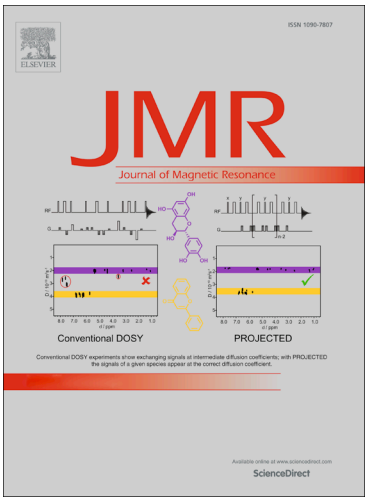

Optimized phases for the acquisition of *J*-spectra in coupled spin systems for thermally and PHIP polarized molecules

S. Bussandri, I. Prina, R.H. Acosta, L. Buljubasich

PII: S1090-7807(18)30043-0
DOI: https://doi.org/10.1016/j.jmr.2018.01.020
Reference: YJMRE 6243

To appear in: *Journal of Magnetic Resonance*

Received Date: 19 December 2017
Revised Date: 25 January 2018
Accepted Date: 28 January 2018

Please cite this article as: S. Bussandri, I. Prina, R.H. Acosta, L. Buljubasich, Optimized phases for the acquisition of *J*-spectra in coupled spin systems for thermally and PHIP polarized molecules, *Journal of Magnetic Resonance* (2018), doi: https://doi.org/10.1016/j.jmr.2018.01.020

Optimized phases for the acquisition of J-spectra in coupled spin systems for thermally and PHIP polarized molecules.

S. Bussandri[a,b], I. Prina[a,b], R. H. Acosta[a,b], L. Buljubasich[*a,b]

[a]*Universidad Nacional de Córdoba - Facultad de Matemática, Atronomía, Física y Computación, Córdoba, Argentina.*
[b]*CONICET - IFEG, Córdoba, Argentina.*

Abstract

We demonstrate that the relative phases in the refocusing pulses of multipulse sequences can compensate for pulse errors and off-resonant effects, which are commonly encountered in J-spectroscopy when CPMG is used for acquisition. The use of supercycles has been considered many times in the past, but always from the view point of time-domain NMR, that is, in an effort to lengthen the decay of the magnetization. Here we use simple spin-coupled systems, in which the quantum evolution of the system can be simulated and contrasted to experimental results. In order to explore fine details, we resort to partial J-spectroscopy, that is, to the acquisition of J-spectra of a defined multiplet, which is acquired with a suitable digital filter. We unambiguously show that when finite radiofrequency pulses are considered, the off-resonance effects on nearby multiplets affects the dynamics of the spins within the spectral window under acquisition. Moreover, the most robust phase cycling scheme for our setup consists of a 4-pulse cycle, with phases $yy\overline{yy}$ or $xx\overline{xx}$ for an excitation pulse with phase x. We show simulated and experimental results in both thermally polarized and PHIP hyperpolarized systems.

Keywords: CPMG, CP, Echo trains, J-spectroscopy, NMR, Hyperpolarization, Parahydrogen, PHIP, Phase cycling, Pulse sequences, J-coupling, Spin dynamics

1. Introduction

Echo trains are at the heart of NMR since the first implementation by Carr and Purcell in 1954 [1]. The original pulse sequence consisted of a train of refocusing radiofrequency pulses preceded by an excitation pulse, all with the same phases. A few years later, Meiboom and Gill presented an alternative to the original pulse sequence, with the π pulses phase shifted 90° with respect to the excitation pulse. The sequence, widely known as CPMG in the realm of NMR, proved to be more efficient in removing cumulative effects of errors caused by π-pulse missetting [2].

The multi refocusing pulse sequences opened the way to a wide range of applications in NMR. The accurate measurements of T_2 is crucial in the analysis of mechanical and thermodynamic properties of polymers [3], in on-line chemical reactions monitoring [4, 5], the study of chemical exchange mechanisms in diluted systems [6–8], or in the study of protein dynamics [9].

Within the ample field of porous media, CPMG is generally used to obtain pore size distributions [10, 11]. Ultra fast MRI pulse sequences for static or dynamic systems like RARE and FLIESSEN [12, 13] are built based on echo trains. Additionally, multiechoes sequences are plugged at the end of many pulse sequences, as an acquisition block in order to improve signal-to-noise ratios by means of echoes addition [14]. The vast amount of applications and its variety manifests the enormous importance of multiechoes sequences in NMR. In terms of spectroscopy, in the 60's and 70's, echo trains played a central role in the determination of indirect spin-spin couplings, or J-couplings, in liquid state NMR [15–17].

ParaHydrogen Induced Polarization (PHIP) is a very popular hyperpolarization technique in constant development. After its first appearance in 1986 [18], the technique has evolved embracing applications ranging from the study of specific kinetics in chemical reactions [19], development of heterogeneous catalysts [20], in the field of MRI [21–25], hyperpolarization transfer via specially designed pulse sequences [26, 27] or physical transport [28–30], and also in the context of long lived

Email address: lbulju@famaf.unc.edu.ar (L. Buljubasich[*])