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

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1 Cross-relaxation in ^{1}H- ^{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 resembles NOE (nuclear Overhauser effect), which has 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 ^{1}H to ^{19}F transfer is caused by the presence of paramagnetic TEMPO radical. When we inadvertently used TEMPOL instead, we discovered that the ^{1}H 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 a levelsystem, 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:

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

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

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

where τ_c is the correlation time of the random process.

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}. 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 written as:

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

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:

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

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:

$$\mathcal{H} = (\omega_H + Am_S(t))H_z + BH_x m_S(t) + +\omega \hat{F}_z + \sum D_{i,j} \hat{H}_i \hat{F}_j \tag{5}$$

The first two terms would collectively correspond to quantization of a nuclear spin along a new effective magnetic field $\tilde{\mathbf{B}} = \dfrac{1}{\gamma}(\omega_H + Am_S(t)), B, 0)$. By rotating the spin operator around H_y by a small angle $\phi(t) = arctan(\dfrac{m_S(t)B}{\omega_H + m_S(t)A}) \approx \dfrac{m_S B}{\omega_H}$ one can rewrite this part of Hamiltonian along the new axis: $B_z(t)H_z + B_x(y)H_x = \tilde{\omega}_H(t)\tilde{H}_z$. Together with the fact that H_y operator generates a rotation in the spin space, the dipolar part of the Hamiltonian will also be transformed as:

$$H_{dip}(t) = exp(-i\phi(t)H_y) \sum D_{i,j} H_i F_j exp(i\phi(t)H_y) \approx$$
$$\approx \phi(t)[\sum D_{i,j} H_i F_j, H_y] = \frac{m_S(t)B}{\omega_H}[\sum D_{i,j} H_i F_j, H_y] \tag{6}$$

It is obvious that such time dependent hamiltonian is capable of inducing flip-flop transitions or zero quantum or double-quantum order. Using equation 1 we can estimate the rate as:

$$W_{ZQ} \sim |\frac{BD}{\omega_H}|^2 J(\omega_{ZQ})$$
$$J(\omega) = \frac{\tau_c}{1 + \omega^2 \tau_c^2} \tag{7}$$

where A - is hyperfine, D - dipolar coupling, ZQ stands for zero-quantum (the case for double-quantum can be calculated in a similar manner), tau_c - electron correlation time, which is our case is determined by electron spin-diffusion (τ_c should be smaller than 100 us based on my CPMG measurements outlined in 2012 JMR paper). At the same time, the electron-induced $W_n = \frac{1}{T_{1n}}$ relaxation of nuclei can be estimated as (Ch. IX.II.A Abragam):

$$W_n \sim |B|^2 J(\omega_F) \tag{8}$$

Since $\omega\tau \gg 1$, $J(\omega) \sim \frac{1}{\omega^2 \tau}$. We can then look that the ratio of two rates:

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

Since t typical dipolar coupling is 100 kHz and ω_{ZQ} 8MHz, the ZQ process is several orders of magnitude slower than nuclear T1 observed in the sample. Similar argument applies to a DQ process.

5 Electron-induced proton-fluorine flip-flops

One could consider an electron hyperfine coupled to both nuclei. The hamiltonian for such a system would therefore be in the following form:

$$\mathcal{H} = \omega_S \hat{S}_z + \sum A_{Hi,j} \hat{S}_i \hat{H}_j + \sum A_{Fi,j} \hat{S}_i \hat{H}_j \omega_H \hat{H}_z + \omega \hat{F}_z, \tag{10}$$

where A_H, A_F are the hyperfine couplings of protons and fluorines respectively. In the electron spin rotating frame, the Hamiltonian can be rewritten as:

$$\mathcal{H} = A_H \hat{S}_z \hat{H}_z + B_H \hat{S}_z \hat{H}_x + \omega_H \hat{H}_z + A_F \hat{S}_z \hat{F}_z + B_F \hat{S}_z \hat{F}_x + \omega \hat{F}_z \tag{11}$$

Since $A_H, A_F, B_H, B_F \ll \omega_H, \omega_F$, the hyperfine terms can be regarded as a perturbation to the nuclear Zeeman interaction. If so, then increasing orders of perturbation theory corrections to the energy would produce terms of the order:

$$E \sim \omega(1 + \frac{A}{\omega} + ()\frac{A}{\omega})^2 + ...) \tag{12}$$

The zeroth order correponds to zeeman interaction and the first order to hyperfine interactions. The second order correction would produce affective three spin terms in the Hamiltonian proportional to $SzH_\pm F_\mp, SzH_\pm F_\pm$ and having a magnitude of $\frac{A^2}{\omega}$ 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.

$$\frac{W_{ZQ}}{W_n} \sim |\frac{A}{\omega_H}|^2 (\frac{\omega_F}{\omega_{ZQ}})^2 \sim (\frac{A}{\omega_{ZQ}})^2 \tag{13}$$

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Hyperfine couplings of protons can be estimated as $A \sim \dfrac{78 \text{ MHz}}{r^3 \text{\AA}^3}$, which for a distance of 2 Å would produce a hyperfine coupling of about 10 MHz. In addition, the protons of nitroxide methyl groups have isotropic hyperfine couplings of about 10 MHz. Altogether it means that nuclei with coupling on the order of 10 MHz are always present in the vicinity of TEMPO. Therefore the rate of ZQ transition, or a flip-flop could be on the order of $\dfrac{1}{T_1 n}$ induced by the presence of electrons.

In other words the process can be viewed as a result of energy transfer between protons and fluorines in the vicinity of paramagnetic center. Such energy transfer takes place due to rapid level crossings induced by the fluctuations of the local magnetic field sensed by the nuclei.