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NMR relaxometry: spin lattice relaxation times in the laboratory frame versus spin lattice relaxation times in the rotating frame

Emilie Steiner¹, Mehdi Yemlou¹, Laouès Guendouz², Sébastien Leclerc³, Anthony Robert¹, Daniel Canet¹*

¹Méthodologie RMN (CRM2, UMR 7036 CNRS- Nancy-Université), Faculté des Sciences et Technologies, BP 70239 54506 Vandoeuvre-lès-Nancy Cedex (France)

²Laboratoire d’Instrumentation Electronique de Nancy (EA 3440) Faculté des Sciences et Technologies BP 70239 54506 Vandoeuvre-lès-Nancy (cedex), France

³LEMTA (UMR 7563 CNRS- Nancy-Université), BP 160, 54504 Vandoeuvre-lès-Nancy (cedex), France

*Corresponding author: Daniel.Canet@crm2.uhp-nancy.fr

Abstract

Relaxometry dispersion curves display the spin lattice relaxation rate as a function of the measurement frequency. However, as far as proton NMR is considered, dispersion curves usually start around 5 kHz and thus miss the very low frequency region. This gap can be filled by the measurement of the spin-lattice relaxation rate in the rotating frame. The issue of connecting both relaxation rates is considered for two relaxation mechanisms: i) randomly varying magnetic fields, ii) dipolar interaction within a system of two equivalent spins. Appropriate data processing is presented and the random field mechanism turns out to be adequate.
1. Introduction

Measurement and interpretation of NMR relaxation times as a function of the measurement frequency $\omega_0$ (or, equivalently, as a function of the NMR static magnetic field $B_0$ through the Larmor equation $\omega_0 = \gamma B_0$, $\gamma$ being the gyromagnetic ratio of the considered nucleus) is called relaxometry. Applications are numerous [1] ranging from the characterization of slow molecular motions in complex systems to the effects of paramagnetic species on biological fluids. Dedicated instruments, called relaxometers (working according to field cycling methodology), are available in a range going from some kHz (say 5 kHz) to some tens of MHz (typically from 10 MHz to 40 MHz). Higher frequencies can be investigated with conventional NMR spectrometers, possibly with variable field electromagnets in the range 10 MHz-100 MHz, or at still higher frequencies with fixed frequency cryomagnets. Results, in terms of the longitudinal relaxation rate $R_1$ (the inverse of the relaxation time $T_1$), are usually presented in the form of a so-called dispersion curve, $R_1$ being the ordinate (with a logarithmic scale if variations are important) and the measurement frequency as abscissa (generally with a logarithmic scale). These dispersion curves present a gap in the frequency range going from zero frequency up to some tens of kHz. The present study is devoted to the way of filling this gap which can contain important information about slow motions or exchange phenomena. One possibility, explored in this paper, is to measure the so-called relaxation time in the rotating frame ($T_{1\rho}$ or its inverse $R_{1\rho}$) as a function of $\omega_1 = \gamma B_1$ where $B_1$ is the amplitude of the radio-frequency (rf) field along which nuclear magnetization is locked (measuring this relaxation time is accomplished by following the decay of locked magnetization). However, the major concern is that $R_{1\rho}$ does not depend on $\omega_1$ in the same way as $R_1$ depends on $\omega_0$ [2,3]. Indeed, in the case of diamagnetic systems, in only one instance [4] (to the best of our knowledge) was the $R_{1\rho}$ dispersion curve directly linked to the $R_1$ dispersion curve.
be mentioned that, in the case of paramagnetic relaxation enhancement (PRE), Fries et al. recently proposed [5] to use a linear combination of $R_1$ and $R_{1p}$. The approach presented here is along the same lines and could be applied to systems which possess a slow electronic spin relaxation [6], thus not overwhelming the low-frequency $R_{1p}$ dispersion. Otherwise $R_{1p}$ has been mostly used to characterize very slow motions [7, 8] or exchange phenomena in biological systems through $^{15}$N [9-14] or proton [15] measurements. It must be noticed that, in order to increase the frequency range, off-resonance experiments, first introduced by Desvaux [16], were employed [8,11-15]. This adds however some complexity in the exploitation of experimental data.

The present work is devoted to a transformation of $R_{1p}$ data so that they can complement the $R_1$ dispersion curve toward the very low frequencies. Obtaining a full dispersion curve presents obviously some advantages in terms of the accuracy of parameters derived from dispersion curves and may reveal relaxation mechanisms undetectable at higher frequencies. Exchange phenomena will not be envisioned here. The proposed procedure will be considered theoretically and two examples will be given: one dealing with a solvent in interaction with the surface of an organogel, the protons of this solvent being subjected in addition to a constant contribution due to paramagnetic relaxation, the other with the different types of water in a mesoporous medium.

2. Theory

The expressions of the three relaxation rates we are concerned with here (the spin-lattice or longitudinal $R_1$, the spin-spin or transverse $R_2$, the spin-lattice in the rotating frame $R_{1p}$) depend obviously on the relaxation mechanisms. We shall be dealing exclusively with dipolar interactions experienced by the proton(s) of the molecules under investigation. Two situations can be envisioned: i) interactions arise from outside; in that case randomly fluctuating
magnetic fields constitute a good approximation for evaluating the spectral densities entering the expression of relaxation parameters; ii) interactions take place inside the set of the considered protons (e.g. the dipolar interaction between the two protons of the water molecule) and one has to take heed of the whole system (constituted of “like spins”, according to Abragam’s terminology [17]) and, as will be seen below, this entails some complications. Of course, the present treatment rests on the hypothesis of classical dipolar interactions and would probably need some modifications in the case of a quantum magnetic moment, e.g. a paramagnetic ion [18].

Equations given below are expressed in terms of spectral densities [19,20], their simplest form being

\[ J(\omega) = \frac{2\tau_c}{1 + \omega^2 \tau_c^2} \]  

where \( \tau_c \) is a correlation time describing a motion supposed isotropic. Of course, the expressions below can accommodate any type of spectral density.

**Random fields**

\( \omega_0 \) and \( \omega'_0 \), being measurement frequencies, one has for the three relaxation rates

\[ R_i(\omega_0) = C2J(\omega_0) + R_{\text{other}} \]  

\[ R_2 = C[J(0) + J(\omega'_0)] + R_{\text{other}} \]  

\[ R_{1\rho}(\omega_1) = C[J(\omega_1) + J(\omega'_0)] + R_{\text{other}} \]  

\( C \) stands for a factor including constants and the amplitude of the relevant dipolar interaction; \( R_{\text{other}} \) stands for the contribution of other relaxation mechanisms. \( \omega_0 \) represents the low frequencies at which \( R_i \) is measured, just above (or overlapping with) the frequency range covered by the \( R_{1\rho} \) measurements. \( \omega'_0 \) is the frequency (relatively high for sensitivity
reasons) of the spectrometer with which these latter measurements have been carried out. (2) arises from the correlation function of the random field transverse components (x and y), hence the \(\omega_0\) dependency which corresponds to the precession of the two homolog magnetization components. Conversely, (3) and (4) depend on one transverse component and of the longitudinal component (z). The latter is responsible for the spectral density at zero frequency (no precession) in (3) and at \(\omega_1\) (nutation around the rf field) in (4). It can be noticed that the only difference between \(R_{1p}\) and \(R_2\) is the substitution of \(J(0)\) by \(J(\omega_1)\).

From equations (2) and (4), it is obvious that, in non extreme narrowing conditions, \(R_{1p}(\omega)\) cannot be equal to \(R_i(\omega)\). \(R_{1p}(\omega)\) can however be processed according to the following algebra. Consider the frequency \(\omega_{lb}\) in the region where \(R_{1p}\) and \(R_i\) overlap. We can always write

\[
2R_{1p}(\omega_{lb}) = 2CJ(\omega_{lb}) + R_{\text{other}} + C'
\]

with the constant \(C'\) defined as

\[
C = 2R_{1p}(\omega_{lb}) - R_i(\omega_{lb}) = 2CJ(\omega_0) + R_{\text{other}}
\]

Consider now a frequency \(\omega_{la}\) where only \(R_{1p}\) is available. In order to compare and eventually to connect \(R_i\) and \(R_{1p}\) data, the latter must be substituted by \(R_{1p}'\), which we define as

\[
R_{1p}'(\omega_{la}) = 2R_{1p}(\omega_{la}) - C'
\]

\(R_{1p}'(\omega_{la})\) should therefore be identical to \(R_i(\omega_{la})\).

Measurements of \(R_{1p}\) are performed for different values of \(\omega_1\) (by varying the amplitude of the rf field). According to equation (7), they are then multiplied by two and subtracted by a quantity independent of \(\omega_1\) and corresponding to \(2J(\omega_0)\) and to other contributions to the relaxation rates, constant at these low frequencies. In practice, this quantity is determined by
making coincident, in the overlap region, the two dispersion curves \( R_1(\omega_0) \) and \( R_{1,\rho}(\omega_0) \). Of course, the rf field amplitude cannot be made infinitely small. Fortunately, \( J(0) \) is better deduced from the measurement of \( R_2 \) to which the above treatment can be applied as well.

\[ \text{Like spins} \]

With the same notations as in the previous section, one has [2,3,17,19,20]

\[
R_1 = C[4J(2\omega_0) + J(\omega_0)] + R^{\text{other}} \approx 5CJ(\sqrt{3}\omega_0) + R^{\text{other}} \quad (8)
\]

\[
R_2 = C[\frac{2}{3}J(0) + \frac{1}{6}J(\omega_0' - \omega_{0''}) + J(2\omega_0') + \frac{3}{2}J(\omega_0')] + R^{\text{other}} \quad (9)
\]

\[
R_{1,\rho} = C[\frac{2}{3}J(2\omega_0) + \frac{1}{6}J(\omega_0' - \omega_{0''}) + J(2\omega_0') + \frac{3}{2}J(\omega_0')] + R^{\text{other}} \quad (10)
\]

The approximation in equation (8) which consists in replacing \( 4J(2\omega_0) + J(\omega_0) \) by \( 5J(\sqrt{3}\omega_0) \) has been shown to be very appropriate [21]. The somewhat complicated expressions of \( R_2 \) and \( R_{1,\rho} \) are due to the existence, in a two-spin system, of a two-quantum coherence (hence the spectral densities at \( 2\omega_0 \) or \( 2\omega_0' \)) and a zero-quantum coherence (emphasized here by \( J(\omega_0' - \omega_{0''}) \) which has not the same physical meaning as \( J(0) \)). There are some important differences with respect to the random field mechanism: \( J(0) \) in \( R_2 \) becomes \( J(2\omega_1) \) in \( R_{1,\rho} \), while \( R_1 \) depends on \( J(\sqrt{3}\omega_0) \). This means that the procedure described in the previous section can be applied with a multiplicative factor of 15/2 (in place of 2) and provided that the frequency scale is adapted to each parameter: \( \omega = \sqrt{3}\omega_0 \) for \( R_1(\omega) \) and \( \omega = 2\omega_0 \) for \( R_{1,\rho}(\omega) \).

3. Experimental
Two systems presently under investigation in this laboratory, with the objective of obtaining full dispersion curves, i.e. from zero up to several hundreds of MHz, were retained for the present study. However, as we are concerned here with the very beginning of the dispersion curve, we shall focus only on the frequency range 0-10 MHz. The first one is the solvent (toluene) necessary to the formation of an organogel built with a modified amino-acid [22]; the problem is to know whether, once the gel is formed, toluene still interacts with its surface (experiments performed at 20°C). An unexpected complication occurs due to dissolved oxygen in pure toluene, providing a strong paramagnetic contribution to relaxation rates [23].

At the time the organogel was prepared, we were not aware of this problem which would anyway be difficult to overcome due to the actual preparation procedure. Fortunately, this paramagnetic contribution is constant at low frequencies and can be simply subtracted thus permitting to examine unambiguously the effects of the toluene-gel interaction. On the other hand, due to the number of interacting protons and because it is the total proton magnetization of toluene which is measured, a random field mechanism can be predicted.

The second system is water within a mesoporous medium. In that case, one could wonder if the dipolar relaxation mechanism is intramolecular (the like spins model would prevail) or intermolecular or both. As further discussed in the conclusion, a random field mechanism will be shown to constitute a good approximation for the two latter cases. Anyway, the problem is to characterize, on the one hand, water inside pores, which presumably manifests itself at low frequencies due to a long correlation time, and, on the other hand, interstitial water, which is expected to contribute predominantly at high frequencies due to a smaller correlation time (experiments performed at 25°C). However, for such a system, the whole dispersion curve must be considered and its behavior at very low frequencies can be important for its global analysis.
Proton longitudinal relaxation times were first measured with a Stelar (Mede, Italy) Smatracer relaxometer operating between 5 kHz and 10 MHz according to field cycling automatic procedures [24]. This instrument requires 10 mm o.d. NMR sample tubes which were therefore utilized for subsequent measurements (so as to investigate the very same sample). A home-made spectrometer operating at 200 MHz was employed for $T_1$, and $T_2$ measurements. A special probe, accommodating 10 mm o.d. sample tubes (see above) and capable of handling relatively high rf power for a relatively long time (spin lock periods), was specially constructed. It involves a saddle-shaped coil of 29 mm height and 14.5 mm diameter (silver coated copper wire of 1.5 mm diameter) for covering a substantial portion of the sample with a homogeneous rf field, and high voltage 0.8-10 pF variable non magnetic capacitors (RP series, Polyflon, Norwalk, CT). Its quality factor is of 470. As a matter of fact, problems were encountered, not with the probe but with the stability and possible droops of the power amplifier. This prevents to go beyond 13 kHz (the rf field amplitude being expressed in frequency units) with durations of the spin-lock period up to 6s. This seemingly modest performance (as compared to a previous probe designed for 5mm o.d. sample tubes [25]) is due to the unfavorable coil geometry adapted to the 10mm o.d. sample tubes.

$T_1$ was deduced from the decay of the locked magnetization [19,20] under on-resonance conditions, implying two distinct experiments in the case of toluene, one for the methyl and the other for the aromatic resonances. The spin locking field amplitude is varied from experiment to the other and calibrated from the duration of a 180° rf pulse. $T_2$ was measured according to the CPMG method [26] in order to compensate imperfections of the 180° rf pulses and with a sufficient number of pulses in order to reduce diffusion effects, which, due to background gradients, could be important in the case of porous media [1].

4. Results and discussion
Figure 1 shows toluene raw data in the range 1 kHz-10 MHz ($R_{1\rho}$, $R_1$) for the pure solvent and for the solvent in the organogel phase. In both cases, one observes, as expected, a plateau at very low frequencies in accord with the first part of a Lorentzian curve (see eq. (1)). In the case of pure toluene, this plateau extends beyond 10 MHz and is attributable to paramagnetic relaxation [23]. Conversely, in the gel phase, the rise beneath 10 MHz is characteristic of a hindered motion, attributable to the interaction with the organogel. The rescaling of $R_{1\rho}$ data against $R_1$ data has been carried out as explained in the theory section according to the random field model. This is shown in figure 2. Owing to these excellent results, it was deemed unnecessary to try the other model (like spins). On the other hand, $T_2$ could actually be measured for the methyl resonance but not for the aromatic resonance because of the echo modulation by spin-spin couplings. Thus, the determination of the global $R_2$ turned out to be impossible. This was not considered as a penalty since $R_{1\rho}$ data just confirm the plateau guessed from $R_1$ data.

The other system dealt with in this study is water in a mesoporous medium [27]. Figure 3 shows the raw $R_1$ and $R_{1\rho}$ data obtained at 25° C. In figure 4, the $R_{1\rho}$ data have been rescaled according to the random field model so as to coincide with $R_1$ data in the overlap region. The consistency of both sets of data is seen to be excellent. Conversely, an attempt to rescale $R_{1\rho}$ data according to the like spins model (see above) is seen to fail (figure 5). Moreover, as shown in figure 6, $R_2$ appears to be in perfect agreement with what should be $R_{1\rho}$ at zero frequency (see equations (3) and (4)). This demonstrates the consistency of all relaxation data ($R_1$, $R_{1\rho}$ and $R_2$). For this system, we have therefore at hand the whole dispersion curve from zero frequency up to several hundreds of MHz (not shown). Indeed, it will be confirmed in a
future work that the data at very low frequencies are essential for properly analyzing dispersion curves.

Conclusion

This study has demonstrated the possibility of obtaining dispersion curves in the whole frequency range, including zero frequency (in the absence of J couplings) and very low frequencies. At least for the two investigated systems (very different in nature), the random field model appears perfectly adequate for linking $R_1$ and $R_{1\rho}$ evolutions. Besides a change in the frequency scale which is almost the same for $R_1$ and $R_{1\rho}$ data and, thus, is not very significant, the major difference between the random field model and the like spins model lies in the multiplicative factor which is applied to $R_{1\rho}$ data: 2 for the former model 15/2 for the latter. As a matter of fact, the failure of the like spins model is not very surprising because it applies strictly to a system made of two isolated spins, a situation which is rarely encountered.

Indeed, it can be shown that this property could be extended to a multi-spin system if and only if all the cross-relaxation rates are identical.

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References


Figure captions

Figure 1. Raw data of pure Toluene (20° C). Filled triangles: \( R_i \). Open triangles: \( R_{i,\rho} \).
Raw data of Toluene in the organogel phase (20° C). Filled squares: \( R_i \). Open squares: \( R_{i,\rho} \).

Figure 2. Filled squares: \( R_i \) data of Toluene in the organogel phase (20° C, identical to fig. 1).
Open squares: \( R_{i,\rho} \) data rescaled for coinciding with \( R_i \) data in the overlap region (see text).

Figure 3. Raw data for water in a porous medium (25°C). Filled squares: \( R_i \). Open squares:
\( R_{i,\rho} \).

Figure 4. Filled squares: \( R_i \) data of water in a porous medium (25° C, identical to fig. 3).
Open squares: \( R_{i,\rho} \) data rescaled for coinciding with \( R_i \) data in the overlap region (according to the random field model, see text).

Figure 5. Same as figure 4 but with the like spins model showing the inadequacy of the model. Note the modifications of the frequency scales according to the procedure detailed in the text.

Figure 6. Same as figure 1 with normal ordinate and abscissa scales (and reduced frequency range) permitting to display the \( R_2 \) value (triangle at zero frequency).
Figure 1
\( R_1 \) (s\(^{-1}\)) vs. \( \nu = \varpi / 2\pi \) (MHz)

Figure 2
Figure 3
\[ u = \frac{\omega}{2\pi} \text{ (MHz)} \]

\[ R_1 \text{ (s}^{-1}) \]

Figure 4
Figure 5
\[ u = \frac{\omega}{2\pi} \text{(MHz)} \]

Figure 6