

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 rapidly to a value higher than thermal equilibrium, and then slowly approaches it. 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. In an experiment where protons were saturated prior the measurement, the ^{19}F magnetization does not overshoot to non-equilibrium values. 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.

In the following we will derive the expression for nuclear relaxation time induced by electron flips. Then we will explore the second order corrections to the Hamiltonian due to a hyperfine interaction and demonstrate that they **could not** produce time-dependent terms leading to relaxation. Next, we will explore the flip-flop rates in a system of one electron, one hyperfine coupled nucleus and another dipolar coupled nucleus. We will show that the flip-flop rates are smaller than nuclear flip rate $1/T_1$, and thus can be neglected.

Finally, we will explore a model where nuclear flip-flops occur due to fast nuclear energy level crossings, produced by random electron spin jumps.

3 Nuclear 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.

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):

$$W_n = |B|^2 \frac{\tau_c}{1 + \omega_n^2 \tau_c^2}, \quad (3)$$

where B is a non-secular part of hyperfine interaction, ω_n is the nuclear Larmor frequency, and τ_c is equal to electron correlation time. Carr-Purcell-Meiboom-Gill experiments have estimated earlier that a correlation time driven by electron flip-flops in 40 mM TEMPO radicals at 9.4 T magnetic field was on the order of 100 μ s (Potapov et al. JMR 2012). The 3.4 T magnetic field used in our experiments, the spectrum would become narrower by a factor of 3, thus effectively increasing the number of pairs producing flip-flops. On the other hand, our measurements are carried out at a lower temperature of 1.4 K, which produces smaller number of flip-flopping pairs due to a strong alignment of electrons. Our estimate of this effect yield a factor of 5 smaller number of pairs compared to higher temperatures. Overall the effects of magnetic field and temperature work in the opposite directions, thus leaving the correlation time about the same i.e. $\approx 100\mu$ s.

Given this correlation time, for most nuclei under our experimental conditions $\omega_n \tau_c \gg 1$, allowing the Eq.3 can be transformed as:

$$W_n \approx \left(\frac{B}{\omega_n}\right)^2 \frac{1}{\tau_c} \quad (4)$$

In an actual sample containing many nuclei the spin diffusion averages the nuclear relaxation times of nuclei, except nuclei in the vicinity of electron which are detuned from the bulk by strong hyperfine interactions.

4 Electron-mediated coupling between nuclei.

In this section we will explore the effective internuclear coupling emerging due to coupling of nuclei to the same electron. 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:

$$\mathcal{H} = \omega_S \hat{S}_z + \sum_{i,j=x,y,z} A_{ij}^{(H)} \hat{S}_i \hat{H}_j + \sum_{i,j=x,y,z} A_{ij}^{(F)} \hat{S}_i \hat{H}_j - \omega_H \hat{H}_z - \omega_F \hat{F}_z, \quad (5)$$

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:

$$\mathcal{H} = A_H \hat{S}_z \hat{H}_z + B_H \hat{S}_z \hat{H}_x - \omega_H \hat{H}_z + A_F \hat{S}_z \hat{F}_z + B_F \hat{S}_z \hat{F}_x - \omega_F \hat{F}_z \quad (6)$$

Since $B_H, B_F \ll \omega_H, \omega_F$, the non-secular terms can be regarded as a perturbation to a secular Hamiltonian. Let's denote the eigenstates of unperturbed Hamiltonian as $|k\rangle$: $|1\rangle = |\alpha_H \alpha_F\rangle$, $|2\rangle = |\alpha_H \beta_F\rangle$, $|3\rangle = |\beta_H \alpha_F\rangle$, $|4\rangle = |\beta_H \beta_F\rangle$. In this basis the matrix of perturbation $\hat{V} = m_S B_H \hat{H}_x + m_S B_F \hat{F}_x = \frac{m_S}{2} (B_H (H_+ + H_-) + B_F (F_+ + F_-))$ would have the following elements:

$$V_{ik} = \frac{m_S}{2} \begin{bmatrix} 0 & B_F & B_H & 0 \\ B_F & 0 & 0 & B_H \\ B_H & 0 & 0 & B_F \\ 0 & B_H & B_F & 0 \end{bmatrix} \quad (7)$$

The unperturbed energies will be:

$$\begin{aligned} E_1^0 &= -\frac{\omega_H + \omega_F}{2} + \frac{m_S}{2} (A_H + A_F) \\ E_2^0 &= -\frac{\omega_H - \omega_F}{2} + \frac{m_S}{2} (A_H - A_F) \\ E_3^0 &= \frac{\omega_H - \omega_F}{2} - \frac{m_S}{2} (A_H - A_F) \\ E_4^0 &= \frac{\omega_H + \omega_F}{2} - \frac{m_S}{2} (A_H + A_F) \end{aligned} \quad (8)$$

In the following we assume that unperturbed energy levels are non-degenerate, i.e. $E_2^0 \neq E_3^0$. The perturbation theory would produce the corrections to the eigenfunctions $|\Psi\rangle = |\phi^{(0)}\rangle + |\phi^{(1)}\rangle + |\phi^{(2)}\rangle \dots$, where $|\phi^{(l)}\rangle$ is the l th order correction. The first order perturbation to the

eigenfunction $|k^{(1)}\rangle$ can be written as:

$$|k^{(1)}\rangle = \sum_{l \neq k} \frac{|l^{(0)}\rangle \langle l^{(0)} | \hat{V} | k^{(0)} \rangle}{E_k^{(0)} - E_l^{(0)}} = \sum_{l \neq k} \frac{|l^{(0)}\rangle V_{lk}}{E_k^{(0)} - E_l^{(0)}} \quad (9)$$

Such first order perturbation only produce mixing with functions differing by $m_H = \pm 1, \Delta m_F = 0$, or $m_H = 0, \Delta m_F = \pm 1$ because $V_{23} = V_{14} = 0$. The second order perturbation contains more additional terms:

$$|k^{(2)}\rangle = \sum_{l \neq k, m \neq l} \frac{|l^{(0)}\rangle \langle l^{(0)} | \hat{V} | m^{(0)} \rangle \langle m^{(0)} | \hat{V} | k^{(0)} \rangle}{(E_k^{(0)} - E_l^{(0)})(E_k^{(0)} - E_m^{(0)})} = \sum_{l \neq k, m \neq l} \frac{|l^{(0)}\rangle V_{lm} V_{mk}}{(E_k^{(0)} - E_l^{(0)})(E_k^{(0)} - E_m^{(0)})} \quad (10)$$

This interaction mixes states differing by $\Delta m_H = \pm 1, \Delta m_F = \mp 1$ and $\Delta m_H = \pm 1, \Delta m_F = \pm 1$. For $|2\rangle = |\alpha_H \beta_F\rangle$, the mixing coefficient for $|3\rangle = |\beta_H \alpha_F\rangle$ can be calculated as:

$$c_{23}^{(2)} = \sum_{m \neq 3} \frac{|l^{(0)}\rangle V_{2m} V_{m3}}{(E_2^{(0)} - E_m^{(0)})(E_3^{(0)} - E_m^{(0)})} = \frac{V_{21} V_{13}}{(E_2^{(0)} - E_1^{(0)})(E_3^{(0)} - E_1^{(0)})} + \frac{V_{24} V_{43}}{(E_2^{(0)} - E_4^{(0)})(E_3^{(0)} - E_4^{(0)})} \approx \approx \frac{m_S^2 B_F B_H}{2 \omega_H \omega_H}$$

Also we can calculate the second order corrections to energies:

$$E_2^{(2)} = \sum_{k \neq 2} \frac{V_{2k}^2}{E_2^{(0)} - E_k^{(0)}} \approx \left(\frac{m_S}{2}\right)^2 \left(\frac{B_H^2}{\omega_H} - \frac{B_F^2}{\omega_F}\right) \quad (11)$$

$$E_3^{(2)} = \sum_{k \neq 3} \frac{V_{3k}^2}{E_3^{(0)} - E_k^{(0)}} \approx \left(\frac{m_S}{2}\right)^2 \left(\frac{B_H^2}{\omega_H} - \frac{B_F^2}{\omega_F}\right) \quad (12)$$

Although \hat{V} does produce mixing of states 2 and 3, the random jumps of an electron between states with $m_S = \pm \frac{1}{2}$ will not produce relaxation, because for an electron spin $\frac{1}{2}$ while m_S randomly fluctuates between $\frac{1}{2}$ and $-\frac{1}{2}$, m_S^2 stays constant $m_S^2 = \frac{1}{4}$. Nevertheless, the presence of such mixing implies that nuclei in the vicinity of an electron can be coupled even if they are spatially remote from one another.

Hyperfine couplings of protons (and fluorines similarly) can be estimated as $B \sim \frac{78 \text{ MHz}}{r^3} \frac{\text{\AA}^3}{\text{\AA}^3}$, 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. This implies that the mixing strength could achieve up to $D = \frac{B_H B_F}{8\omega_H \omega_F} \approx 0.01$ at 3.3 T field, while the dipolar couplings among methylene or methyl protons with couplings of ≈ 50 kHz might produce mixing of $\sim \frac{D}{\Delta\omega}$, which for proton-fluorine pair produces mixing of $\sim \frac{D}{\Delta\omega} \approx 0.01$.¹

The case for degenerate levels $|2\rangle, |3\rangle$ with $E_2^0 = E_3^0$ can also be treated, however interaction \hat{V} does not lift the degeneracy and requires treatment of the other states as well, which we will skip because it is quite lengthy. When other states are included the interaction \hat{V} does lift the degeneracy, with eigenfunction being almost pure $|2\rangle, |3\rangle$ with little admixtures of $|3\rangle, |2\rangle$ respectively. In effect the mixing produces terms on the order of $\frac{B^2}{\omega^2}$ just the same as in the non-degenerate case.

Overall it means that while the effective coupling between nuclei is present it does not produce a very significant mixing of states $|2\rangle, |3\rangle$ and is independent on the spin $\frac{1}{2}$ electron orientation.

5 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:

$$\mathcal{H} = \omega_S \hat{S}_z + \sum_{i,j=x,y,z} A_{i,j} \hat{S}_i \hat{H}_j + \omega_H \hat{H}_z + \omega_F \hat{F}_z + \sum_{i,j=x,y,z} D_{ij} \hat{H}_i \hat{F}_j, \quad (13)$$

¹Interestingly, the effect of mixing among nuclei in the vicinity of electron will be more pronounced for nuclei with lower γ , because the mixing coefficient does not scale with γ , while the mixing due to dipolar couplings will scale as γ

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:

$$\mathcal{H} = A\hat{S}_z\hat{H}_z + B\hat{S}_z\hat{H}_x + D_{i,j}\hat{H}_i\hat{F}_j + \omega_H\hat{H}_z + \omega\hat{F}_z + \sum D_{i,j}\hat{H}_i\hat{F}_j, \quad (14)$$

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:

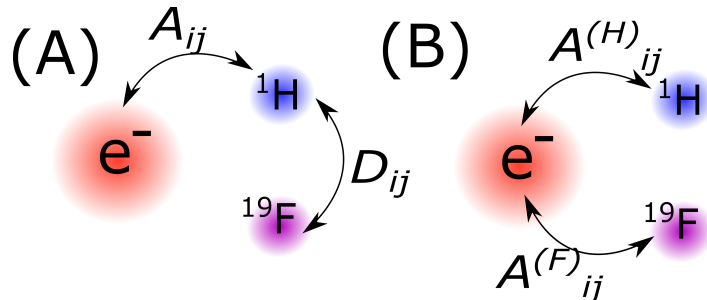
$$\mathcal{H} = (\omega_H + Am_S(t))H_z + BH_xm_S(t) + \omega\hat{F}_z + \sum D_{i,j}\hat{H}_i\hat{F}_j \quad (15)$$

The first two terms would collectively correspond to quantization of a nuclear spin along a new effective magnetic field $\tilde{\mathbf{B}} = \frac{1}{\gamma}(\omega_H + Am_S(t), \gamma B, 0)$. 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 the spin space, the dipolar part of the Hamiltonian can will then be transformed as:

$$\begin{aligned} \hat{\tilde{H}}_{dip}(t) &= \exp(-i\phi(t)\hat{H}_y) \sum_{i,j=x,y,z} D_{i,j}\hat{H}_i\hat{F}_j \exp(i\phi(t)\hat{H}_y) \approx \\ &\approx \phi(t) \left[\sum_{i,j=x,y,z} D_{ij}\hat{H}_i\hat{F}_j, \hat{H}_y \right] = \frac{m_S(t)B}{\omega_H} \left[\sum_{i,j=x,y,z} D_{ij}\hat{H}_i\hat{F}_j, \hat{H}_y \right] \end{aligned} \quad (16)$$

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

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.



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:

$$W_{ZQ} \sim \left| \frac{BD}{\omega_H} \right|^2 J(\omega_{ZQ})$$

$$J(\omega) = \frac{\tau_c}{1 + \omega^2 \tau_c^2} \quad (17)$$

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):

$$W_n \sim |B|^2 J(\omega_F) \quad (18)$$

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 $\omega_H \approx \omega_F$:

$$\frac{W_{ZQ}}{W_n} \sim \left| \frac{D}{\omega_H} \right|^2 \left(\frac{\omega_F}{\omega_{ZQ}} \right)^2 \sim \left(\frac{D}{\omega_{ZQ}} \right)^2 \quad (19)$$

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 a double-quantum process.

6 Cross-relaxation due to level-crossings.

As appears from Eq.8 the energy levels E_2 and E_3 could be rather close in energy, and could momentarily cross during the electron flip. We can neglect the perturbation \hat{V} because it does not produce a significant mixing of levels ($|2\rangle$ and $|3\rangle$ in particular). The effective Hamiltonian for a system of two nuclei is:

$$\mathcal{H} = A_H m_S \hat{H}_z + B_H m_S \hat{H}_x - \omega_H \hat{H}_z + A_F m_S \hat{F}_z + B_F m_S \hat{F}_x - \omega_F \hat{F}_z + D(\hat{H}_z \hat{F}_z + \frac{1}{2}(\hat{H}_+ \hat{F}_- + \hat{H}_- \hat{F}_+)), \quad (20)$$

where D is either a dipolar coupling. The Hamiltonian matrix in basis $|1\rangle, |2\rangle, |3\rangle, |4\rangle$ is:

$$\hat{H}_{ik} = \begin{bmatrix} -\frac{\omega_H + \omega_F}{2} + \frac{m_S}{2}(A_H + A_F) + \frac{D}{4} & 0 & 0 & 0 \\ 0 & -\frac{\omega_H - \omega_F}{2} + \frac{m_S}{2}(A_H - A_F) - \frac{D}{4} & D & 0 \\ 0 & D & \frac{\omega_H - \omega_F}{2} - \frac{m_S}{2}(A_H - A_F) - \frac{D}{4} & 0 \\ 0 & 0 & 0 & \frac{\omega_H + \omega_F}{2} - \frac{m_S}{2}(A_H + A_F) + \frac{D}{4} \end{bmatrix} \quad (21)$$

Let's focus on the evolution among states $|2\rangle$ and $|3\rangle$. Then we could introduce some effective spin $\hat{I}^{(23)}$. The effective Hamiltonian driving the evolution of such spin is:

$$\hat{H}_{eff} = \left(-\frac{\omega_H - \omega_F}{2} + \frac{m_S}{2}(A_H - A_F)\right)\hat{I}_z^{(23)} + D\hat{I}_x^{(23)}, \quad (22)$$

where diagonal dipolar interaction can be neglected because it is proportional to an identity matrix. This Hamiltonian is very simple, which is why we could replace its action by the vector model. Effectively, the rotation of magnetization in this model takes place around effective fields $\omega_+ = (D, 0, \Omega + a)$ and $\omega_- = (D, 0, \Omega - a)$ depending on the electron state m_S , where $\Omega = \frac{\omega_H - \omega_F}{2}$ and $a = \frac{A_H - A_F}{4}$. Consider initial magnetization $M = (0, 0, 1)$ at $t = 0$ aligned along z-axis, it rotates around ω_+ field, followed by a an electron flip at time τ_1 , rotation around ω_- field for interval τ_2 and a second electron flip. The rotation along the direction of ω_- would produce a vector:

$$\begin{aligned} \mathbf{M}(\tau_1) &= \mathbf{M}_{\parallel} + \mathbf{M}_{\perp x} \sin \omega_+ \tau_1 + \mathbf{M}_{\perp y} \cos \omega_+ \tau_1 \\ \mathbf{M}_{\parallel} &= \frac{(\mathbf{M}_0 \cdot \boldsymbol{\omega}_+)}{|\boldsymbol{\omega}_+|^2} \boldsymbol{\omega}_+ \\ \mathbf{M}_{\perp x} &= \frac{(\mathbf{M}_0 \times \boldsymbol{\omega}_+)_x}{|\boldsymbol{\omega}_+|} \\ \mathbf{M}_{\perp y} &= \mathbf{M}_0 - \mathbf{M}_{\perp x} - \mathbf{M}_{\parallel}, \end{aligned} \quad (23)$$

where \mathbf{M}_{\parallel} is the projections of vector \mathbf{M} along the direction of $\boldsymbol{\omega}_+$, $\mathbf{M}_{\perp x}$, $\mathbf{M}_{\perp y}$ are directional vectors in the plane perpendicular to $\boldsymbol{\omega}_+$. Vector \mathbf{M} will have a defined projection along the $\boldsymbol{\omega}_+$ and some additional component which orientation depends on τ_1 . An electron flip which follows next changes the direction of the effective field to ω_- , and magnetization continues to precess around this new direction. The component along the ω_- can be found as:

$$q = \frac{(\boldsymbol{\omega}_+ \cdot \boldsymbol{\omega}_-)}{|\boldsymbol{\omega}_+| |\boldsymbol{\omega}_-|} = \frac{D^2 + \Omega^2 - a^2}{\sqrt{D^2 + (\Omega + a)^2} \sqrt{D^2 + (\Omega - a)^2}}, \quad (24)$$

while the rest of vector \mathbf{M} will have a dependence on τ_1, τ_2 . Since electron flips are random, then realization of a random process is different in all three spin systems, i.e. time intervals τ_1, τ_2 are random. Since $D\tau_c \gg 1$ the time-dependent component is completely random in various three spin systems, and averaging over ensemble produces zero. (In other words, the nuclear coherences decay very quickly.)

Lets consider several scenarios.

Scenario 1. If $D \ll \Omega, a, |\Omega - a|$ the equation for q simplifies to:

$$q \approx 1 - \frac{D^2 a^2}{(\Omega^2 - a^2)^2} \quad (25)$$

After n step of random electron jumps taking place during interval $t = n\tau_c$, the magnetization will decrease by a factor:

$$q^n = \left(1 - \frac{D^2 a^2}{(\Omega^2 - a^2)^2}\right)^n = \exp\left(-\ln\left(1 - \frac{D^2 a^2}{(\Omega^2 - a^2)^2}\right)n\right) \approx \exp\left[-\frac{D^2 a^2}{(\Omega^2 - a^2)^2} \frac{t}{\tau_c}\right] \quad (26)$$

In other words the rate of nuclear flip-flop is $W_{ff} = \frac{D^2 a^2}{(\Omega^2 - a^2)^2} \frac{1}{\tau_c}$. Taking the ratio of a flip-flop rate and nuclear relaxation rate and assuming $B \sim a$ one obtains:

$$\frac{W_{ff}}{W_n} \approx \left(\frac{D\omega_H}{\Omega^2 - a^2}\right)^2 \quad (27)$$

For the smallest $a \ll \Omega$ under our experimental conditions is $\frac{W_{ff}}{W_n} < 1$. For nuclei located closer to the electron and thus having larger hyperfine couplings $\frac{W_{ff}}{W_n} \approx 1$.

Scenario 2.

However, there is chance that some nuclear pairs have frequency difference $a \approx \Omega$. For those the value of $q = \frac{D}{\sqrt{D^2 + 4\Omega^2}} \ll 1$. In practice it means that for one of the electron m_S states the levels of nuclear subsystem become degenerate and large D mixes them very rapidly.

Scenario 3. Another interesting case is of $\Omega = 0$, i.e. when both nuclei have the same Larmor frequency. The q then is:

$$q = \frac{D^2 - a^2}{D^2 + a^2} \quad (28)$$

For small $D \ll a$ this can be simplified as $q \approx 1 - \frac{D^2}{a^2}$, and the ratio of a flip-flop rate to nuclear

relaxation time is:

$$\frac{W_{ff}}{W_n} \approx \left(\frac{D\omega_H}{a^2}\right)^2 \quad (29)$$

For $a \approx 3$ this ratio becomes ≈ 1 and for smaller a it becomes even bigger. In practice it means that **flip-flops among nuclei of one kind are very likely to occur with nuclear magnetization lifetime.**

7 Conclusions.

We have shown that the flip-flip rate may be rather significant for fluorine-proton and proton-proton transfer.