Wiederholung letzte Vorlesungsstunde
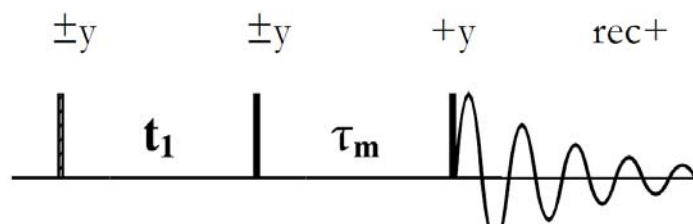

NOESY
Nuclear Overhauser Enhancement and Exchange Spectroscopy

Schneller / häufiger Austausch → $T > T_c$

Koaleszenz → T_c

$T < T_c$

langsamer/ seltener Austausch → $T \ll T_c$

trans $\delta_{(N)H} \sim 8.8ppm$ cis $\delta_{(N)H} \sim 8.2ppm$
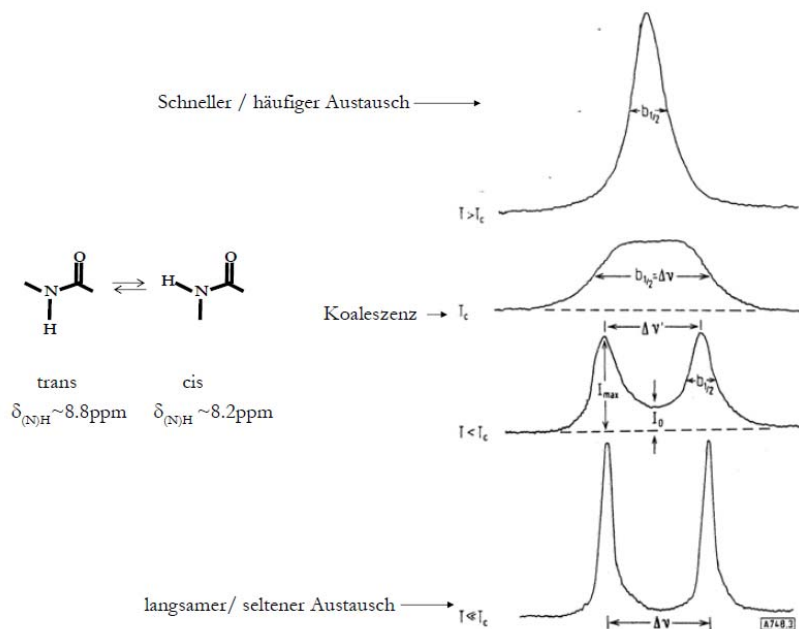
NOESY
Pulssequenz

NOESY
Evolution der Magnetisierung vor τ_M

$$I_{Az} \xrightarrow{\;90°_y\;} I_{Ax}$$

$$\xrightarrow{\;\Omega I_z t\;} I_{Ax} \cos\Omega_A t_1 + I_{Ay} \sin\Omega_A t_1$$

$$\xrightarrow{\;90°_y\;} -I_{Az} \cos\Omega_A t_1 + I_{Ay} \sin\Omega_A t_1$$

$$I_{Az} \xrightarrow{\;90°_{-y}\;} -I_{Ax}$$

$$\xrightarrow{\;\Omega I_z t\;} -I_{Ax} \cos\Omega_A t_1 - I_{Ay} \sin\Omega_A t_1$$

$$\xrightarrow{\;90°_{-y}\;} -I_{Az} \cos\Omega_A t_1 - I_{Ay} \sin\Omega_A t_1$$

NOESY
Evolution der Magnetisierung vor τ_M

$$\pm y \qquad \pm y \qquad +y \qquad rec+$$

$$t_1 \qquad \tau_m$$

$$I_{Az} \xrightarrow{90^\circ_y} I_{Ax}$$

$$\xrightarrow{\Omega I_z t} I_{Ax}\cos\Omega_A t_1 + I_{Ay}\sin\Omega_A t_1$$

$$\xrightarrow{90^\circ_y} -I_{Az}\cos\Omega_A t_1 + I_{Ay}\sin\Omega_A t_1$$
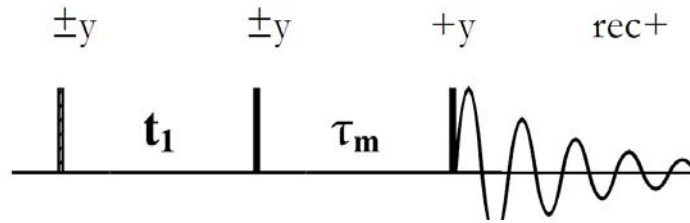
$$I_{Bz} \xrightarrow{90^\circ_y} I_{Bx}$$

$$\xrightarrow{\Omega I_z t} I_{Bx}\cos\Omega_B t_1 + I_{By}\sin\Omega_B t_1$$

$$\xrightarrow{90^\circ_y} -I_{Bz}\cos\Omega_B t_1 + I_{By}\sin\Omega_B t_1$$

$$I_{Az} \xrightarrow{90^\circ_{-y}} -I_{Ax}$$

$$\xrightarrow{\Omega I_z t} -I_{Ax}\cos\Omega_A t_1 - I_{Ay}\sin\Omega_A t_1$$

$$\xrightarrow{90^\circ_{-y}} -I_{Az}\cos\Omega_A t_1 - I_{Ay}\sin\Omega_A t_1$$
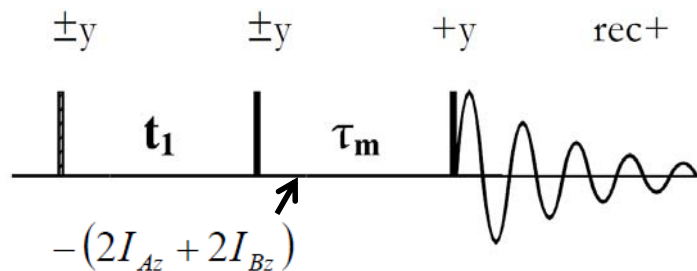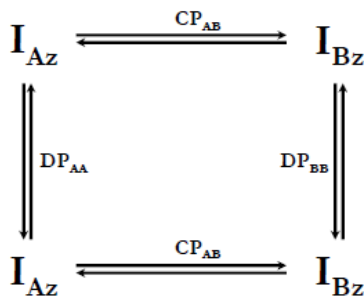
$$I_{Bz} \xrightarrow{90^\circ_{-y}} I_{Bx}$$

$$\xrightarrow{\Omega I_z t} I_{Bx}\cos\Omega_B t_1 + I_{By}\sin\Omega_B t_1$$

$$\xrightarrow{90^\circ_{-y}} -I_{Bz}\cos\Omega_B t_1 - I_{By}\sin\Omega_B t_1$$

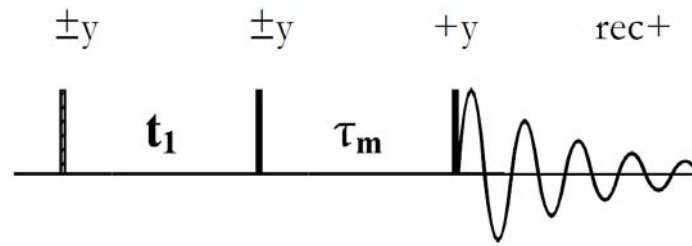
NOESY
Evolution der Magnetisierung während τ_M

$$\mathbf{I_{Az}} \xrightleftharpoons{CP_{AB}} \mathbf{I_{Bz}}$$

$$\Big\Updownarrow DP_{AA} \qquad\qquad DP_{BB}\Big\Updownarrow$$

$$\mathbf{I_{Az}} \xrightleftharpoons{CP_{AB}} \mathbf{I_{Bz}}$$

$$\pm y \qquad \pm y \qquad +y \qquad rec+$$

$$t_1 \qquad \tau_m$$

$$-(2I_{Az} + 2I_{Bz})$$

$$-2I_{Az}\cos\Omega_A t_1 \qquad \xrightarrow{\tau_m} \qquad (-2\cos\Omega_A t_1)\left(I_{Az}\cdot DP_{AA}\tau_m + I_{Bz}CP_{AB}\tau_m\right)$$

$$-2I_{Bz}\cos\Omega_B t_1 \qquad \xrightarrow{\tau_m} \qquad (-2\cos\Omega_B t_1)\left(I_{Bz}\cdot DP_{BB}\tau_m + I_{Az}CP_{AB}\tau_m\right)$$

NOESY
Evolution der Magnetisierung nach τ_M

$$\xrightarrow{90°_y} (-2\cos\Omega_A t_1)(I_{Ax} \cdot DP_{AA}\tau_m + I_{Bx}CP_{AB}\tau_m)$$

$$(-2\cos\Omega_B t_1)(I_{Bx} \cdot DP_{BB}\tau_m + I_{Ax}CP_{AB}\tau_m)$$

$$\xrightarrow{\Omega I_z t} (-2\cos\Omega_A t_1)(DP_{AA}\tau_m(I_{Ax}\cos\Omega_A t_2 + I_{Ay}\sin\Omega_A t_2) + CP_{AB}\tau_m(I_{Bx}\cos\Omega_B t_2 + I_{By}\sin\Omega_B t_2))$$

$$(-2\cos\Omega_B t_1)(DP_{BB}\tau_m(I_{Bx}\cos\Omega_B t_2 + I_{By}\sin\Omega_B t_2) + CP_{AB}\tau_m(I_{Ax}\cos\Omega_A t_2 + I_{Ay}\sin\Omega_B t_2))$$
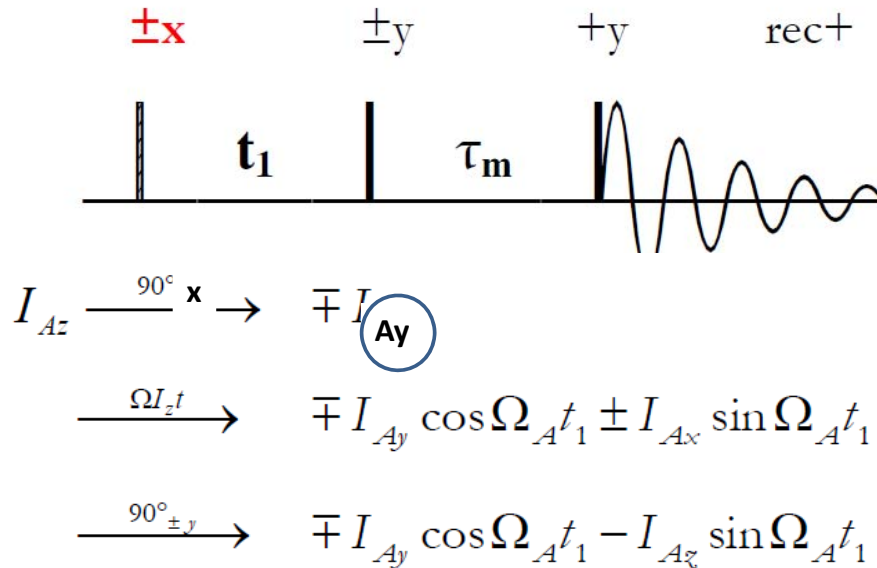

NOESY
Evolution der Magnetisierung nach τ_M

$$\xrightarrow{90°_y} (-2\cos\Omega_A t_1)(I_{Ax} \cdot DP_{AA}\tau_m + I_{Bx}CP_{AB}\tau_m)$$

$$(-2\cos\Omega_B t_1)(I_{Bx} \cdot DP_{BB}\tau_m + I_{Ax}CP_{AB}\tau_m)$$

$$\xrightarrow{\Omega I_z t} (-2\cos\Omega_A t_1)(DP_{AA}\tau_m(I_{Ax}\cos\Omega_A t_2 + I_{Ay}\sin\Omega_A t_2) + CP_{AB}\tau_m(I_{Bx}\cos\Omega_B t_2 + I_{By}\sin\Omega_B t_2))$$

$$(-2\cos\Omega_B t_1)(DP_{BB}\tau_m(I_{Bx}\cos\Omega_B t_2 + I_{By}\sin\Omega_B t_2) + CP_{AB}\tau_m(I_{Ax}\cos\Omega_A t_2 + I_{Ay}\sin\Omega_B t_2))$$

$$(-2\cos\Omega_A t_1)(DP_{AA}\tau_m)e^{i\Omega_A t_2} +$$

$$(-2\cos\Omega_A t_1)(CP_{AB}\tau_m)e^{i\Omega_B t_2} +$$

$$(-2\cos\Omega_B t_1)(DP_{BB}\tau_m)e^{i\Omega_B t_2} +$$

$$(-2\cos\Omega_B t_1)(CP_{AB}\tau_m)e^{i\Omega_A t_2}$$

NOESY
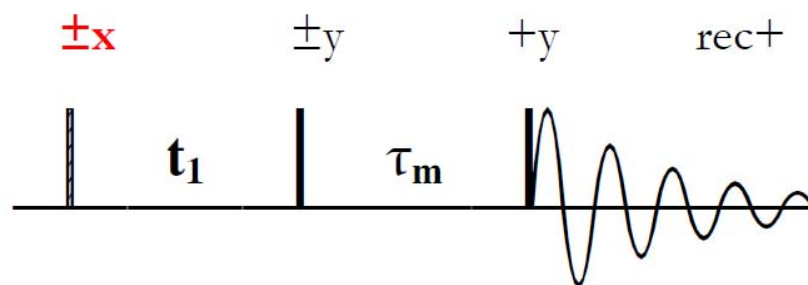## Vorzeichenunterscheidung in t_1

$$I_{Az} \xrightarrow{\quad 90° \; x \quad} \mp I_{Ay}$$

$$\xrightarrow{\quad \Omega I_z t \quad} \mp I_{Ay}\cos\Omega_A t_1 \pm I_{Ax}\sin\Omega_A t_1$$

$$\xrightarrow{\quad 90°_{\pm y} \quad} \mp I_{Ay}\cos\Omega_A t_1 - I_{Az}\sin\Omega_A t_1$$

NOESY
Vorzeichenunterscheidung in t_1

$$\left(-2\sin\Omega_A t_1\right)\left(DP_{AA}\tau_m\right)e^{i\Omega_A t_2} +$$
$$\left(-2\sin\Omega_A t_1\right)\left(CP_{AB}\tau_m\right)e^{i\Omega_B t_2} +$$
$$\left(-2\sin\Omega_B t_1\right)\left(DP_{BB}\tau_m\right)e^{i\Omega_B t_2} +$$
$$\left(-2\sin\Omega_B t_1\right)\left(CP_{AB}\tau_m\right)e^{i\Omega_A t_2}$$

NOESY
Peaks im NOESY

$$\text{I} \quad : \quad e^{i\Omega_A t_1} \cdot DP_{AA} \tau_m \cdot e^{i\Omega_A t_1} \cdot e^{\frac{-t_1}{T_2^A}} \cdot e^{\frac{-t_2}{T_2^A}}$$

$$\text{II} \quad : \quad e^{i\Omega_A t_1} \cdot CP_{AB} \tau_m \cdot e^{i\Omega_B t_1} \cdot e^{\frac{-t_1}{T_2^A}} \cdot e^{\frac{-t_2}{T_2^B}}$$

$$\text{III} \quad : \quad e^{i\Omega_B t_1} \cdot DP_{BB} \tau_m \cdot e^{i\Omega_B t_1} \cdot e^{\frac{-t_1}{T_2^B}} \cdot e^{\frac{-t_2}{T_2^B}}$$

$$\text{IV} \quad : \quad e^{i\Omega_B t_1} \cdot CP_{AA} \tau_m \cdot e^{i\Omega_A t_1} \cdot e^{\frac{-t_1}{T_2^B}} \cdot e^{\frac{-t_2}{T_2^A}}$$

Frequenzen in t_1 Frequenzen in t_2

Signalamplituden   Relaxation

NOESY
Peaks im NOESY