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Through-space R^3-HETCOR experiments between spin-1/2 and half-integer quadrupolar nuclei in solid-state NMR

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Abstract

We present several new methods that allow to obtain through-space 2D HETCOR spectra between spin-1/2 and half-integer quadrupolar nuclei in the solid state. These methods use the rotary-resonance concept to create hetero-nuclear coherences through the dipolar interaction instead of scalar coupling into the HMQC and refocused INEPT experiments for spin $n/2$ ($n > 1$). In opposite to those based on the cross-polarization transfer to quadrupolar nuclei, the methods are very robust and easy to set-up.

Keywords: Solid-state NMR; Quadrupolar nuclei; HETCOR; Dipolar coupling; HMQC; R-INEPT

1. Introduction

Most of the experimental nuclear magnetization resonance (NMR) methods for spin-1/2 nuclei in the solid-state, utilize indirect excitation via cross-polarization (CP). Nuclear polarization is usually transferred from abundant spins I with large gyromagnetic ratio γ_I and short longitudinal relaxation time T_{1I} to diluted spins S with small γ_S or long T_{1S}, in order to increase the magnetization of S and the repetition rate of the experiment. For resolution enhancement, CP is very often combined with magic-angle spinning (MAS) and various radio frequency (rf) pulse sequences to overcome the dipolar interactions [1]. The CP-MAS method has played an instrumental role in extending the analytical capabilities of solid-state NMR to the studies of 'rare' nuclei such as ^{13}C, ^{15}N and ^{29}Si. The widespread use of this method is not limited to signal enhancement, but also includes spectral editing and various 2D techniques, such as hetero-nuclear correlation (HETCOR) experiments. These experiments can provide detailed information about complex structures in chemistry, biology and materials science by identifying atoms in local 'proximity' to one another. Two-dimensional HETCOR methods have been well established in solution NMR [2,3] and solid-state NMR of spin-1/2 nuclei [4,5]. In the latter case, hetero-nuclear through-space connectivities, which are related to the dipolar interactions, are usually analyzed using the CP transfer [4,5]. For reasons of resolution and sensitivity, experiments are performed at increasingly high magnetic fields, which often leads to very fast MAS rates (presently up to 90 kHz) to minimize the occurrence of spinning sidebands due to chemical-shift anisotropy (CSA). However, the homo- and hetero-nuclear dipolar interactions are also drastically reduced at very large spinning speeds. In such a situation, the CP matching condition between the two rf-fields becomes very narrow and thus very sensitive to rf-inhomogeneity, and this led to the development of improved CP-MAS schemes involving amplitude and/or frequency rf modulations [6].

The use of CP involving half-integer quadrupolar nuclei ($S = 3/2$, 5/2, 7/2, 9/2) presents additional challenges due to the convoluted spin dynamics involved in the spin-locking and polarization transfer, especially under MAS conditions. In the powdered samples, these CP dynamics are

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strongly anisotropic with respect to crystalline orientation and they depend on numerous experimental parameters. As a result, methods including a CP transfer to or from half-integer quadrupolar nuclei present many important experimental and theoretical limitations. In this article, we would like to describe a new hetero-nuclear dipolar transfer, based on the rotary-resonance recoupling (R^3) concept, [7–12] that avoids most of the previous CP limitations. After recalling the limitations of CP-transfers including quadrupolar nuclei, we describe the R^3 concept and its application in two different HETCOR-types of experiments, based either on the HMQC [13] (hetero-nuclear multiple-quantum coherence) or the R-INEPT [14–16] (refocused insensitive nuclei enhanced by polarization transfer) principles. In the third part, we give several examples of R^3 HETCOR experiments obtained either with ^{1}H or ^{31}P spin-1/2 nuclei, and either with ^{23}Na ($S = 3/2$), or ^{27}Al ($S = 5/2$) quadrupolar nuclei. In the following, the observed nucleus will always be denoted S and the non-observed I.

2. Fast MAS CP transfer involving one half-integer quadrupolar nucleus

In the case of fast MAS, CP transfers between two (I and S) spin-1/2 nuclei, are only observable under the modified Hartmann–Hann condition [17,18]:

$$\nu_{1S} + \varepsilon\nu_{1I} = j\nu_R \quad (\varepsilon = \pm 1;\ j = \pm 1,\ \pm 2), \tag{1}$$

where ν_{1I} and ν_{1S} are the rf-fields, and ν_R is the spinning speed. With respect to the signal that should be observed after a $\pi/2$ pulse, the cross-polarized signal of S nuclei is enhanced proportionally to the ratio of the ν_0 Larmor frequencies:

$$\mathrm{Signal}_{cp}/\mathrm{Signal}_{\pi/2} = 0.725\nu_{0I}/\nu_{0S} \tag{2}$$

Cross-polarization between one spin-1/2 nucleus (I) and one half-integer ($S = n/2$, $n > 1$) nucleus submitted to the quadrupole interaction (defined by the quadrupole frequency $\nu_Q = 3e^2qQ/2S(2S-1)$), presents a considerable challenge due to the very complex spin dynamics involved in both the spin-locking of S nucleus and the I → S CP transfer itself. These dynamics are strongly anisotropic with respect to crystallite orientation and they depend on the relative size of several parameters: ν_{1I}, ν_{1S}, ν_R, the irradiation offsets, and the dipolar and quadrupolar interactions. The effect of MAS is of particular consequence, as it makes these two interactions time dependent. The efficiency of such CP experiments is much lower than the value given by Eq. (2), and the sensitivity is rarely enhanced with respect to the direct excitation method. However, CP remains useful to record through-space HETCOR spectra. The effect of MAS on spin-locking of S magnetization can be categorized based on the magnitude of the adiabaticity parameter:

$$\alpha_{ad} = \nu_{1S}^2/\nu_Q\nu_R \tag{3}$$

that is related to the speed at which the quadrupole interaction crosses zero as the sample rotates [19,20]. The efficiency of spin-locking increases when $\alpha_{ad} \ll 1$ or when $\alpha_{ad} \gg 1$, whereas the intermediate case $\alpha_{ad} \approx 1$ results in a loss of spin-locked states. In case of strong quadrupole interaction and fast spinning speed, only the first case, called sudden passage, is most of the time accessible. Under typical conditions, the sudden passage condition requires that $\nu_{1S} \ll 100$ kHz, and in practice, ν_{1S} of a few kHz is often used. In the case of weak ν_{1S}, the nutation frequency acting on the central-transition (CT) is multiplied by $(S + 1/2)$, and the fast MAS previous Hartmann–Hahn matching condition [Eq. (1)] translates to:

$$(S + 1/2)\nu_{1S} + \varepsilon\nu_{1I} = j\nu_R \quad (\varepsilon = \pm 1;\ j = \pm 1,\ \pm 2) \tag{4}$$

This small rf-value may result in vastly different spin-locking and polarization transfer efficiencies for different S resonances. As an example, the efficiency of S spin-locking degrades largely when the rotary-resonance condition:

$$\nu_{1S} = \mathrm{d}\nu_R/(S + 1/2), \quad (\mathrm{d} : \mathrm{integer}) \tag{5}$$

is met, and when the second-order quadrupole interaction ($\approx \nu_Q^2/\nu_{0S}$) increases [21]. In addition, the I → S CP transfer by itself introduces additional dips of efficiency with respect to those only due to the spin-locking process of the quadrupolar nucleus [Eq. (5)] [21]. As a conclusion, the CP method applied to quadrupolar nuclei is not an easy and robust experiment. In most cases, the CP transfer becomes much less sensitive than with spin-1/2 nuclei only. To be efficient, the rf-fields must be weak, which leads to a large sensitivity to off-resonance irradiation and rf-mismatch. This is the reason why MAS HETCOR spectra are often recorded with several complementary experiments performed with different irradiation offsets, especially at high magnetic field. rf matching curves [Eq. (4)] present numerous dips, which means that setting up the CP transfer is not easy, especially with samples of low sensitivity, and moreover, the efficiency of the CP transfer being C_Q dependent, sites with very different C_Q may not be observable simultaneously.

3. The rotary-resonance recoupling phenomenon

3.1. R^3 concept

The rotary-resonance recoupling (R^3) phenomenon occurs when the irradiation of one nucleus with an rf-field amplitude ν_1 is related to the spinning speed ν_R by a ratio $q = \nu_1/\nu_R$, that is equal to an integer or a fraction. This effect allows to re-introduce anisotropic interactions under MAS.

Under such conditions, dephasings due to homo-nuclear dipolar interactions occur for $q = 1/2$ (also known as HORROR condition [10]) and $q = 1$, while CSA and the hetero-nuclear dipolar interactions are re-introduced for $q = 1$ and $q = 2$ [22]. Rotary-resonance has the specific property that a delay introduced during the R^3 irradiation