

Frequency-selective quadrupolar MRI contrast

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Abstract

A method for the selective detection of quadrupolar nuclei located in anisotropic environments is presented. The image contrast can be tuned to the degree of anisotropy in the sample by using frequency-swept pulsed. These methods are particularly useful in the field of sodium-MRI, where sodium signals from locally-ordered environments provide diagnostic information. In solid-state MRI, these methods could be useful for probing structural defects within the sample. We demonstrate here one-dimensional images, in which the pixel contrast indicates the presence or absence of quadrupolar coupling within a certain frequency range.

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1. Introduction

Nuclei with spins $I > \frac{1}{2}$ are subject to a quadrupolar coupling mechanism, originating from the electrostatic interactions between non-uniform nuclear and electronic charge distributions [1]. The Hamiltonian for this interaction, truncated by the Zeeman interaction, can be written as $H_Q = A_Q \frac{1}{2} [I_z^2 - I(I+1)/3]$, with the time-averaged quadrupolar coupling given by $A_Q = \langle 3\omega_Q [P_2(\cos \beta) + (\eta/2) \cos 2\alpha \sin^2 \beta] \rangle$. Here ω_Q is the quadrupolar coupling constant, $\omega_Q = e^2 q Q / 2I(2I-1)$, usually given in angular frequency units, and η is the asymmetry parameter. The strength of the interaction varies with the orientation of the electric field gradient (EFG) tensor with respect to the static magnetic field (via the Euler angles α and β). For a single orientation and axial symmetry, this interaction gives rise to $2I$ resonance lines, equally spaced by $A_Q/2\pi$. For half-integer quadrupolar nuclei, the position of the central transition (between the levels $-\frac{1}{2}$ and $\frac{1}{2}$) does not vary with orientation, while the positions of the outer transitions (satellite transitions) do. For a random collection of crystallites with different orientations of the EFGs with respect to the static magnetic field, the positions of the satellite transitions vary and a powder spectrum is obtained

[2]. The same situation occurs when motional averaging is incomplete. Such is the case when the ions are associated with macromolecular structures in the sodium-proteoglycan/collagen systems of cartilage tissue [3]. The central transition ($-\frac{1}{2} \rightarrow \frac{1}{2}$) does not experience any orientational dependence and stays narrow, except for very large quadrupolar coupling constants, which typically only arise in solid systems [4].

Sodium concentrations monitored in cartilage tissue by ^{23}Na -MRI show a strong correlation with charge densities and thereby proteoglycan content [5]. Proteoglycan depletion is accompanied by a decrease of the sodium concentration [6]. This has been demonstrated both in in vivo models [7,8], and in vivo [9–11]. Another example of the application of ^{23}Na -MRI is the study of brain tumors [12]. Distinguishing between free sodium and sodium associated with macromolecules has the potential to provide strong diagnostic power for cartilage tissue disorders [13].

The central transition of ordered sodium overlaps frequently with the signal arising from free sodium. Chemical shift reagents may help to distinguish, for example, intracellular from extracellular sodium [14,15]. On the other hand, only the ordered sodium exhibits a quadrupolar interaction and therefore broadened satellite transition signals [16]. Techniques have been developed that allow one to selectively observe the signals from

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ordered environments, i.e. from those ions that exhibit a nonvanishing quadrupolar interaction [3,13,16,17]. These experiments are best described using spherical tensor operators [3,13,18,19]. After a hard 90° pulse the density matrix can be written in terms of the transverse magnetization components $T_{\pm 1}^1$, which represent spherical tensor operators of rank one and order plus or minus one. In general, one distinguishes between two scenarios of their time evolution. Under the action of the quadrupolar Hamiltonian this operator transforms into a mixture of $T_{\pm 1}^2$. These terms can be converted into double quantum coherence, $T_{\pm 2}^2$. A double-quantum filter experiment selects the signals arising from ordered sodium. On the other hand, ions that experience slow isotropic motion, may also contribute to a double-quantum signal via a relaxation-induced pathway described by $T_{\pm 1}^1 \rightarrow T_{\pm 1}^3 \rightarrow T_{\pm 2}^3$ [3,20]. The spectroscopic signature of this signal can in some cases be distinguished from the former [3,13]. Specialized pulse sequences can further minimize the appearance of the free sodium signals [3,13].

The modified Jeener–Broekaert experiment [3] selects the signals of ordered-sodium ions using a z -filter. The coherence transfer in this experiment can be described by the following trajectory: $T_{\pm 1}^1 \rightarrow T_{\pm 1}^2, T_{\pm 1}^3 \rightarrow T_0^2 \rightarrow T_{-1}^2 \rightarrow T_{-1}^1$ (the $T_{\pm 1}^3$ components cancel each other by applying the z -filter). The advantage of this sequence is that the selection of T_0^2 over T_0^3 is insensitive to B_1 field inhomogeneities. However, as Navon et al. pointed out [13], and we noticed in testing this sequence, the leakage due to T_0^1 may be problematic. Therefore, the appearance of the free sodium signal may hamper its applicability.

The double-quantum sequence selects the coherence corresponding to ordered ions solely by the flip angle setting, and it is therefore, extremely sensitive to B_1 field inhomogeneity. Leakage of the $T_{\pm 2}^3$ term often occurs. Another disadvantage of both sequences is that since the lineshape of the filtered component is dispersive, it is not a desirable method for imaging purposes, especially when a broad distribution of quadrupolar coupling constants is present.

A marked improvement of above methods was originally developed by Wimperis et al. [3], in which the coherence present in the satellite transitions is transferred into the central transition, via a double Jeener–Broekaert experiment. The advantage of this sequence is that the signal from ordered sodium may be converted into a central transition component with a large signal-to-noise ratio due to a narrow lineshape. Unfortunately, the aforementioned disadvantages of the Jeener–Broekaert sequence also apply here.

Recently, a relatively simple approach was described that allows one to suppress the central transition signals using two soft pulses [16], but the back-transfer into the central transition was not developed.

We described recently how frequency-swept pulses can be used to perform this back transfer, and demonstrated this technique with simple one-dimensional imaging [17].

The advantages of this technique are its potential of B_1 robustness, as it does not rely on precise flip-angle settings. Furthermore, we demonstrated that one may perform this experiment in a regime in which the satellite transitions appear saturated. This is potentially useful in order to prevent the satellite and central images from overlapping. In addition, this technique allows one to design efficient experiments for filtering the signals from ordered environments for spins larger than $\frac{3}{2}$. In contrast to previous methods, this approach also allows one to easily obtain a quadrupolar-coupling-selective contrast mechanism. In this article, we demonstrate this useful aspect by showing how one may obtain different image contrast based on the frequency-selective magnetization transfer from the satellite to the central transitions.

2. Experimental

All experiments were performed on a Bruker Avance 500 MHz spectrometer with a BBI probe tuned to the sodium frequency and equipped with a single-axis gradient accessory with a maximum strength of 50 G/cm.

The sample was prepared by placing two capillaries (i.d. 1 mm, o.d. 1.5 mm) in an NMR tube and filling them with two different liquid crystalline solutions. One capillary was filled with a mixture of 38.8 wt% sodium decyl sulfate (SDS), 6.7 wt% of decanol, and 54.5 wt% of water to give a quadrupolar splitting of 9.4 kHz. The other capillary was filled with a mixture of 37 wt% SDS, 7.2 wt% of decanol, and 55.8 wt% of water to give a quadrupolar splitting of 5.6 kHz. The sample was maintained at a temperature of 20°C .

The pulse sequences are represented in Fig. 1. The double-frequency-sweep (DFS) pulses were created according to $\omega_1(t) = \omega_1 \cos[\omega_1 t - (\omega_s - \omega_f)t^2/2\tau]$, where ω_1 is the overall rf field, ω_s and ω_f are the start and final sweep frequencies, and t is the duration of the pulse. The phase cycle was as follows: $\varphi(\text{CT}_{\text{sat}}) = m \times 90^\circ$, $\varphi(\text{DFS}) = l \times 90^\circ$, the hard pulse phase = $k \times 90^\circ$, and the receiver phase $\varphi_R = k \times 90^\circ$, where m , k and l assume the values $\{0, 1, 2, 3\}$ independently. The parameters of the soft pulse were $\omega_1/2\pi = 200$ Hz, pulse length 800 μs , and for the hard pulse, $\omega_1/2\pi = 21.4$ kHz, pulse length 3.6 μs . All DFS pulses had a duration of 400 μs . The DFS1 pulse had a power of 900 Hz, and the sweep was from 8.5 to 11.5 kHz. The DFS2 pulse had a power of 800 Hz and the sweep was from 4 to 6.5 kHz. The DFS3 pulse had a power of 1500 Hz and the sweep was from 2 to 12.5 kHz. For the 1D imaging profile, the gradient strength was 3 G/cm. The gradient echo time was 1 ms and 2048 data points were acquired to cover a spectral window of 50 kHz. 64 transients were co-added.

3. Results and discussion

The pulse sequences shown in Fig. 1 are used to demonstrate this method. The first rf irradiation is a soft pulse designed to saturate the central transition popula-

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