Optical relaxation is negligible in NMR

For molecular absorption in the visible and ultraviolet the emission of light either by spontaneous (fluorescence) or stimulated (lasing) processes is an important mechanism for relaxation of the excited state. Neither of these mechanisms is important in NMR.

The Einstein relations tell us that the spontaneous emission Decreases as the third power of frequency. Thus, in the radio-Frequency range spontaneous emission becomes truly tiny.

For an isolated dipole the rate of relaxation can be Calculated based on the Fermi Golden Rule:

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This rate is approximately W = 10^{-21} s^{-1}, which is so small
that we can neglect it.

Even stimulated emission is extremely small in NMR such
that the mechanisms of relaxation are all non-radiative. The
mechanisms of nuclear spin relaxation involve coupling of
the spin with the surroundings, which can mean the
environment (called the lattice for historical reasons) and
other spins.

The relaxation Hamiltonian

We can include the terms leading to relaxation conceptually
In the Hamiltonian as follows.
We can represent the fluctuating terms in the Hamiltonian
as $Hl_{ocal}(t)$ such that the total Hamiltonian is

$$\mathcal{H} = \mathcal{H}_z + \mathcal{H}_{local}(t)$$

The local can be decomposed into isotropic and anisotropic
contributions

$$\mathcal{H}_{local}(t) = \mathcal{H}_{local}^{iso}(t) + \mathcal{H}_{local}^{aniso}(t)$$

Finally the anisotropic contributions consist of both
longitudinal and transverse terms

$$\mathcal{H}_{local}^{aniso}(t) = \mathcal{H}_{long}^{aniso}(t) + \mathcal{H}_{trans}^{aniso}(t)$$

# The relationship between molecular rotation and the correlation time

Spontaneous relaxation of nuclear spin orientations is extremely slow. almost zero. T_1 relaxation is caused by transient magnetic fields caused by molecular motion. T_1 relaxation is optimal if molecular rotations also occur at the Larmour precession frequency. In non-viscous liquids molecular rotation frequencies are several orders of magnitude higher than ω_0. Therefore, only a small fraction of the moleculars in the sample have the correct frequency To relax the spins. T_1 relaxation is very inefficient under these circumstances. For larger molecules and more viscous solutions molecular motions become slower and T_1 Becomes shorter.. At some point the average molecular motions become slower than ω_0, and T_1 becomes longer again

The correlation time

The trend for T_1 is shown in the Figure below. T_2 slows
As the molecular rotations slow. Thus, larger molecules
And more viscous solutions lead to smaller T_2 values.
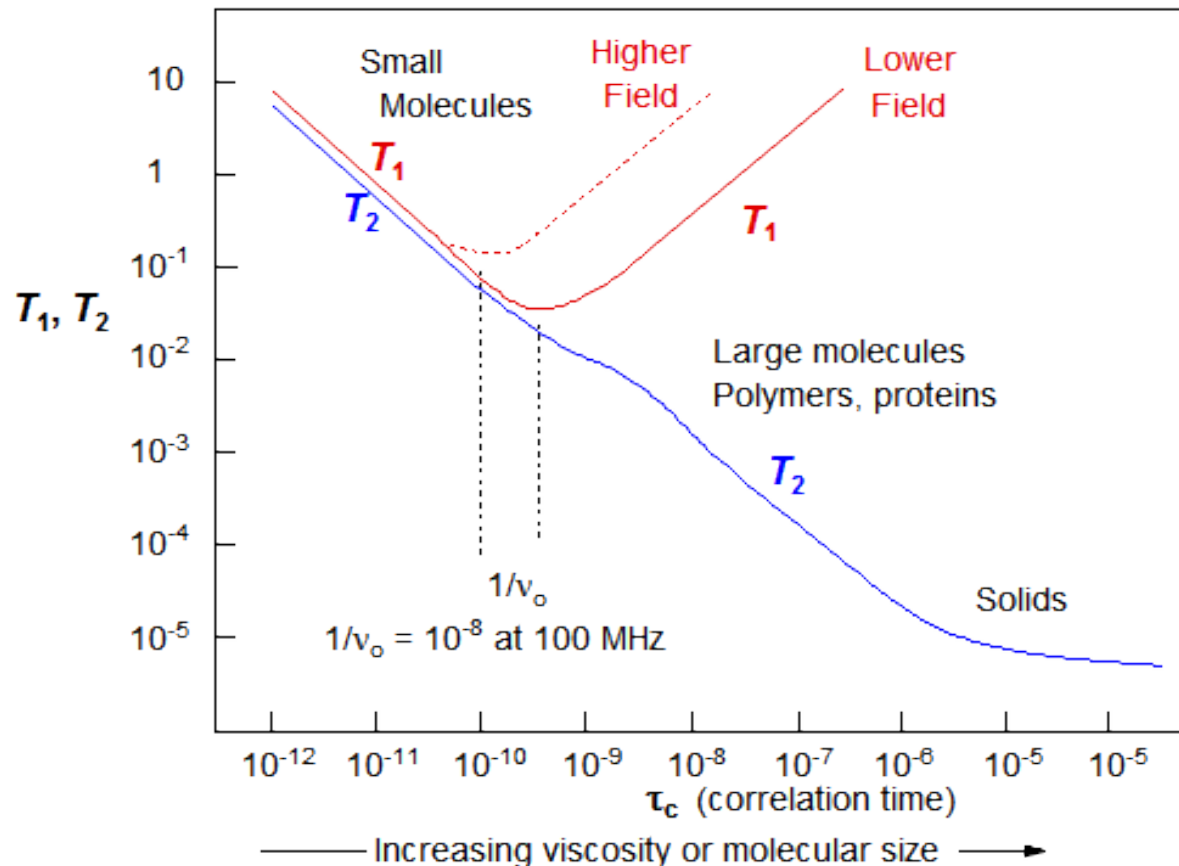
Two-spin population diagram
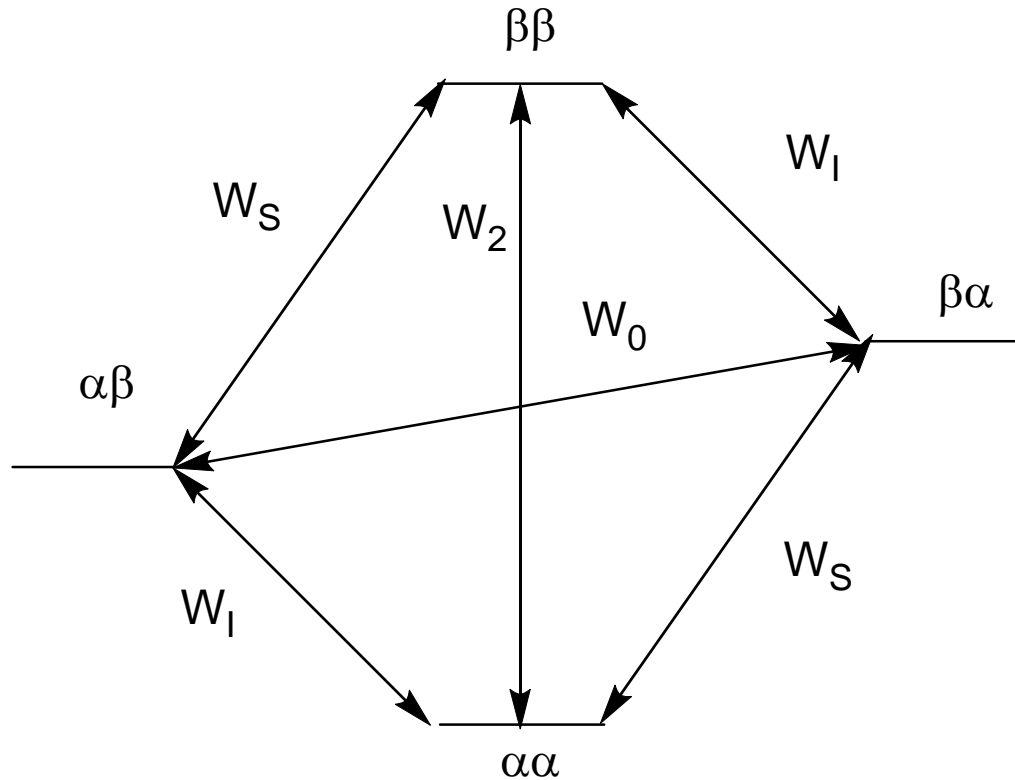
Rate equations for relaxation

The Solomon equations are the rate equations that describe the various populations of these states. For example, the aa population equation is:

$$\frac{dP_{\alpha\alpha}}{dt} = -(W_I + W_S + W_2)P_{\alpha\alpha} + W_I P_{\beta\alpha} + W_S P_{\alpha\beta} + W_2 P_{\beta\beta} + K$$

where $P_{\gamma\delta}$ is the population of the spin state $|\gamma\delta>$. K is a constant chosen to ensure that the population returns to the equilibrium value $P_{\alpha\alpha}^0$. At equilibrium

$$\frac{dP_{\alpha\alpha}}{dt} = 0$$

$$K = (W_I + W_S + W_2)P_{\alpha\alpha}^0 - W_I P_{\beta\alpha}^0 - W_S P_{\alpha\beta}^0 - W_2 P_{\beta\beta}^0$$

Rate equations in terms of population

Treating the difference in population relative to the equilibrium value as:

$$\Delta P_{\gamma\delta} = P_{\gamma\delta} - P_{\gamma\delta}^0$$

$$\frac{d\Delta P_{\alpha\alpha}}{dt} = -(W_I + W_S + W_2)\Delta P_{\alpha\alpha} + W_I\Delta P_{\beta\alpha} + W_S\Delta P_{\alpha\beta} + W_2\Delta P_{\beta\beta}$$

Similar equations can be written for the other three states:

$$\frac{d\Delta P_{\alpha\beta}}{dt} = -(W_I + W_S + W_0)\Delta P_{\alpha\beta} + W_0\Delta P_{\beta\alpha} + W_I\Delta P_{\beta\beta} + W_S\Delta P_{\alpha\alpha}$$

$$\frac{d\Delta P_{\beta\alpha}}{dt} = -(W_I + W_S + W_0)\Delta P_{\beta\alpha} + W_0\Delta P_{\alpha\beta} + W_I\Delta P_{\alpha\alpha} + W_S\Delta P_{\beta\beta}$$

$$\frac{d\Delta P_{\beta\beta}}{dt} = -(W_I + W_S + W_2)\Delta P_{\beta\beta} + W_I\Delta P_{\alpha\beta} + W_S\Delta P_{\beta\alpha} + W_2\Delta P_{\alpha\alpha}$$

Rate equations in terms of magnetization

These population equations can be cast in terms of the magnetization of a two-spin system as follows:

$$\frac{d\Delta I_z(t)}{dt} = -(W_0 + 2W_I + W_2)\Delta I_z(t) - (W_2 - W_0)\Delta S_z(t)$$

$$\frac{d\Delta S_z(t)}{dt} = -(W_0 + 2W_S + W_2)\Delta S_z(t) - (W_2 - W_0)\Delta I_z(t)$$

$$\Delta I_z(t) = \langle I_z \rangle(t) - \langle I_z^0 \rangle$$

$\langle I_z^0 \rangle$ is the equilbirium value of the I_z operator.

The Solomon equations

We can define the quantities

$$\rho_I = W_0 + 2W_I + W_2$$
$$\rho_S = W_0 + 2W_S + W_2$$
$$\sigma_{IS} = W_2 - W_0$$

Where ρ_I and ρ_S are the autorelaxations of spins I and S and σ_{IS} is the cross relaxation. Using these definitions we can recast the magnetization equations so that it is evident that they comprise a pair of coupled first order differential equations.

$$\frac{d\Delta I_z(t)}{dt} = -\rho_I \Delta I_z(t) - \sigma_{IS}\Delta S_z(t)$$
$$\frac{d\Delta S_z(t)}{dt} = -\rho_S \Delta S_z(t) - \sigma_{IS}\Delta I_z(t)$$

Extension to N coupled spins

The Solomon equations can be extended to N non-interacting spins

$$\frac{d\Delta I_{kz}(t)}{dt} = -\rho_k \Delta I_{kz}(t) - \sum_{j \neq k} \sigma_{kj} \Delta S_{jz}(t)$$

$$\sum_{j} \rho_{jk} = \rho_k$$

The sum of the individual magnetizations gives the net magnetization vector equation.

$$\frac{d\Delta \boldsymbol{M_z}(t)}{dt} = -\boldsymbol{R} \Delta \boldsymbol{M_z}(t)$$

Solution of the eigenvalue problem

In which R is a NxN matrix with elements

$$R_{kk} = \rho_k$$
$$R_{jk} = \sigma_{jk}$$

and $\Delta \boldsymbol{M_z}(t)$ is a column vector with dimension Nx1 and elements $\Delta I_{kz}(t)$. The magnetization decays exponentially due both to the autorelaxation and cross relaxation terms, which gives rise to magnetization transfer.

$$\Delta \boldsymbol{M_z}(t) = \mathrm{e}^{-\boldsymbol{R}t} \Delta \boldsymbol{M_z}(0)$$

The solution can be expressed as a dimilarity transfer form

$$\Delta \boldsymbol{M_z}(t) = \boldsymbol{U}^{-1} \mathrm{e}^{-\boldsymbol{D}t} \boldsymbol{U} \Delta \boldsymbol{M_z}(0)$$

$$\boldsymbol{R} = \boldsymbol{U}^{-1} \boldsymbol{D} \boldsymbol{U}$$

Solution of the eigenvalue problem

The matrices are given below and the evaluation of the eigenvalues $\lambda_{\pm}$ gives the provides the solution to the Solomon equations

$$\boldsymbol{R} = \boldsymbol{U}^{-1}\boldsymbol{D}\boldsymbol{U}$$

$$\boldsymbol{R} = \begin{bmatrix} \rho_I & \sigma_{IS} \\ \sigma_{IS} & \rho_S \end{bmatrix}$$

$$\boldsymbol{D} = \begin{bmatrix} \lambda_+ & 0 \\ 0 & \lambda_- \end{bmatrix}$$

$$\lambda_{\pm} = \frac{1}{2}\left[(\rho_I + \rho_S) \pm \sqrt{(\rho_I - \rho_S)^2 + 4\sigma_{IS}^2} \right]$$

The similarity transform

The eigenvalues $\lambda_{\pm}$ are substituted back into the eigenvector equation to obtain the the U matrix.

$$\boldsymbol{U} = \begin{bmatrix} \dfrac{-\sigma_{IS}}{\sqrt{(\rho_I - \lambda_+)^2 + 4\sigma_{IS}^2}} & \dfrac{-\sigma_{IS}}{\sqrt{(\rho_I - \lambda_-)^2 + 4\sigma_{IS}^2}} \\[4ex] \dfrac{\rho_I - \lambda_+}{\sqrt{(\rho_I - \lambda_+)^2 + 4\sigma_{IS}^2}}\sigma_{IS} & \dfrac{\rho_I - \lambda_-}{\sqrt{(\rho_I - \lambda_-)^2 + 4\sigma_{IS}^2}} \end{bmatrix}$$

Finally we write the equation for the time-dependent net magnetization relaxation:

$$\begin{bmatrix} \Delta M_I(t) \\ \Delta M_S(t) \end{bmatrix} = \begin{bmatrix} a_{II}(t) & a_{IS}(t) \\ a_{SI}(t) & a_{SS}(t) \end{bmatrix} \begin{bmatrix} \Delta M_I(0) \\ \Delta M_S(0) \end{bmatrix}$$