Relaxation in EPR

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Content of the lecture:

- Why bothering about relaxation ?
- What can we learn from relaxation ?
- How do we measure T_1 and T_2 ?
- How do T_1 and T_2 appear in the Bloch equations ?
- What dynamical processes contribute to T_1 and T_2 ?

- Some application examples of relaxation processes

Understanding of relaxation is necessary to optimize experimental conditions

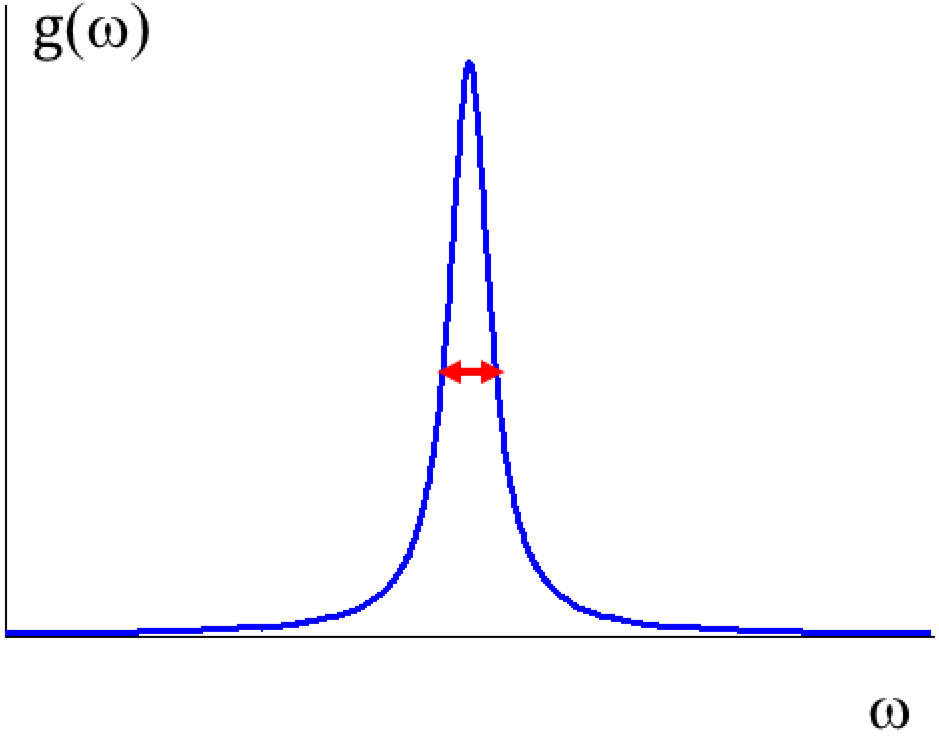
1) cw-EPR Experiments

In liquids the homogeneous lineshape is given by a Lorentz function:

$$g(\omega) = \frac{T_2}{\pi} \cdot \frac{1}{1 + [T_2(\omega - \omega_\mathrm{L})]^2}$$

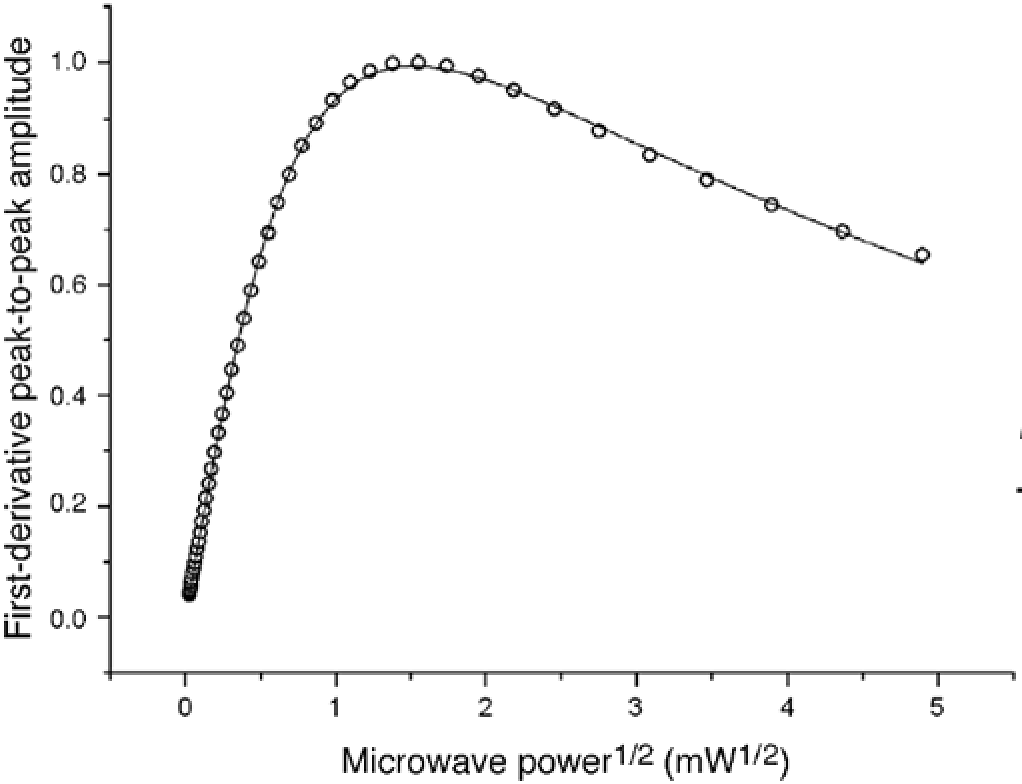
with a linewidth $\Delta\omega_{1/2} = \frac{2}{T_2}$

(if MW power is not too high)



The observed cw-EPR signal is given as $M_y = \frac{\pi \omega_1 M_0}{\sqrt{1+\omega_1{}^2 T_1 T_2}}\ g'(\omega)$

where $g'(w)$ is a Lorentz function with an increased linewidth defined by $\frac{2}{T_2{}'} = \frac{2}{T_2}\sqrt{1+\omega_1{}^2 T_1 T_2}$ (see *Abragam Bible for details)*



ω_1 is the strength of the MW excitation magnetic field (in rad/s)

The maximum of the cw-EPR signal is reached for $\omega_1{}^2 T_1 T_2 = 1$

Example:

Radical in liquid solution at RT:
$T_2 \sim T_1 \sim 0.1\ \mu s \rightarrow \omega_1 = 10$ MHz rad $\rightarrow B_1 = 0.56$ G

MW-power to MW-magnetic field conversion:

$$B_1 = c \cdot \sqrt{Q \cdot P_{MW}}$$

With a standard rectangular cw-EPR TE_{102} resonator:
$Q=2500$ $c = 0.028\ \mathrm{G}/\sqrt{\mathrm{W}}$

→ Optimal MW-Power $P_{MW} = \frac{{B_1}^2}{c^2 \cdot Q}$ ~160 mW

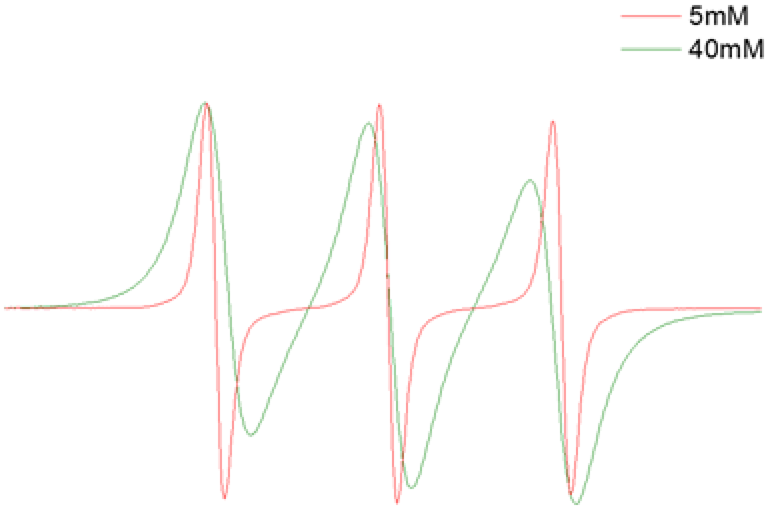
Example:

Organic Radicals in liquid solution at RT:

$T_2 \sim 1\ \mu s \longrightarrow$ Linewidth ~ 300 KHz (0.1 G)

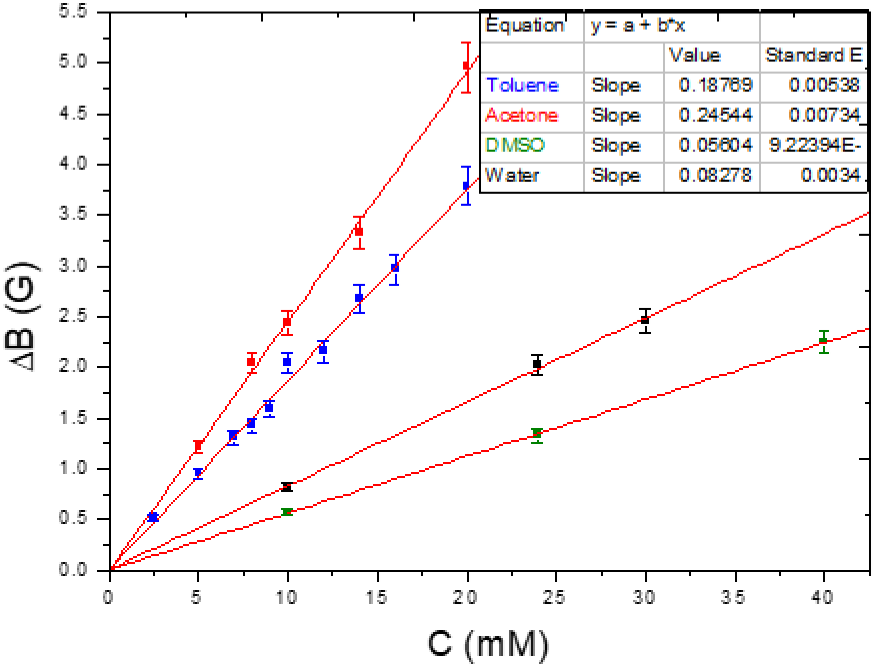
Line-Broadening by Heisenberg Exchange

$$R_2 = \frac{1}{T_2} = \frac{1}{T_2{}^{intrinsic}} + \kappa_{ex} \cdot c$$



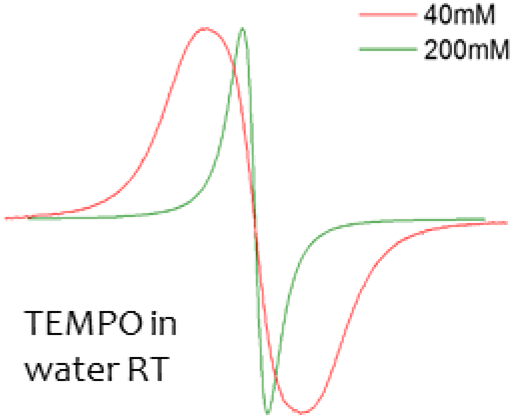
(Neugebauer et al PCCP 2014)

TEMPO Radical in different Solvents



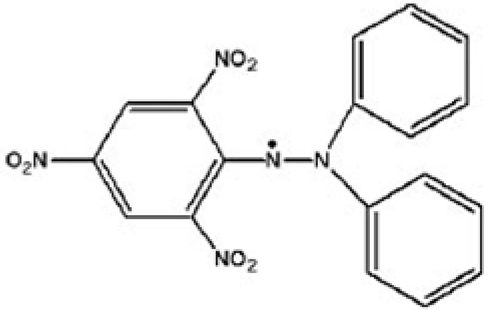
Equation	y = a + b*x		
		Value	Standard E
Toluene	Slope	0.18769	0.00538
Acetone	Slope	0.24544	0.00734
DMSO	Slope	0.05604	9.22394E-
Water	Slope	0.08278	0.0034

But – for high concentrations of Radicals the opposite effect is observed !



TEMPO in
water RT

Line becomes narrower with higher concentrations of radicals!



DPPH

Linewidth in solid sample is only **3 G** (compared to the value of > 100 G expected from dipol-dipol and hyper-fine interactions)
Exchange frequency 20 GHz narrows the line!

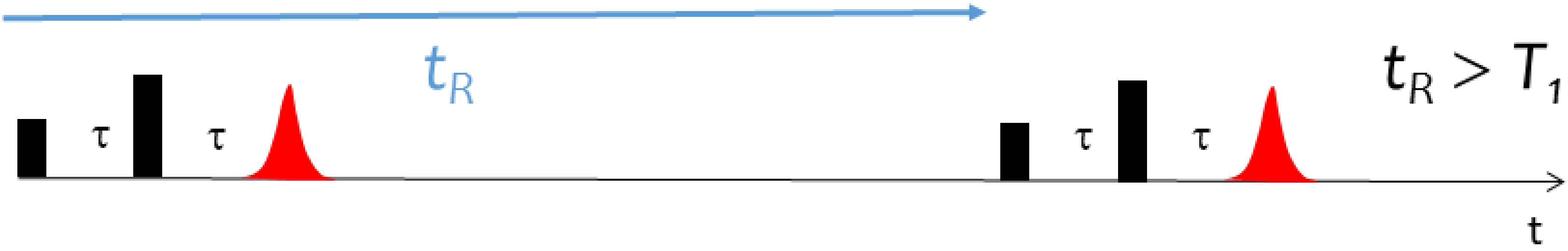
Complicated non-linear dependence of relaxation!
More detailed understanding of the phenomena is required!
Narrowing plays an important role for the understanding of the different contributions to lineshapes in MR
(Dipolar couplings, Exchange couplings, Liquids, etc.)

2) Pulse EPR Experiments:

In solids lines are inhomogeneous broadened
The FID signal decay does not decay with T_2

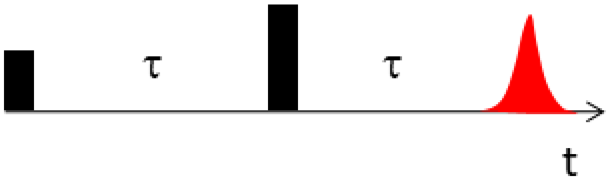
(and in most cases also does not reflect the full inhomogeneous linewidth but just the excitation bandwidth of the pulses)

- The repetition rate of the experiment is limited by T_1



$t_R > T_1$

- The time interval for transversal evolution is limited by T_2



$2\tau \sim T_2$

Relaxation is necessary for some experiment to work:

PRE: Paramagnetic relaxation enhancement
NOE: Nuclear Overhauser Enhancement

MRI: Magnetic Resonance Imaging

ODNP: Overhauser Dynamic Nuclear Polarization

RIDME: Relaxation Induced Dipolar Modulation Enhancement
REFINE: Relaxation Filtered Hyperfine Spectroscopy

But of course in principle for any experiment!

Relaxation can be used as information tool:

Contrast agents / Functional imaging

ODNP: rotational and translational dynamics of radicals
SS-DNP: spin diffusion between nuclear spins

Anisotropy of T_2: Librational dynamics of radicals

RIDME: Distance between radicals

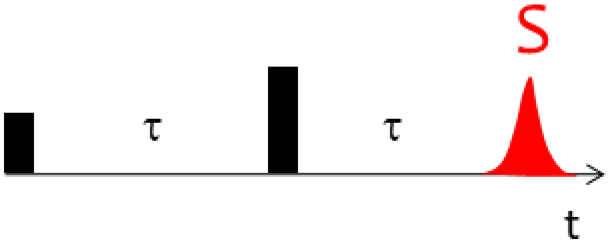
EPR Linewidth: - Oxygen in close contact
- Local nuclear spins
- Mobility of spin label
……

Determination of relaxation rates:

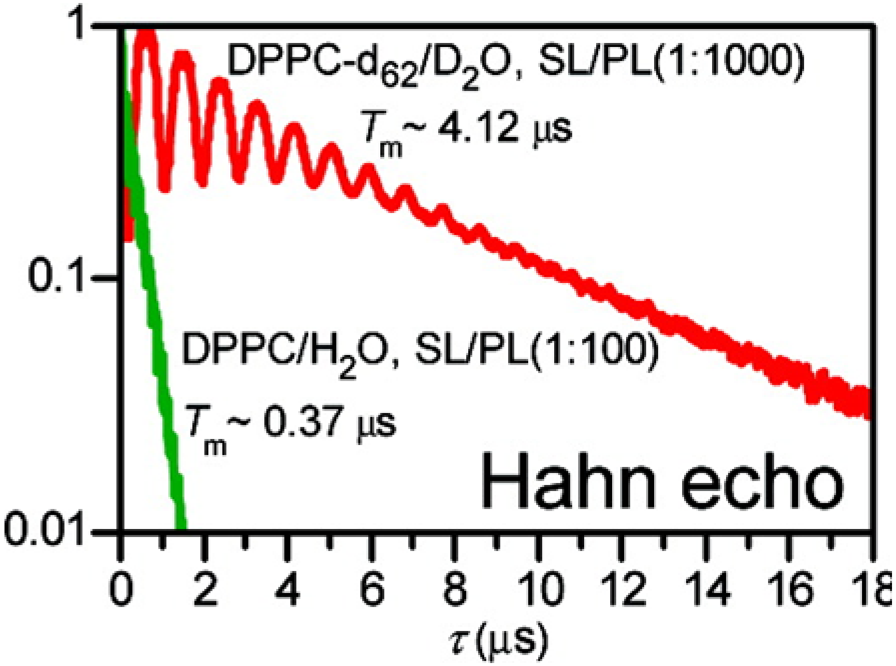
Cw-EPR: Linewidth (T_2) and Saturation Curve (T_1 T_2)

Pulse-EPR:

Hahn-Echo Decay for T_2



$$S(2\tau) = S(0)exp\left\{-\frac{2\tau}{T_2}\right\}$$



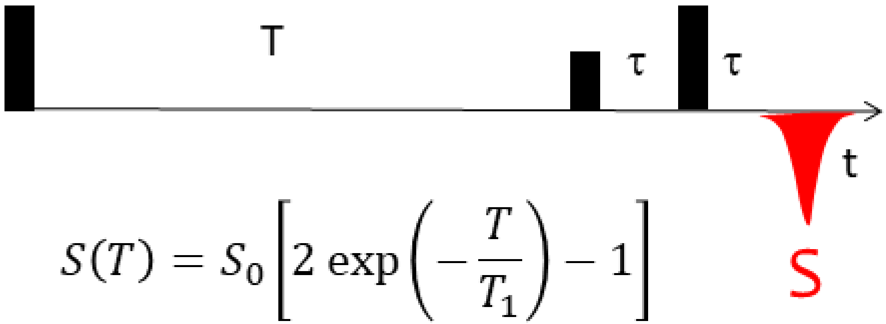
Relaxation of steric acid nitroxide spin labels (at 40 K and 0.3 T) in lipids under different experimental conditions

(Dastvan et al. JPC 2010)

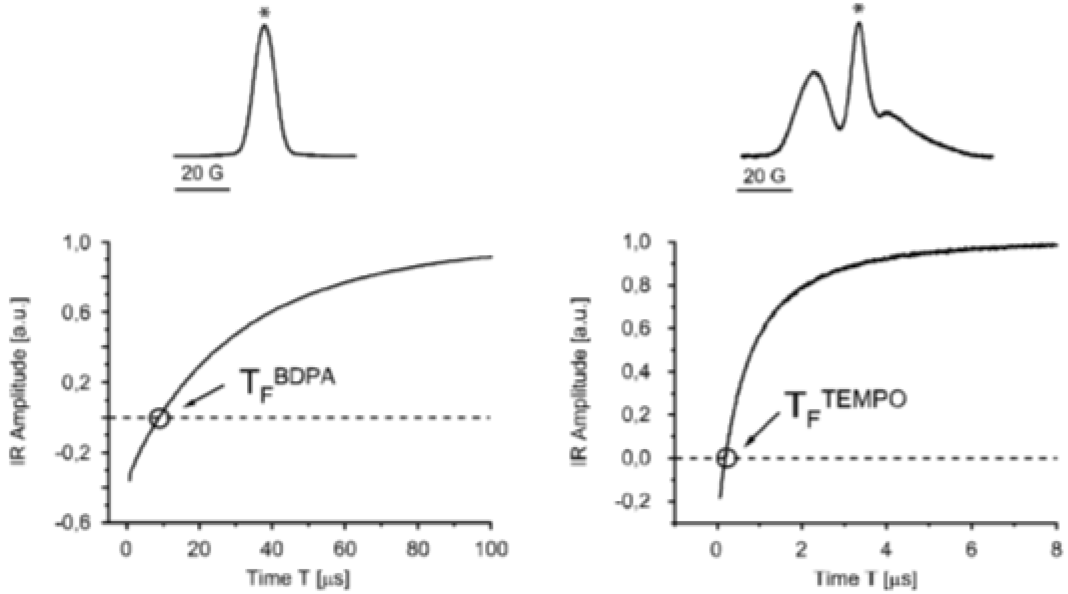
Determination of relaxation rates:

Pulsed EPR measurements for the determination of T_1

Inversion Recovery for T_1



$$S(T) = S_0\left[2\exp\left(-\frac{T}{T_1}\right) - 1\right]$$



At RT in polystyrene

(Maly et al. Biochem. 2004)

In the case of inhomogeneous linewidth > pulse excitation width:
Spectral diffusion will complicate the analysis of the experiments !

Simple description of relaxation rates

S=1/2 with Larmor-Frequency $\omega_L = \gamma B_0$

Coupling to a **stochastic perturbation field *B*(t)**

$B_x(t), B_y(t), B_y(t)$ Uncorrelated

$\langle B_x(t)\rangle_t = \left\langle B_y(t)\right\rangle_t = \langle B_z(t)\rangle_t = 0$ Zero Mean Value

$\langle B_x(t)^2\rangle_t = \left\langle B_y(t)^2\right\rangle_t = \langle B_z(t)^2\rangle_t \neq 0$ Random Orientation

$$\langle B_x(t)\cdot\ B_x(t+\tau)\rangle_t = \langle B_x(t)^2\rangle_t \cdot \exp\left\{-\frac{\tau}{\tau_c}\right\}$$

Exponential Autocorrelation Function

Solve the Bloch-Equation with fluctuating field (but without MW)

$$\frac{d\vec{M}}{dt} = \vec{M} \times \gamma \vec{B}_0 + \vec{M} \times \gamma \overline{B}(t)$$

Look on this in a frame rotating with the Larmor frequency:

$$\frac{d\vec{M}'}{dt} = \vec{M}' \times \gamma \vec{B}'(t)$$

$$\boxed{\begin{aligned} \dot{M}_x' &= \gamma \left(M_y' B_z'(t) - M_z' B_y'(t) \right) \\ \dot{M}_y' &= \gamma \left(M_z' B_x'(t) - M_x' B_z'(t) \right) \\ \dot{M}_z' &= \gamma \left(M_x' B_y'(t) - M_y' B_x'(t) \right) \end{aligned}}$$

<u>with</u>

$$\begin{aligned} B_x' &= B_x \cos \omega_L t + B_y \sin \omega_L t \\ B_y' &= -B_x \sin \omega_L t + B_y \cos \omega_L t \\ B_z' &= B_z \end{aligned}$$

To observe relaxtion processes, chose a starting condition depart from the equilibrium condition. Let‘s first search for the T_1 effects:

$$\left(M_z'(0) \neq 0 \; , \quad M_x'(0) = M_y'(0) = 0 \right)$$

Chose first order perturbation theory to look for the change in the magnetization:

$$M_x'(t_1) = -\gamma M_z'(0) \int_0^{t_1} B_y'(t_2)\, dt_2$$

$$M_y'(t_1) = \gamma M_z'(0) \int_0^{t_1} B_x'(t_2)\, dt_2$$

$$M_z'(t_1) = M_z'(0)$$

As can be seen on this approximation level, no change in M_z can be observed……

Go to second order perturbation theory for M_z (meaning to include the 1. Order expressions for M_x and M_y)

$$M_z'(T) - M_z'(0) = \gamma \int_0^T \left[M_x'(t_1) B_y'(t_1) - M_y'(t_1) B_x'(t_1)\right] dt_1$$

$$M_z'(T) = M_z'(0) \left\{ 1 - \gamma^2 \int_0^T \underbrace{\left(\int_0^{t_1} B_y'(t_2) B_y'(t_1) + B_x'(t_2) B_x'(t_1)\, dt_2 \right)}_{\text{replace by } B_x,\, B_y} dt_1 \right.$$

$$M_z'(T) - M_z'(0) = -\gamma^2 M_z'(0) \cdot \int_0^T \left(\int_0^{t_1} \left\{ \cos \omega_L (t_1 - t_2) \left[B_x(t_1) B_x(t_2) + B_y(t_1) B_y(t_2) \right] - \sin \omega_L (t_1 - t_2) \left[B_x(t_1) B_y(t_2) - B_y(t_1) B_x(t_2) \right] \right\} dt_2 \right) dt_1$$

Use the known properties of the fluctuation $B(t)$

Finally, this leads to expressions for the relaxation rates R_1 and R_2

$$R_1 = \frac{1}{T_1} = \gamma^2\left[\langle {B_x}^2\rangle + \langle {B_y}^2\rangle\right]\frac{\tau_c}{1+{\omega_L}^2{\tau_c}^2}$$

$$R_2 = \frac{1}{T_2} = \gamma^2\left[\tau_c\langle {B_z}^2\rangle\right] + \frac{1}{2T_1}$$

Two cases can be considered:

A) Fast correlation time limit $\omega_L\tau_c \ll 1$ ‘Redfield Limit‘

$$R_1 \approx \gamma^2\left[\langle {B_x}^2\rangle + \langle {B_y}^2\rangle\right]\tau_c$$

$$R_2 \approx \gamma^2\left[\langle {B_z}^2\rangle\right]\tau_c + \frac{R_1}{2}$$

$$with\ \langle {B_x}^2\rangle = \langle {B_y}^2\rangle = \langle {B_z}^2\rangle \qquad \gamma^2\langle {B_i}^2\rangle = \langle \Delta{\omega_B}^2\rangle$$

$$R_1 = R_2 = 2\,\langle \Delta{\omega_B}^2\rangle\,\tau_c$$

Easy expression for T_1 (T_2)

Both are equal

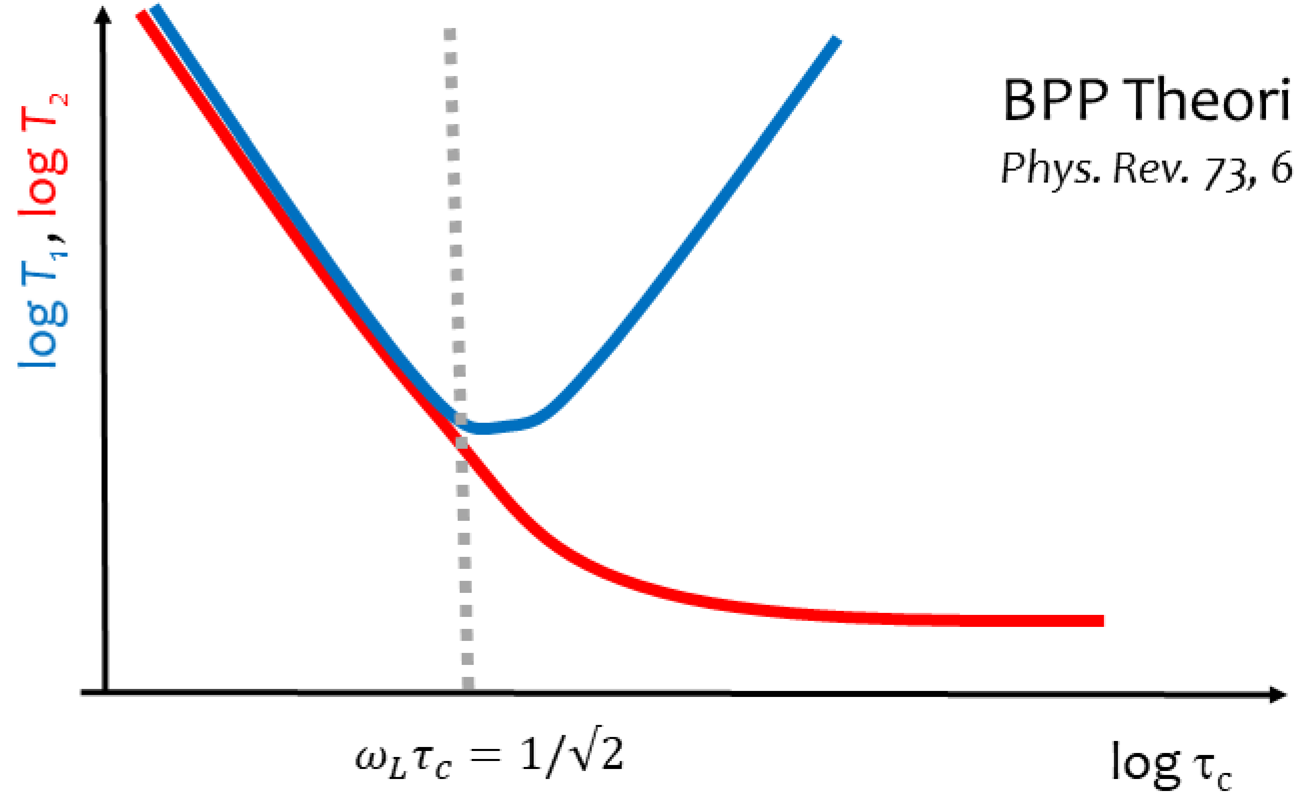
Holds for liquids

B) Slow correlation time limit $\omega_L \tau_c \gg 1$

$$R_2 \approx \langle \Delta\omega_B{}^2 \rangle \, \tau_c$$

$$R_1 \approx \frac{\langle \Delta\omega_B{}^2 \rangle}{\langle \omega_L{}^2 \rangle} \cdot \frac{1}{\tau_c} = \frac{1}{\langle \tau_c^2 \rangle \langle \omega_L{}^2 \rangle} \cdot \langle \Delta\omega_B{}^2 \rangle \, \tau_c \ll R_2$$

T_1 is much longer than T_2. This holds for solids



BPP Theorie

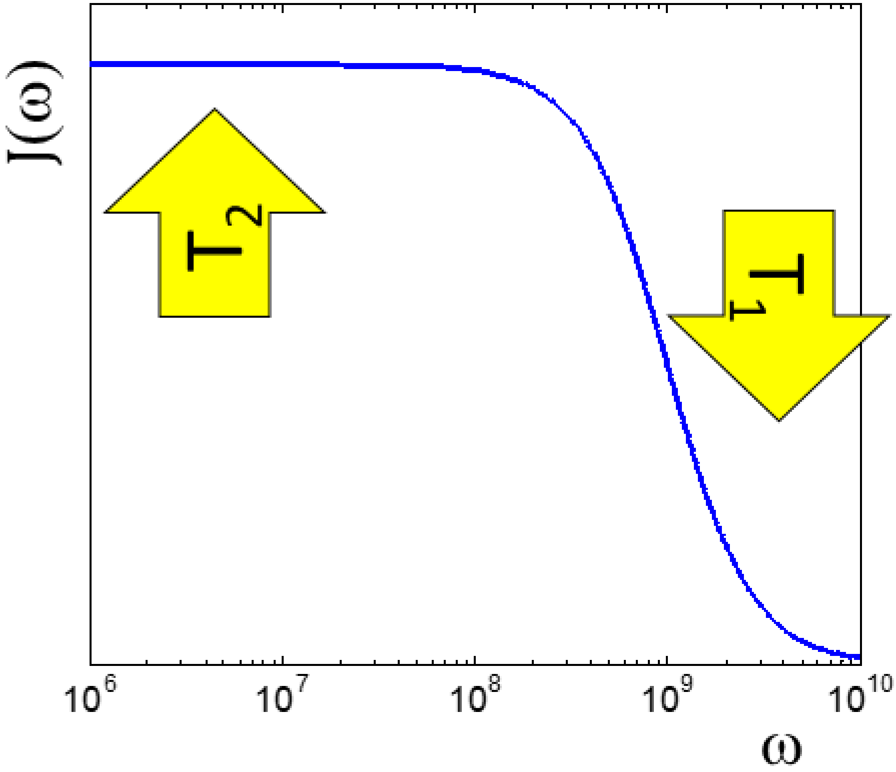
Phys. Rev. 73, 679 1948

The fluctuating field *B(t)* can also be described by the spectral densities $J(\omega)$:

$\langle B(t) \cdot B(t+\tau) \rangle_t = G(\tau)$ Autocorrelation-Function of fluctuating field *B(t)*

$J(\omega) = \int G(\tau) e^{i\omega\tau} d\tau$ Spectral density of the fluctuating field *B(t)*

If $G(\tau)$ is an exponential decaying function, $J(\omega)$ is a Lorentz function

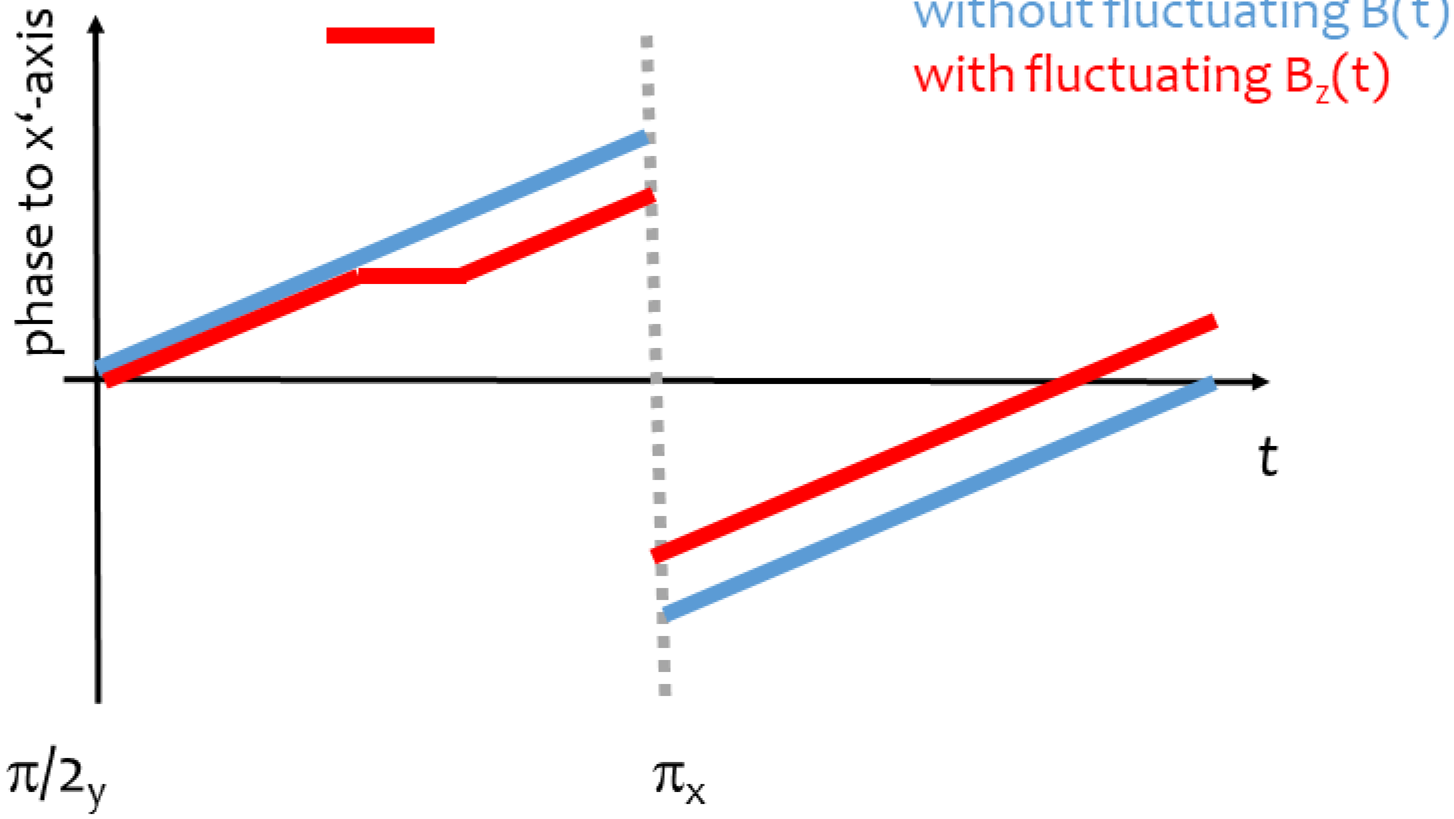


$R_1 \sim J(\omega_L)$
$R_2 \sim J(0)$

Simple intuitive visualization of relaxation processes for longitudinal and transversal magnetiziation:

Transversal Magnetization: $R_2 = \frac{1}{T_2} = \gamma^2[\tau_c\langle {B_z}^2\rangle]$

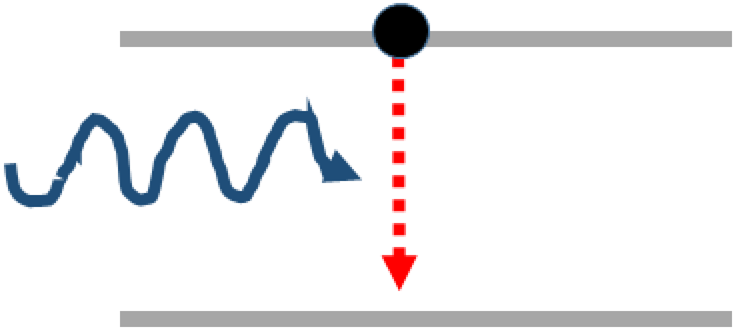
Every fluctuating field B_z leads to dephasing of transversal magnetization



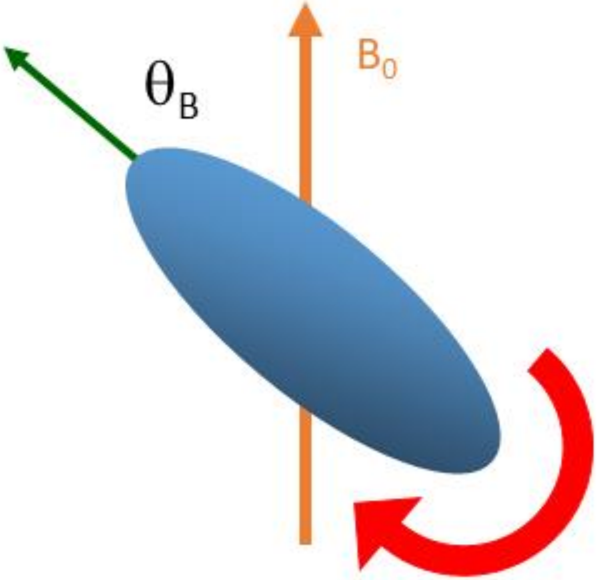
Longitudinal relaxation of spins by fluctuating field:

$$R_1 = \frac{1}{T_1} = \gamma^2\left[\langle {B_x}^2\rangle + \langle {B_y}^2\rangle\right]\frac{\tau_c}{1+{\omega_L}^2{\tau_c}^2}$$

Fluctuations perpendicular to B_0 with a correlation time τ_c of ~ $1/\omega_L$ acts like a MW pulse on-resonance and induces a stochastic transition between α and β spin states.



Example: Transversal Relaxation of Radicals by small angle librational dynamics in a glassy matrix

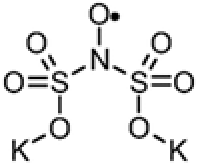


Molecular rotation modulates the anisotropic tensor interactions *A* and *g*

$$\frac{1}{T_2(\theta_B)} = \Delta\omega(\theta_B)^2 \cdot \boldsymbol{\tau}_c$$

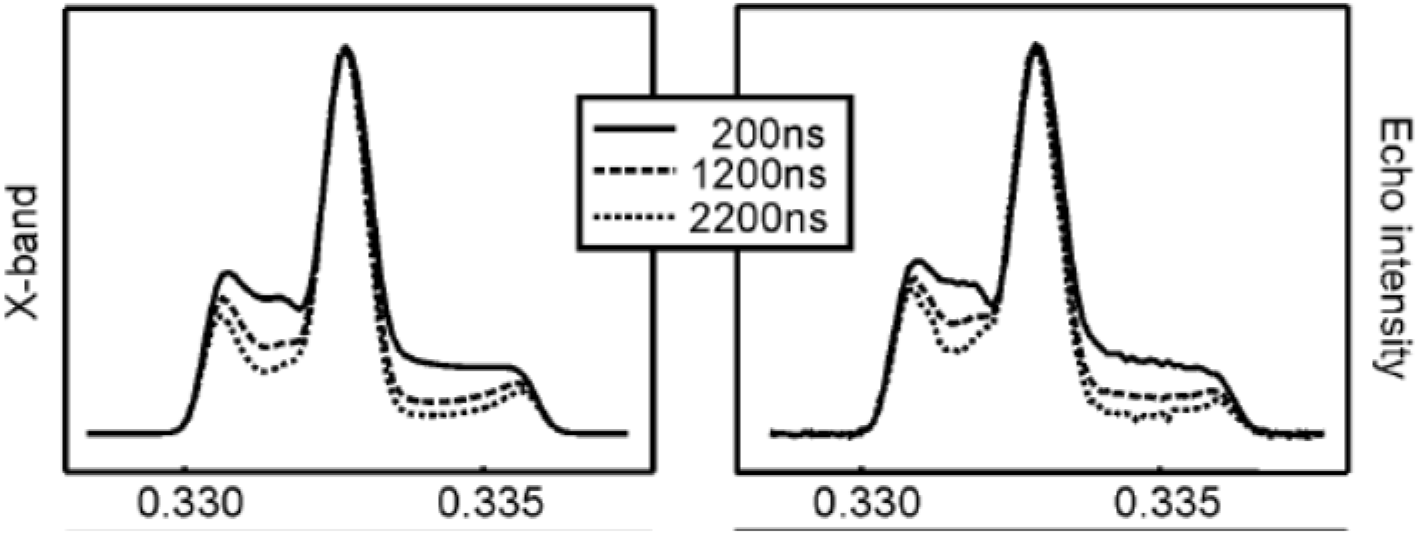
Rotation of Molecule modulates the anisotropic ^{14}N hyperfine coupling seen at the electron spin S → $B(t)$

Rotational correlation time τ_c is defined as the time to rotate the molecule 1 radian (1/2π)

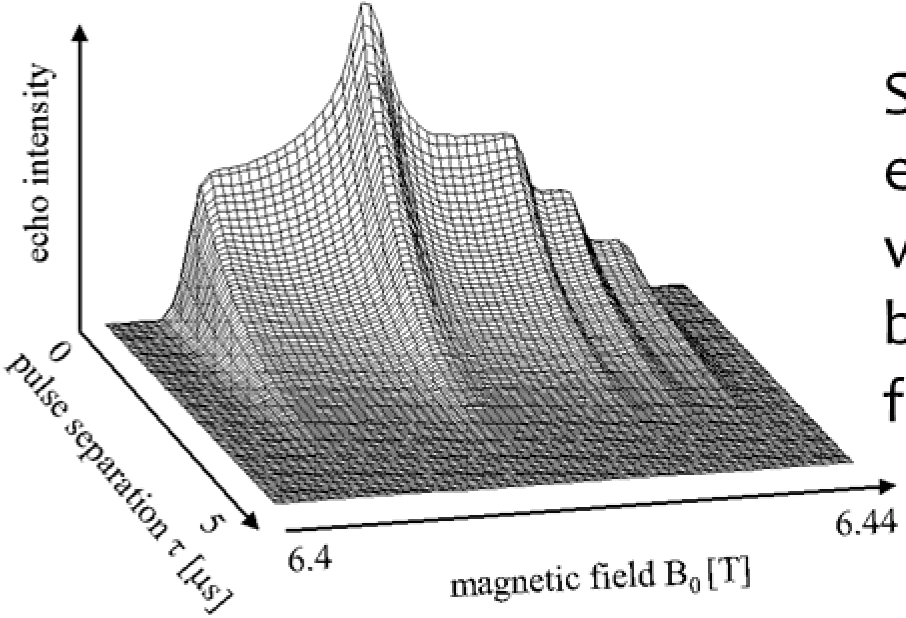


Fremy‘s Salt in glycerol at 185 K

(*Kirilina Mag. Res. Chem. 2005*)



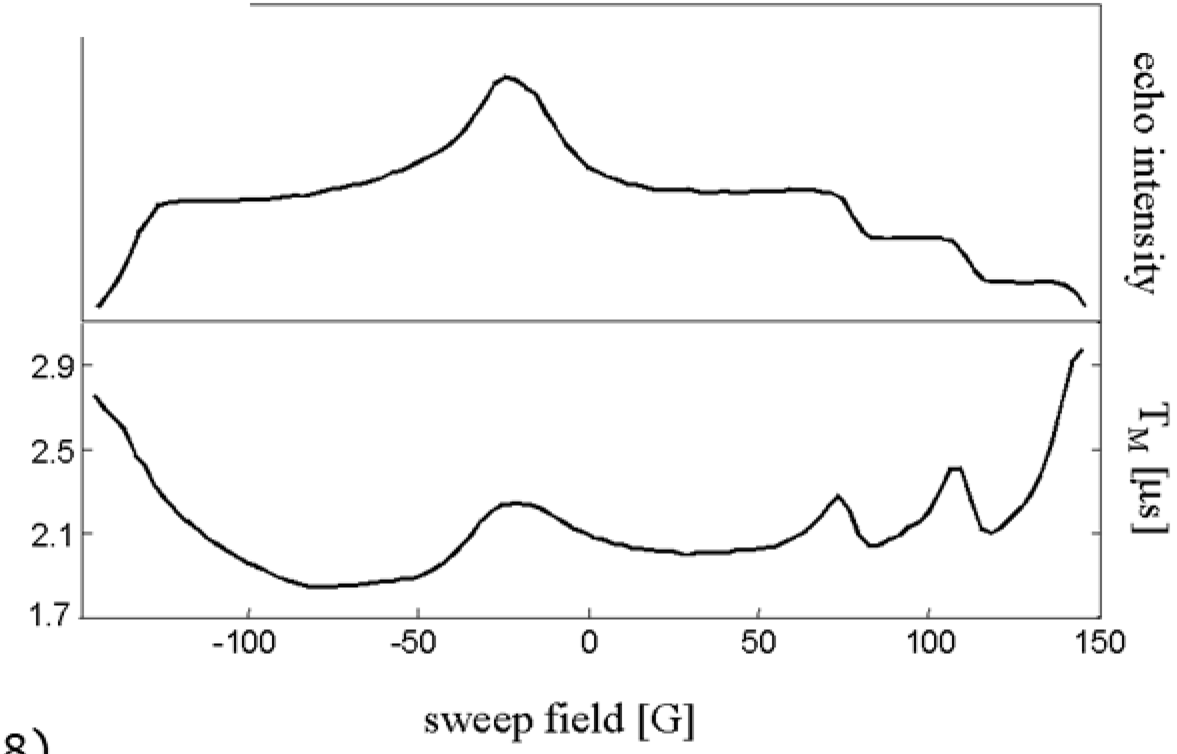
Field swept echo detected spectra (normalized to maximum) show dependence of T_2 on spectral position (orientation)



Similar tranlational relaxation effects can be observed by the variation of the Larmor-Frequency by rotation of the molecule at high fields by the anisotropic g-Tensor

TEMPO in Toluene measured at 180 GHz (G-band) and at a temperature of ? K

Combined A and g tensor relaxation is visible



(Prisner, Biol. Mag. Res. 1998)

Other Example:

Relaxation by a closeby fast relaxing spin *I*

Fluctuating field introduced on spin *S* by fast relaxing spin *I* closeby

Fluctuating field *B(t)* is given by magnetic dipol-dipol interaction:

$$\Delta\omega_B(t) = \frac{g_s g_I \beta_s \beta_I}{R^3}(1 - 3\;cos^2\theta)$$

Correlation time of fluctuation is given by relaxation time of spin I:

$$\tau_c = \; {T_1}^I$$

But: Autokorrelation function is not a exponential decaying function in this case! Only jump between two field values *B(t)* possible!

(see also sudden jump model: *Hu & Hartmann Phys. Rev. B 1974 and* BBP-Theory (*Bloembergen et al Phys. Rev. 1948*).

For this case there exists an analytical expression for the decay of the spin echo signal (*Salikov et al. Sov. Phys JETP (1969)*):

$$S(2\tau) = \frac{1}{C^2}\left[\frac{K}{2}\left\{(K+C)e^{-(K-C)2\tau} + (K-C)e^{-(K+C)2\tau} - \Delta^2 e^{-K2\tau}\right\}\right]$$

$$with\ \Delta = \frac{\Delta\omega_B}{2}, K = \frac{1}{\tau_c}, C^2 = K^2 - \Delta^2$$

$If\ K \ll \Delta\ (\omega_B \tau_c \gg 1)$ (slow relaxing regime)

$$S(2\tau) = exp\left\{-\frac{2\tau}{{T_1}^I}\right\} \Rightarrow {T_2}^S = {T_1}^I$$

Each jump of I leads to a dephasing of the S spin

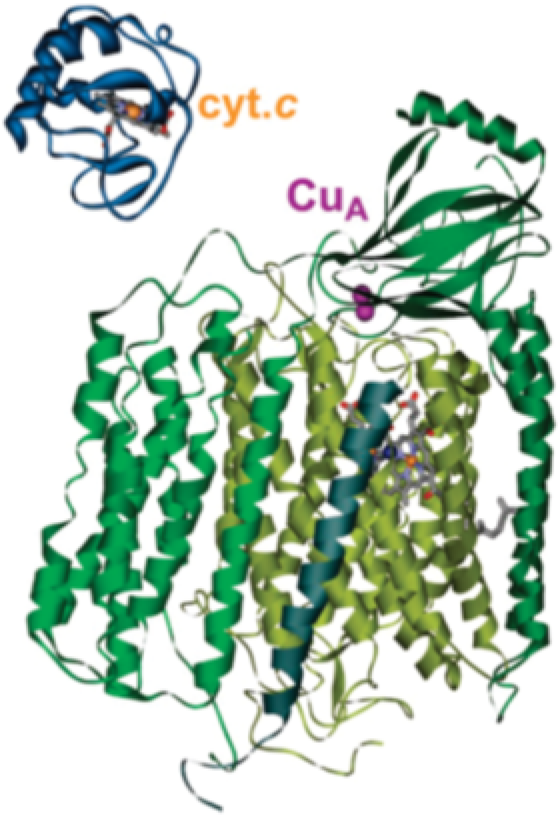
$If\ K \gg \Delta\ (\omega_B \tau_c \ll 1)$ (fast relaxing regime)

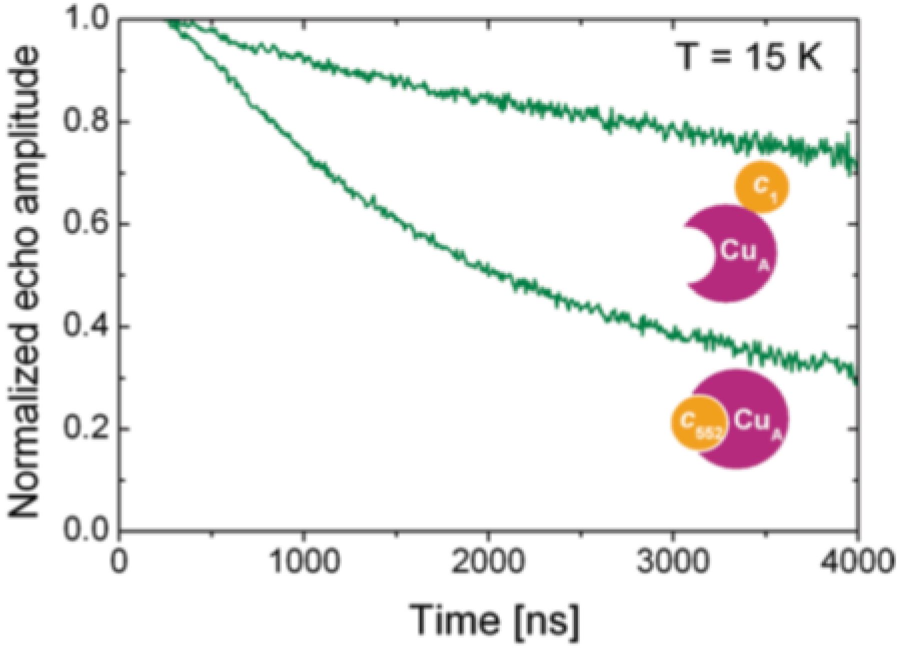
$$S(2\tau) = exp\left\{-\Delta^2 {T_1}^I \tau\right\} \Rightarrow \frac{1}{{T_2}^S} = \frac{\Delta^2}{2}{T_1}^I$$

More jumps lead to less dephasing (Redfield Narrowing Limit)

Interaction of cytochrome c with cytochrome c oxidases

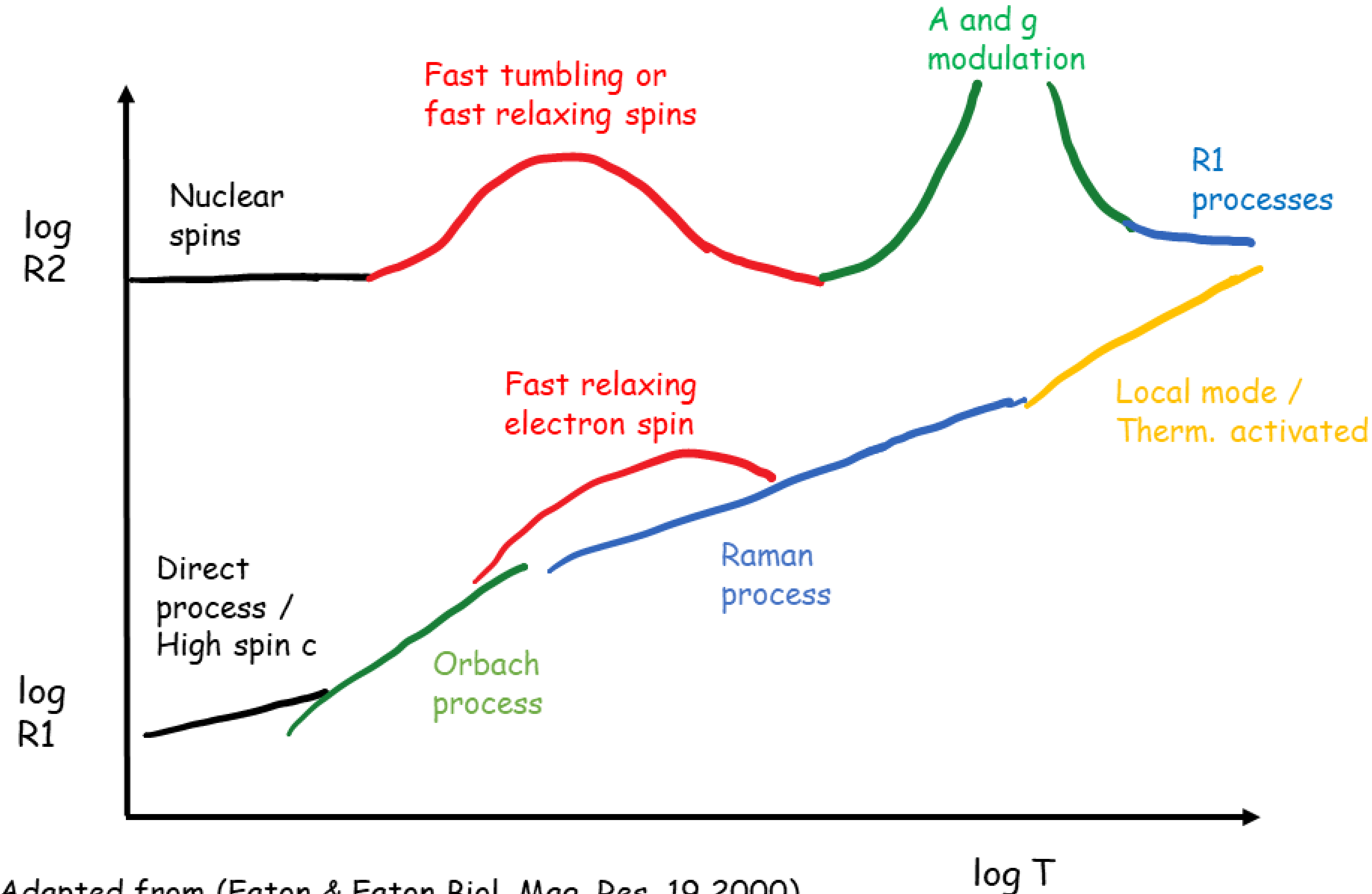
Dipolar relaxation strength and therefore dipolar relaxation rate depends on the distance between specific cytochrome and Cu_A





(*Lyubenova et al Account Chem. Res. 2010*)

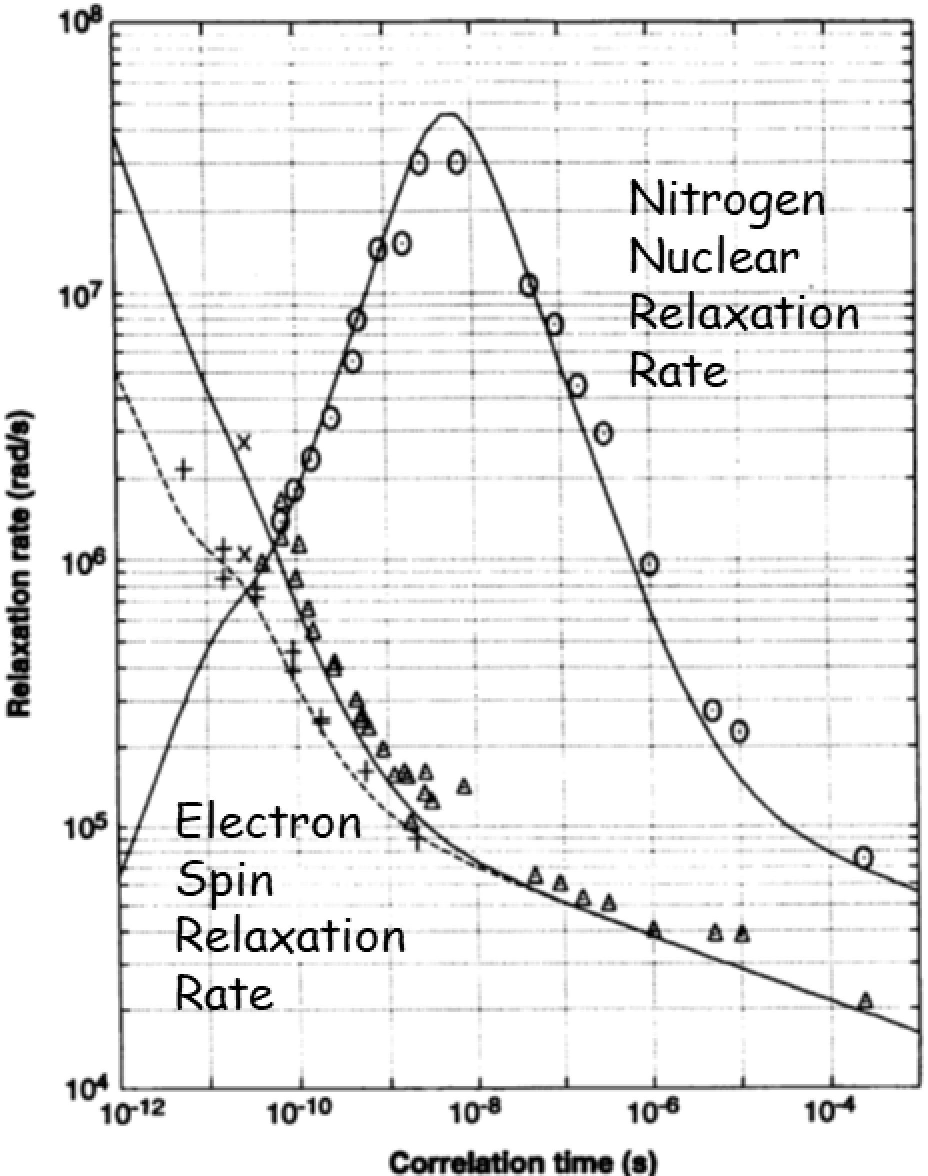
Relaxation sources for nitroxide radicals in solids



Adapted from (Eaton & Eaton Biol. Mag. Res. 19 2000)

T_1 Relaxation of nitroxide radicals in liquid solutions

(B. Robinson et al. Science 1994)



Anisotropic A and g Interaction:

$$R_1 = \frac{1}{6}\sum\left(A_i - \overline{A}\right)^2 \frac{\tau_c}{1+(\omega_S\,\tau_c)^2}$$

Spin-Rotation Interaction:

$$R_1 \sim \frac{\sum(g_i - g_e)^2}{9\,\tau_c}$$

Heisenberg Exchange Interaction:

$$R_1 \sim K \cdot\, c_S$$

Spin diffusion with Solvent Nuclei:

$$R_1 \sim \sqrt[4]{\frac{2\,\omega_s\,\tau_c}{1+\ (\omega_s\,\tau_c)^{3/4}}}$$

Lineshape by rotational tumbling (g & A)

Relaxation rates of isotropic tumbling molecules with only g-tensor anisotropy:

$$\frac{1}{T_2} = \frac{\Delta g^2 \beta^2 {B_0}^2}{30}\left[4\tau_c + \frac{3\tau_c}{1+{\omega_L}^2{\tau_c}^2}\right]$$

With: $\Delta g^2 = (g_{xx} - g_{\mathrm{av}})^2 + (g_{yy} - g_{\mathrm{av}})^2 + (g_{zz} - g_{\mathrm{av}})^2$

Relaxation rates of isotropic tumbling molecules with correlated g-tensor and A-tensor anisotropy:

$$\frac{1}{T_2} = a + bm_I + c{m_I}^2$$

With:

$$a = \frac{1}{T_2{}'} + \frac{2}{15}\Delta g^2(\beta B_0)^2\tau_c + \frac{1}{20}\gamma^2\Delta A^2 I(I+1)\tau_c$$

$$b = -\frac{4}{15}(\beta B_0)\gamma(\Delta g\Delta A)\tau_c$$

$$c = \frac{1}{12}\gamma^2\Delta A^2\tau_c$$

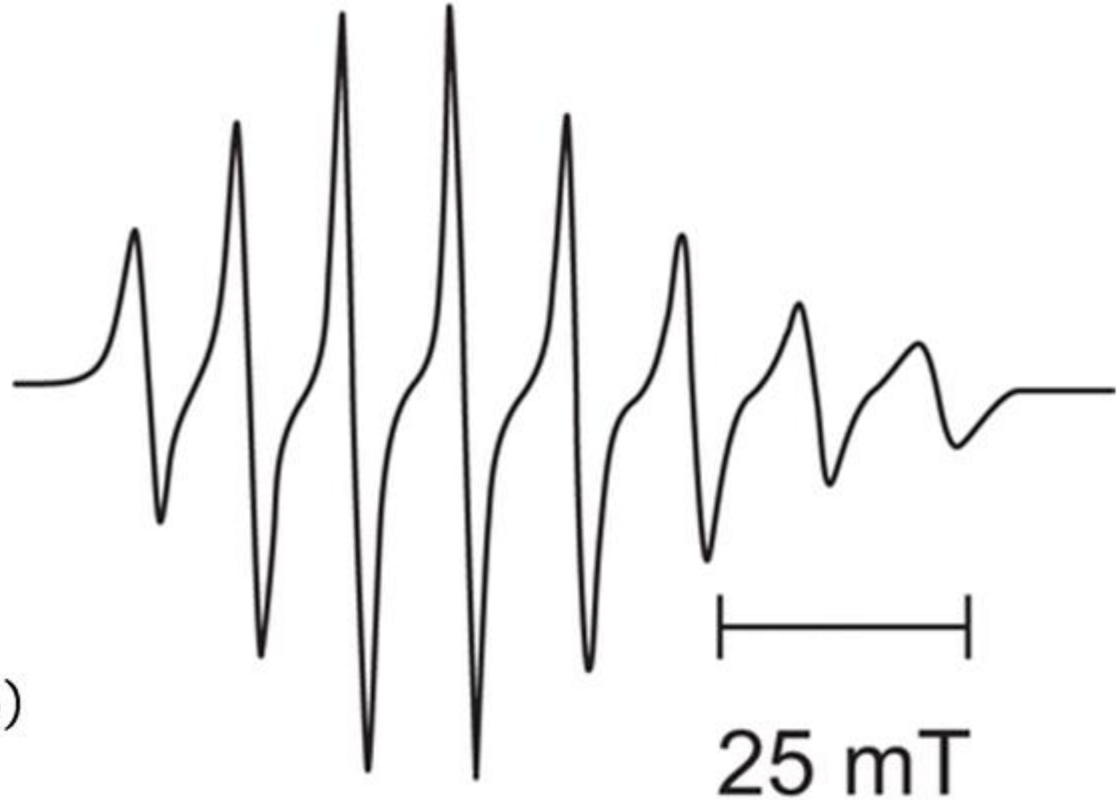
and

$$\Delta g\Delta A = (A_{xx} - A_{av})(g_{xx} - g_{av}) + \left(A_{yy} - A_{av}\right)\left(g_{yy} - g_{av}\right) + (A_{zz} - A_{av})(g_{zz} - g_{av})$$

Example:

Vanadyl (IV) acetylacetonate in tolune at 263 K (S=1/2, I=7/2)

(Wilson, Kivelson JCP 1966)



→ Asymmetry of EPR hyperfine line widths comes from b-Term in the relaxation expression

$$\frac{1}{T_2} = a + bm_I + cm_I{}^2$$

Literature:

Abragam Principles of NMR
Carrington, McLachlan Introduction to MR
Levitt Spin Dynamics
Slichter Principles of Magnetic Resonance
Bloembergen Nuclear Magnetic Relaxation
Poole/Farach Relaxation in Magnetic Resonance

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