¹H NUCLEAR MAGNETIC RELAXATION DISPERSION AS A SOURCE OF INFORMATION ON ELECTRON SPIN RELAXATION

DANUTA KRUK, AGNIESZKA MILEWSKA

Institute of Physics, Jagiellonian University, Reymonta 4, PL-30-059 Kraków, Poland

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The measurement of water proton ¹H spin-lattice relaxation rates in aqueous solutions of paramagnetic compounds provides information about electron relaxation times and the effective electron spin – nuclear spin dipole-dipole coupling. Relaxation dispersion profiles for water solution of 4-carboxy-TEMPO have been collected and analyzed in terms of Solomon-Bloemebergen-Morgan relaxation theory. The electron spin relaxation rates and the dipole-dipole constant have been estimated versus temperature.

INTRODUCTION

Nuclear Magnetic Resonance (NMR) field cycling (FC) relaxometry refers to experiments in which nuclear spin - lattice relaxation (typically for ¹H) is detected versus magnetic field (frequency). Field dependent relaxation studies are a unique source of information on structural and dynamical features of molecules. Especially NMR relaxometry is a well established experimental method for studying liquids dynamics. Performing relaxation experiments in different frequency ranges, one detects motional processes occurring on different time scales. In the low frequency range one observes slow dynamics while for successively higher frequencies spin interactions mediated by progressively faster motional processes become efficient. Due to the modern FC technology it has recently become possible to measure nuclear spin relaxation as a function of frequency in the range of 10 kHz – 20 MHz or more (for 1 H).

The FC sequence consists of three main blocks, separated by a very short times (0,2-2,0 ms):

- Polarization a magnetic field B_{pol} is applied until the magnetization reaches equilibrium. This block does not appear in a nonpolarization variant of FC ($B_{pol}=0$).
- Evolution the magnetic field is reduced to a lower value, B_{rlx}. The magnetization evolves in time adjusting itself to the new condition.
- Detection the magnetization is detected by applying a pi/2 pulse (B_{ACO}).

A schematic view of the experimental procedure is shown in Fig.1.

Paramagnetic species influence the NMR spectra of

liquids in several ways. NMR paramagnetic relaxation enhancement (PRE) refers to an enhancement of spinlattice relaxation of solvent nuclei (typically water protons) due to the presence of the paramagnetic species in solution (Bloembergen, Purcell & Pound, 1948).



Fig. 1. A schematic representation of the Fast Field Cycling (FFC) method of measuring nuclear spin-lattice relaxation.

measurements Relaxometric on solutions of paramagnetic solutes are often a convenient way for obtaining the nuclear spin-lattice relaxation rate versus the magnetic field and the electron spin-lattice and spinspin relaxation rates. In the case of nuclear spins in a paramagnetic substance, the largest source of nuclear relaxation is often the modulation of the coupling to the electron spin magnetic dipole. In liquids the dominating mechanism of the fluctuations of the mutual electron spin - nuclear spin dipole-dipole coupling is provided by molecular tumbling electron spin relaxation. Therefore, the field dependence of the PRE (commonly referred to as Nuclear Magnetic Relaxation Dispersion, NMRD, profile) carries potentially a wealth of information on structure and dynamics of the species involved (Strandberg & Westlund, 1996).

RELAXATION THEORY FOR PARAMAGNETIC SYSTEMS – A BACKGROUND

The dipole-dipole Hamiltonian $H_{DD}(I,S)$ (I and S denote the nuclear and electron spin, respectively) is given in the laboratory frame (defined by the direction of the external magnetic field) as (Kruk, 2007, Solomon & Bloembergen, 1956):

$$H_{DD}(I,S) = a_{DD}^{IS} \sum_{m=-2}^{2} (-1)^{m} F_{-m}^{2} T_{m}^{2}(I,S)$$
(1)

The components $T_m^2(I, S)$ of the two-spin tensor operator have the form:

$$T_0^2(I,S) = \frac{1}{\sqrt{6}} \left[2I_z S_z - \frac{1}{2} (I_+ S_- + I_- S_+) \right]$$
(2a)

$$T_{\pm 1}^{2}(I,S) = \mp \frac{1}{2} [I_{z}S_{\pm} + I_{\pm}S_{z}]$$
(2b)

$$T_{\pm 2}^{2}(I,S) = \frac{1}{2}I_{\pm}S_{\pm}$$
(2c)

The dipole-dipole coupling constant is defined as: $a_{DD}^{IS} = \sqrt{6} \frac{\mu_0}{4\pi} \frac{\gamma_I \gamma_S \hbar^2}{r_{IS}^3}$ where r_{IS} is the inter-spin distance, γ_I and γ_S are gyromagnetic factors for the spins *I* and *S*, respectively. The dipole-dipole interaction is axially symmetric. This implies that the special functions, F_{-m}^2 , involve only two Euler angles, namely:

$$F_{-m}^{2}(t) = D_{0,-m}^{2}(0,\beta_{DDL}(t),\gamma_{DDL}(t))$$
(3)

where the index 'DDL' denotes the angle between the dipole-dipole (DD) axis and the direction of the external magnetic field (L), $D_{0,-m}^2$ are Wigner rotation matrices of rank two. When the Redfield condition is fulfilled for the nuclear spin – electron spin system, i.e. a product of the amplitude of the dipole-dipole coupling and the correlation time, τ_c , describing its fluctuations is much smaller than one, $|H_{DD}|\tau_c <<1$, the nuclear spin-lattice relaxation rate, R_{1I} , are expressed as a linear combination of spectral densities (Slichter, 1990). A spectral density function, $J(\omega)$, is given as Fourier transform of a time correlation function, C(t). The time

correlation function for a stochastic quantity A(t) is defined as:

$$\left\langle A^*(t)A(0)\right\rangle = \iint A(x)A(x_0)P(x,x_0,\tau)P_{eq}(x_0)dx_0dx$$
(4)

The function $P(x, x_0, \tau)$ describes the probability that our system is in the state x at time τ if it has been in the state x' at time zero, while P_{eq} is the equilibrium distribution of states; in particular $P_{eq}(x_0)$ describes the probability of finding the state x_0 in equilibrium. The probability is obtained as a solution of the isotropic rotational diffusion equation:

$$P(\Omega, \Omega_0, t) = \frac{2l+1}{4\pi} \sum_{l,m} D_{0,m}^{l*}(\Omega_0) D_{0,m}^l(\Omega) \exp\left(-\frac{t}{\tau_R}\right)$$
(5)

where the characteristic time constant τ_R is the rotational correlation time for second rank Wigner rotational matrices. Substituting this series into the general definition of Eq.4, taking into account that $P_{eq}(\Omega_0) = 1/4\pi$ and making use of orthogonal properties of the Wigner rotation matrices, one obtains:

$$C(t) = \frac{1}{5} \exp\left(-\frac{t}{\tau_R}\right) \tag{6}$$

Fourier transform of such a correlation function (which has in this case Lorentzian form) reflects the spectral features of the motional processes leading to relaxation.

SOLOMON-BLOEMBERGEN-MORGAN RELAXATION THEORY

According to the Solomon – Bloembergen - Morgan (SBM) relaxation theory for paramagnetic systems, the nuclear spin lattice relaxation rate, R_{1I} , is described by the formula (Westlund, 1995; Solomon, 1955, Bertini, Luchinat & Parigi, 2001):

$$R_{1I} = \frac{1}{60} \left(a_{DD}^{IS} \right)^2 \times \left[\frac{\tau_{c2}}{1 + (\omega_I - \omega_S)^2 \tau_{c2}^2} + \frac{3\tau_{c1}}{1 + \omega_I^2 \tau_{c1}^2} + \frac{6\tau_{c2}}{1 + (\omega_I + \omega_S)^2 \tau_{c1}^2} \right]$$
(7)

where ω_I and ω_S denote the nuclear and electron spin Larmor frequencies. The correlation times entering Eq.7 are defined as follows:

$$\tau_{ci}^{-1} = \tau_R^{-1} + R_{i,e} \qquad (i = 1, 2)$$
(8)

The first term in the sum is the correlation rate originating from reorientation of the nuclear-electron spin vector, while the second one represents the electron spin relaxation rates: $R_{i,1}$ is the electron spin-lattice relaxation rate, while $R_{i,2}$ is the electron spin-spin relaxation rate. At this stage a qualitative explanation might be of help. The dipole-dipole interaction is a twospin interaction and therefore transitions of the nuclear spin between its energy levels are associated with transitions of the electron one (Bloembergen & Morgan, 1961). The terms in Eq.7 which contains ω_s reflect the contributions to the nuclear spin relaxation which are associated with the electron spin coherences involving its two energy levels (i.e. with the spin-spin relaxation process), while the terms which does not contain the transition frequency ω_s is associated with the populations of the electron spin energy levels (i.e. with its spin-lattice relaxation time).

EXPERIMENTAL RESULTS AND ANALYSIS

4-carboxy-Tempo belongs to the TEMPO group of radicals. It has one unpaired electron trapped between four methyl groups adjacent to the nitroxyl group (Fig. 2) which makes the radical stable. This compound is widely used in electron spin resonance spectroscopy as a structural probe for biological systems.



Fig. 2. Structure of 4-carboxy-TEMPO

The NMRD profiles for 10mM concentration water solution of 4-carboxy-TEMPO have been collected in the frequency range 10 kHz - 20 MHz at four temperatures: 288K, 298K, 308K and 318K. The obtained relaxation rates contain the diamagnetic (water) and the paramagnetic contribution (Bloembergen, 1957):

$$R_{1,observed} = R_{1,diamagnetic} + R_{1,paramagnetic}$$
(9)

To separate $R_{1,paramagnetic}$ from $R_{1,observed}$ the relaxation rates of pure water have been measured. It has been obtained: R_1^{288} =0,446 s⁻¹, R_1^{298} =0,365 s⁻¹, R_1^{308} =0,303s¹

and $R_1^{318}=0,254$ s⁻¹. The longitudinal relaxation time of water is in a very good approximation frequency independent. After extracting the diamagnetic contribution to the overall relaxation, the obtained relaxation rates have been normalized to the concentration of 1mM (i.e. divided by the concentration). The data are shown in Fig. 3. The SBM equation has been then applied to interpret the ¹H spinlattice relaxation profiles. A simplified form of this equation, obtained by taking $|\omega_1 \pm \omega_s| \cong \omega_s$, has been used:

$$R_{1I} = CK \left[\frac{3\tau_{c1}}{1 + \omega_I^2 \tau_{c1}^2} + \frac{7\tau_{c2}}{1 + \omega_S^2 \tau_{c2}^2} \right]$$
(10)

here C=0,001 is the concentration of 4-carboxy-TEMPO in the solution. The obtained results are collected in Table 1.



Fig. 3. ¹H spin-lattice relaxation dispersion profiles for 4carboxy-Tempo in solution normalized to 1mM concentration. Solid lines show results predicted by Eq.10 for the parameters given in Table 1.

Table 1. Parameters obtained from the least-square fits of Eq.10 to the relaxation data shown in Fig. 3.

Т	Κ	τ_{c1}	τ_{c2}
[K]	$[10^{6} Hz^{2}]$	$[10^{-8} s]$	$[10^{-8} s]$
288	920	8,9±2,7	2,22±0,36
298	690	8,4±1,8	1,95±0,23
308	600	7,7±3,2	1,67±0,35
318	358	8,5±1,9	1,82±0,21

DISCUSSION AND CONCLUSIONS

The observed dispersion of the relaxation data is, in fact, reflected by the second term in Eq.10, which is associated with the electron spin-spin relaxation time, T_{2e} . Since the correlation time, τ_{c2} , contains also the rotational component, one should treat the values given in Table 1. as the lower limit of T_{2e} (*i.e.* this relaxation process cannot be faster than it is described by these times). The spin-lattice relaxation time, T_{1e} , can be estimated from an almost "plateau" (frequency independent) contribution to the nuclear relaxation, given by the first term of Eq.10. Therefore the error of τ_{c1} is relatively large. K gives the amplitude of the effective electron spin - nuclear spin dipole-dipole constant. Its decrease with temperature can be explained by a progressively faster exchange processes between the water molecules belonging to the coordination sphere of the paramagnetic species and the solvent water molecules.

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