Singlet States: Relaxation Properties

1. Relaxation Mechanisms

So far we have restricted our attention to the case of a two-spin-1/2 system. Real molecules are often made by more than two spins. In addition, macroscopic samples may have more than one molecular species, each carrying one or more nuclear spins. For any practical purpose it is sufficient to introduce a 3rd spin and then replicate the treatment for any other spin. The general situation is sketched in Fig.1.

![Figure 1](image)

In such a spin-system there are a number of interactions that may lead to singlet state relaxation and indeed to longitudinal relaxation. These are summarized in the graph in Fig. 2.

![Figure 2](image)

1.1 Singlet relaxation via coherent singlet-triplet mixing interactions

The existence of a finite difference in chemical shift between the two spins of the singlet spin-pair induces relaxation via mixing of singlet with triplet states.\(^1\)\(^2\). Basically, the singlet state is mixed with a triplet state that is, for example, affected by DD relaxation. Hence the singlet state decays as a function of the intra-pair dipole-dipole relaxation. The situation becomes clearer by writing down the Liouvillian superoperator for a system containing \(H_{CS}, H_J\) and \(\Gamma_{DD}\) and expressing it as a matrix in the following zero-quantum operator basis:
\[
\begin{pmatrix}
\frac{1}{2} (I_1^2 - I_2^2 + I_{1z}^2 - I_{2z}^2) \\
\frac{1}{2} (-I_1^2 + I_2^2 + I_{1z}^2 - I_{2z}^2) \\
\frac{1}{\sqrt{6}} (I_1^2 + I_2^2 - 4I_{1z}I_{2z}) \\
\frac{1}{\sqrt{2}} (I_{1z}^2 + I_{2z}^2) \\
-\frac{1}{\sqrt{3}} (I_1^2 + I_2^2 + 2I_{1z}I_{2z}) \\
\frac{1}{2}
\end{pmatrix}
\]  

(1.1)

to obtain:

\[
\begin{pmatrix}
-i2\pi J_{1z} - \frac{b_{1z}^2}{2} & 0 & -i\Delta\omega & 0 & i\Delta\omega & 0 \\
0 & i2\pi J_{1z} - \frac{b_{1z}^2}{2} & \frac{i\Delta\omega}{\sqrt{6}} & 0 & -i\Delta\omega & 0 \\
-\frac{i\Delta\omega}{\sqrt{6}} & \frac{i\Delta\omega}{\sqrt{6}} & -\frac{9b_{1z}^2}{10} & 0 & 0 & 0 \\
0 & 0 & 0 & \frac{-3b_{1z}^2}{2} & 0 & 0 \\
i\Delta\omega & -i\Delta\omega & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0
\end{pmatrix}
\]

(1.2)

It is now clear that the singlet state, 5th row, 5th column is mixed with triplet states as a function of the difference in chemical shift (\(\Delta\omega\)). The analytical form of the eigenvalues of this matrix is not known. However, second order perturbation theory yield the following eigenvalue for the decay rate of the singlet state population:

\[
R_{CS}^S = \frac{\Delta\omega^2 b_{1z}^2}{12\pi^2 J_{1z}^3}
\]

(1.3)

In the most general case, triplet states are relaxed by other mechanisms like CSA, SR, etc., therefore the singlet-triplet mixing makes the singlet relaxation to depend on these mechanisms too. The inclusion of CSA relaxation, for example, leads to:

\[
R_{CS}^S = \frac{\Delta\omega^2}{60\pi J_{1z}^3} \left\{ 5b_{1z}^2 + \gamma' B_0 \left[ \|\sigma_1^z\| + \|\sigma_2^z\| \right] \tau_1 + \left[ \|\sigma_1^z\| + \|\sigma_2^z\| \right] \tau_2 \right\}
\]

(1.4)

where \(||\ldots||\) indicates the Frobenius norm, \(\sigma\) the traceless chemical shift tensor, + and – indicates its symmetric and anti-symmetric and where \(\tau_1\) and \(\tau_2\) are the rank-1 and rank-2 correlation times, respectively. Note that for isotropic rotational diffusion \(\tau_1=3\tau_2\).

In a similar fashion, if the singlet spin pair is coupled via a scalar-J-coupling interaction to a 3rd spin one can work out the coherent-J coupling contribution to singlet relaxation rates as:

\[
R_{J}^S = \frac{b_{1z}^2}{3J_{1z}^2} \sum_q (I_q + 1) (J_{1q} - J_{2q})^2
\]

(1.5)
where \( I_q \) is the spin quantum number for the q-th spin.

1.2 Singlet relaxation via incoherent interactions

In an analogous fashion one can work out the contribution to the singlet relaxation rate due to every other mechanism indicated in Fig. 2. This has been done for all the mechanism indicated with the following results:

- **CSA\(^3\) (Chemical Shift Anisotropy)**

\[
R_{S}^{\text{CSA}} = \frac{2}{9} \gamma^2 B_0^2 \left[ \left\| \sigma_1^z - \sigma_2^z \right\| \tau_1 + \left\| \sigma_1^z - \sigma_2^z \right\| \tau_2 \right] \tag{1.6}
\]

- **SR (Spin Rotation)**

\[
R_{S}^{\text{SR}} = \frac{2k_B T}{3\hbar} \text{Tr} \left\{ i \bar{\gamma}_{\text{SR}} \left[ \Delta C_0^z + \Delta C_1^z + \Delta C_2^z \right] \right\} \tag{1.7}
\]

where \( k_B \) is the Boltzmann constant, \( T \) the temperature, \( \hbar \) the reduced-Planck constant, \( \bar{\gamma} \) the inertia vector made by the three principal values of the inertia tensor, \( \bar{\gamma}_{\text{SR}} \) the spin-rotation correlation time vector. \( \Delta C_q = C_{q,q} - C_{q,q} \) indicate the difference between the n=0,+,- components of the spin-rotation tensor for the two nuclei, with ‘0’ indicating the isotropic and ‘+’ and ‘-’ the symmetric and anti-symmetric components, respectively.

- **DD\(^4\) (Dipole-Dipole)**

\[
R_{S}^{\text{DD}} = \frac{4}{3} \tau_2 \sum_q I_q (I_q + 1 \left[ b_{q,1}^2 + b_{q,2}^2 - 2 b_{q,1} b_{q,2} d_{q}^0 (\beta_{q,2}) \right] q \neq 1,2 \tag{1.8}
\]

with \( d_{q}^0 (\beta_{q,2}) = \frac{1}{2} (3 \cos^2 \beta_{q,2} - 1) \) being the rank-2, component-00 element of a reduced Wigner matrix and \( \beta_{q,2} \) is the angle in q of the triangle with vertices at spin 1, 2 and q.

- **JSK (scalar J coupling of Second Kind)**

\[
R_{S}^{\text{JSK}} = \frac{16 \pi^2}{9} \sum_q T_{q,q} \left( \sum_{j} \{ 2 + b_{q,j}^2 \} I_q \left( I_q + 1 \right) \right)^2 \left( \frac{T_{q,q}}{1 + 2 + b_{q,j}^2 \tau_2} \right)^2 \tag{1.9}
\]

where \( T_{q,q} \) is the T1 for the q-th spin, that in the fast-motion-limit case is equivalent to T2,q. If the 3rd nucleus is a quadrupolar nucleus then:

\[
T_{q,q} = \frac{40 S^2 (2 S - 1)^2}{(3 + 2 S)(3 + \eta) Q^2 \tau_2} \tag{1.10}
\]

with \( Q \) being the quadrupolar constant and \( \eta \) the asymmetry parameter of the quadrupolar tensor.
2. External Random Field approach\(^1\)

Spin relaxation can often be represented as due to external random magnetic fields fluctuating in solutions (ERF). These fields would have the following Hamiltonian:

\[
H_{ERF}^j = -\gamma B_j(t) \hat{I} = -\gamma \left( B_{j,x}(t) \hat{I}_x + B_{j,y}(t) \hat{I}_y + B_{j,z}(t) \hat{I}_z \right) = c \sum_{m=-1}^1 (-1)^m A_m^j(t) T_m^j
\]  

(2.1)

with the following equalities:

\[
l = 1 \\
c = -\gamma \\
A_m^j(t) = \begin{cases} 
B_{j,z}(t) & m = 0 \\
\frac{1}{\sqrt{2}} \left( B_{j,x}(t) \pm i B_{j,y}(t) \right) & m = \pm 1
\end{cases}
\]

(2.2)

\[
T_m^j = \begin{cases} 
\hat{I}_z & m = 0 \\
\frac{1}{\sqrt{2}} \hat{J}^x & m = \pm 1
\end{cases}
\]

Within the assumption that random field on a nucleus are isotropic, i.e.:

\[
\left( B_{j,x} \right)^{1/2} = \left( B_{j,y} \right)^{1/2} = \left( B_{j,z} \right)^{1/2} = B_j
\]

(2.3)

their correlation can be described by a single parameter:

\[
C_{ERF}^{j} = \frac{B_{j,x} B_{j,y}}{B_{j}^2} = \frac{B_{j,z}}{B_{j}^2} = \frac{0}{1} \text{ if } \alpha \neq \beta \\
\frac{1}{|0,1|} \text{ if } \alpha = \beta \text{ AND } j = k
\]

(2.4)

In this case, the relaxation superoperator for random field interactions in the fast motion limit becomes:

\[
\hat{\Gamma}_{ERF} = \sum_{j,k} \tilde{\Gamma}_{j,k}^{ERF} \\
\tilde{\Gamma}_{j,k}^{ERF} = \frac{\gamma_j \gamma_k T_1}{3} C_{ERF}^{j} B_j B_k \sum_{m=-1}^1 (-1)^m \hat{T}_{m,m} \hat{T}_{m,m}
\]

(2.5)

Relaxation rates are eigenvalues of the relaxation superoperator. The following steps are needed for their analytical determination:

1. Choose a suitable base of spin operators
2. Represent the superoperator in that base (In the limit here chosen the basis is block diagonal according to coherence orders. The single state has coherence order zero therefore the zero-order block can be isolated)
3. The block is diagonalised and eigenvector are taken (if not exactly solvable one can use perturbative approaches to get the relevant eigenvalues)

When these steps are applied to the superoperator in Eq. 2.5 we have:

\[
R_{ERF}^j = 2\gamma_j \gamma_k T_1 \left( B_j^2 + B_k^2 - 2C_{ERF}^j B_j B_k \right)
\]

(2.6)
In the case of fully correlated fields \( C_{\text{corr}}^\beta = 1 \) of equal magnitude, the ERF mechanism is not able to relax the singlet state \( R_{\text{ERF}}^{\text{SSF}} = 0 \). On the contrary, for fully uncorrelated fields \( C_{\text{corr}}^\beta = 0 \) of equal magnitude the singlet state decay rate do coincide with the rate of longitudinal magnetization, i.e. \( R_{\text{SSF}}^{\text{SSF}} = 2 \gamma \mu \tau (B_1^2 + B_2^2) = \frac{1}{T_1^{\text{SSF}}} \).

3. Intermolecular dipole-dipole relaxation

The case of relaxation due to intermolecular interactions is even more complex because both rotational and translational dynamics has to be taken into account. In the case of dipole-dipole interaction one need to be careful about the time dependence of inter-nuclear distances occurring in the expression of the dipolar coupling. Thus, the correct Hamiltonian would be:

\[
H_{\text{dd}}(t) = \frac{\mu_0 \gamma \mu_0}{4\pi} \sum_{n=2} r_n^2 (t) T_{2-n} \left( \Omega_{2-n} (t) \right) T_{2-n}^* = b_0 \sum_{n=2} r_n^2 (t) T_{2-n} \left( \Omega_{2-n} (t) \right) T_{2-n}^* \tag{3.1}
\]

This Hamiltonian can then be plug into the usual form for the relaxation superoperator to give:

\[
\Gamma_{\text{dd}}^{\sigma \tau} = -\int_0^\infty b_0^* b_\alpha T_{2-n} \left( \Omega_{2-n} (0) \right) D_{2-n}^2 \left( \Omega_{2-n} (\tau) \right) \frac{1}{r_\alpha^2 (0) r_\alpha^2 (\tau)} \hat{T}_{2-n}^* \hat{T}_{2-n} e^{i\omega \tau} d\tau \tag{3.2}
\]

Defining the correlation function:

\[
G_{\text{dd}}^{\sigma \tau} (\tau) = \left( \frac{D_{2-n}^2 \left( \Omega_{2-n} (0) \right) D_{2-n}^2 \left( \Omega_{2-n} (\tau) \right)}{r_\alpha^2 (0) r_\alpha^2 (\tau)} \right) \delta_{\omega \omega} \tag{3.3}
\]

eq 3.2 simplifies to:

\[
\Gamma_{\text{dd}}^{\sigma \tau} = -b_0^* b_\alpha \sum_n \int_0^\infty G_{\text{dd}}^{\sigma \tau} (\tau) e^{i\omega \tau} d\tau \tag{3.4}
\]

where we can isolate the intermolecular spectral density functions:

\[
J_{\text{dd}}^{\sigma \tau} (\omega_\alpha) = \int_0^\infty G_{\text{dd}}^{\sigma \tau} (\tau) e^{i\omega \tau} d\tau \tag{3.5}
\]

whose ridiculously complicated analytical expression, know only for selected cases, is reported in ref.\(^5\) and references therein.

As above, to find the relaxation of the singlet state due to intermolecular dipole-dipole coupling we need to diagonalise the zero-quantum block of the matrix representation of the following relaxation superoperator:

\[
\Gamma_{\text{dd}} = \sum_{\sigma \tau} \Gamma_{\text{dd}}^{\sigma \tau} \tag{3.6}
\]

thus obtaining:
\[ R_{ij}^{(0)} = \frac{\xi}{3} \left[ 3 \left( J_x^{(0)} + J_y^{(0)} + J_z^{(0)} \right) + 2 \left( J_x^{(0)} \omega_j + J_y^{(0)} \omega_j + J_z^{(0)} \omega_j \right) \right] \]

\[ \xi = \left( \frac{\gamma J R_H}{6 \pi} \right) I_q \left( I_q + 1 \right) \]

\[ J^i_x (\omega_n) = J^{\alpha \beta}_{\omega_0} (\omega_n) \quad jk = rs \quad \text{(auto-correlation)} \]

\[ J^i (\omega_n) = J^{\alpha \alpha}_{\omega_0} (\omega_n) \quad jk \neq rs \quad \text{(cross-correlation)} \]
References


