



Methodology for solid state NMR off-resonance study of molecular dynamics in heteronuclear systems



Kazimierz Jurga, Aneta Woźniak-Braszak*, Mikołaj Baranowski

High Pressure Physics Division, Faculty of Physics, Adam Mickiewicz University, Umultowska 85, 61-614 Poznan, Poland

ARTICLE INFO

Article history:

Received 16 March 2015

Received in revised form

11 May 2015

Accepted 3 August 2015

Available online 4 August 2015

Keywords:

Solid-state NMR

Cross-relaxation

Heteronuclear interactions

The Nuclear Overhauser Effect

ABSTRACT

Methodology for the study of dynamics in heteronuclear systems in the laboratory frame was described in the previous paper [1]. Now the methodology for the study of molecular dynamics in the solid state heteronuclear systems in the rotating frame is presented. The solid state NMR off-resonance experiments were carried out on a homemade pulse spectrometer operating at the frequency of 30.2 MHz for protons. This spectrometer includes a specially designed probe which contains two independently tuned and electrically isolated coils installed in the coaxial position on the dewar. A unique probe design allows working at three slightly differing frequencies off and on resonance for protons and at the frequency of 28.411 MHz for fluorine nuclei with complete absence of their electrical interference. The probe allows simultaneously creating rf magnetic fields at off-resonance frequencies within the range of 30.2–30.6 MHz and at the frequency of 28.411 MHz. Presented heteronuclear cross-relaxation off-resonance experiments in the rotating frame provide information about molecular dynamics.

© 2015 Elsevier Inc. All rights reserved.

1. Introduction

The NMR off-resonance technique is a useful tool for studying internal motion in liquids and solid-state systems [2–7]. But its use for typical solid state systems requires overcoming the limitation of apparatus [8–10]. Another issue limiting the application of the off-resonance NMR technique for the study of molecular motion is an additional dipolar cross-relaxation in heteronuclear systems [11]. The heteronuclear ^{19}F – ^1H dipolar interactions contribute to the biexponential ^1H magnetization recovery and introduce multiple spectral density components into the relaxation matrix characterized by frequencies which are the sums and differences of the fluorine and proton Larmor frequencies [11–13]. The non-exponential nature of the spin-relaxation times in the laboratory and rotating frames requires making a more careful mathematical analysis and performing more relaxation experiments which could detect the varied internal dynamics.

Solid-state NMR experiments in which ^1H spins are detected while ^{19}F spins are continuously saturated for a long time $t \gg T_{11}$ simplify the procedure for the analysis of experimental data. Furthermore, if the value of the nuclear Overhauser effect NOE is close to the value of -1 , the precision of the determination of the correlation time is very small using techniques in the laboratory

frame [1], and the solution to this problem is to use the NMR off-resonance technique in which it is possible to determine the dispersion of the spin–lattice relaxation and dispersion NOE in the rotating frame. Only a few authors present expressions for the off-resonance spin lattice relaxation rate ρ_p^l and for the cross-relaxation rate σ_p in the rotating frame. The first field-cycling NMR investigation of ^1H – ^{13}C polarization transfer using cross-relaxation and the nuclear solid effect (NSE) was performed by Horsewill [14,15].

In this paper, a new off-resonance NMR technique for the study of molecular dynamics in heteronuclear ^1H – ^{19}F systems is described. Some solid state NMR experiments, in which detected ^1H spins are spin-locked in the effective field \vec{B}_e while ^{19}F spins are continuously saturated for a long time are proposed. By applying this idea the heteronuclear ^1H – ^{19}F dipolar interactions are suppressed.

The construction of an efficient probe with high sensitivity, where three different frequencies are close to each other, was a big challenge. A specially designed and constructed probe of NMR spectrometer contains two independently tuned and electrically isolated coils installed in the coaxial position on the dewar. A unique probe design allows working at three slightly differing frequencies off and on resonance for protons and at the frequency of 28.411 MHz for fluorine nuclei with complete absence of their electrical interference. The probe allows simultaneously creating rf magnetic fields at off-resonance frequencies within the range of

* Corresponding author.

E-mail address: abraszak@amu.edu.pl (A. Woźniak-Braszak).

30.2–30.6 MHz and at the frequency of 28.411 MHz.

From the dispersion of the off-resonance spin lattice relaxation rate ρ_ρ^I in the rotating frame the correlation times τ_c which describe the molecular dynamics were obtained. Moreover, the dependence of the steady-state NOE_ρ as a function of the effective frequency ω_e was presented giving also correlation times τ_c . So far, in the literature of the world, there are no published results for the dispersion NOE_ρ factor in off-resonance rotating frame.

2. Theory

2.1. The expressions for the off-resonance spin lattice relaxation rate ρ_ρ^I in the rotating frame and the cross-relaxation rate σ_ρ^{IS}

For the study of relaxation in the rotating frame, we are using the effective magnetic field \vec{B}_e which is given by the following expression:

$$\vec{B}_e = B_1 \hat{i} + \Delta B \hat{k}, \quad (1)$$

where B_1 is the amplitude of the component of rf magnetic field perpendicular to the static magnetic field \vec{B}_0 , rotating with the off-resonance angular frequency ω and $\Delta B = B_0 - \frac{\omega}{\gamma}$ is the off-resonance magnetic field [8,9].

The angle β between the effective field \vec{B}_e and the static magnetic field \vec{B}_0 is defined by the equation

$$\beta = \arctan\left(\frac{B_1}{\Delta B}\right) \quad (2)$$

The macroscopic differential equation for the longitudinal rotating frame relaxation of spin I by dipolar interaction with spin S was derived by Peng and co authors [12]. In our case spin I refers to protons and S refers to fluorines. The decay of the polarizations $\langle I_z \rangle(t)$ along the effective field \vec{B}_e is given by the following equation [12,16]:

$$\frac{d\langle I_z \rangle(t)}{dt} = -\rho_\rho^I (\langle I_z \rangle(t) - I'(\infty)) - \frac{N_I}{N_S} \sigma_\rho^{IS} (\langle S_z \rangle(t) - S(\infty)), \quad (3)$$

where ρ_ρ^I is the off-resonance spin lattice relaxation rate in the rotating frame, σ_ρ^{IS} is the cross-relaxation rate, $I'(\infty)$ is the equilibrium polarization for the I spins in the rotating frame, $S(\infty)$ is the polarization of the S spins at thermal equilibrium in the laboratory frame projected on the direction of the effective field \vec{B}_e ; N_I and N_S describe the number of nuclei I and S , respectively.

The off-resonance spin lattice relaxation rate in the rotating frame ρ_ρ^I is described by the following equation [12]:

$$\begin{aligned} \rho_\rho^I = & \frac{\alpha^2 \hbar^2}{10} \{ 2 \sin^2(\beta) J(\omega_e) + \sin^4\left(\frac{\beta}{2}\right) J(\omega_l - \omega_S + \omega_e) \\ & + \cos^4\left(\frac{\beta}{2}\right) J(\omega_l - \omega_S - \omega_e) + \\ & 3 \cos^4\left(\frac{\beta}{2}\right) J(\omega_l + \omega_e) + 3 \sin^4\left(\frac{\beta}{2}\right) J(\omega_l - \omega_e) \\ & + \frac{3}{2} \sin^2(\beta) J(\omega_S + \omega_e) + \frac{3}{2} \sin^2(\beta) J(\omega_S - \omega_e) \\ & + 6 \cos^4\left(\frac{\beta}{2}\right) J(\omega_S + \omega_l + \omega_e) + 6 \sin^4\left(\frac{\beta}{2}\right) J(\omega_S + \omega_l - \omega_e) \}, \end{aligned} \quad (4)$$

where $\alpha = \frac{\gamma_I \gamma_S}{r_{IS}^3}$, γ_S and γ_I are magnetogyric ratios, r_{IS} is the I–S bond vector.

For $\omega_e \ll \omega_l, \omega_S, \omega_l + \omega_S$; $\omega_e \approx \omega_l - \omega_S$ and the limit where $\beta \leq 10^\circ$, Eq. (4) reduces to the expressions

$$\begin{aligned} \rho_\rho^I = & \frac{\alpha^2 \hbar^2}{10} \{ 2 \sin^2(\beta) J(\omega_e) + J(\omega_l - \omega_S - \omega_e) + 3J(\omega_l) \\ & + 6J(\omega_S + \omega_l) \}. \end{aligned} \quad (5)$$

In on-resonance limit where β approaches 90° and taking into account the following limit $\omega_e \ll \omega_l, \omega_S, \omega_l \pm \omega_S$, Eq. (4) goes into expression

$$\begin{aligned} \rho_\rho^I = & \frac{\alpha^2 \hbar^2}{20} \{ 4J(\omega_e) + J(\omega_l - \omega_S) + 3J(\omega_l) + 6J(\omega_S) \\ & + 6J(\omega_S + \omega_l) \}. \end{aligned} \quad (6)$$

The cross-relaxation rate σ_ρ^{IS} is described by the formula

$$\begin{aligned} \sigma_\rho^{IS} = & \frac{\alpha^2 \hbar^2}{10} \{ \sin^4\left(\frac{\beta}{2}\right) J(\omega_l - \omega_S + \omega_e) \\ & - \cos^4\left(\frac{\beta}{2}\right) J(\omega_l - \omega_S - \omega_e) \\ & + \frac{3}{2} \sin^2(\beta) J(\omega_S + \omega_e) - \frac{3}{2} \sin^2(\beta) J(\omega_S - \omega_e) \\ & + 6 \cos^4\left(\frac{\beta}{2}\right) J(\omega_S + \omega_l + \omega_e) \\ & - 6 \sin^4\left(\frac{\beta}{2}\right) J(\omega_S + \omega_l - \omega_e) \}. \end{aligned} \quad (7)$$

Having regard to $\omega_e \ll \omega_l, \omega_S, \omega_l + \omega_S$; $\omega_e \approx \omega_l - \omega_S$ and to the limit $\beta \leq 10^\circ$, we find that Eq. (7) reduces to the equation

$$\sigma_\rho^{IS} = \frac{\alpha^2 \hbar^2}{10} \{ -J(\omega_l - \omega_S - \omega_e) + 6J(\omega_S + \omega_l) \}. \quad (8)$$

And for on-resonance limit $\beta = 90^\circ$ we get that

$$\sigma_\rho^{IS} = 0, \quad (9)$$

which means that the cross-relaxation vanishes. In the next part of the paper the IS superscripts in the symbol σ_ρ^{IS} will be omitted leaving only σ_ρ .

2.2. Heteronuclear NMR off-resonance experimental procedure

When the S spins are saturated for a long time, the equation $\langle S_z \rangle(t) = 0$ is satisfied and Eq. (3) can be rewritten as

$$\frac{d\langle I_z \rangle(t)}{dt} = -\rho_\rho^I (\langle I_z \rangle(t) - I'(\infty)) + \frac{N_I}{N_S} \sigma_\rho S(\infty) \quad (10)$$

The analytical solution to Eq. (10) is monoexponential [13] and is presented by the following equation:

$$\begin{aligned} \langle I_z \rangle(t) - I'(\infty) = & \frac{N_I \sigma_\rho}{N_S \rho_\rho^I} S(\infty) + \left(\langle I_z \rangle(0) - I'(\infty) - \frac{N_I \sigma_\rho}{N_S \rho_\rho^I} S(\infty) \right) \exp(-\rho_\rho^I \cdot t) \end{aligned} \quad (11)$$

Taking into account that [14]

$$\frac{I(\infty)}{S(\infty)} = \frac{\gamma_I}{\gamma_S}, \quad (12)$$

one can find that Eq. (11) can be rewritten as follows:

$$\begin{aligned} \langle I_z \rangle(t) - I'(\infty) = & \frac{N_I \sigma_\rho}{N_S \rho_\rho^I} I(\infty) \frac{\gamma_S}{\gamma_I} + \left(\langle I_z \rangle(0) - I'(\infty) - \frac{N_I \sigma_\rho}{N_S \rho_\rho^I} I(\infty) \frac{\gamma_S}{\gamma_I} \right) \exp(-\rho_\rho^I \cdot t). \end{aligned} \quad (13)$$

where $\langle I_z \rangle(0)$ is the polarization of spins I at time $t=0$ dependent on the initial conditions of the experiment.

Download English Version:

<https://daneshyari.com/en/article/5420318>

Download Persian Version:

<https://daneshyari.com/article/5420318>

[Daneshyari.com](https://daneshyari.com)