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2_4-SEMA as a sensitive and offset compensated SLF sequence

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ABSTRACT

Separated Local Field (SLF) spectroscopy is a powerful tool for the determination of structure and dynamics of oriented systems such as membrane proteins oriented in lipid bilayers and liquid crystals. Of many SLF techniques available, Polarization Inversion Spin Exchange at Magic Angle (PISEMA) has found wide application due to its many favorable characteristics. However the pulse sequence suffers from its sensitivity to proton resonance frequency offset. Recently we have proposed a new sequence named 2_4-SEMA (J. Chem. Phys. 132 (2010) 134301) that overcomes this problem of PISEMA. The present work demonstrates the advantage of 2_4-SEMA as a highly sensitive SLF technique even for very large proton offset. 2_4-SEMA has been designed for obtaining reliable dipolar couplings by switching the magic-angle spin-lock for protons over four quadrants as against the use of only two quadrants in PISEMA. It is observed that for on-resonance condition, 2_4-SEMA gives rise to signal intensity comparable to or slightly higher than that from PISEMA. But under off-resonance conditions, intensities from 2_4-SEMA are several fold higher than those from PISEMA. Comparison with another offset compensated pulse sequence, SAMPI4, also indicates a better intensity profile for 2_4-SEMA. Experiments carried out on a single crystal of ^{15}N labeled N-acetyl–DL-valine and simulations have been used to study the relative performance of the pulse sequences considered.

1. Introduction

Dipolar couplings provide structural information due to their dependence on molecular orientation and inter-atomic distances. They are also sensitive to molecular dynamics and can provide information about local motion. There exist a wide range of NMR methods which help in extracting heteronuclear dipolar coupling in the solid state which are known as Separated Local Field (SLF) techniques [1,2]. SLF experiment resolves in two dimensions heteronuclear dipolar couplings on the basis of the chemical shifts. Such experiments are used extensively to characterize the structure of magnetically and mechanically oriented membrane proteins in lipid bilayers [3–11] and also to study liquid crystalline systems [12–14]. Out of the several possible SLF methods available for measuring dipolar couplings, the technique Polarization Inversion Spin Exchange at Magic Angle (PISEMA) [15,16] is being used extensively. This technique utilizes the exchange of spin polarization between ^{1}H and a low γ nucleus such as ^{15}N. In this experiment, during t_1, proton magnetization is spin-locked along an effective field at the magic angle. ^{15}N magnetization also remains spin-locked at the Hartman–Hahn match during this time period with phases following the proton. During spin exchange, magnetization evolves under the heteronuclear dipolar couplings while the homonuclear dipolar couplings are removed. For efficient removal of proton homonuclear dipolar couplings there exist many effective methods [17–22]. Out of these Lee–Goldburg (LG) homonuclear decoupling sequence [17] provides efficient averaging of the couplings and a large scaling factor. Though robust in several aspects, the major disadvantage of PISEMA is that the measured dipolar couplings depend largely on the proton offsets. This may be a major limitation of this sequence for experiments performed at higher magnetic fields. Especially in the case of proteins, where amide proton chemical shifts span a range of about 14 ppm, the effects are very significant [23,24]. To address this issue, several approaches have been proposed in the literature [25–28]. One such pulse sequence that retains the advantage of PISEMA (Fig. 1a) and at the same time removes its proton offset dependence is the recently reported SLF sequence, 2_4-SEMA [29] (Fig. 1). The sequence is designed in such a way that the effective field is cycled through all the four quadrants during t_1 evolution (Fig. 1b), whereas in PISEMA it is cycled only through two quadrants (Fig. 1a). Switching the effective field through all the quadrants has been achieved by changing the offset and r.f. phase of the spin-lock appropriately.

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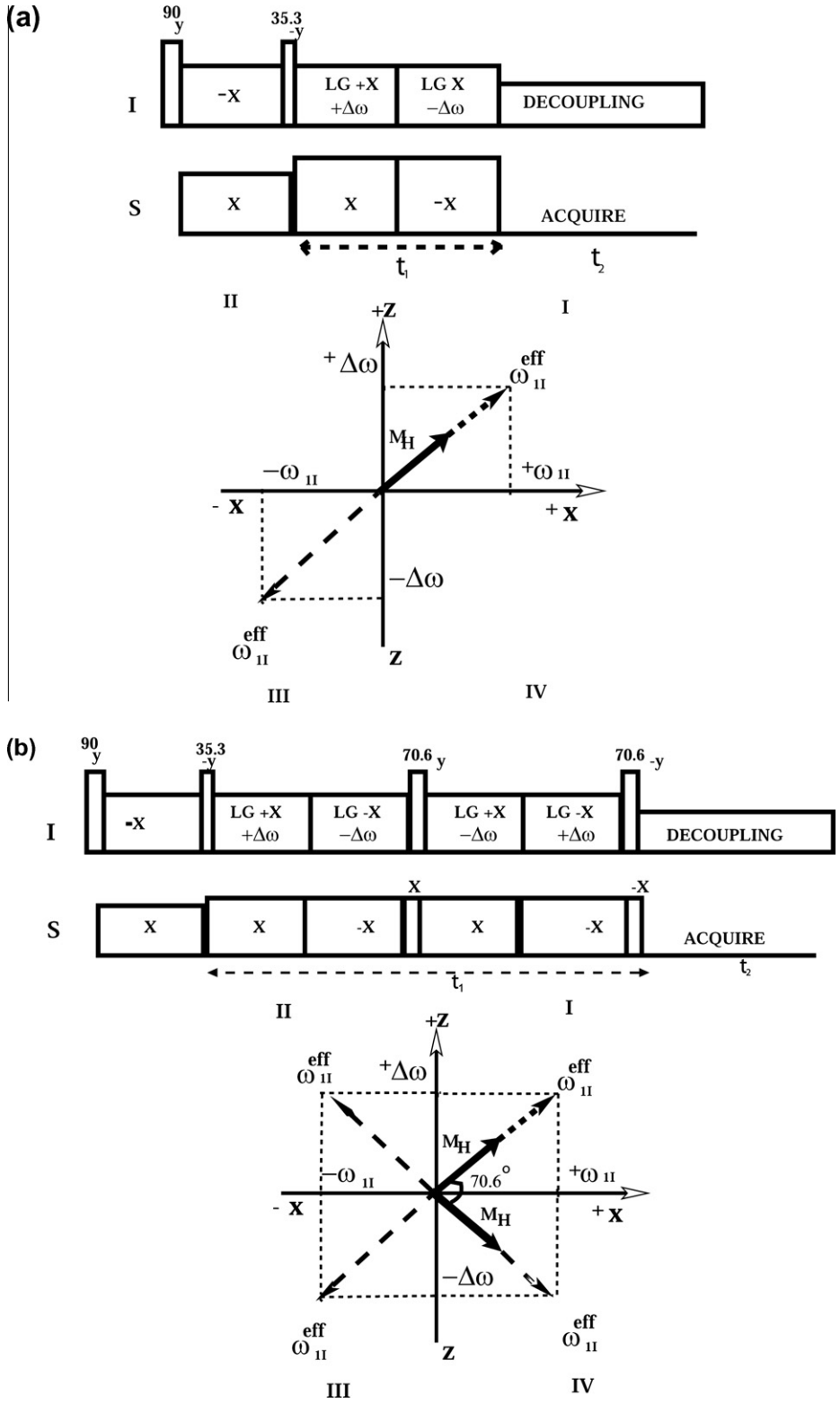

Fig. 1. (a) PISEMA and (b) 2_4-SEMA pulse sequence with their respective effective fields.

Proton magnetization is appropriately switched to retain the spin-lock with the use of additional 70.6° pulses. Since the magnetization is switched between two quadrants and the effective field between all the four quadrants in one t_1 evolution, the sequence is named as 2_4-SEMA, where '2' represents the magnetization and the subscript, '4' represents the effective field. Contrary to the expectation that the efficiency of homonuclear decoupling might deteriorate with the insertion of additional on-resonance pulses in the middle of the decoupling sequence for back and forth switching of magnetization, we have observed with 2_4-SEMA good resolution and sensitivity for the peaks even at extreme proton offsets. This is a feature which was not reported earlier.