

Cross relaxation mechanisms in fluorine-containing sample under conditions of DNP.

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1 Cross-relaxation in ^1H - ^{19}F system.

While searching for optimal DNP conditions for DNP in fluorinated samples, we stumbled upon a peculiar phenomenon, where after shutting down the MW irradiation, the ^{19}F magnetization builds up quickly to some higher than equilibrium value, then slowly reaches thermal equilibrium. These observations suggest that ^{19}F nuclei are in contact with some other reservoir of energy, which is colder than lattice. The most obvious candidate for such a reservoir are abundant protons. This fact however, is yet to be fully confirmed. In the following we'll try to take a closer look at the mechanisms, which might be responsible for this transfer process.

2 NOE.

The transfer process is very similar to NOE (nuclear Overhauser effect), which has been observed in solids quite a while ago. The latest reports published by the groups of Corzillius and Buntkowsky, describe NOE-like transfer from protons to carbons under conditions of MAS DNP (magnetic field of 9.4 T and temperature 100 K). Such transfer is induced by the motion of methyl groups, similarly other reports from the early days of NMR (Pines & Waugh etc.) also attribute the transfer to some molecular motion. Our experiments however were carried at much lower temperatures of 1.4 K amplitudes, where motions are quite suppressed. Our main hypothesis is that ^1H to ^{19}F transfer is caused by the presence of paramagnetic TEMPO

radical. When we inadvertently used TEMPOL instead, we discovered that the ^1H to ^{19}F transfer was either significantly suppressed, or disappeared altogether. In order to show that in more detail we need to demonstrate what happens to the cross-polarization effect, when TEMPO concentration varies.

3 Relaxation and Cross-relaxation.

In the following we estimate the rates of cross-relaxation based on the time-dependent perturbation theory (Ch. VIII.II.C on Abragam's book). Consider a two level system, with $|i\rangle$ - initial, and $|f\rangle$ - final states, and the time-dependent perturbation to a system Hamiltonian $V(t) = \hat{A}f(t)$, where $\overline{f(t)} = 0$. The transfer rate from the $|i\rangle$ - to $|f\rangle$ state can be calculated as:

$$W_{if} = \frac{|A_{if}|^2}{\hbar^2} J(\omega_{if}) \quad (1)$$

where $|A_{if}|$ is the matrix element between the two states, and $J(\omega_{if})$ is the spectral density at the transition frequency $\omega_{if} = \frac{E_f - E_i}{\hbar}$. For a stationary random process with exponentially decaying correlation function, the spectral density has the following form:

$$J(\omega) = \frac{\tau_c}{1 + \omega^2 \tau_c^2}, \quad (2)$$

where τ_c is the correlation time of the random process.

In a three spin system, consisting of an electron and two nuclei, the pairwise interactions between all of them should be taken into account. However, in order to simplify the calculation we split this into two separate cases.

4 One hyperfine and one dipolar coupling

In this section we will consider a cross-relaxation mechanism arising due to rapid changes of nuclear spin quantization axis due to random electron spin flips. Random tilting of quantization axis affects the dipolar interaction between nuclear spins, giving rise to rapidly changing flip-flop terms. In our calculation, we electron is coupled to a nearby proton via a hyperfine interaction, represented by a 2nd rank tensor A_{ij} ($i, j = x, y, z$); the proton in turn is coupled to a nearby

fluorine via a dipolar interaction with components D_{ij} as shown schematically in Figure 1A.

We neglect the hyperfine interactions of ^{19}F nuclei at this stage to simplify the calculation and evaluate the effect of hyperfine and dipolar interaction on relaxation exclusively. The spin Hamiltonian for such coupled three spin system can be written as:

$$\mathcal{H} = \omega_S \hat{S}_z + \sum_{i,j=x,y,z} A_{i,j} \hat{S}_i \hat{H}_j + \omega_H \hat{H}_z + \omega_F \hat{F}_z + \sum_{i,j=x,y,z} D_{ij} \hat{H}_i \hat{F}_j, \quad (3)$$

where $\hat{H}_i, \hat{F}_i, \hat{S}_i$ - are the angular momenta of proton, fluorine and electron spins respectively. Taking into account that electron Zeeman interaction is greater than any other terms, the Hamiltonian in the electron spin rotating frame would take a form:

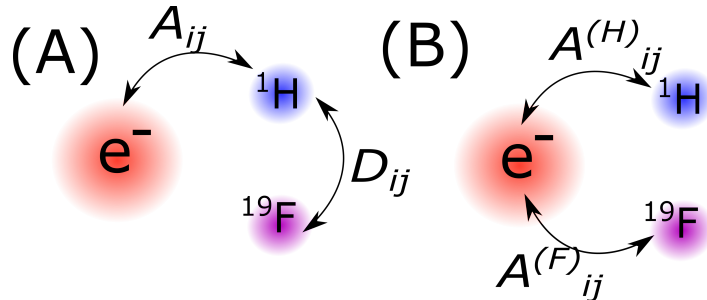
$$\mathcal{H} = A \hat{S}_z \hat{H}_z + B \hat{S}_z \hat{H}_x + D_{i,j} \hat{H}_i \hat{F}_j + \omega_H \hat{H}_z + \omega_F \hat{F}_z + \sum D_{i,j} \hat{H}_i \hat{F}_j, \quad (4)$$

where A and B are the secular and non-secular terms of the hyperfine interaction (term proportional to $\hat{S}_z \hat{H}_y$ was eliminated by a rotation in the spin space). The time-dependence in this Hamiltonian arises due to random flips of an electron spin, having a projection $m_S(t) = \pm \frac{1}{2}$ projection on the z-axis:

$$\mathcal{H} = (\omega_H + A m_S(t)) H_z + B H_x m_S(t) + \omega_F \hat{F}_z + \sum D_{i,j} \hat{H}_i \hat{F}_j \quad (5)$$

The first two terms would collectively correspond to quantization of a nuclear spin along a new effective magnetic field $\tilde{\mathbf{B}} = \frac{1}{\gamma}(\omega_H + A m_S(t), \gamma B, 0)$. By rotating the spin operator around H_y by a small angle $\phi(t) = \arctan(\frac{m_S(t)B}{\omega_H + m_S(t)A}) \approx \frac{m_S B}{\omega_H}$ one can rewrite this part of Hamiltonian along the new axis: $B_z(t) \hat{H}_z + B_x(t) \hat{H}_x = \tilde{\omega}_H(t) \hat{\tilde{H}}_z$. The \hat{H}_y operator generates a rotation in

Figure 1: Interactions used to calculation. (A) Electron spin is hyperfine coupled to a proton, which is dipolar coupled to nearby fluorine. (B) Electron spin is hyperfine coupled to both a proton and a fluorine nuclei.



the spin space, the dipolar part of the Hamiltonian can will then be transformed as:

$$\begin{aligned}\hat{H}_{dip}(t) &= \exp(-i\phi(t)\hat{H}_y) \sum_{i,j=x,y,z} D_{i,j} \hat{H}_i \hat{F}_j \exp(i\phi(t)\hat{H}_y) \approx \\ &\approx \phi(t) \left[\sum_{i,j=x,y,z} D_{i,j} \hat{H}_i \hat{F}_j, \hat{H}_y \right] = \frac{m_S(t)B}{\omega_H} \left[\sum_{i,j=x,y,z} D_{i,j} \hat{H}_i \hat{F}_j, \hat{H}_y \right]\end{aligned}\quad (6)$$

This time dependent Hamiltonian contains terms such as $\hat{H}_\pm \hat{F}_\mp$ and $\hat{H}_\pm \hat{F}_\pm$ is capable of inducing zero quantum (flip-flop) or double-quantum (flop-flop) transitions respectively. We will skip obtaining the exact equation for the rate, but rather focus in evaluating it by the order of magnitude. Using equation 1 we can estimate the zero-quantum transfer rate as:

$$\begin{aligned}W_{ZQ} &\sim \left| \frac{BD}{\omega_H} \right|^2 J(\omega_{ZQ}) \\ J(\omega) &= \frac{\tau_c}{1 + \omega^2 \tau_c^2}\end{aligned}\quad (7)$$

where B - is non-secular proton hyperfine interaction, D - dipolar coupling, ZQ stands for zero-quantum ($\omega_{ZQ} = \omega_H - \omega_F$), τ_c - electron correlation time, which is case is determined by electron spin-diffusion (τ_c should be smaller than 100 μs based on my CPMG measurements outlined in 2012 JMR paper - **this requires more explanations**). At the same time, the electron-induced $W_n = \frac{1}{T_{1n}}$ relaxation of ^{19}F nuclei can be estimated as (Ch. IX.II.A Abragam):

$$W_n \sim |B|^2 J(\omega_F) \quad (8)$$

Since $\omega_F \tau_c \gg 1$ and $\omega_{ZQ} \tau_c \gg 1$, the spectral densities are equal to $J(\omega_F) \approx \frac{1}{\omega_F^2 \tau_c}$ and $J(\omega_{ZQ}) \approx \frac{1}{\omega_{ZQ}^2 \tau_c}$. We can then look that the ratio of two rates, assuming that $\omega_H \approx \omega_F$:

$$\frac{W_{ZQ}}{W_n} \sim \left| \frac{D}{\omega_H} \right|^2 \left(\frac{\omega_F}{\omega_{ZQ}} \right)^2 \sim \left(\frac{D}{\omega_{ZQ}} \right)^2 \quad (9)$$

Since a typical dipolar coupling is $D \sim 100$ kHz and $\omega_{ZQ} \sim 8$ MHz, then $W_{ZQ} \ll W_n$ i.e. the ZQ process is several orders of magnitude slower than nuclear relaxation rate $\frac{1}{T_1}$ due to presence of electrons. Similar argument is true for for a double-quantum process.

5 Electron-induced proton-fluorine flip-flops

Now we will include the hyperfine interactions for both nuclei, while neglecting the dipolar interaction between them as shown schematically in Figure 1B. The Hamiltonian for such a system would therefore be in the following form:

$$\mathcal{H} = \omega_S \hat{S}_z + \sum_{i,j=x,y,z} A_{ij}^{(H)} \hat{S}_i \hat{H}_j + \sum_{i,j=x,y,z} A_{ij}^{(F)} \hat{S}_i \hat{H}_j + \omega_H \hat{H}_z + \omega_F \hat{F}_z, \quad (10)$$

where $A_{ij}^{(H)}, A_{ij}^{(F)}$ are the hyperfine interaction tensors of protons and fluorines respectively. In the electron spin rotating frame, using $A_{H,F}$ and $B_{H,F}$ for secular and non-secular terms of a hyperfine interaction the Hamiltonian can be rewritten as:

$$\mathcal{H} = A_H \hat{S}_z \hat{H}_z + B_H \hat{S}_z \hat{H}_x + \omega_H \hat{H}_z + A_F \hat{S}_z \hat{F}_z + B_F \hat{S}_z \hat{F}_x + \omega_F \hat{F}_z \quad (11)$$

Since $B_H, B_F \ll \omega_H, \omega_F$, the non-secular terms can be regarded as a perturbation to a secular Hamiltonian. For simplicity, let's consider the action of this perturbation of an eigestate $|\Psi^{(0)} = |\alpha_H \beta_F\rangle$. In the first order of perturbation theory, this function will transform into:

$$\Psi^{(1)} = |\alpha_H \beta_F\rangle + c_1 |\beta_H \alpha_F\rangle + c_2 |\beta_H \alpha_F\rangle, \quad (12)$$

where $c_1, c_2 \sim \frac{B_{H,F}}{\omega_{H,F}}$. All the mixed states differ from one another only by a flip of one nucleus.

The second order of perturbation theory will mix addition states:

$$\Psi^{(2)} = |\alpha_H \beta_F\rangle + c_1 |\alpha_H \alpha_F\rangle + c_2 |\beta_H \beta_F\rangle + d_1 |\beta_H \alpha_F\rangle + d_2 (\dots \text{all other functions} \dots), \quad (13)$$

The coefficient $d_1, d_2 \sim \frac{B^2}{\omega^2}$, where B is a combination of hyperfine couplings of protons and fluorines, and ω - the energy difference between the levels.

Also, then increasing orders of perturbation theory corrections to the energy would produce terms of the order:

$$E \sim \omega \left(1 + \frac{B}{\omega} + \left(\frac{B}{\omega} \right)^2 + \dots \right) \quad (14)$$

The zeroth order corresponds to a Zeeman interaction, the first order should be zero in our case. The second order correction would produce effective three spin terms in the Hamiltonian

proportional to $S_z H_{\pm} F_{\mp}, S_z H_{\pm} F_{\pm}$ and having a magnitude of $\frac{B^2}{\omega} \sim 1 \text{ MHz} \gg D$. Such terms are time dependent and are capable to producing nuclear zero-quantum and double-quantum transitions respectively. Similarly to section 4 we can estimate the ratio of zero-quantum relaxation rate and the nuclear relaxation rate.

$$\frac{W_{ZQ}}{W_n} \sim \left| \frac{B}{\omega_H} \right|^2 \left(\frac{\omega_F}{\omega_{ZQ}} \right)^2 \sim \left(\frac{B}{\omega_{ZQ}} \right)^2 \quad (15)$$

Hyperfine couplings of protons can be estimated as $B \sim \frac{78}{r^3} \frac{\text{MHz}}{\text{\AA}^3}$, which for a distance of 2 \AA would produce a hyperfine coupling of about 10 MHz. In addition, the protons of nitroxide methyl groups have large anisotropic hyperfine couplings of about 10 MHz (J. Phys. Chem. 1982, 86, 4011). Altogether it means that proton nuclei with coupling on the order of 10 MHz are always present in the vicinity of TEMPO. Therefore the rate of a ZQ transition, or a flip-flop and relaxation rate due to presence of electrons, will have the same order of magnitude as the electron-induce nuclear relaxation time $\frac{1}{T_{1n}}$.

6 Conclusions.

In this sketchy calculations we have compared two potential mechanisms for proton to fluorine magnetization transfer induced by the electron spin flips. When electron is strongly hyperfine coupled to both fluorine and proton nuclei, its fluctuations induce nuclei flip-flop transitions.