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Cross-polarisation method for improvement of ^{14}N NQR signal detectability

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Abstract

This is a study of the cross-polarization effects in the case of ^{14}N quadrupolar spin-system with a long spin–lattice relaxation time. Two important benefits of the cross-polarization technique were demonstrated for PETN: (i) a polarization transfer resulting in increased NQR single shot signal response and (ii) a dynamic reduction in recovery time of the NQR system allowing scan repetition on a much shorter timescale. It was proved that this technique can reduce the optimal waiting time between pulse sequences up to 60 times through a significant reduction of the relaxation time of the quadrupolar spin-system. All experiments were carried out at room temperature using spin-locking multi-pulse sequences and small external magnetic field.

Keywords: Nuclear Quadrupole Resonance (NQR); Cross-polarization; Nitrogen-14; Free induction decay; Spin-echo

1. Introduction

As a radio-frequency spectroscopic technique, nuclear quadrupole resonance (NQR) is a powerful chemically specific method for the detection of illicit substances, such as explosives [1–3]. The NQR frequency of an explosive is very sensitive to its molecular environment and is therefore unique to each explosive chemical structure. Most explosives contain nitrogen-14 (^{14}N) nuclei whose spectral lines are usually located at low RF from 0.4 to 6 MHz. NQR signals are weak because of the small energy level separation and hence considerable effort is employed to optimally detect them. In order to improve sensitivity, it is common to employ a pulsed technique based on using special multi-pulse sequences [4–8]. However a long spin–lattice relaxation time (T_1) in some explosive types significantly reduces the efficiency of applied multi-pulse sequences. Examples of these explosives include PETN (pentaerythritol tetranitrate), Ammonium Nitrate (AN) and TNT (trinitrotoluene).

A quadrupolar spin-system once excited by an RF pulse or pulse sequence recovers to thermal equilibrium with the lattice in a time T_1. To take PETN as a specific example, a long T_1 time of about 32 s means that the ^{14}N NQR signal which decays throughout the application of a first pulse sequence over a few seconds cannot be efficiently re-excited by the application of a second pulse sequence until around a T_1 time has elapsed. In most applications, this period is excessive and so detection results are generally based on the single application of a pulse sequence. Being able to effectively manipulate the recovery time allows a pulse sequence to be repeated on a much shorter timescale resulting in major improvements in the effectiveness of such techniques.

The cross-polarisation methods [9,10] can be used to reduce the recovery time after excitation of a quadrupole spin-system in hydrogen (^{1}H) containing solids. The recovery time reduction can be achieved by using contact between the proton and quadrupolar spin-systems, when the energy level separations in these systems are made the same and level crossings take place. According to the spin-temperature concept [11,12], for the technique to be effective the proton system should be much "cooler" than

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the RF pulse sequence "heated" quadrupolar spin-system. It is important to point out that efficiency of the method is not critically dependent on the uniformity of the magnetic field. Removing uniformity requirements lowers the hardware cost of generating a static magnetic field considerably and makes the use of these techniques over large inspection volumes or stand-off feasible.

This paper presents new results of applying the cross-polarisation technique for effective detection of plastic explosives with long T_1. The particular task of this work was to show an effectiveness of the method for the detection of PETN contained explosives, PETN being chosen because it posses very long T_1 and it is used in many plastic explosives throughout the world. In these experiments, we have used a relatively small magnetic field which can be easily provided by a permanent magnet or simple solenoid. We have proved that the cross-polarisation technique can reduce the optimal waiting time between pulse sequences up to 60 times demonstrating the significant reduction of the relaxation time of the quadrupolar spin-system. All experiments were carried out at room temperature using spin-locking multi-pulse sequences.

2. Background

Cross-polarisation is used to enhance the signal-to-noise ratio in both nuclear magnetic resonance (NMR) and NQR. In NMR experiments, the signal enhancement is normally achieved by transferring magnetisation from abundant spins like protons ^1H to rare spins [9,10]. In the case of NQR, magnetisation is transferred to quadrupolar nuclei from ^1H nuclei previously polarised in a reference magnetic field [13–17]. Two important benefits can be obtained (i) polarization transfer resulting in increased NQR single shot signal response and (ii) a dynamic reduction in recovery time of the NQR system allowing scan repetition on a much shorter timescale. Both enhancements offer a leap forward for QR explosive detection capability.

Let us consider the sample containing two spin-systems, namely magnetic nuclei, usually protons (P) with spin–lattice relaxation time T_{1P} and quadrupolar nuclei (Q) with spin–lattice relaxation time T_{1Q} (Fig. 1). We assume that spin-systems P and Q are connected via dipole–dipole interactions and relaxation times T_{1P} and T_{1Q} are long enough for the experiment. The typical cross-polarisation experiment is clearly illustrated in Fig. 2. A basic approach of this sort of experiment is to initially polarize the P spins using a static magnetic field so that the P energy levels have much greater energy separation than the Q levels. Given time to equilibrate the P levels will have relative occupation numbers determined by the Boltzman distribution. Thus the relative population difference between the two P levels, hence polarisation, will correspondingly be much greater than the Q levels of interest. By reducing the external magnetic field adiabatically the P level splitting is reduced such that the proton and quadrupolar energy levels separations equalise allowing a transfer of polarisation. This results in a net polarisation flow from protons to the quadrupolar nuclei. This effect can also be explained through the concept of spin temperatures, where energy flows from the "hot" Q spin-system to the "cold" P spin-system "cooling" the Q spin-system. Applying conventional pulse detection techniques soon after removing the magnetic field, the NQR response can be improved according to the ratio of the proton NMR to NQR frequency [15]. Thus, the Q signal enhancement becomes greater the higher the initial polarization for P system. It should be noted that the efficiency of cross-polarisation also depends on the strength of the dipole–dipole interactions between the Q and P spins and the relaxation times T_{1P} and T_{1Q}. An NQR signal increase by using level crossing technique was recently demonstrated for such explosives as TNT [16] and PETN [17].

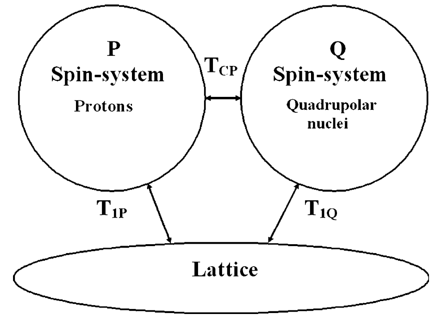

Fig. 1. Proton (P) spin-system, quadrupolar (Q) spin-system and lattice. Spin systems P and Q are connected with a lattice and this connection may be by the spin–lattice relaxation time T_{1P} and T_{1Q} accordingly. Connection between P and Q spin-systems via dipole–dipole interactions may be characterised by the cross-correlation time T_{CP}.

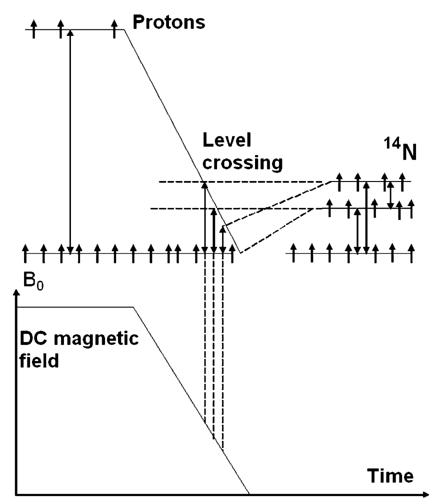

Fig. 2. Cross-polarizations NQR experiment. The static magnetic field initially polarizes the P spins using a static magnetic field so that the P energy levels have much greater energy separation than the Q levels. By reducing the external magnetic field adiabatically the P level splitting is reduced such that the proton and quadrupolar energy levels separations equalise allowing a transfer of polarisation.

The cross-polarisation method can be very efficient for reducing the relaxation time of Q spins previously excited (or "heated") by a sequence of RF pulses. In order to achieve