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Quadrupole Sensitive Pulse for Signal Filtering

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Abstract

A longstanding problem in quadrupolar NMR of semi-solids is the selection of signals originating from ordered nuclei, i.e. those that experience a non-vanishing quadrupolar coupling. Established techniques, such as for example multiple-quantum filters are not adequate in situations when the radio frequency power is on the order of the quadrupolar coupling or the quadrupolar relaxation rates, such as may be the case on an MRI scanner, or in ex situ applications. In this manuscript we show a new method for the selective excitation of ordered spin-3/2 nuclei, which produces the desired results when the radio frequency power is approximately equal or smaller than quadrupolar frequency. Using a combination of simulations and experiments with ²³Na in NaCl solution, Pf1-solutions, and bovine patellar cartilage samples we further show how the value of the quadrupolar frequency and global features of a quadrupolar coupling distribution can be extracted from these experiments.

Introduction

Sodium ions play important roles in human physiology. In the body, sodium ions can either exist in their free form, or restricted in their motion. Typically, the extracellular compartment contains freely moving sodium ions, with a few exceptions, such as for example cartilage tissue, where sodium ions are associated with macromolecular constructs, and motion is restricted via binding to negatively charged entities.^{1,2} Anisotropic motion, or motion with partial averaging leads to the appearance of a residual quadrupolar coupling.^{3,4} Biexponential relaxation is observed when sodium ions are tumbling relatively slowly, such as in the crowded intra-cellular environment⁵. Although the concentration of the extracellular sodium is about 10 times larger than the one of intra-cellular sodium, monitoring the latter and sodium in cartilage tissue is of greater interest for indicating physiological changes^{2,6}. Several methods exist for diagnosing either restricted or slow motion, which include the multiple quantum filtered sequence⁷⁻¹⁸, sequences based on mixed selective and non-selective pulse sequences^{19,20} and a quadrupolar jump-and-return sequence²¹. The multiple-quantum filtered sequences, although very powerful, require strong pulses and a relatively long phase cycle for these to be useful. In cases where the quadrupolar frequency ν_Q is not significantly smaller than the Rabi frequency ν_{rf} , large losses and artifacts are observed, which prevent these methods from being used reliably in vivo^{7,22}.

In this article, we describe a new method, called Quadrupole Sensitive Pulse (QSP), for the selective excitation of ordered quadrupolar spins only (i.e. those that display residual quadrupolar couplings) when the radio frequency fields (rf-field, ν_{rf}) of the pulses are approximately equal or smaller than a given quadrupolar frequency. One feature of QSP is that it is a central transition (CT) measurement and therefore it can also be used as either a preparation module or an excitation module in other sequences,

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