Solid State Nuclear Magnetic Resonance 74-75 (2016) 1–9

Contents lists available at ScienceDirect

Solid State Nuclear Magnetic Resonance

journal homepage: www.elsevier.com/locate/ssnmr

A novel pulse scheme for multiple quantum excitation, SFAM to enhance the sensitivity of MQMAS experiments

Bálint Koczor, János Rohonczy *

Eötvös Loránd University, Department of Inorganic Chemistry, Pázmány Péter sétány 1/A, 1117 Budapest, Hungary

ARTICLE INFO

Article history:
Received 20 November 2015
Received in revised form
11 February 2016
Accepted 17 February 2016
Available online 22 February 2016

Keywords:
SFAM
Shifted FAM
MQMAS
FAM
DFS
Quadrupole NMR

ABSTRACT

The basic MQMAS sequence consists of two hard pulses, one excites the equilibrium population to MQ (Multiple Quantum) coherence, and the other converts back to detectable coherence after some evolution time t_1 (Medek et al., 1995 [1]). Unfortunately the MQ excitation and conversion processes are very inefficient due to the nonlinear nature of MQ processes. MQ conversion (converting MQ back to detectable coherence) efficiency can significantly be enhanced with DFS (Double Frequency Sweep) or FAM (Fast Amplitude Modulation) type pulses instead of rectangular pulse irradiation (Goldbourt and Madhu, 2002 [2]). In contrary to conversion, it is more challenging to enhance MQ excitation in MQMAS experiments, since most methods result in distorted lineshapes (Goldbourt and Madhu, 2002 [2]; Lim and Grey, 1998 [3]). In the present work MQ excitation of single crystals was studied, and the understanding of the process led to a principle, which was extended to the excitation of powder samples as well. The resulting method was implemented into the MQMAS sequence to enhance MQ excitation of powder samples under MAS condition. The new sequence called SFAM (Shifted Fast Amplitude Modulation) can provide high enhancements at low RF powers ($\epsilon > 4$ at $\nu_{rf} = 40$ kHz) compared to rectangular pulses. Although simulated lineshapes of SFAM predict only minor deviations from ideal lineshapes, experimentally obtained lineshapes along the anisotropic dimension show rather strong distortions. SFAM is relatively simple to optimize, and shows robustness with respect to the miscalibration or inhomogeneity of the RF power as well as to other parameters of the pulse scheme. A good agreement was found between numerically and experimentally optimized parameters.

1. Introduction

1.1. MQMAS experiments

NMR combined with MAS offers a sensitive probe of the atomic-scale environment in the solid state, since most of anisotropic interactions [4] can be removed by rotating the sample around the magic angle 54.736°. However, most NMR active nuclei posses a spin $I > 1/2$, thus yielding a quadrupole coupling due to interaction with the surrounding electronic environment. The second order quadrupole coupling is not removed by rotating around the magic angle, obscuring the chemical shift differences between chemically distinct sites in case of strong couplings. The effect of second order quadrupole coupling on symmetric transitions can be expressed as a linear combination of Legendre polynomials [2]. DAS (Dynamic Angle Spinning) [5,6] and DOR (DOuble Rotation) [5,7] methods both utilize the manipulation of the spatial part of the quadrupole Hamiltonian involving special hardware, utilizing the fact that the second and fourth order Legendre polynomial contributions can be removed by rotations around different axes. STMAS [8] was also developed to obtain high resolution MAS NMR spectrum of quadrupolar nuclei with half-integer spin, however, it requires a very precise setting of the magic angle.

On the contrary, MQMAS was developed to obtain high resolution NMR spectra of quadrupolar nuclei with commercial MAS probes, utilizing the manipulation of both spatial and spin parts of the spin Hamiltonian. Radio frequency pulses are used to create symmetric multiple quantum coherent spin states, which are correlated with the CT (Central Transition) detectable coherence during the experiment, resulting in a 2D spectrum. Both isotropic and anisotropic projections can be obtained from MQMAS spectra. The simplest realization of this method consists of two hard pulses separated by a variable delay [1] corresponding to the $t1$ evolution time. The first pulse excites the nuclei into the multiple quantum coherence state, and the other converts the MQ density to detectable CT signal. The coherence order selection is performed with proper phase cycling [1].

* Corresponding author.
E-mail address: rohonczy@chem.elte.hu (J. Rohonczy).

http://dx.doi.org/10.1016/j.ssnmr.2016.02.001
0926-2040/

1.2. Sensitivity enhancement of MQMAS

Although MQMAS is extensively used to study the atomic-scale environment of solids containing quadrupolar nuclei, it suffers from poor sensitivity due to the need of filtration through multiple quantum coherences. This problem gets more significant in cases, when the RF power is limited, since nonlinear MQ excitation and conversion processes require extremely large RF fields in case of strong quadrupole couplings.

Several methods have been developed to improve the sensitivity of MQMAS so far, mainly focusing on the enhancement of the second, conversion pulse, the conversion from multiple to single quantum coherence. DFS (Double Frequency Sweep) [9], FAM (Fast Amplitude Modulation) [10–12], SPAM (Soft Pulse Added Mixing) [13,14], WURST (Wideband, Uniform Rate, Smooth Truncation) [15] and HS (Hyperbolic Secant) [16] methods can result in a significant enhancement of the multiple to single quantum coherence conversion of quadrupolar nuclei. FAM methods consist of a number of oppositely phased high-power pulses and optionally short delays separating these pulses. Significant enhancement of the conversion process is expected with FAM at the cost of the optimization of the pulse lengths and RF powers. DFS utilizes a cosine type amplitude and corresponding phase modulation of the pulse, sweeping through the satellite region of the involved nuclei. Even higher enhancements can be achieved with DFS at the cost of a more challenging optimization process. Pulse schemes employing low RF powers but longer pulse lengths were also developed. FASTER (FAst Spinning gives Transfer Enhancement at Rotary resonance) [17] utilizes rotary resonance conditions of the RF power resulting in about a threefold conversion enhancement, but causing relatively strong lineshape distortions.

In contrary to conversion, only few methods have been developed for the enhancement of the multiple quantum excitation process. Mainly rectangular pulses are used to excite quadrupolar nuclei if high RF fields are available. FASTER was optimized for triple quantum (TQ) excitation with the powerful tool provided by optimal control theory, resulting in a pulse scheme [18] requiring less RF power than the original one and yielding more enhancement, but involving longer pulses than 4 rotor periods $\tau_p > 4\tau_r$. RIACT (Rotation Induced Adiabatic Coherence Transfer) [19] can be used to enhance the excitation involving a CT selective 90° pulse creating the CT coherence immediately followed by a 1/4 rotor period long hard CW pulse. The main drawback of this method is the lineshape distortions introduced in the anisotropic dimension [3,20]. RAPT (Rotation Assisted Population Transfer) [21], the realization of population transfer for powder samples, can be used to redistribute the equilibrium populations resulting in additional CT intensity. This enhanced CT starting coherence was excited with RIACT [22] resulting in a significant signal enhancement with relatively small lineshape distortions [22,23]. This method is advantageous [2] considering signal enhancement, and the difficulty of optimization, but still suffers from minor lineshape distortions.

In this work we propose a method which utilizes both MQ excitation and population transfer techniques in a single pulse scheme, used to enhance the MQ excitation of MQMAS experiments. Based on an analytical model, it is shown how the theoretically possible maximum TQ intensity is achieved on single crystals.

In order to achieve the maximum TQ excitation in case of spin 3/2 nuclei of a single crystal, its satellite transitions must be irradiated selectively with half of the RF power at the same time as the central transition. This is achieved with a cosine modulated pulse, shifted with a constant factor $\lambda=1$, where λ is the ratio of the constant shift and the amplitude of the cosine function.

This method can be extended to powder samples by implementing the shifting factor to either the DFS or FAM pulses. In this work we propose the SFAM (Shifted Fast Amplitude Modulated) scheme, which is used to enhance the excitation process in MQMAS experiments. This scheme provides significant signal enhancement over rectangular pulse excitation in case of medium and small RF fields ($\epsilon > 4$ at $\nu_{rf} = 40$ kHz). This property is very advantageous in case of small gamma nuclei or if only limited RF power is available. Our method is relatively simple to optimize, and very robust with respect to its parameters (RF power, pulse separation delay and repetition number). A good agreement was found between numerically and experimentally optimized parameters. SFAM is robust with respect to the quadrupole coupling constant C_Q and the RF field inhomogeneity as well.

In this paper we first derive the model of single crystal excitation, then we demonstrate the usefulness of SFAM, particularly the optimization process and the enhancement achieved with SFAM with respect to the quadrupole coupling and RF field strengths. We also compare lineshapes obtained using SFAM. Finally we provide an experimental demonstration of SFAM enhanced MQMAS.

2. MQ excitation and conversion in single crystals

2.1. Model to describe selective irradiations

The Liouville–von Neumann equation is used to describe the time evolution of individual density matrix elements. The evolution of $\rho^{\beta\gamma}$ matrix element is written as

$$i\frac{\partial\rho^{\beta\gamma}}{\partial t} = \left[\hat{\mathcal{H}}, \rho^{\beta\gamma}\right] = \omega_{rf}\left[\hat{I}_x, |\beta\rangle\langle\gamma|\right] + \omega_{0ff}\left[\hat{I}_z, |\beta\rangle\langle\gamma|\right] + \left[\hat{\mathcal{H}}_Q^{(1)}, |\beta\rangle\langle\gamma|\right] \quad (1)$$

Matrix elements of the density operator are treated as state projectors $\rho^{\beta\gamma} = |\beta\rangle\langle\gamma|$. The rotating frame first order Hamiltonian includes the interaction with the external RF field $\omega_{rf}\hat{I}_x$, assuming a pulse with $\Phi=0$ phase, the first order quadrupole interaction $\hat{\mathcal{H}}_Q^{(1)}$, and the $\hat{I}_z$ contribution due to offset irradiation $\omega_{0ff}\hat{I}_z$.

This model leads to a coupled differential equation system of the matrix elements. From now on spin 3/2 nuclei with a positive gamma factor are considered according to the notation of matrix elements defined in Appendix A. Assume a quadrupole frequency $\frac{1}{2}\omega_Q/2\pi$ that defines the offset of satellite transitions relative to the central transition. Assume a pure triple-quantum starting density operator $\hat{\rho}_0 = \hat{I}^+\hat{I}^+\hat{I}^+$. In case of selective irradiation at one of the satellite transitions' frequency $\frac{1}{2}\omega_Q/2\pi$, it is a good approximation to keep only two equations corresponding to TQ and DQ matrix elements (see detailed evaluation in Appendix B). This assumption corresponds to the limit $\omega_Q \gg \omega_{rf}$. Contributions from neighboring matrix elements are neglected in the limit, thus as a consequence of selective satellite irradiation, the coupled differential equation system reduces to the following form:

$$\frac{\partial(TQ)_{\alpha\delta}}{\partial t} = i\omega_{rf}\frac{\sqrt{3}}{2}(DQ)_{\alpha\gamma} - i\frac{3}{2}\omega_Q(TQ)_{\alpha\delta} \quad (2)$$

$$\frac{\partial(DQ)_{\alpha\gamma}}{\partial t} = i\omega_{rf}\frac{\sqrt{3}}{2}(TQ)_{\alpha\delta} - i\frac{3}{2}\omega_Q(DQ)_{\alpha\gamma} \quad (3)$$

The analytical solution of the differential equation system defines a sinusoidal transformation of the TQ density to DQ density. See Appendix C for more details:

$$(TQ)_{\alpha\delta}(t) = C_1\cos\left(\frac{\sqrt{3}}{2}\omega_{rf}t\right)\exp\left(-i\frac{3}{2}\omega_Q t\right) \quad (4)$$