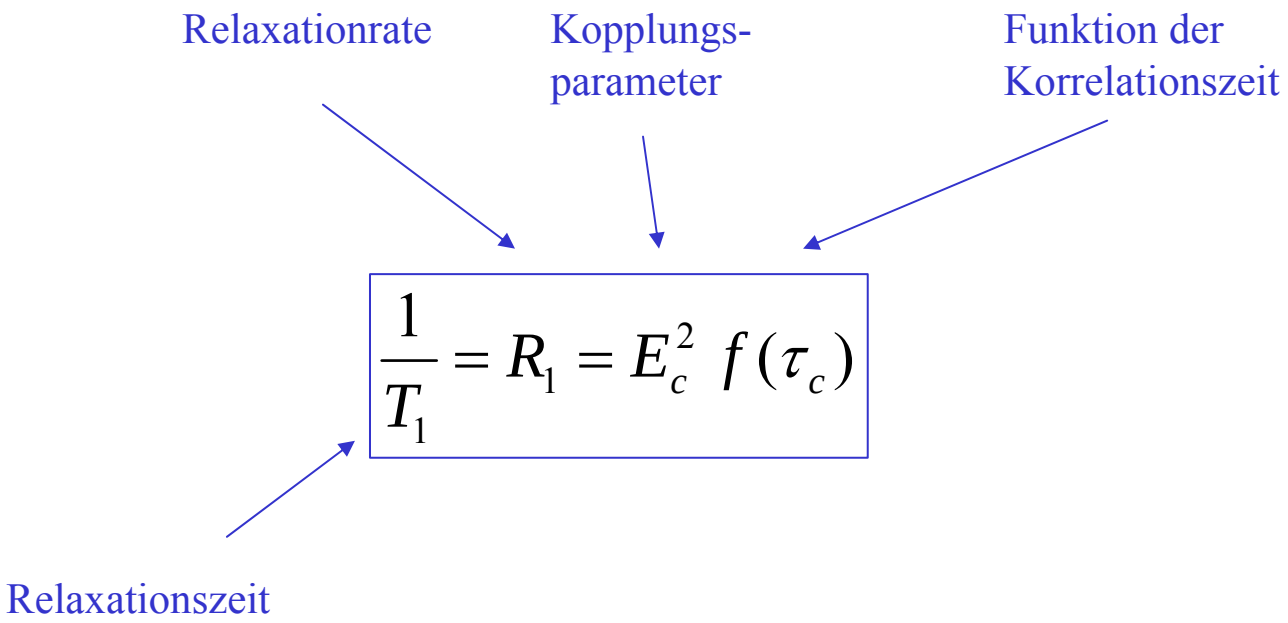
5. Spin-Rotations-Wechselwirkung (SR)



Relaxationsmechanismen



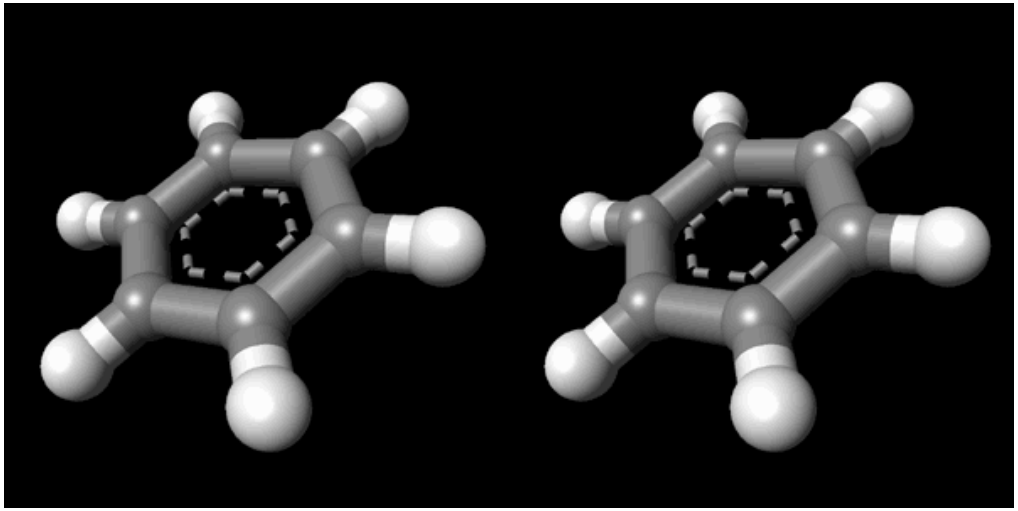
Relaxationsmechanismen

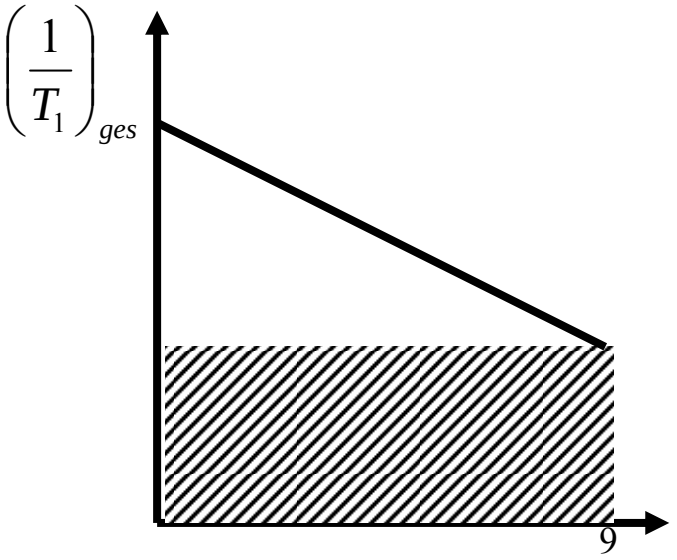


Dipolare Wechselwirkung

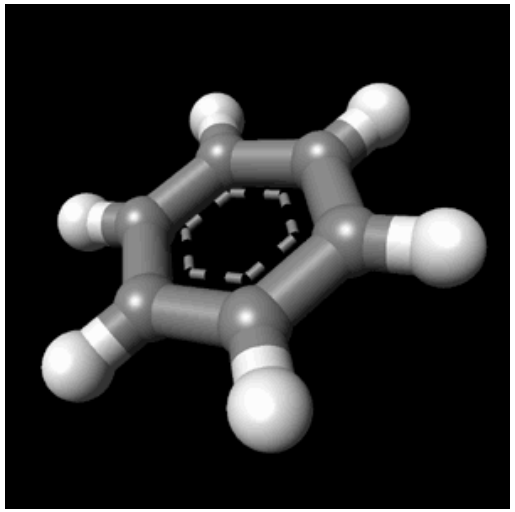
$$\left(\frac{1}{T_1}\right)_{ges} = \left(\frac{1}{T_1}\right)_{intra}^{H,H} + \left(\frac{1}{T_1}\right)_{inter}^{H,H}$$

$$\left(\frac{1}{T_1}\right)_{ges} = \left(\frac{1}{T_1}\right)_{intra}^{H,H} + \left(\frac{1}{T_1}\right)_{inter}^{H,D}$$





Dipolare Wechselwirkung



^{13}C-^{1}H

$$\frac{1}{T_1} = \frac{1}{T_1^{DD}} + \frac{1}{T_1^{Q}} + \frac{1}{T_1^{CSA}} + \frac{1}{T_1^{SC}} + \frac{1}{T_1^{SR}}$$

$$\left(\frac{1}{T_1}\right)^{DD} = \frac{\eta}{\eta_{\max}} \cdot \left(\frac{1}{T_1}\right)_{ges}$$

Dipolare Wechselwirkung

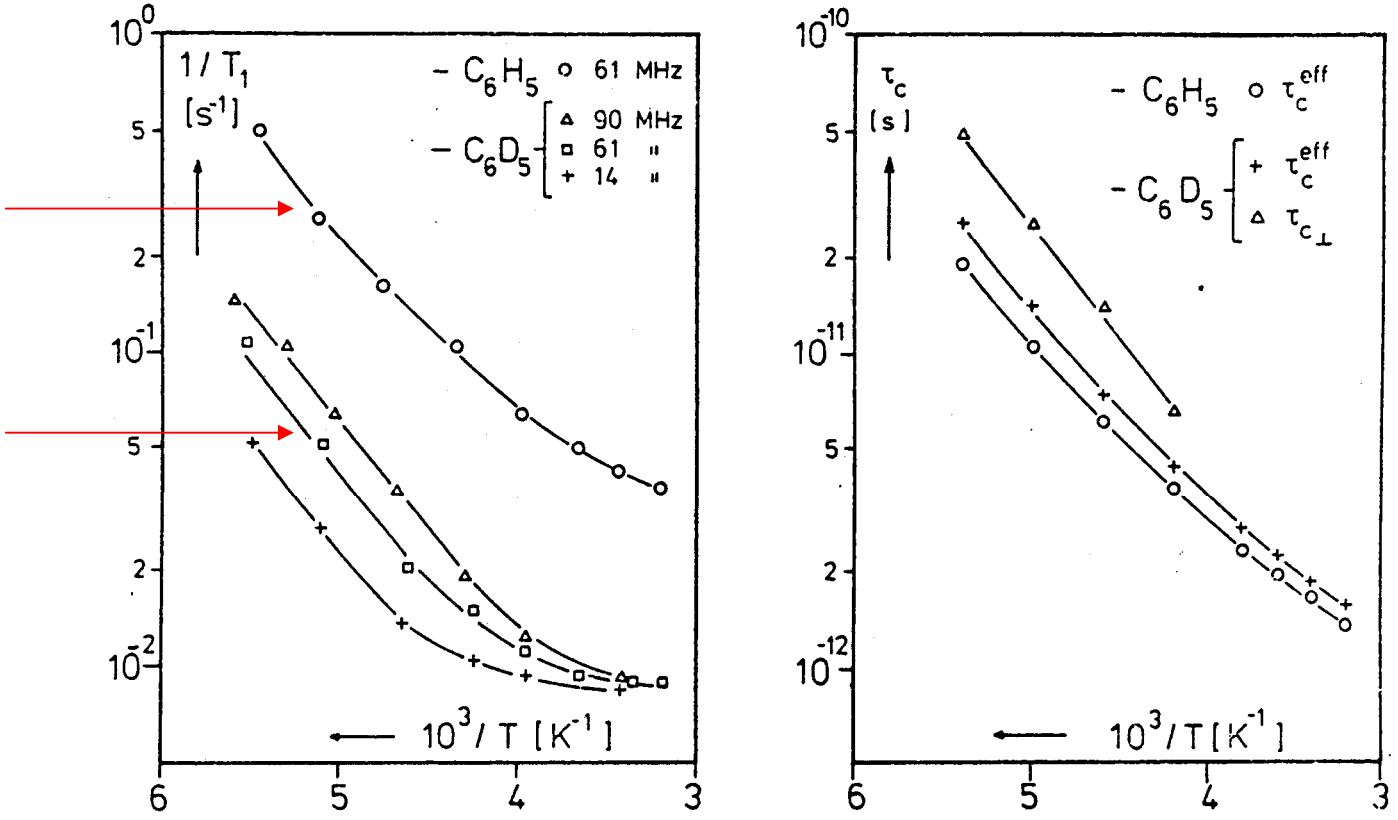


Abbildung 43 ^{13}C-Relaxationsraten und Korrelationszeiten für den Phenylring in Toluol.

Dipolare Wechselwirkung

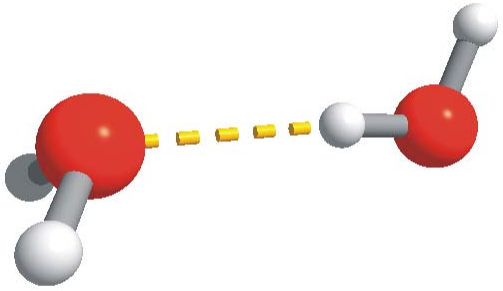
1-Decanol

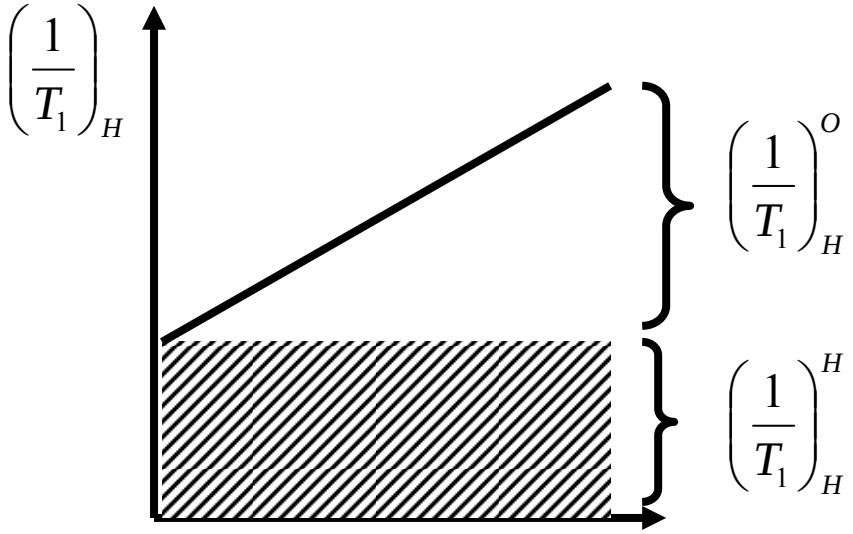
CH_3-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2- CH_2-OH

T_1	3.10	2.20	1.60	1.10	0.84	0.84	0.84	0.77	0.77	0.65
τ_c		11	15	21	28	28	28	30	30	36

Dipolare Wechselwirkung

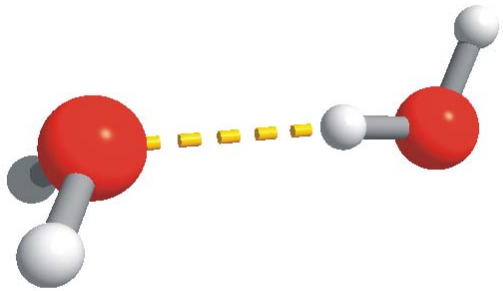
$$\left(\frac{1}{T_1}\right)_H = \left(\frac{1}{T_1}\right)_H^H + X_{^{17}O}\left(\frac{1}{T_1}\right)_H^O$$



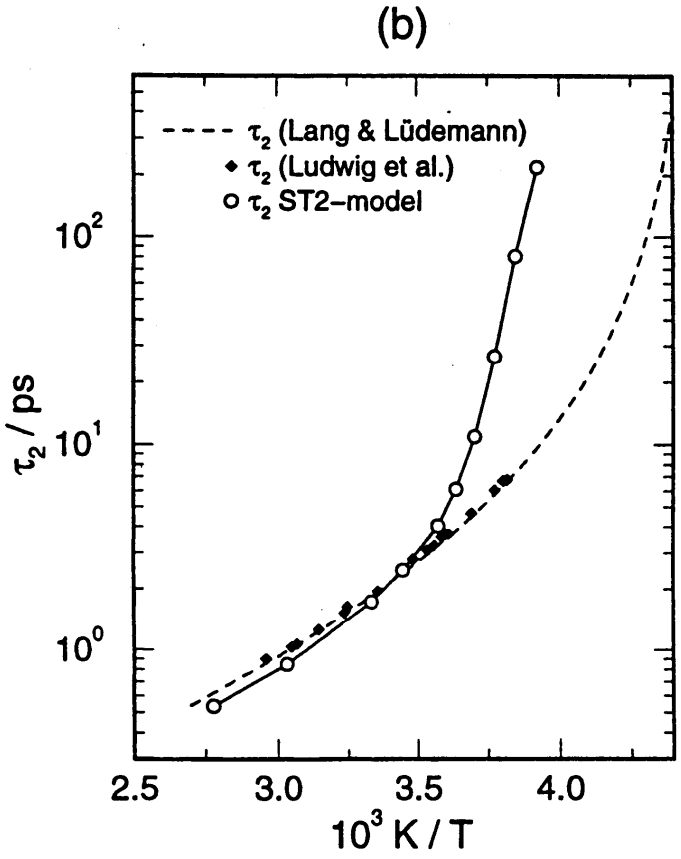


Dipolare Wechselwirkung

$$\left(\frac{1}{T_1}\right)_H^O = \frac{4}{3}\gamma_H^2\gamma_O^2 S(S+1)\frac{1}{r_{OH}^6}\tau_{OH}$$



J. Phys. Chem. B, Vol. 103, No. 20, 1999

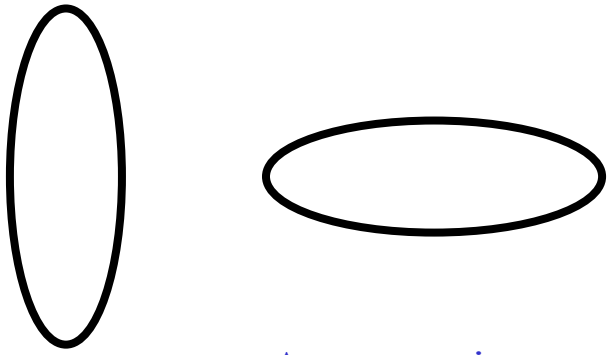


Dipolare Wechselwirkung

Wechselwirkung	T_1-Bereich	E_c	Typische Systeme
Dipol-Dipol	$10^{-2}<T_1<100$	$\gamma_I\gamma_S\hbar/r^3$	CH_3I
Quadrupol	$10^{-7}<T_1<100$	e^2Qq/h	$\mathbf{N}H_3$, $\mathbf{D}_2O$
Anisotropie der chemischen Verschiebung	$10^{-3}<T_1<100$	$\gamma B_0(\sigma_{\|}-\sigma_{\perp})$	$H^{13}\mathbf{C}{\equiv}CH$
Skalare Kopplung	$10^{-2}<T_1<100$	$2A^2/3[S(S+1)]^{1/2}$	$^{13}\mathbf{C}HBr_3$, $\mathbf{P}Br_3$
Spin Rotation	$10^{-5}<T_1<100$	$(C_{\|}+2C_{\perp})/h)$	$ClO_3\mathbf{F}$, $^{15}\mathbf{N}H_4^+$

Quadrupolare Wechselwirkung

I>1/2



elektrischer Feldgradient

Asymmetrie-parameter

$$R_1 = R_2 = \left(\frac{3}{40}\right)\left[\frac{2I+3}{I^2(2I-1)}\right]\left[1+\frac{\eta^2}{3}\right]\left(\frac{eQeq_{zz}}{h}\right)^2 \tau_c$$

Quadrupol-Kopplungs-konstante

$$\eta = \frac{V_{xx} - V_{yy}}{V_{zz}} = \frac{eq_{xx} - eq_{yy}}{eq_{zz}}$$

Quadrupolare Wechselwirkung

NH_4^+	eQeq/h≈0 Hz	T_1≈50s	
CH_3CN	eQeq/h≈4 MHz	T_1≈22ms	
$HCONH_2$	eQeq/h≈2-4 MHz	T_1≈2ms	

Quadrupolare Wechselwirkung

		fest	flüssig	gasförmig
D_2O	eQeq/h	215 kHz	253 kHz	308 kHz
	η	0.112		0.135
$D_2{}^{17}O$	eQeq/h	6.14 MHz	8.1 MHz	10.175 kHz
	η	0.93		0.75

Quadrupolare Wechselwirkung

Wechselwirkung	T_1-Bereich	E_c	Typische Systeme
Dipol-Dipol	$10^{-2}<T_1<100$	$\gamma_I\gamma_S\hbar/r^3$	CH_3I
Quadrupol	$10^{-7}<T_1<100$	e^2Qq/h	$\mathbf{N}H_3$, $\mathbf{D}_2O$
Anisotropie der chemischen Verschiebung	$10^{-3}<T_1<100$	$\gamma B_0(\sigma_{\parallel}-\sigma_{\perp})$	$H^{13}\mathbf{C}\equiv CH$
Skalare Kopplung	$10^{-2}<T_1<100$	$2A^2/3[S(S+1)]^{1/2}$	$^{13}\mathbf{C}HBr_3$, $\mathbf{P}Br_3$
Spin Rotation	$10^{-5}<T_1<100$	$(C_{\parallel}+2C_{\perp})/h)$	$ClO_3\mathbf{F}$, $^{15}\mathbf{N}H_4^+$

Anisotropie der chemischen Verschiebung

$$B_{loc} = B_0 - \sigma B_0 = B_0(1-\sigma)$$

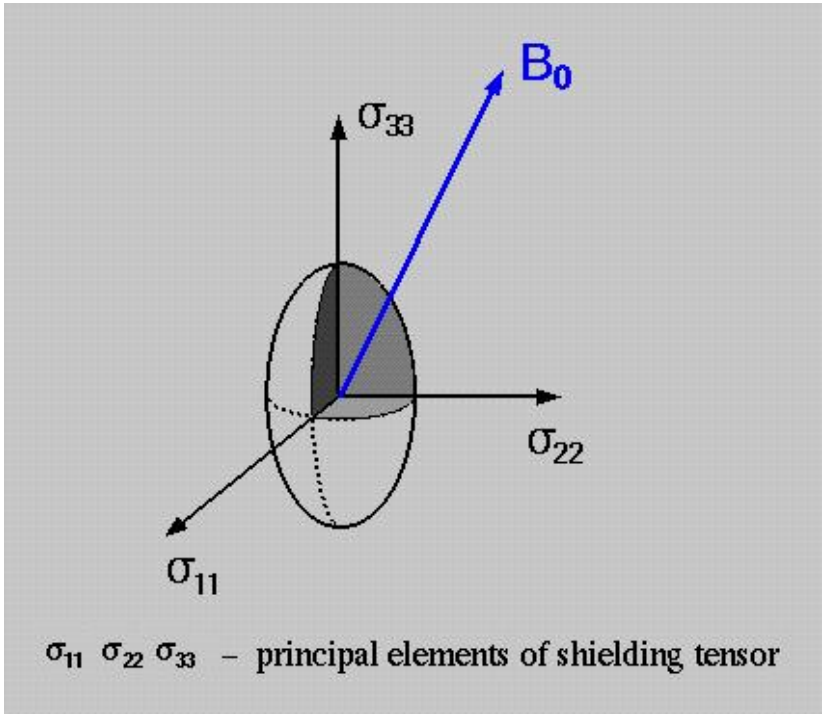
$$\sigma = \frac{1}{3}(\sigma_{xx} + \sigma_{yy} + \sigma_{zz})$$

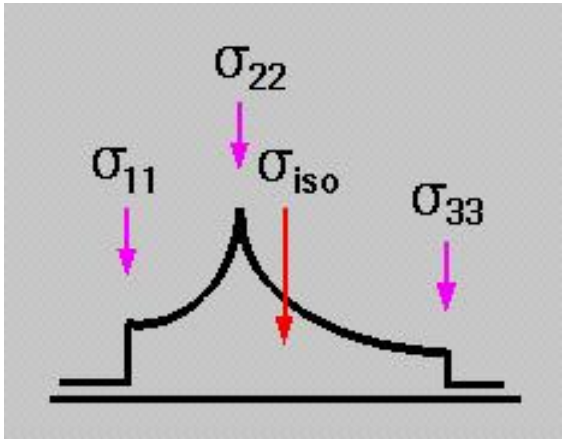
in der Flüssigkeit !!!

Anisotropie der chemischen Verschiebung

$$\sigma = \frac{1}{3}(\Sigma_{xx} + \Sigma_{yy} + \Sigma_{zz})$$

lokale
Fluktuationen





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

Anisotropie der chemischen Verschiebung

$$R_1 = \frac{1}{15}\gamma^2 B_0^2 (\sigma_{\parallel} - \sigma_{\perp})^2 \frac{2\tau_c}{1+\omega^2\tau_c^2}$$

$$R_2 = \frac{1}{90}\gamma^2 B_0^2 (\sigma_{\parallel} - \sigma_{\perp})^2 \left[\frac{6\tau_c}{1+\omega^2\tau_c^2} + 8\tau_c \right]$$

Anisotropie der chemischen Verschiebung

$$R_1 = \frac{2}{15}\gamma^2 B_0^2 (\sigma_{\parallel} - \sigma_{\perp})^2 \tau_c$$

$$R_2 = \frac{7}{45}\gamma^2 B_0^2 (\sigma_{\parallel} - \sigma_{\perp})^2 \tau_c$$

$$R_1 / R_2 = 6/7$$

$^{13}CS_2$ $T_1(^{13}C) \approx 20\text{-}60$ s, ^{33}S: 0.75%, γ klein, SR

$CH_3{}^{13}COOH$ $T_1(^{13}C)$: 40s bei 9 MHz und 21s bei 63 MHz

Anisotropie der chemischen Verschiebung

Wechselwirkung	T_1-Bereich	E_c	Typische Systeme
Dipol-Dipol	$10^{-2}<T_1<100$	$\gamma_I\gamma_S\hbar/r^3$	CH_3I
Quadrupol	$10^{-7}<T_1<100$	e^2Qq/h	$\mathbf{N}H_3$, $\mathbf{D}_2O$
Anisotropie der chemischen Verschiebung	$10^{-3}<T_1<100$	$\gamma B_0(\sigma_{\parallel}-\sigma_{\perp})$	$H^{13}\mathbf{C}\equiv CH$
Skalare Kopplung	$10^{-2}<T_1<100$	$2A^2/3[S(S+1)]^{1/2}$	$^{13}\mathbf{C}HBr_3$, $\mathbf{P}Br_3$
Spin Rotation	$10^{-5}<T_1<100$	$(C_{\parallel}+2C_{\perp})/h)$	$ClO_3\mathbf{F}$, $^{15}\mathbf{N}H_4^+$

Skalare Kopplung

Spin I und Spin S mit I=1/2 und S≥1/2, beide zeitabhängig

$T_1(S)$ kurz im Vergleich zu 1/A, dann fluktuiert $AS(t)/\gamma_I$ mit $\tau_S=T_1(S)$

$$R_1^I = \frac{2A^2}{3} S(S+1) \frac{\tau_S}{1+(\omega_I-\omega_S)^2\tau_S^2}$$

$$R_2^I(SC) = \frac{2A^2}{3} S(S+1) \left[\tau_S + \frac{\tau_S}{1+(\omega_I-\omega_S)^2\tau_S^2} \right]$$

Skalare Kopplung

$HCCl_3$: $R_1(I)_{total} = R_1^I(DD) + R_1^I(SC)$ $J_{H\text{-}Cl}$ und $J_{C\text{-}Cl}$

$$R_2(I)_{total} = R_2^I(DD) + R_2^I(SC)$$

$T_1(H)$=90s, $T_2(H)$=10s, $T_1(^{13}C)$=33s, $T_2(^{13}C)$=0.35s

$$R_1(I)(total) = R_1^I(DD) = R_2^I(DD) \qquad \boxed{R_2^I - R_1^I = \frac{A^2}{3} S(S+1)\tau_S}$$

$T_1(^{35}Cl)$=34μs > $J_{H\text{-}Cl}$≅6.9Hz

Skalare Kopplung

^{13}C-^{1}H: $T_1(^{13}C) > T_1(^{1}H)$

$R_1(^{1}H) = 1/T_1(^{1}H) << 2\pi J = A$ $T_2(^{13}C) < T_1(^{13}C)$

$^{13}CH_3I$:

$J_{CH} = 152Hz$
$T_1(^{13}C) = 13.4s$
$T_2(^{13}C) = 3.9s$
$T_1(^{1}H) = 10.9s$

Skalare Kopplung

Wechselwirkung	T_1-Bereich	E_c	Typische Systeme
Dipol-Dipol	$10^{-2}<T_1<100$	$\gamma_I\gamma_S\hbar/r^3$	CH_3I
Quadrupol	$10^{-7}<T_1<100$	e^2Qq/h	$\mathbf{N}H_3$, $\mathbf{D}_2O$
Anisotropie der chemischen Verschiebung	$10^{-3}<T_1<100$	$\gamma B_0(\sigma_{\|}-\sigma_{\perp})$	$H^{13}\mathbf{C}{\equiv}CH$
Skalare Kopplung	$10^{-2}<T_1<100$	$2A^2/3[S(S+1)]^{1/2}$	$^{13}\mathbf{C}HBr_3$, $\mathbf{P}Br_3$
Spin Rotation	$10^{-5}<T_1<100$	$(C_{\|}+2C_{\perp})/h)$	$ClO_3\mathbf{F}$, $^{15}\mathbf{N}H_4^+$

Spinrotation

Rotationsfrequenz der Elektronen um den Kern: $V = hJ / 2\pi I$

Rotationszustand

Strom durch Elektron: $i = (e/c)V$

Magnetisches Moment: $\mu_J = i(\pi R^2) = (eh/2\pi Mc)J \cong \mu_N J$

$$R_1 = 2(IkT/\hbar^2)C_{eff}^2 \tau_J \qquad C_{eff}^2 = 1/3(2C_\perp^2 + C_\parallel^2)$$

$$\tau_c \tau_J = I/6kT$$

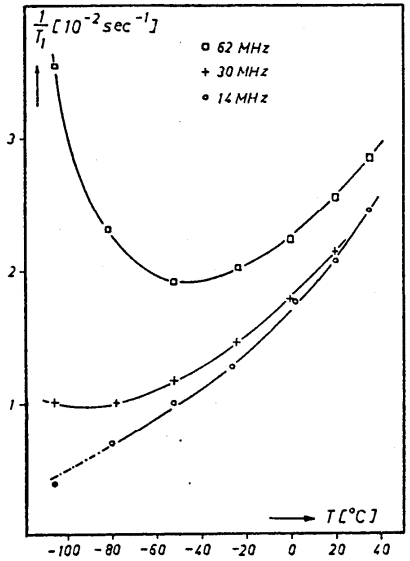
Spinrotation

Wechselwirkung	T_1-Bereich	E_c	Typische Systeme
Dipol-Dipol	$10^{-2}<T_1<100$	$\gamma_I\gamma_S\hbar/r^3$	CH_3I
Quadrupol	$10^{-7}<T_1<100$	e^2Qq/h	$\mathbf{N}H_3$, $\mathbf{D}_2O$
Anisotropie der chemischen Verschiebung	$10^{-3}<T_1<100$	$\gamma B_0(\sigma_{\parallel}-\sigma_{\perp})$	$H^{13}\mathbf{C}{\equiv}CH$
Skalare Kopplung	$10^{-2}<T_1<100$	$2A^2/3[S(S+1)]^{1/2}$	$^{13}\mathbf{C}HBr_3$, $\mathbf{P}Br_3$
Spin Rotation	$10^{-5}<T_1<100$	$(C_{\parallel}+2C_{\perp})/h)$	$ClO_3\mathbf{F}$, $^{15}\mathbf{N}H_4^+$

CSA- und SR-Wechselwirkung

CS_2

$$\frac{1}{T_1} = \frac{1}{T_1^{CSA}} + \frac{1}{T_1^{SR}}$$



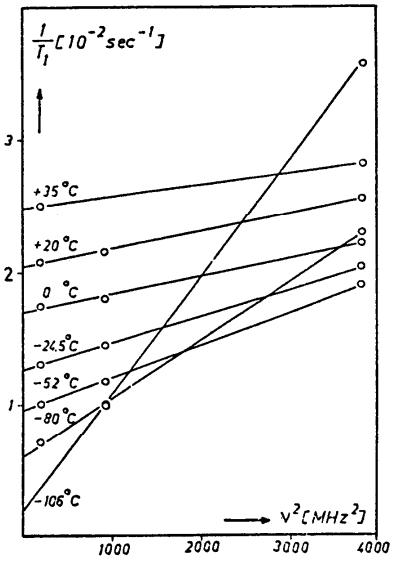


Abbildung 37 Temperatur- und Frequenzabhängigkeit der ^{13}C-Relaxationsrate in CS_2.

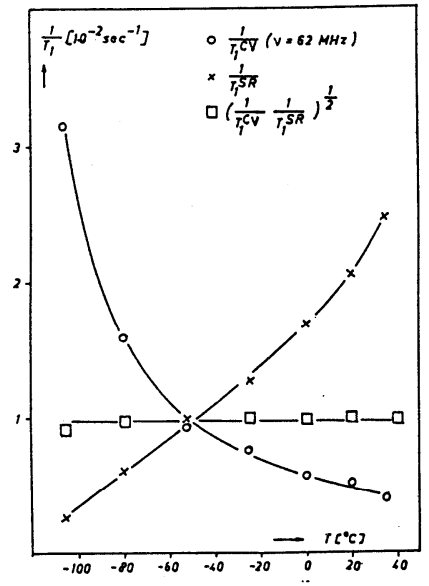


Abbildung 38 ^{13}C-Relaxationsraten durch anisotrope Abschirmung bei 62 MHz und durch Spin-Rotationswechselwirkung in CS_2.

DD-, CSA- und SR-Wechselwirkung

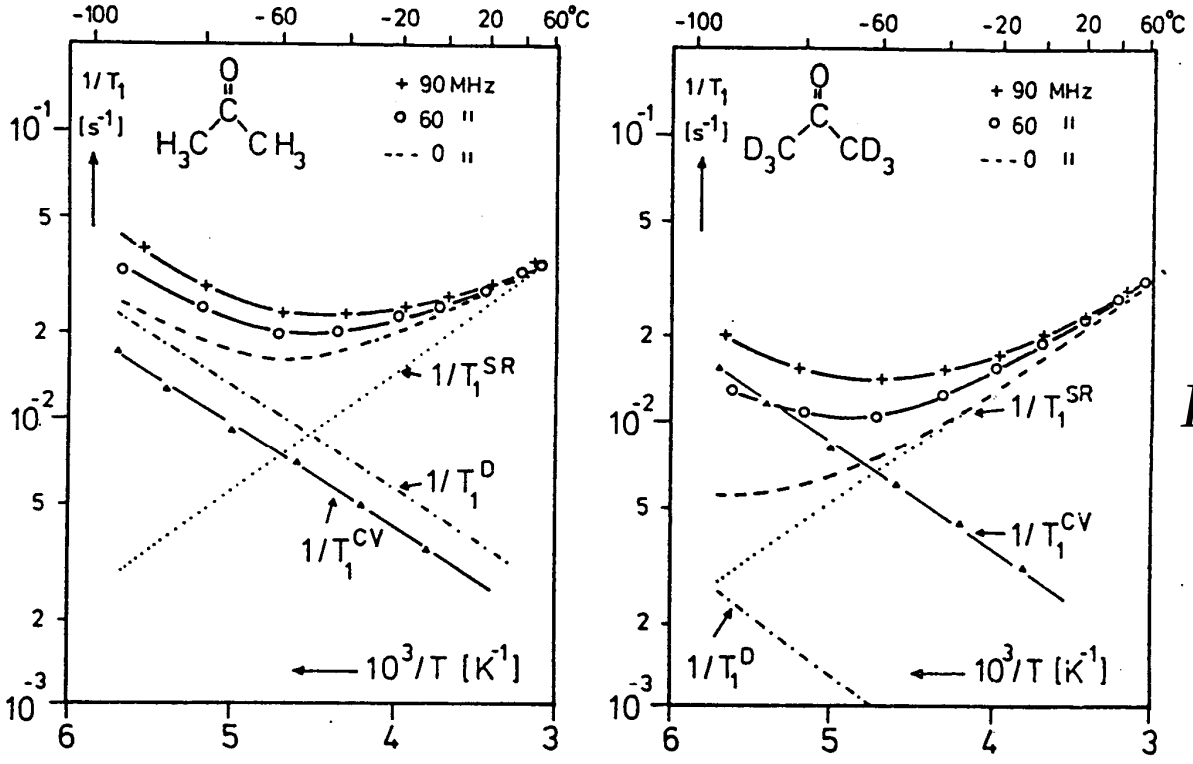


Abbildung 39 ^{13}C-Relaxationsraten des Carbonylkohlenstoffs in Aceton-h_6 und -d_6.

$$\frac{1}{T_1} = \frac{1}{T_1^{DD}} + \frac{1}{T_1^{CSA}} + \frac{1}{T_1^{SR}}$$

$\omega \rightarrow 0$: $(1/T_1)_{CSA}$

$$R_1 = \frac{2}{15}\gamma^2 B_0^2 (\sigma_{\parallel} - \sigma_{\perp})^2 \tau_c$$

$\Delta\sigma$ aus FK $\rightarrow \tau_c$

$(1/T_1)_{DD}$ mit $r_{C..H}$

$(1/T_1)_{SR}$: $(1/T_1)_{DD}$