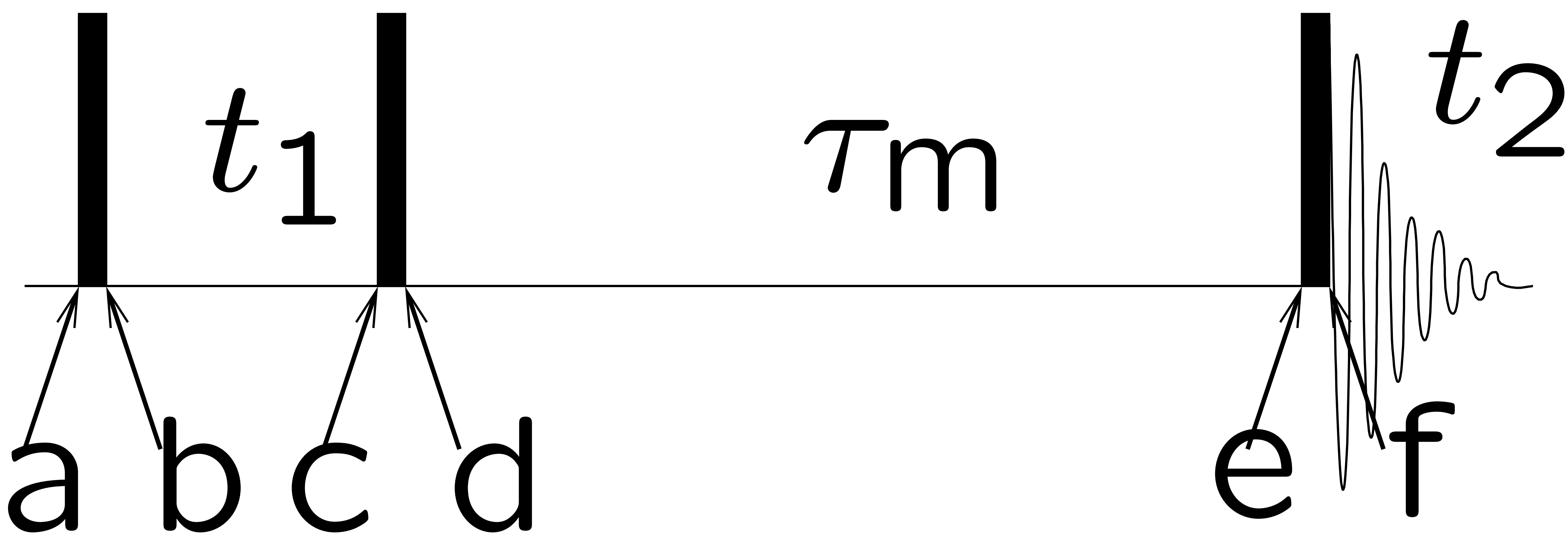
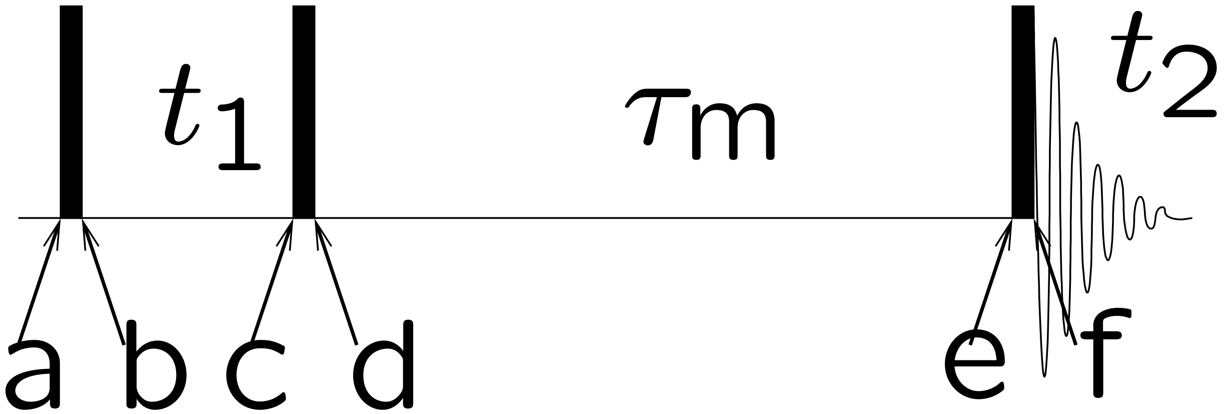
Lecture 9: 2D spectroscopy, NOESY

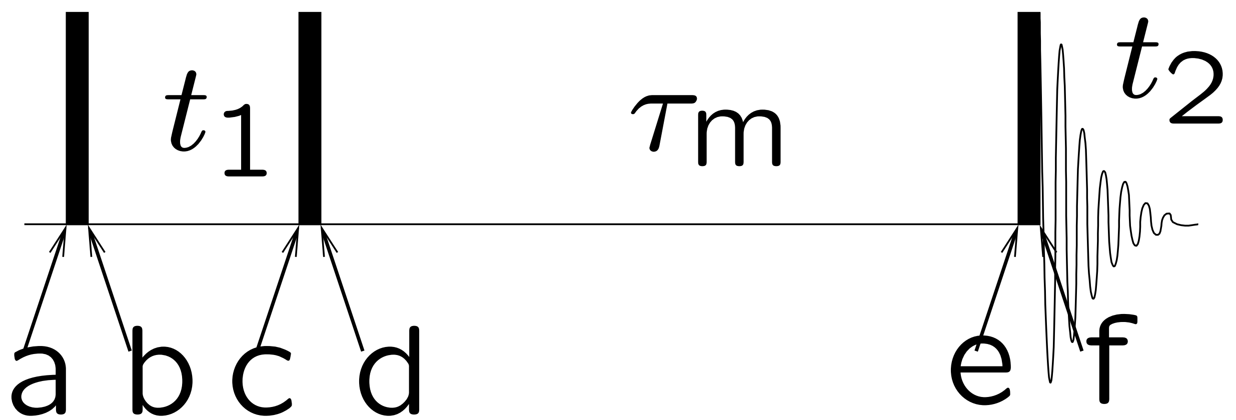

t_1
τ_m
t_2
a
b
c
d
e
f

HOMEWORK:



$$\hat{\rho}(\mathrm{a}) = \frac{1}{2}\mathscr{I}_t + \frac{1}{2}\kappa(\mathscr{I}_{1z} + \mathscr{I}_{2z})$$

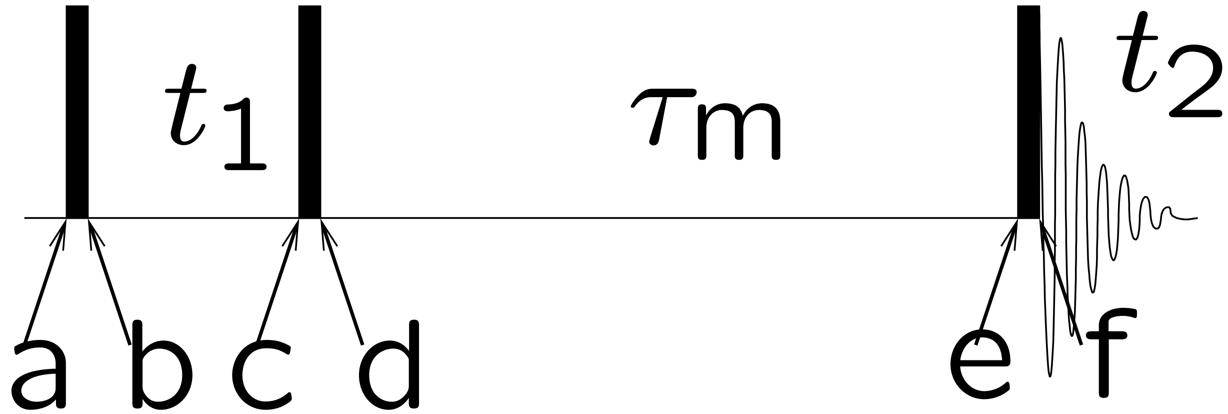
HOMEWORK:



$$\widehat{\rho}(\mathrm{a}) = \frac{1}{2}\mathscr{I}_t + \frac{1}{2}\kappa(\mathscr{I}_{1z} + \mathscr{I}_{2z})$$

$$\widehat{\rho}(\mathrm{b}) = \frac{1}{2}\mathscr{I}_t + \frac{1}{2}\kappa(-\mathscr{I}_{1y} - \mathscr{I}_{2y})$$

HOMEWORK:



$$\hat{\rho}(\mathrm{a}) = \frac{1}{2}\mathscr{I}_t + \frac{1}{2}\kappa(\mathscr{I}_{1z} + \mathscr{I}_{2z})$$

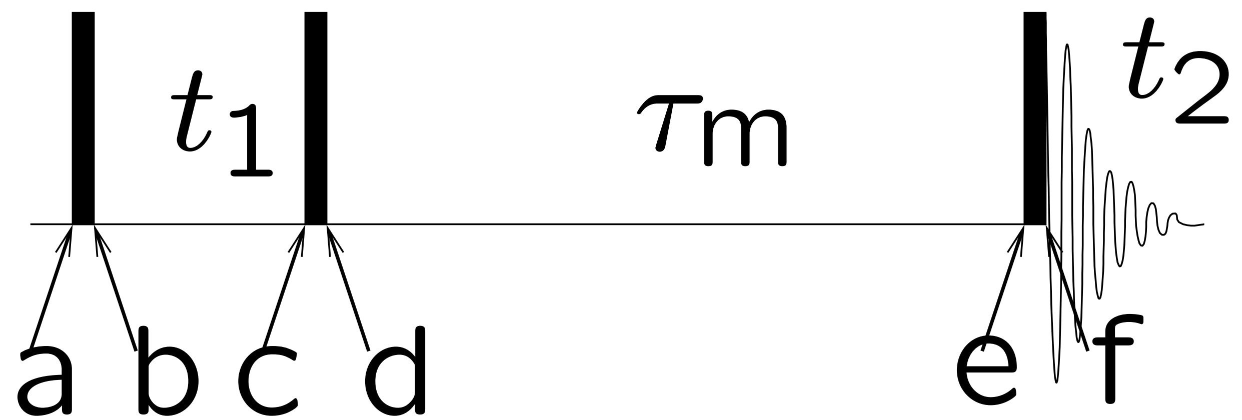
$$\hat{\rho}(\mathrm{b}) = \frac{1}{2}\mathscr{I}_t + \frac{1}{2}\kappa(-\mathscr{I}_{1y} - \mathscr{I}_{2y})$$

$$\hat{\rho}(\mathrm{c}) = \frac{1}{2}\mathscr{I}_t + \frac{1}{2}\kappa\left(-c_{11}\mathscr{I}_{1y} + s_{11}\mathscr{I}_{1x} - c_{21}\mathscr{I}_{2y} + s_{21}\mathscr{I}_{2x}\right)$$

$$c_{11} \rightarrow \mathrm{e}^{-R_{2,1}t_1}\cos(\Omega_1 t_1) \qquad s_{11} \rightarrow \mathrm{e}^{-R_{2,1}t_1}\sin(\Omega_1 t_1)$$

$$c_{21} \rightarrow \mathrm{e}^{-R_{2,2}t_1}\cos(\Omega_2 t_1) \qquad s_{21} \rightarrow \mathrm{e}^{-R_{2,2}t_1}\sin(\Omega_2 t_1)$$

HOMEWORK:



$$\hat{\rho}(\mathrm{a}) = \frac{1}{2}\mathscr{I}_t + \frac{1}{2}\kappa(\mathscr{I}_{1z} + \mathscr{I}_{2z})$$

$$\hat{\rho}(\mathrm{b}) = \frac{1}{2}\mathscr{I}_t + \frac{1}{2}\kappa(-\mathscr{I}_{1y} - \mathscr{I}_{2y})$$

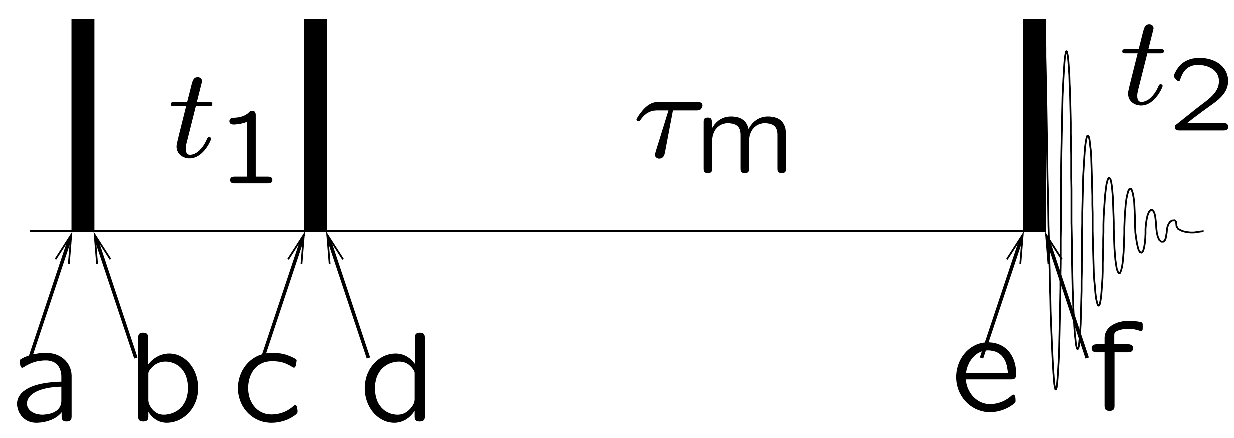
$$\hat{\rho}(\mathrm{c}) = \frac{1}{2}\mathscr{I}_t + \frac{1}{2}\kappa\left(-c_{11}\mathscr{I}_{1y} + s_{11}\mathscr{I}_{1x} - c_{21}\mathscr{I}_{2y} + s_{21}\mathscr{I}_{2x}\right)$$

$$c_{11} \rightarrow \mathrm{e}^{-R_{2,1}t_1}\cos(\Omega_1 t_1) \qquad s_{11} \rightarrow \mathrm{e}^{-R_{2,1}t_1}\sin(\Omega_1 t_1)$$

$$c_{21} \rightarrow \mathrm{e}^{-R_{2,2}t_1}\cos(\Omega_2 t_1) \qquad s_{21} \rightarrow \mathrm{e}^{-R_{2,2}t_1}\sin(\Omega_2 t_1)$$

$$\hat{\rho}(\mathrm{d}) = \frac{1}{2}\mathscr{I}_t + \frac{1}{2}\kappa\left(-c_{11}\mathscr{I}_{1z} + s_{11}\mathscr{I}_{1x} - c_{21}\mathscr{I}_{2z} + s_{21}\mathscr{I}_{2x}\right)$$

HOMEWORK:



$$\hat{\rho}(\mathrm{d}) = \frac{1}{2}\mathscr{I}_t + \frac{1}{2}\kappa\left(-c_{11}\mathscr{I}_{1z} + s_{11}\mathscr{I}_{1x} - c_{21}\mathscr{I}_{2z} + s_{21}\mathscr{I}_{2x}\right)$$

M_z relaxes with R_1, M_x, M_y relax with R_2:

$\tau_\mathrm{m} = 0.2\,\mathrm{s}$, $R_1 = 1\,\mathrm{s}^{-1}$, and $R_2 = 20\,\mathrm{s}^{-1}$

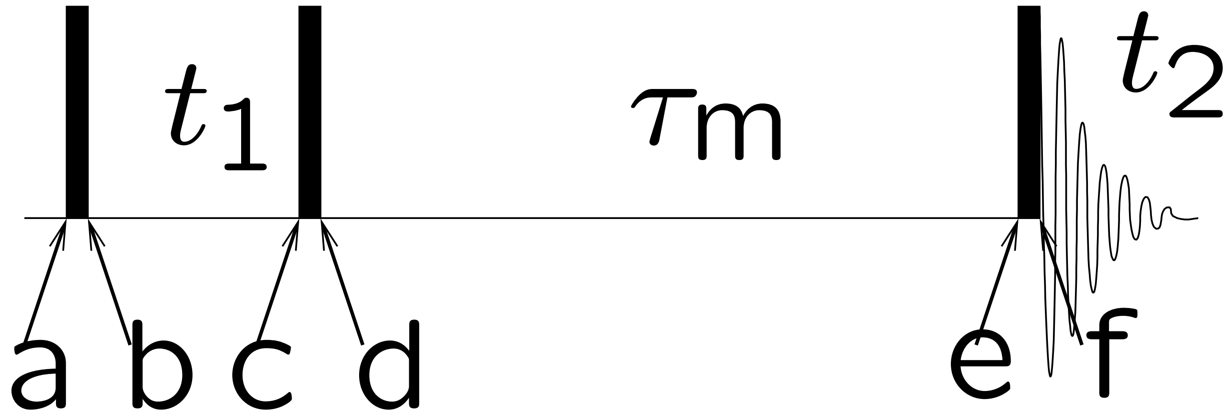
$$\Rightarrow \quad \mathrm{e}^{-R_2\tau_\mathrm{m}} = \mathrm{e}^{-20\times 0.2} = \mathrm{e}^{-4} \approx 0.02$$

$\mathscr{I}_{1x}, \mathscr{I}_{1y}, \mathscr{I}_{2x}, \mathscr{I}_{2y}$ contributions reduced to $2\,\% \approx 0$

$$\Rightarrow \quad \mathrm{e}^{-R_1\tau_\mathrm{m}} = \mathrm{e}^{-1\times 0.2} = \mathrm{e}^{-0.2} \approx 0.82$$

$\mathscr{I}_{1z}, \mathscr{I}_{2z}$ contributions survive ($82\,\% \approx 1$)

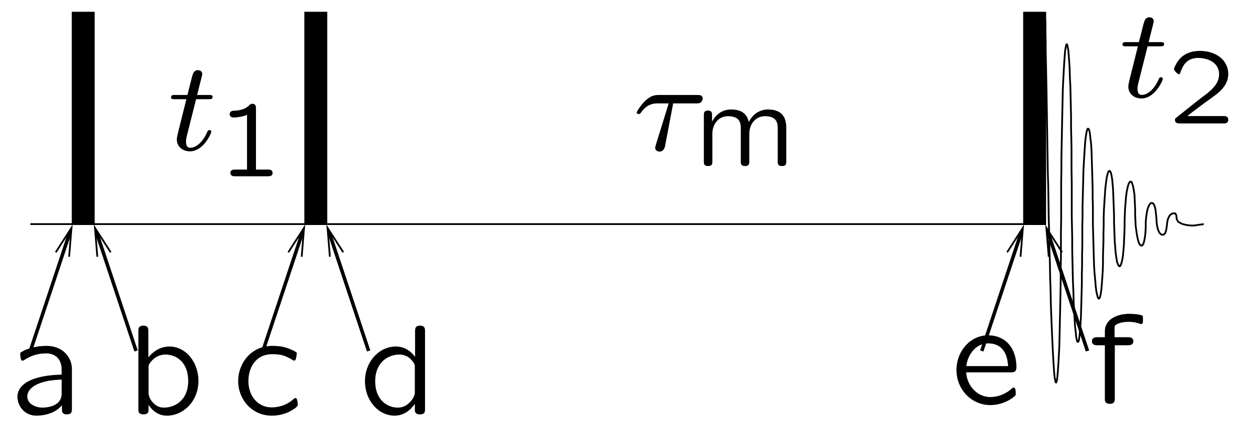
HOMEWORK:



$$\hat{\rho}(\mathrm{e}) = \frac{1}{2}\mathscr{I}_t - \mathcal{A}_1\mathscr{I}_{1z} - \mathcal{A}_2\mathscr{I}_{2z}$$

$$\mathcal{A}_1 = -\mathrm{e}^{-R_1\tau_\mathrm{m}}c_{11} \qquad \mathcal{A}_2 = -\mathrm{e}^{-R_1\tau_\mathrm{m}}c_{21}$$

HOMEWORK:

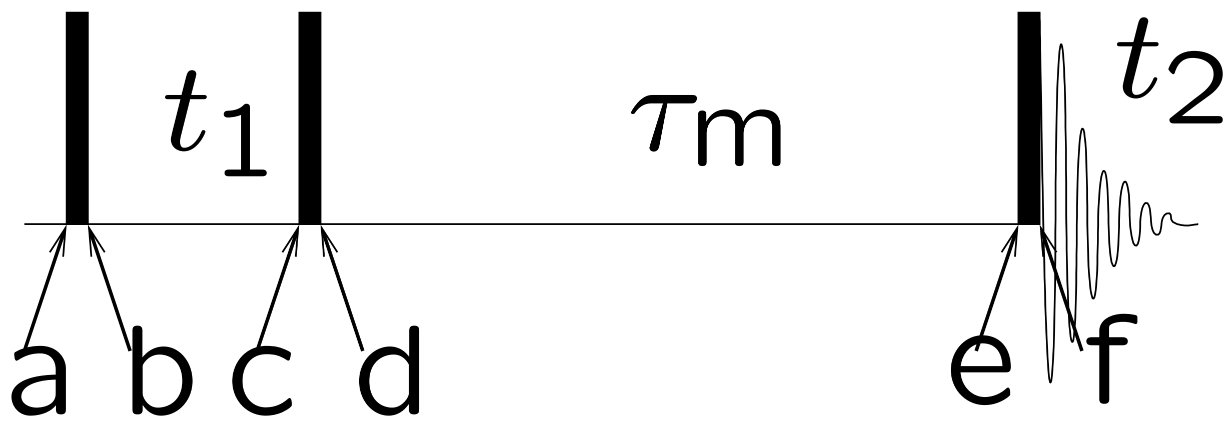


$$\hat{\rho}(\mathrm{e}) = \frac{1}{2}\mathscr{I}_t - \mathcal{A}_1\mathscr{I}_{1z} - \mathcal{A}_2\mathscr{I}_{2z}$$

$$\mathcal{A}_1 = -\mathrm{e}^{-R_1\tau_\mathrm{m}}c_{11} \qquad \mathcal{A}_2 = -\mathrm{e}^{-R_1\tau_\mathrm{m}}c_{21}$$

$$\hat{\rho}(\mathrm{f}) = \frac{1}{2}\mathscr{I}_t + \mathcal{A}_1\mathscr{I}_{1y} + \mathcal{A}_2\mathscr{I}_{2y}$$

HOMEWORK:



$$\hat{\rho}(\mathrm{e}) = \frac{1}{2}\mathscr{I}_t - \mathcal{A}_1\mathscr{I}_{1z} - \mathcal{A}_2\mathscr{I}_{2z}$$

$$\mathcal{A}_1 = -\mathrm{e}^{-R_1\tau_\mathrm{m}}c_{11} \qquad \mathcal{A}_2 = -\mathrm{e}^{-R_1\tau_\mathrm{m}}c_{21}$$

$$\hat{\rho}(\mathrm{f}) = \frac{1}{2}\mathscr{I}_t + \mathcal{A}_1\mathscr{I}_{1y} + \mathcal{A}_2\mathscr{I}_{2y}$$

$$\hat{\rho}(t_2) = \frac{1}{2}\mathscr{I}_t$$

$$+\mathcal{A}_1(\cos(\Omega_1 t_2)\mathscr{I}_{1y} - \sin(\Omega_1 t_2)\mathscr{I}_{1x})$$

$$+\mathcal{A}_2(\cos(\Omega_2 t_2)\mathscr{I}_{2y} - \sin(\Omega_2 t_2)\mathscr{I}_{2x})$$

MODULATION IN 2D EXPERIMENT

$$\widehat{M}_+ = \mathcal{N}\left(\gamma_1(\widehat{I}_{1x} + \mathrm{i}\widehat{I}_{1y}) + \gamma_2(\widehat{I}_{2x} + \mathrm{i}\widehat{I}_{2y})\right)$$

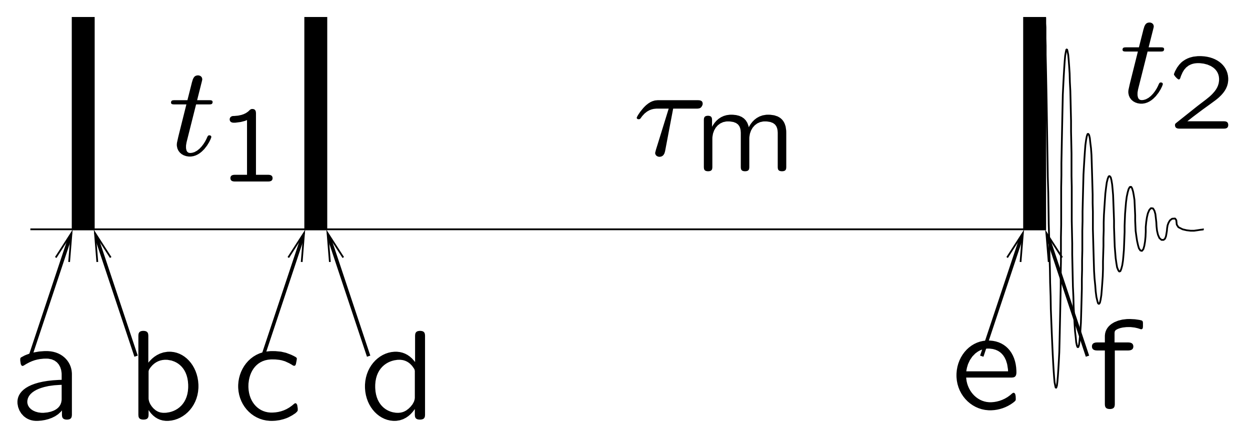
$$\mathrm{Tr}\left\{\mathscr{I}_{nx}(\mathscr{I}_{nx} + \mathrm{i}\mathscr{I}_{ny})\right\} = 1$$

$$\mathrm{Tr}\left\{\mathscr{I}_{ny}(\mathscr{I}_{nx} + \mathrm{i}\mathscr{I}_{ny})\right\} = \mathrm{i}$$

$$\begin{aligned}\langle M_+\rangle &= \mathrm{Tr}\{\widehat{\rho}(t_2)\widehat{M}_+\} \\ &= \mathcal{N}\gamma\hbar\mathcal{A}_1\left(\mathrm{e}^{-R_{2,1}t_2}\cos(\Omega_1 t_2) - \mathrm{i}\mathrm{e}^{-R_{2,1}t_2}\sin(\Omega_1 t_2)\right) \\ &+ \mathcal{N}\gamma\hbar\mathcal{A}_2\left(\mathrm{e}^{-R_{2,2}t_2}\cos(\Omega_2 t_2) - \mathrm{i}\mathrm{e}^{-R_{2,2}t_2}\sin(\Omega_2 t_2)\right)\end{aligned}$$

$$\begin{aligned}Y(\omega) &= \mathcal{N}\gamma\hbar\left(\frac{\mathcal{A}_1 R_{2,1}}{R_{2,1}^2 + (\omega - \Omega_1)^2} + \frac{\mathcal{A}_2 R_{2,2}}{R_{2,2}^2 + (\omega - \Omega_2)^2}\right) \\ &- \mathrm{i}\mathcal{N}\gamma\hbar\left(\frac{\mathcal{A}_1(\omega - \Omega_1)}{R_{2,1}^2 + (\omega - \Omega_1)^2} + \frac{\mathcal{A}_2(\omega - \Omega_2)}{R_{2,2}^2 + (\omega - \Omega_2)^2}\right)\end{aligned}$$

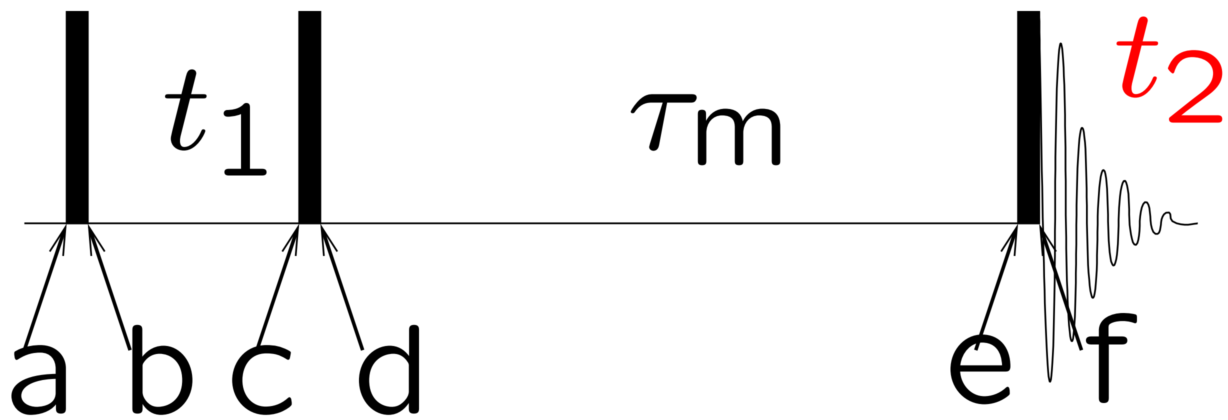
MODULATION IN 2D EXPERIMENT



$$\langle M_+\rangle = \mathcal{N}\frac{\gamma^2\hbar^2 B_0}{8k_\mathrm{B}T}\Big(
\mathrm{e}^{-R_{1,1}\tau_\mathrm{m}}\mathrm{e}^{-R_{2,1}t_1}\cos(\Omega_1 t_1)\left(\mathrm{e}^{-R_{2,1}t_2}\cos(\Omega_1 t_2) - \mathrm{i}\mathrm{e}^{-R_{2,1}t_2}\sin(\Omega_1 t_2)\right) +
\mathrm{e}^{-R_{1,2}\tau_\mathrm{m}}\mathrm{e}^{-R_{2,2}t_1}\cos(\Omega_2 t_1)\left(\mathrm{e}^{-R_{2,2}t_2}\cos(\Omega_2 t_2) - \mathrm{i}\mathrm{e}^{-R_{2,2}t_2}\sin(\Omega_2 t_2)\right)
\Big)$$

$$\Re Y = \mathcal{N}\frac{\gamma^2\hbar^2 B_0}{8k_\mathrm{B}T}\mathrm{e}^{-R_{1,1}\tau_\mathrm{m}}\mathrm{e}^{-R_{2,1}t_1}\cos(\Omega_1 t_1)\frac{R_{2,1}}{R_{2,1}^2 + (\omega - \Omega_1)^2}
+\mathcal{N}\frac{\gamma^2\hbar^2 B_0}{8k_\mathrm{B}T}\mathrm{e}^{-R_{1,2}\tau_\mathrm{m}}\mathrm{e}^{-R_{2,2}t_1}\cos(\Omega_2 t_1)\frac{R_{2,2}}{R_{2,2}^2 + (\omega - \Omega_2)^2}$$

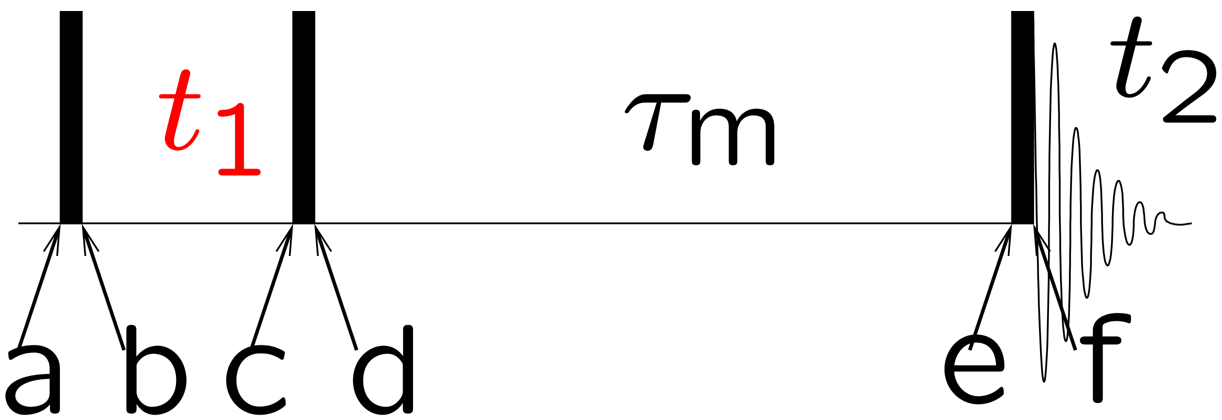
MODULATION IN 2D EXPERIMENT



$$\langle M_+\rangle = \mathcal{N}\frac{\gamma^2\hbar^2 B_0}{8k_\mathrm{B}T}\Big($$
$$\mathrm{e}^{-R_{1,1}\tau_\mathrm{m}}\mathrm{e}^{-R_{2,1}t_1}\cos(\Omega_1 t_1)\left(\mathrm{e}^{-R_{2,1}t_2}\cos(\Omega_1 t_2) - \mathrm{i}\mathrm{e}^{-R_{2,1}t_2}\sin(\Omega_1 t_2)\right) +$$
$$\mathrm{e}^{-R_{1,2}\tau_\mathrm{m}}\mathrm{e}^{-R_{2,2}t_1}\cos(\Omega_2 t_1)\left(\mathrm{e}^{-R_{2,2}t_2}\cos(\Omega_2 t_2) - \mathrm{i}\mathrm{e}^{-R_{2,2}t_2}\sin(\Omega_2 t_2)\right)$$
$$\Big)$$

$$\Re Y = \mathcal{N}\frac{\gamma^2\hbar^2 B_0}{8k_\mathrm{B}T}\mathrm{e}^{-R_{1,1}\tau_\mathrm{m}}\mathrm{e}^{-R_{2,1}t_1}\cos(\Omega_1 t_1)\frac{R_{2,1}}{R_{2,1}^2 + (\omega - \Omega_1)^2}$$
$$+\mathcal{N}\frac{\gamma^2\hbar^2 B_0}{8k_\mathrm{B}T}\mathrm{e}^{-R_{1,2}\tau_\mathrm{m}}\mathrm{e}^{-R_{2,2}t_1}\cos(\Omega_2 t_1)\frac{R_{2,2}}{R_{2,2}^2 + (\omega - \Omega_2)^2}$$

MODULATION IN 2D EXPERIMENT



$$\langle M_+\rangle = \mathcal{N}\frac{\gamma^2\hbar^2 B_0}{8k_\mathrm{B}T}\Big($$

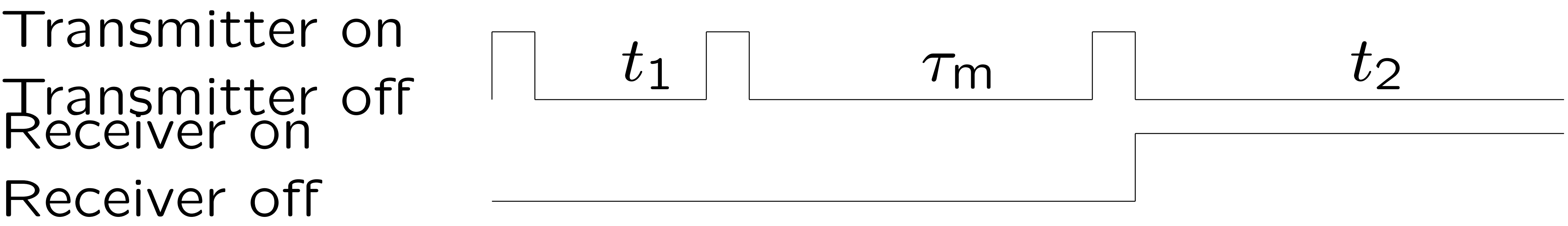
$$\mathrm{e}^{-R_{1,1}\tau_\mathrm{m}}\mathrm{e}^{-R_{2,1}t_1}\cos(\Omega_1 t_1)\left(\mathrm{e}^{-R_{2,1}t_2}\cos(\Omega_1 t_2) - \mathrm{i}\mathrm{e}^{-R_{2,1}t_2}\sin(\Omega_1 t_2)\right) +$$

$$\mathrm{e}^{-R_{1,2}\tau_\mathrm{m}}\mathrm{e}^{-R_{2,2}t_1}\cos(\Omega_2 t_1)\left(\mathrm{e}^{-R_{2,2}t_2}\cos(\Omega_2 t_2) - \mathrm{i}\mathrm{e}^{-R_{2,2}t_2}\sin(\Omega_2 t_2)\right)$$

$$\Big)$$

$$\Re Y = \mathcal{N}\frac{\gamma^2\hbar^2 B_0}{8k_\mathrm{B}T}\mathrm{e}^{-R_{1,1}\tau_\mathrm{m}}\mathrm{e}^{-R_{2,1}t_1}\cos(\Omega_1 t_1)\frac{R_{2,1}}{R_{2,1}^2 + (\omega-\Omega_1)^2}$$

$$+\mathcal{N}\frac{\gamma^2\hbar^2 B_0}{8k_\mathrm{B}T}\mathrm{e}^{-R_{1,2}\tau_\mathrm{m}}\mathrm{e}^{-R_{2,2}t_1}\cos(\Omega_2 t_1)\frac{R_{2,2}}{R_{2,2}^2 + (\omega-\Omega_2)^2}$$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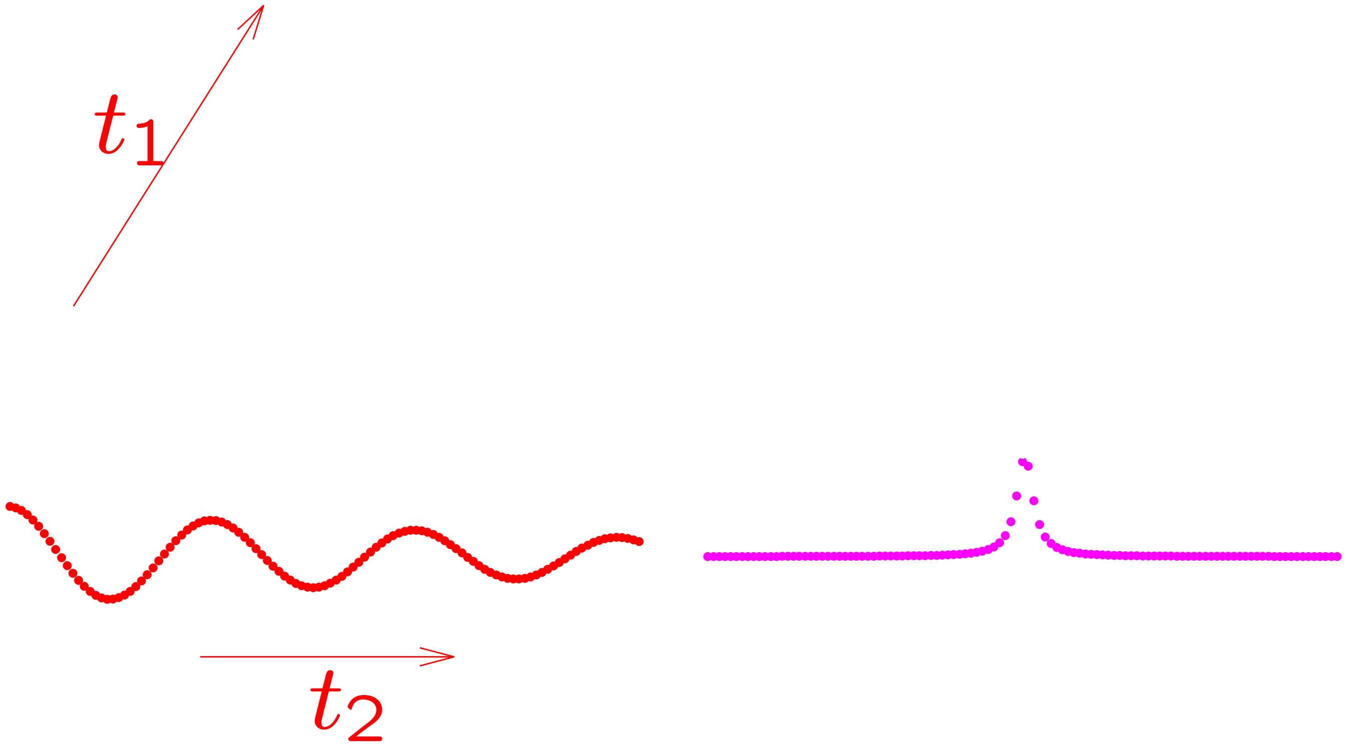
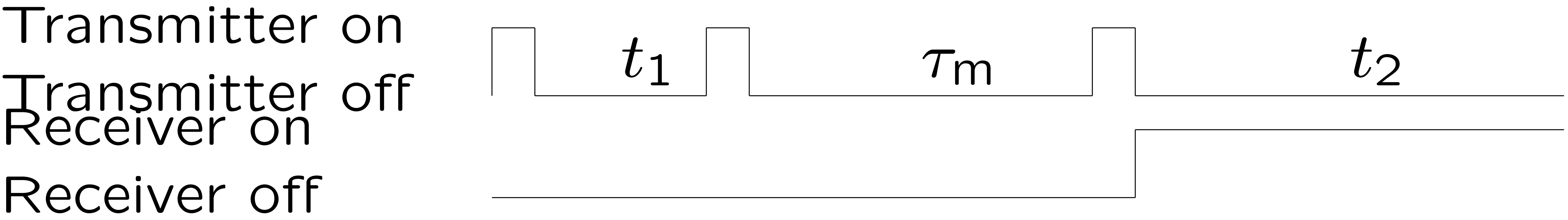
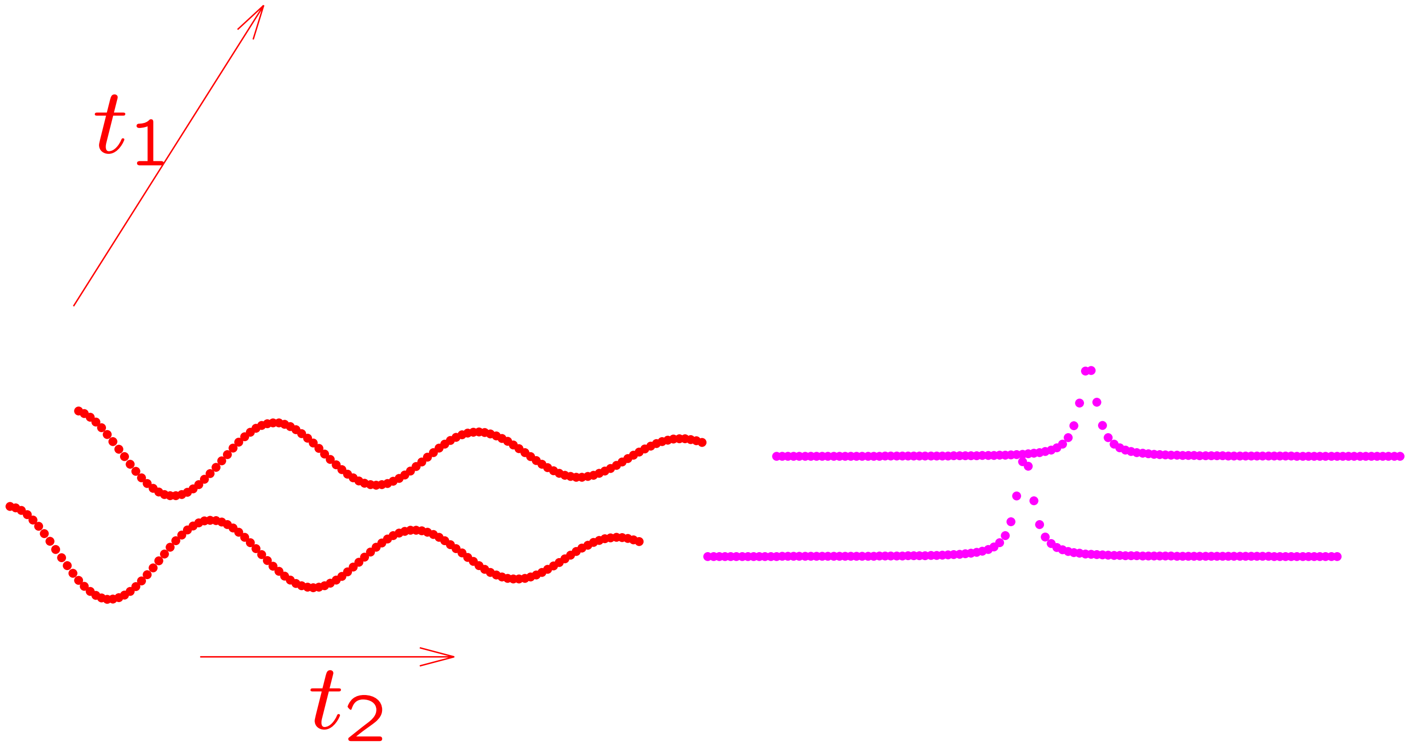
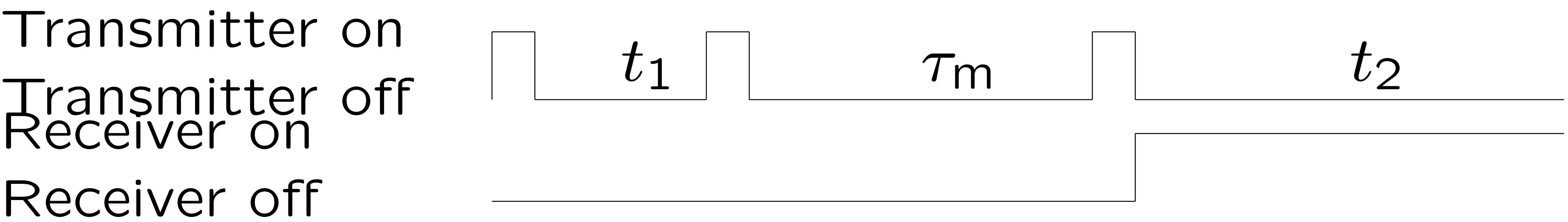
Transmitter off
Receiver on
Receiver off
t_1
τ_m
t_2


t_1
t_2


Transmitter on
Transmitter off
Receiver on
Receiver off
t_1
τ_m
t_2


t_1
t_2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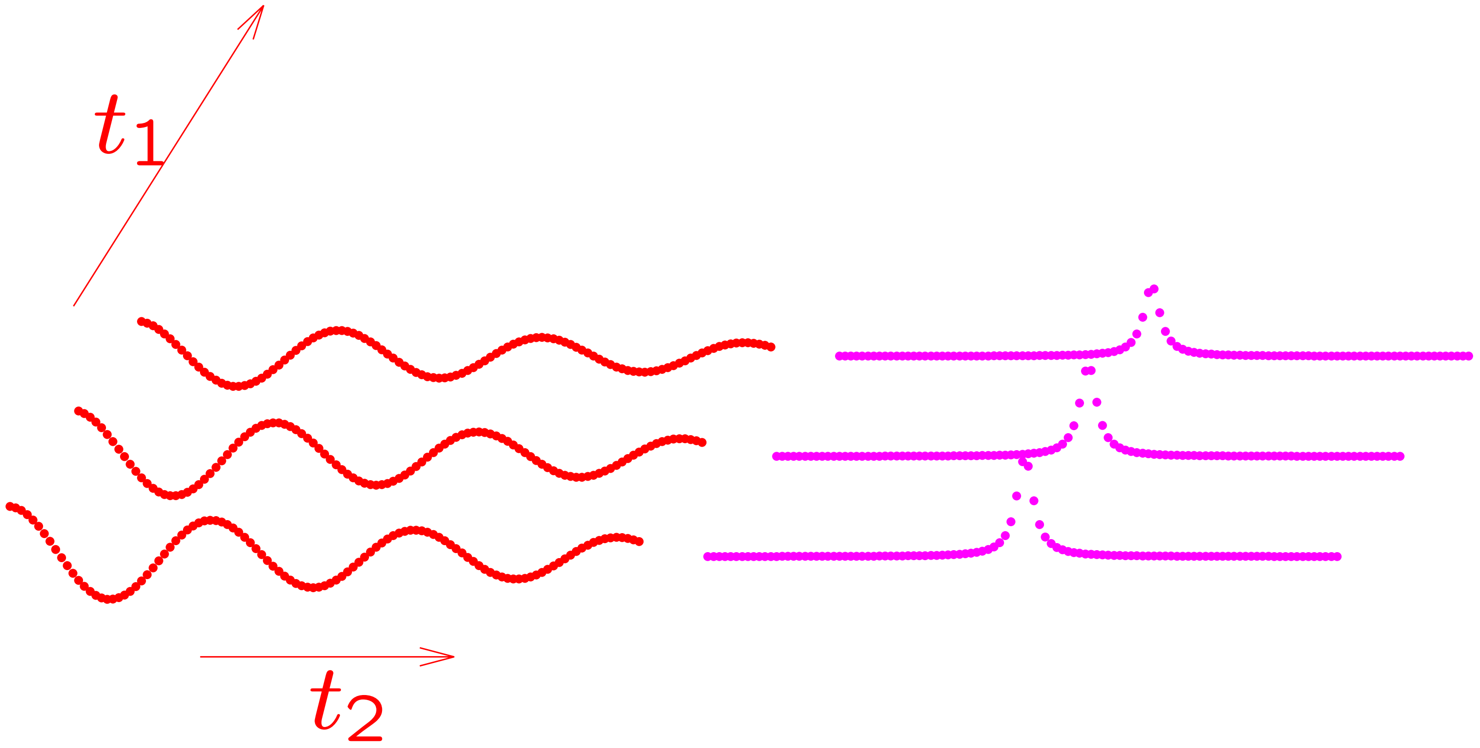
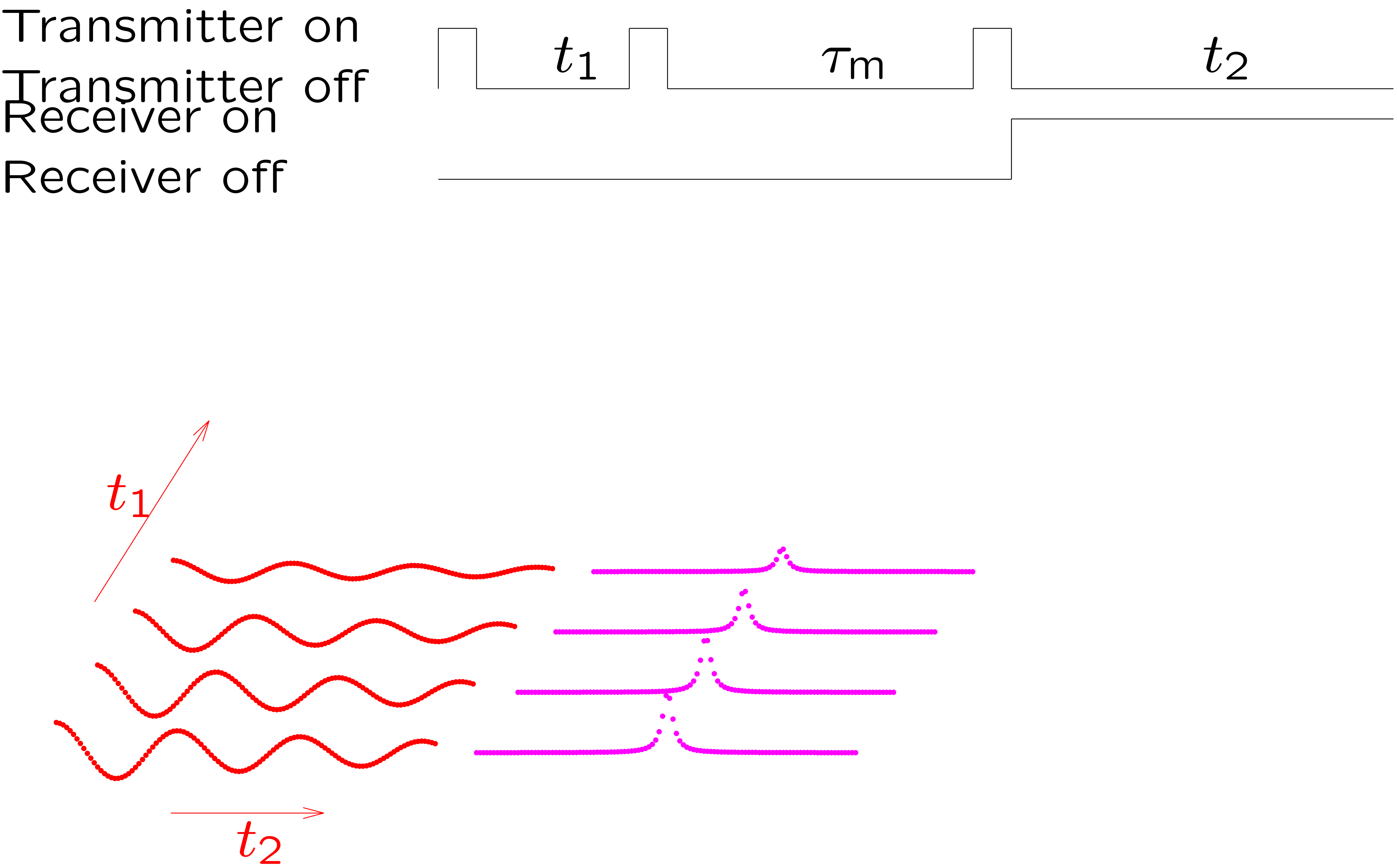
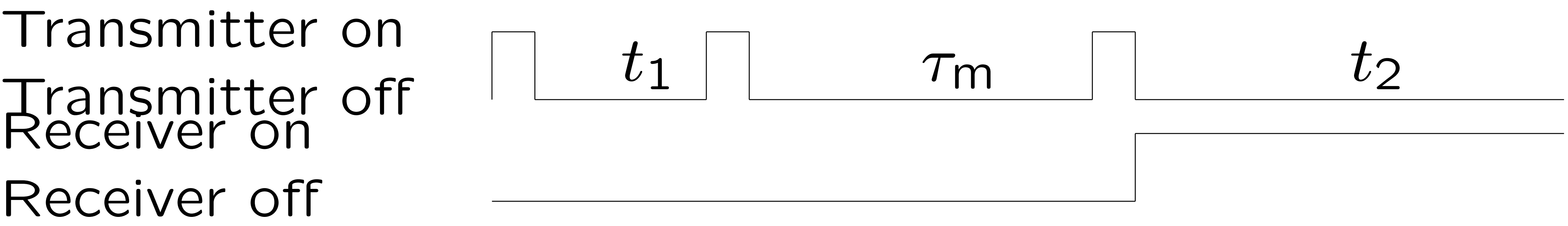
t_1
τ_m
t_2

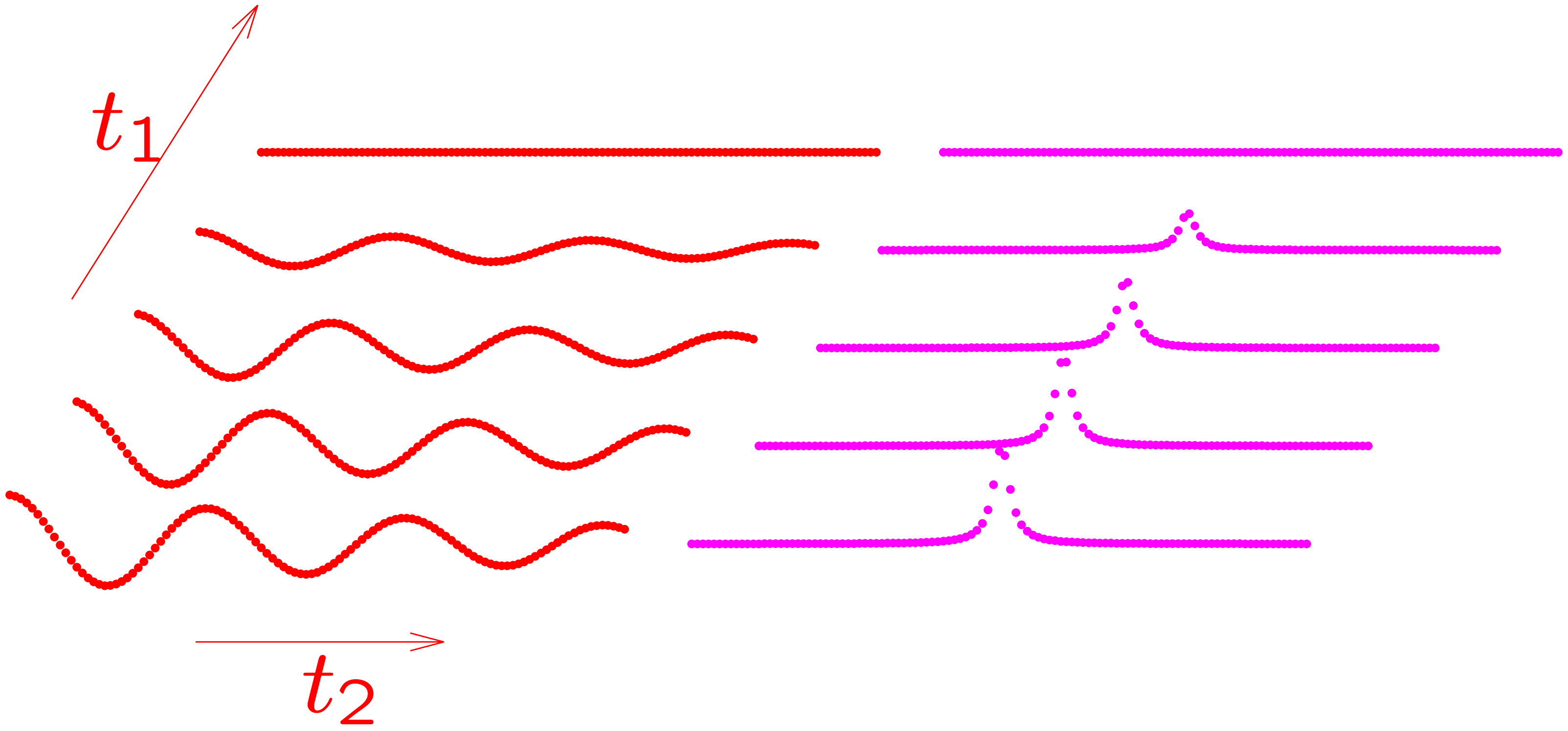

t_1
t_2



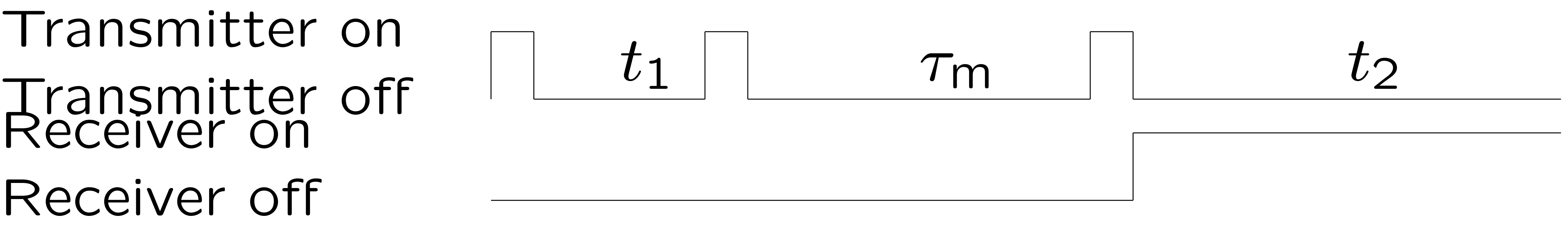
Transmitter on
Transmitter off
Receiver on
Receiver off
t_1
τ_m
t_2
t_1
t_2

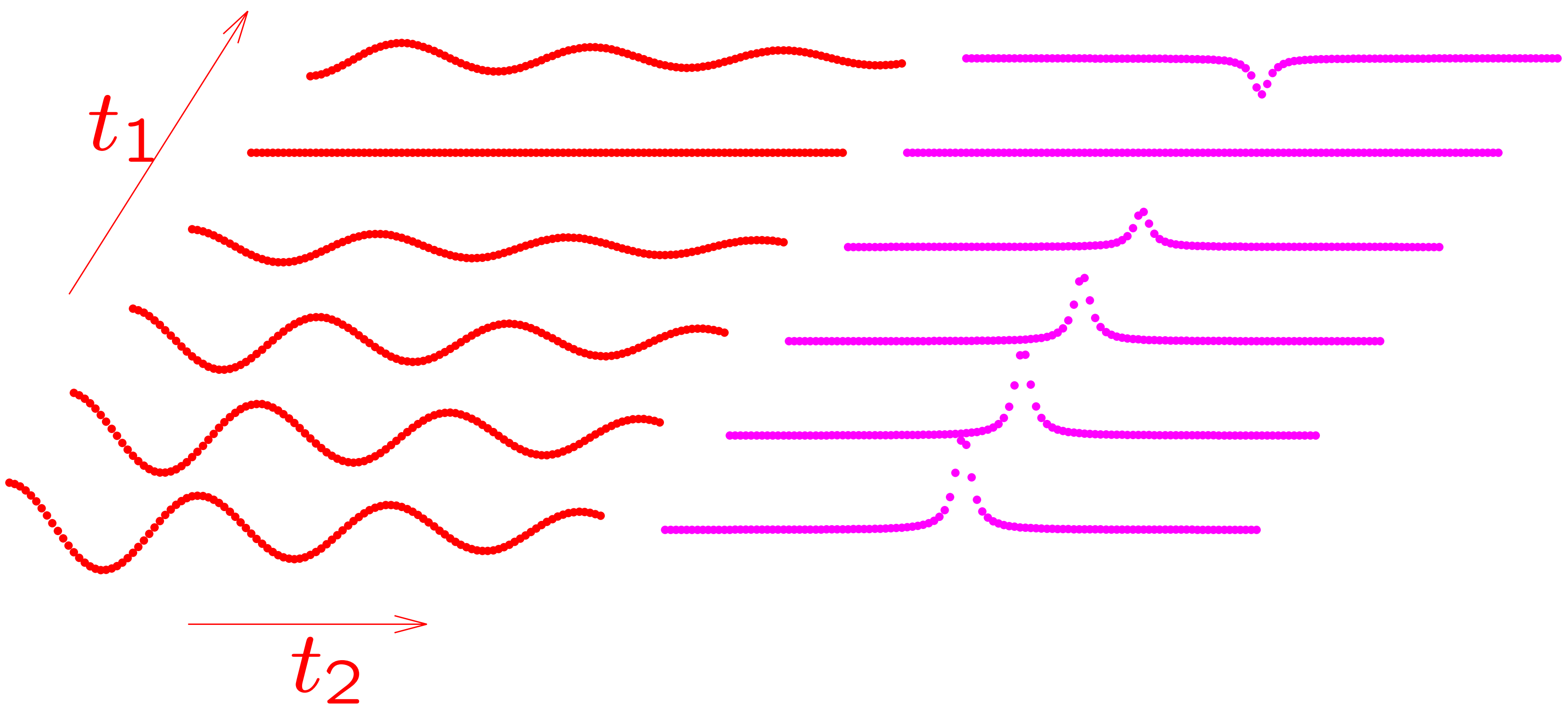


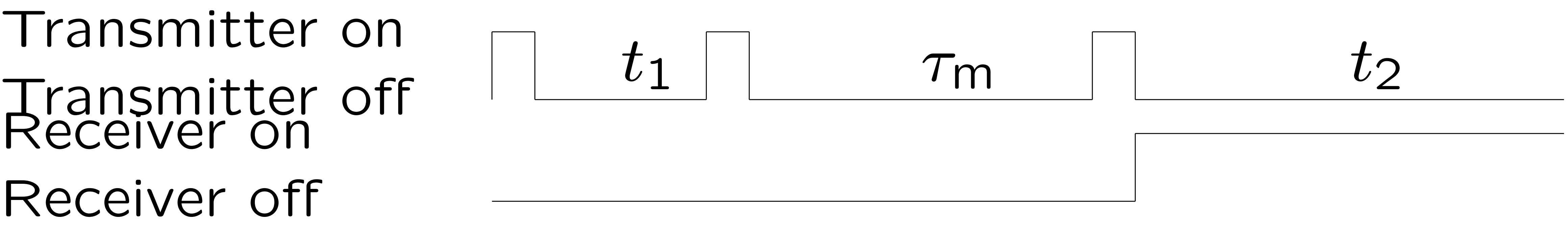
Transmitter on
Transmitter off
Receiver on
Receiver off
t_1
τ_m
t_2

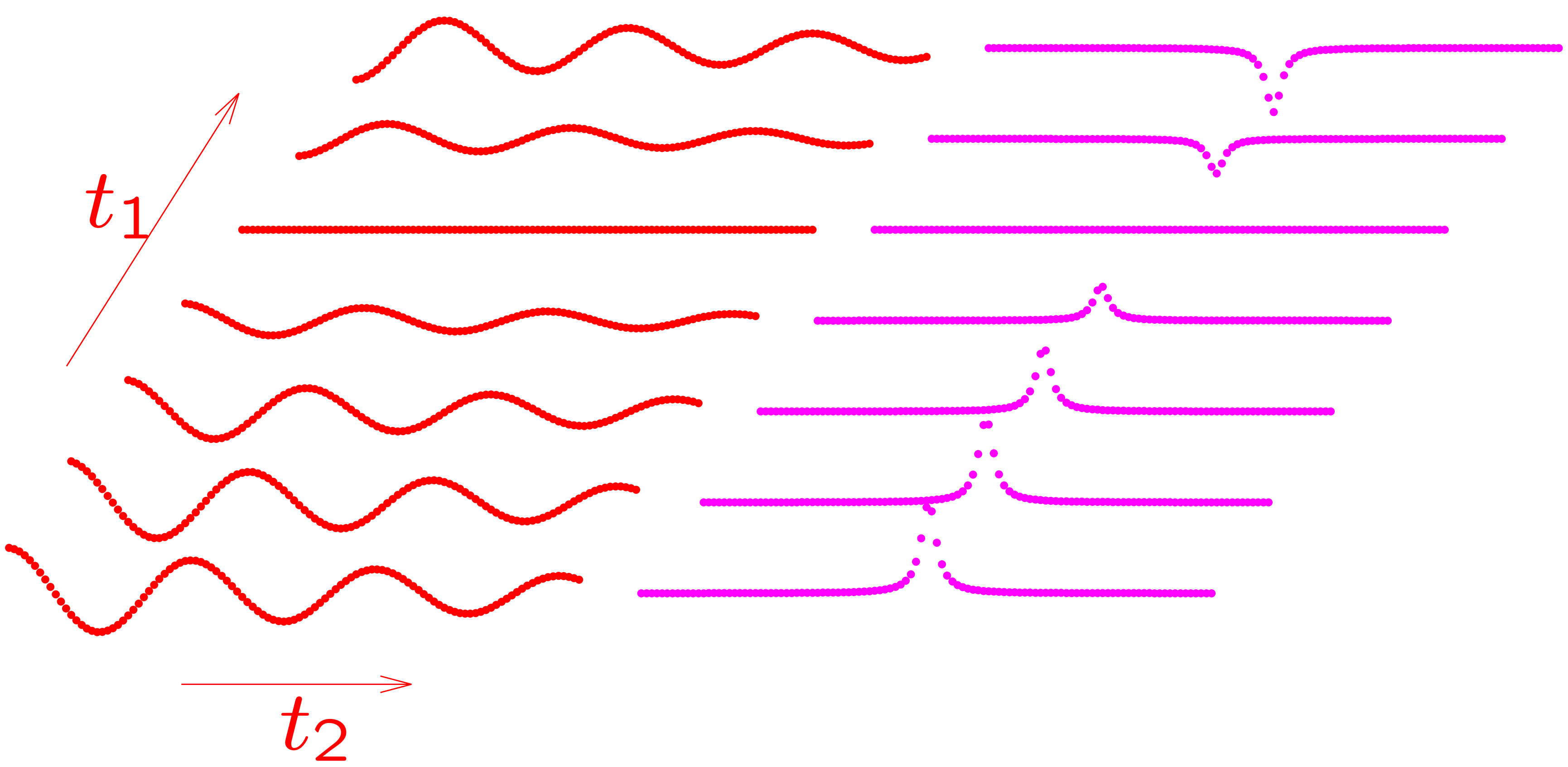


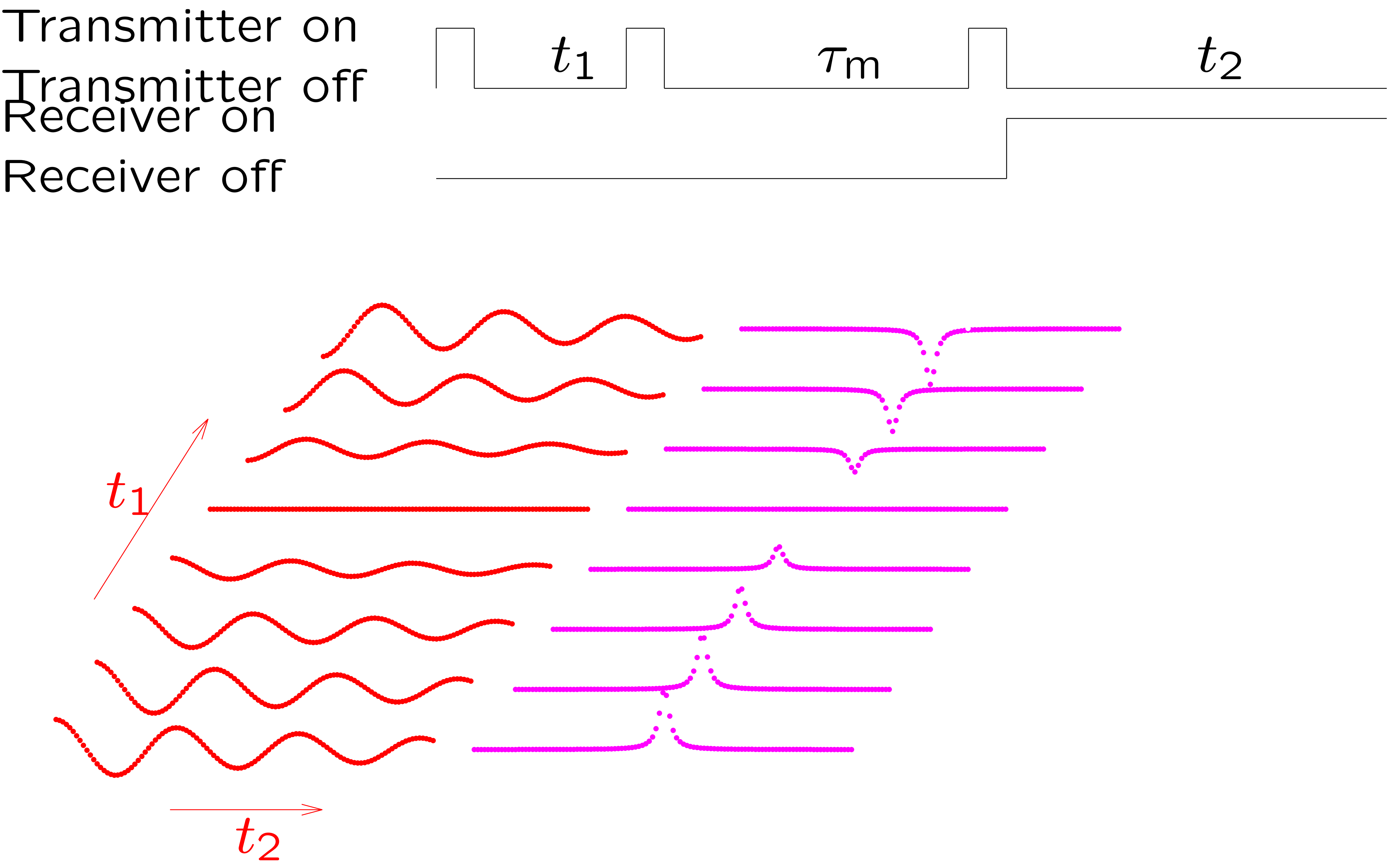
t_1
t_2


Transmitter on
Transmitter off
Receiver on
Receiver off
t_1
τ_m
t_2

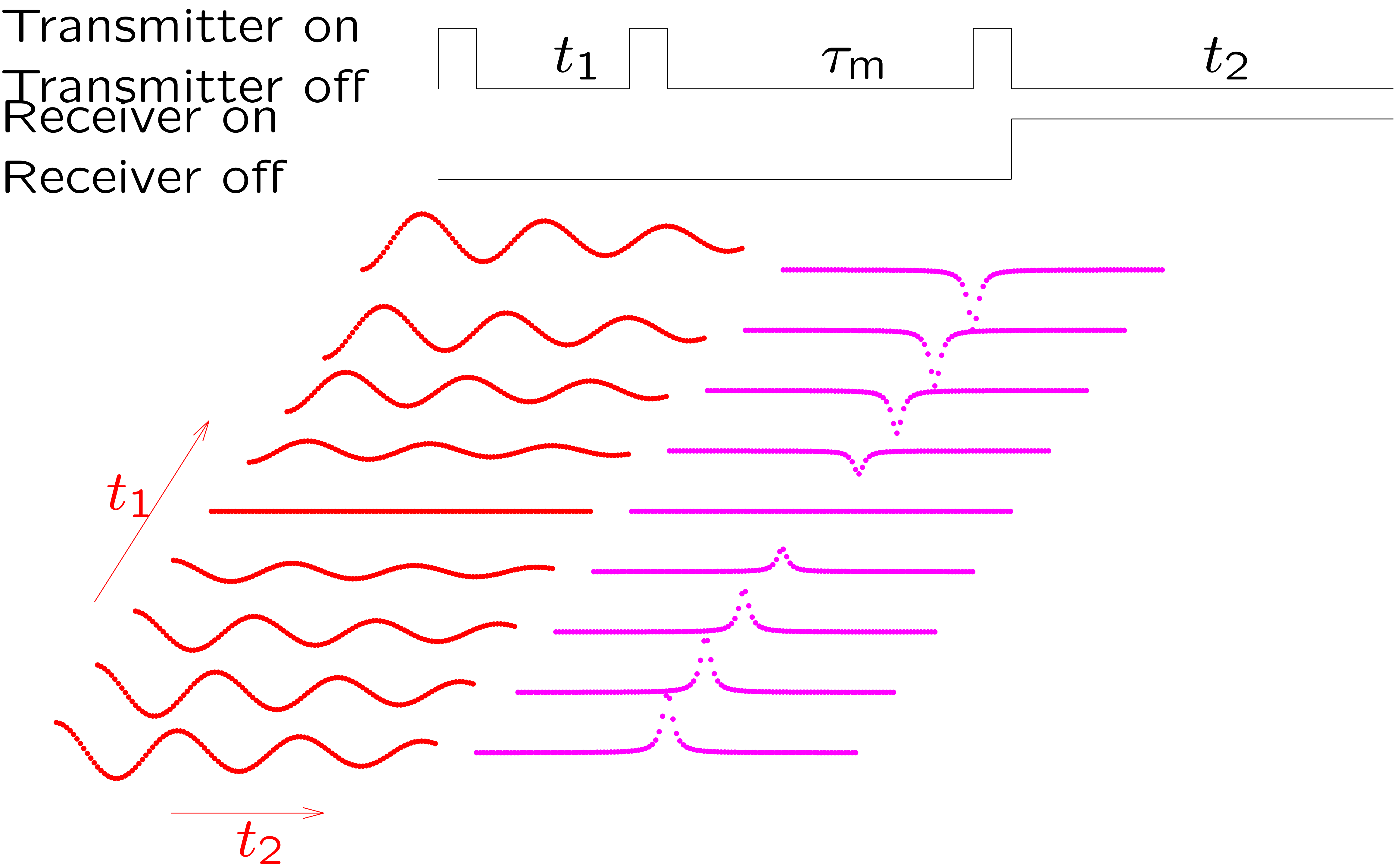

t_1
t_2


Transmitter on
Transmitter off
Receiver on
Receiver off
t_1
τ_m
t_2

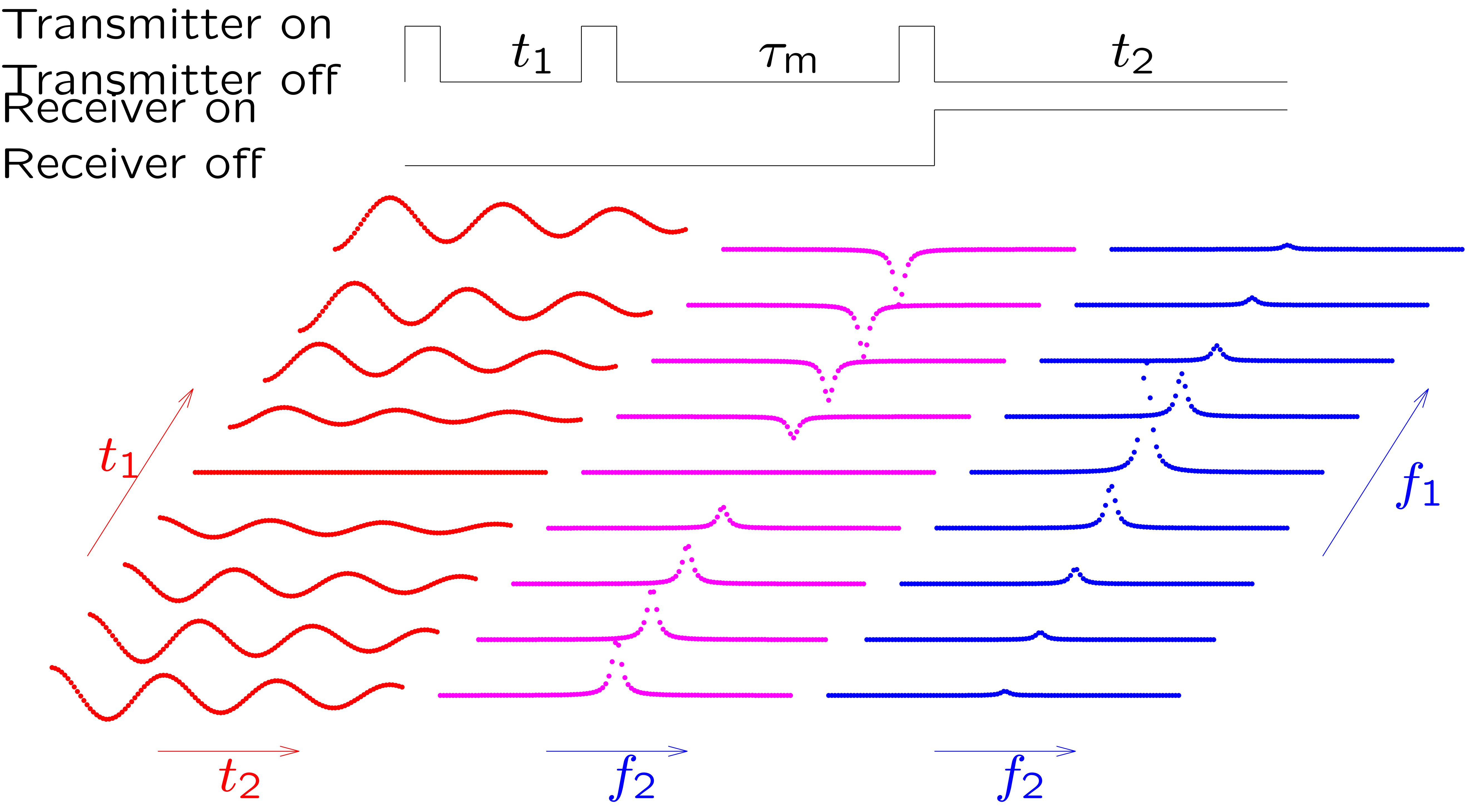

t_1
t_2



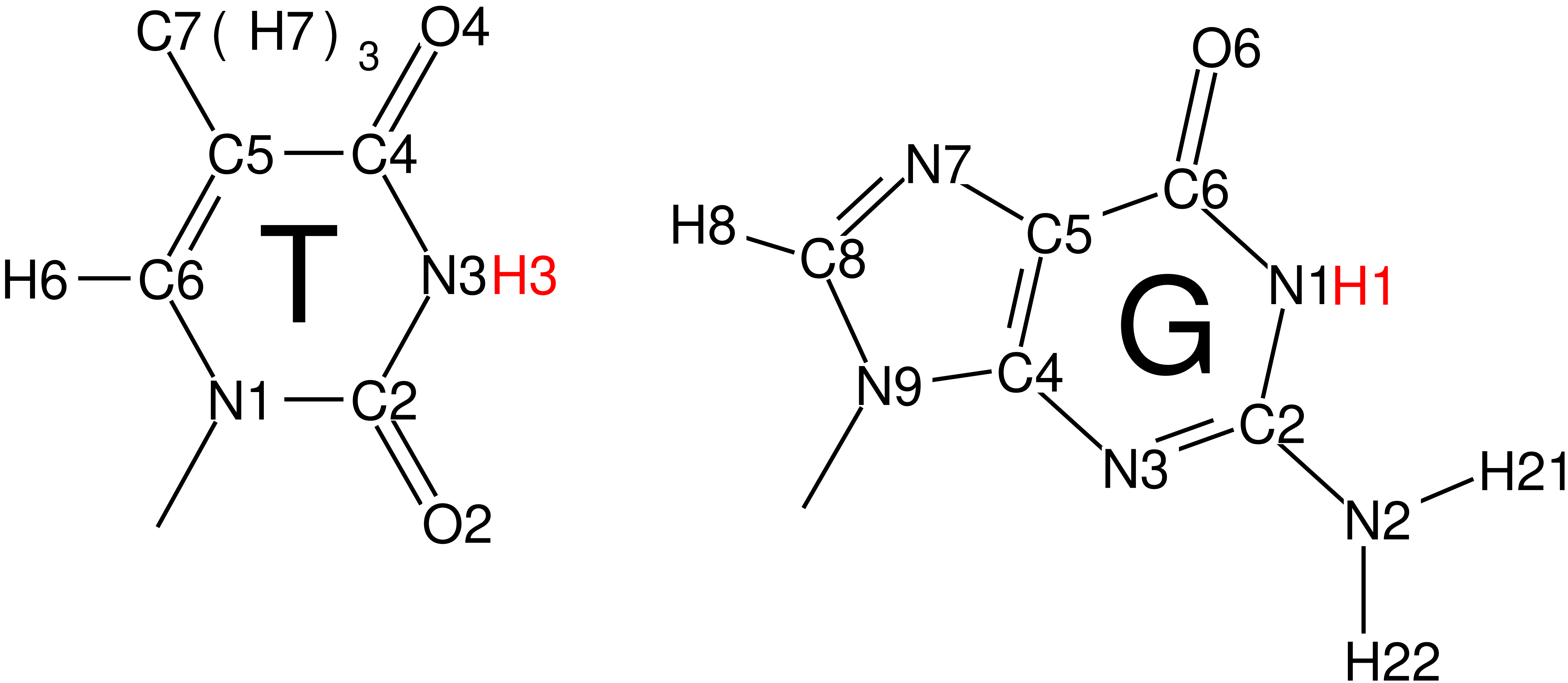
Transmitter on
Transmitter off
Receiver on
Receiver off
t_1
τ_m
t_2
t_1
t_2

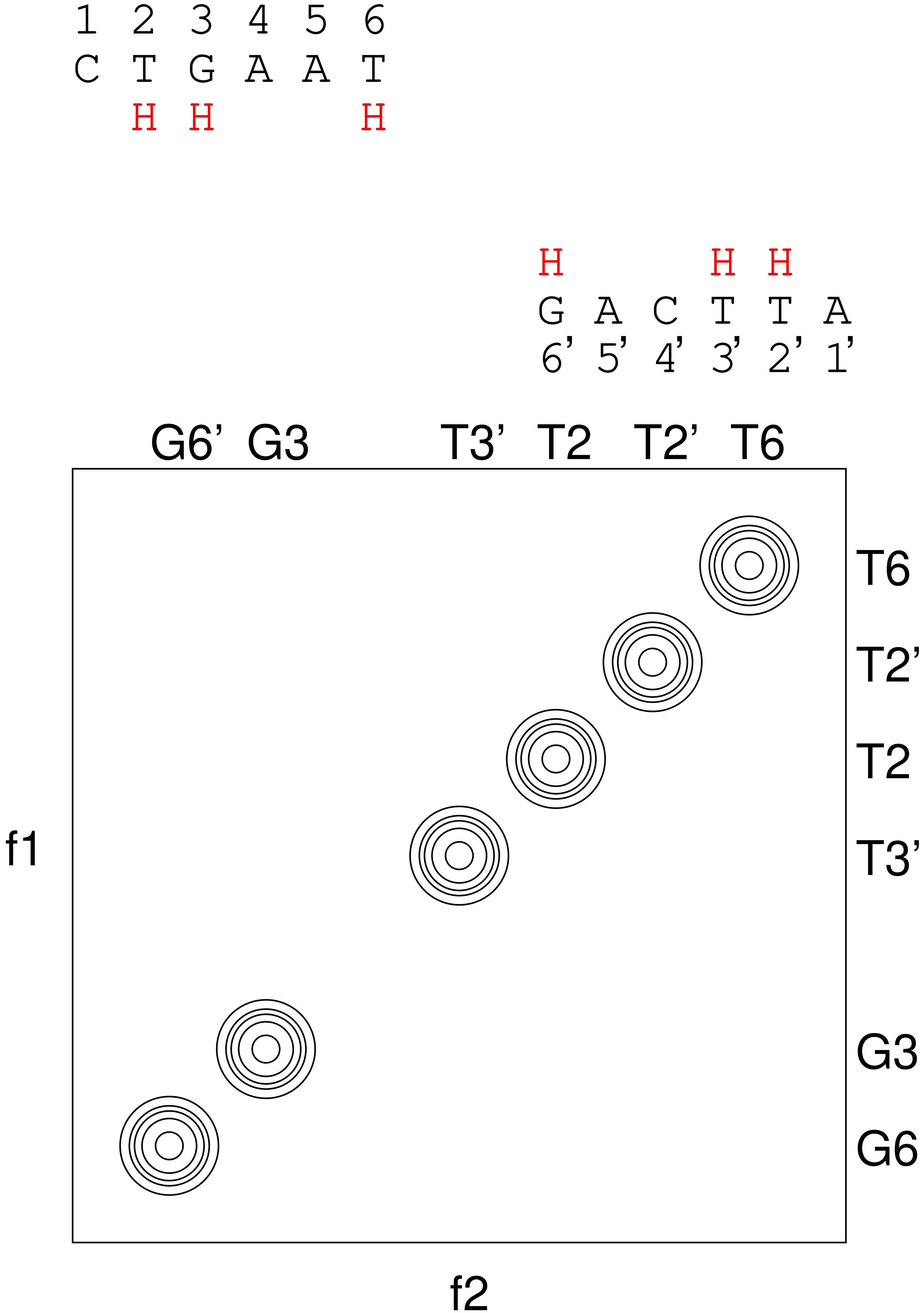


Transmitter on
Transmitter off
Receiver on
Receiver off
t_1
τ_m
t_2
t_1
t_2



Transmitter on
Transmitter off
Receiver on
Receiver off
t_1
τ_m
t_2
t_1
f_1
t_2
f_2
f_2


C7(H7)3
O4
C5
C4
T
H6
C6
N3H3
N1
C2
O2
O6
N7
C6
H8
C8
C5
N1H1
G
N9
C4
C2
N3
H21
N2
H22



1 2 3 4 5 6
C T G A A T
H H H
H H H
G A C T T A
6' 5' 4' 3' 2' 1'
G6' G3 T3' T2 T2' T6
T6
T2'
T2
T3'
G3
G6
f1
f2

Relaxation due to dipolar coupling

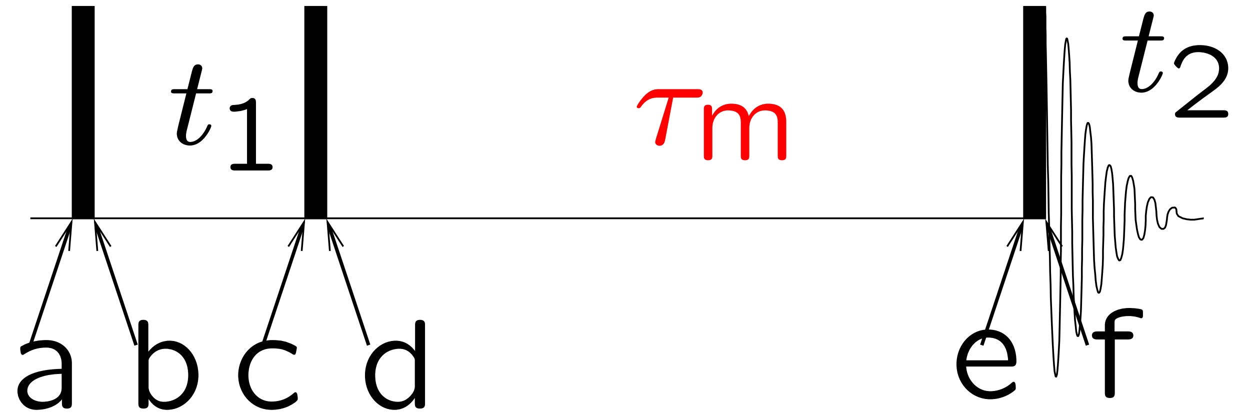
Bloch-Wangsness-Redfield theory applicable

dipolar coupling: different Hamiltonian, large effect

$$\text{dipolar } b = -\frac{\mu_0\gamma_1\gamma_2\hbar}{4\pi r^3}$$

$$\begin{aligned}
\frac{\mathrm{d}\Delta\langle M_{1z}\rangle}{\mathrm{d}t} &= -\frac{b^2}{8}(6J(\omega_{0,1})+2J(\omega_{0,1}-\omega_{0,2})+12J(\omega_{0,1}+\omega_{0,2}))\Delta\langle M_{1z}\rangle \\
&+ \frac{b^2}{8}(2J(\omega_{0,1}-\omega_{0,2})-12J(\omega_{0,1}+\omega_{0,2}))\Delta\langle M_{2z}\rangle \\
&= -R_{\mathrm{a}1}\Delta\langle M_{1z}\rangle - R_{\mathrm{x}}\Delta\langle M_{2z}\rangle \\
\frac{\mathrm{d}\Delta\langle M_{2z}\rangle}{\mathrm{d}t} &= -\frac{b^2}{8}(6J(\omega_{0,2})+2J(\omega_{0,1}-\omega_{0,2})+12J(\omega_{0,1}+\omega_{0,2}))\Delta\langle M_{2z}\rangle \\
&+ \frac{b^2}{8}(2J(\omega_{0,1}-\omega_{0,2})-12J(\omega_{0,1}+\omega_{0,2}))\Delta\langle M_{1z}\rangle \\
&= -R_{\mathrm{a}2}\Delta\langle M_{2z}\rangle - R_{\mathrm{x}}\Delta\langle M_{1z}\rangle \\
\frac{\mathrm{d}\langle M_{1+}\rangle}{\mathrm{d}t} &= -\frac{b^2}{8}(4J(0)+3J(\omega_{0,1})+6J(\omega_{0,2}) \\
&\quad +J(\omega_{0,1}-\omega_{0,2})+6J(\omega_{0,1}+\omega_{0,2}))\langle M_{1+}\rangle \\
&= -\left(R_{0,1}+\frac{1}{2}R_{\mathrm{a}1}\right)\langle M_{1+}\rangle = -R_{2,1}\langle M_{1+}\rangle
\end{aligned}$$

NOESY



$$\langle M_+\rangle = \mathcal{N}\gamma\hbar\,\Big(\mathcal{A}_1 \quad \left(\mathrm{e}^{-R_{2,1}t_2}\cos(\Omega_1 t_2) - \mathrm{i}\mathrm{e}^{-R_{2,1}t_2}\sin(\Omega_1 t_2)\right) + \mathcal{A}_2 \quad \left(\mathrm{e}^{-R_{2,2}t_2}\cos(\Omega_2 t_2) - \mathrm{i}\mathrm{e}^{-R_{2,2}t_2}\sin(\Omega_2 t_2)\right)\Big)$$

$$\Re Y = \mathcal{N}\gamma\ \mathcal{A}_1\ \frac{R_{2,1}}{R_{2,1}^2 + (\omega - \Omega_1)^2} + \mathcal{N}\gamma\hbar\ \mathcal{A}_2\ \frac{R_{2,2}}{R_{2,2}^2 + (\omega - \Omega_2)^2}$$

NOESY

$$-\frac{\mathrm{d}\Delta\langle M_{1z}\rangle}{\mathrm{d}t} = R_{\mathrm{a}1}\Delta\langle M_{1z}\rangle + R_{\mathrm{x}}\Delta\langle M_{2z}\rangle$$

$$-\frac{\mathrm{d}\Delta\langle M_{2z}\rangle}{\mathrm{d}t} = R_{\mathrm{a}2}\Delta\langle M_{2z}\rangle + R_{\mathrm{x}}\Delta\langle M_{1z}\rangle$$

NOESY

$$-\frac{\mathrm{d}\Delta\langle M_{1z}\rangle}{\mathrm{d}t} = R_\mathrm{a}\Delta\langle M_{1z}\rangle + R_\mathrm{x}\Delta\langle M_{2z}\rangle$$

$$-\frac{\mathrm{d}\Delta\langle M_{2z}\rangle}{\mathrm{d}t} = R_\mathrm{a}\Delta\langle M_{2z}\rangle + R_\mathrm{x}\Delta\langle M_{1z}\rangle$$

NOESY

$$-\frac{\mathrm{d}\Delta\langle M_{1z}\rangle}{\mathrm{d}t} = R_{\mathrm{a}}\Delta\langle M_{1z}\rangle + R_{\mathrm{x}}\Delta\langle M_{2z}\rangle$$

$$-\frac{\mathrm{d}\Delta\langle M_{2z}\rangle}{\mathrm{d}t} = R_{\mathrm{a}}\Delta\langle M_{2z}\rangle + R_{\mathrm{x}}\Delta\langle M_{1z}\rangle$$

HOMEWORK

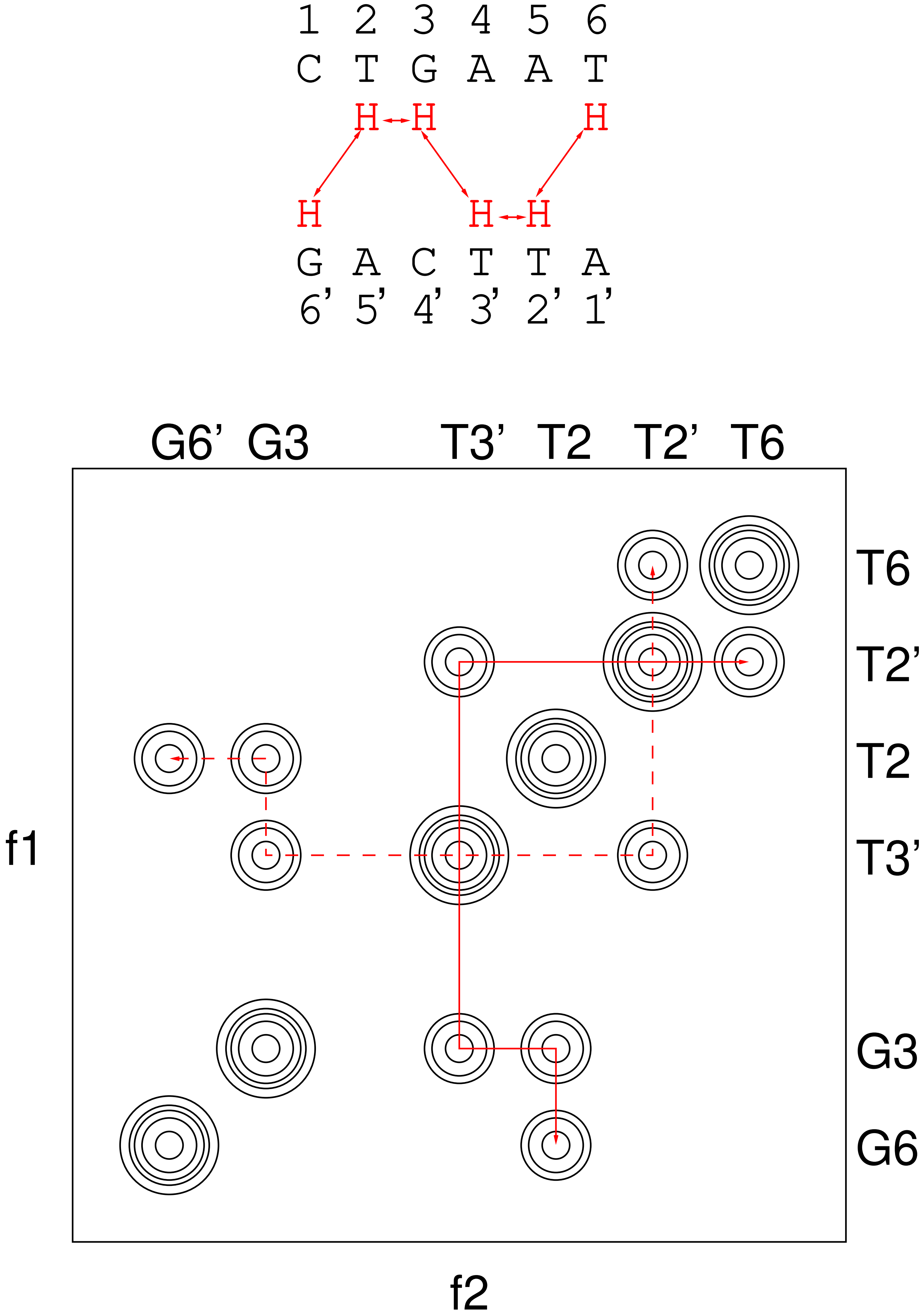
Sections 9.4, 9.5.1, 9.5.2

NOESY

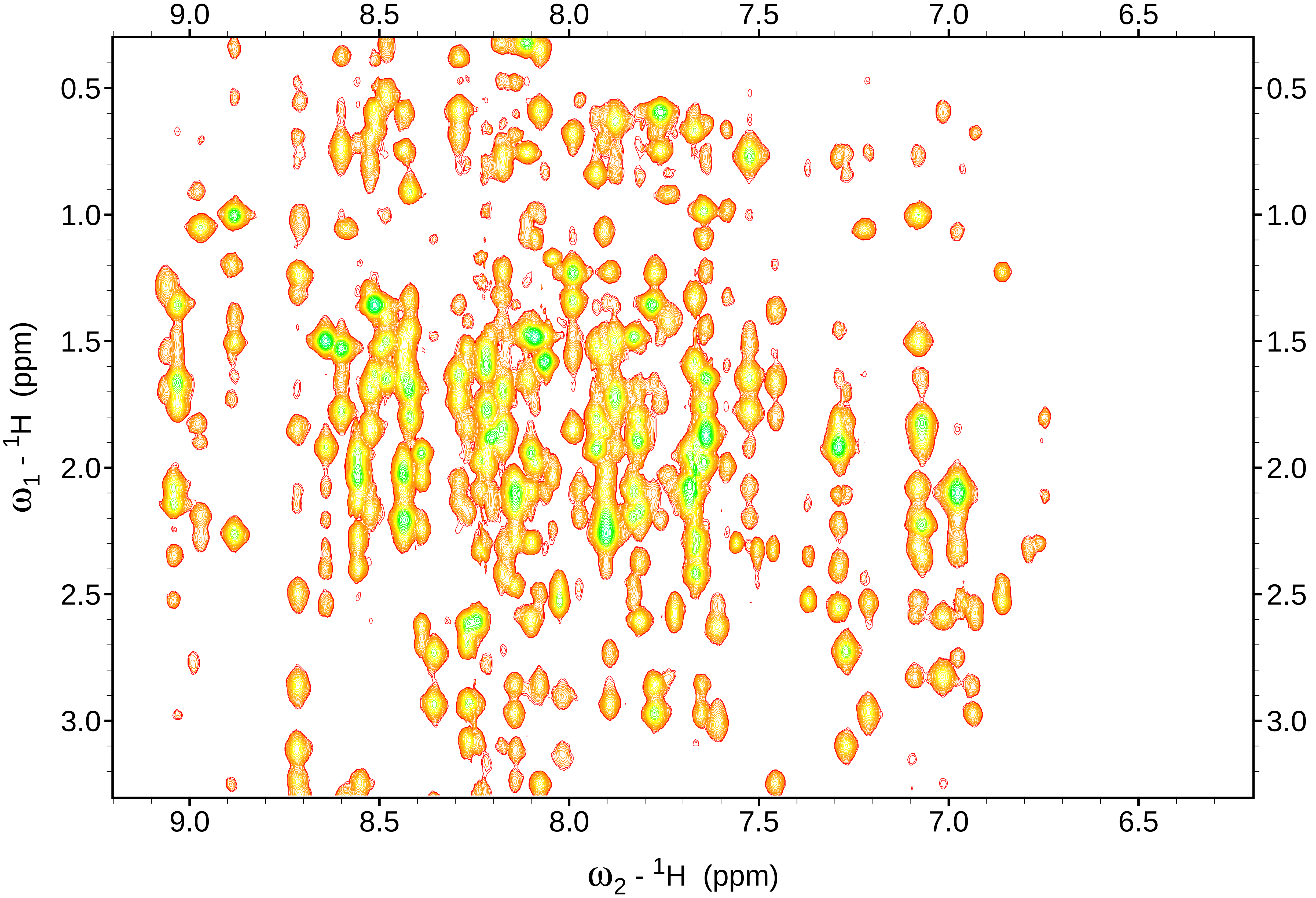
$$-\frac{\mathrm{d}\Delta\langle M_{1z}\rangle}{\mathrm{d}t} = R_\mathrm{a}\Delta\langle M_{1z}\rangle + R_\mathrm{x}\Delta\langle M_{2z}\rangle$$
$$-\frac{\mathrm{d}\Delta\langle M_{2z}\rangle}{\mathrm{d}t} = R_\mathrm{a}\Delta\langle M_{2z}\rangle + R_\mathrm{x}\Delta\langle M_{1z}\rangle$$

$$\mathcal{A}_1 = \frac{\kappa}{2}((1-\zeta)\mathrm{e}^{-R_{2,1}t_1}\cos(\Omega_1 t_1) + \zeta\mathrm{e}^{-R_{2,2}t_1}\cos(\Omega_2 t_1))\mathrm{e}^{-(R_\mathrm{a}+R_\mathrm{x})\tau_\mathrm{m}}$$

$$\mathcal{A}_2 = \frac{\kappa}{2}((1-\zeta)\mathrm{e}^{-R_{2,2}t_1}\cos(\Omega_2 t_1) + \zeta\mathrm{e}^{-R_{2,1}t_1}\cos(\Omega_1 t_1))\mathrm{e}^{-(R_\mathrm{a}+R_\mathrm{x})\tau_\mathrm{m}}$$


1 2 3 4 5 6
C T G A A T
H H H
H H H
G A C T T A
6' 5' 4' 3' 2' 1'
G6' G3 T3' T2 T2' T6
T6
T2'
T2
T3'
G3
G6
f1
f2

10 kDa protein:



NOESY CROSS-PEAK HEIGHT Y_{max}

If $\tau_{\text{m}} < 1/R_{\text{x}}$:

$$Y_{\text{max}} \propto -\frac{1}{2}\left(e^{R_{\text{x}}\tau_{\text{m}}} - e^{-R_{\text{x}}\tau_{\text{m}}}\right)e^{-R_{\text{a}}\tau_{\text{m}}} \approx -R_{\text{x}}\tau_{\text{m}}$$

$$= \left(\frac{\mu_0}{8\pi}\right)^2 \frac{\gamma^4\hbar^2}{r^6}(J(0) - 6J(2\omega_0))\tau_{\text{m}}$$

$$J(0) = \frac{2}{5}\tau_{\text{C}} \qquad J(2\omega_0) = \frac{2}{5}\frac{\tau_{\text{C}}}{1 + (2\omega_0\tau_{\text{C}})^2}$$

Slow motions, long τ_{C}:

$2\omega_0\tau_{\text{C}} \gg 1 \Rightarrow J(0) = \frac{2}{5}\tau_{\text{C}} > 6J(2\omega_0) \approx 0 \Rightarrow Y_{\text{max}} > 0$

Fast motions, short τ_{C}:

$2\omega_0\tau_{\text{C}} \ll 1 \Rightarrow J(0) = \frac{2}{5}\tau_{\text{C}} < 6J(2\omega_0) \approx 6 \times \frac{2}{5}\tau_{\text{C}} \Rightarrow Y_{\text{max}} < 0$

NOESY CROSS-PEAK HEIGHT Y_{max}

If $\tau_{\mathrm{m}} < 1/R_{\mathrm{x}}$:

$$Y_{\mathrm{max}} \propto -\frac{1}{2}\left(\mathrm{e}^{R_{\mathrm{x}}\tau_{\mathrm{m}}} - \mathrm{e}^{-R_{\mathrm{x}}\tau_{\mathrm{m}}}\right)\mathrm{e}^{-R_{\mathrm{a}}\tau_{\mathrm{m}}} \approx -R_{\mathrm{x}}\tau_{\mathrm{m}}$$

$$= \left(\frac{\mu_0}{8\pi}\right)^2 \frac{\gamma^4\hbar^2}{r^6}(J(0) - 6J(2\omega_0))\tau_{\mathrm{m}}$$

$$J(0) = \frac{2}{5}\tau_{\mathrm{C}} \qquad J(2\omega_0) = \frac{2}{5}\,\frac{\tau_{\mathrm{C}}}{1 + (2\omega_0\tau_{\mathrm{C}})^2}$$

Slow motions:

$$2\omega_0\tau_{\mathrm{C}} \gg 1 \Rightarrow J(0) = \tfrac{2}{5}\tau_{\mathrm{C}} > 6J(2\omega_0) \approx 0 \Rightarrow Y_{\mathrm{max}} > 0$$

Fast motions:

$$2\omega_0\tau_{\mathrm{C}} \ll 1 \Rightarrow J(0) = \tfrac{2}{5}\tau_{\mathrm{C}} < 6J(2\omega_0) \approx 6 \times \tfrac{2}{5}\tau_{\mathrm{C}} \Rightarrow Y_{\mathrm{max}} < 0$$

NOESY CROSS-PEAK HEIGHT Y_{max}

$$\frac{Y_{\text{max}}}{Y_{\text{max,ref}}} = \left(\frac{r_{\text{ref}}}{r}\right)^6$$

$$r = r_{\text{ref}} \sqrt[6]{\frac{Y_{\text{max,ref}}}{Y_{\text{max}}}}$$

Reference protons		distance
geminal in methylene	H–C–H	0.17 nm
vicinal in aromatic ring	H–C=C–H	0.25 nm
meta in aromatic ring	H–C=CH–C–H	0.42 nm