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Nitrogen-14 nuclear quadrupole resonance (NQR): Dramatic sensitivity enhancement by large and fast temperature lowering

Maude Ferrari, Alain Retournard, Daniel Canet *

Méthodologie RMN (UMR CNRS-UHP 7565), Nancy-Université, Université Henri Poincaré, B.P. 239, 54506-Vandoeuvre-les-Nancy (cedex), France

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Abstract

We have observed that, when going rapidly from ambient temperature down to liquid nitrogen temperature, the nitrogen-14 NQR signal (for transitions involving the $m = 0$ spin state, nitrogen-14 being a quadrupolar nucleus of spin $I = 1$) is increased by a factor of ca. 10^2. While Boltzmann statistics cannot explain this enhancement, the strong temperature dependence of the quadrupolar interaction is very likely to be at the origin of this phenomenon. Indeed, the quadrupolar Hamiltonian becomes time dependent and is prone to induce transitions toward the spin state associated with $m = 0$. Its binding and slow relaxing properties result in a durable increased population and consequently in an increased intensity of NQR lines originating from the state $m = 0$.

Keywords: Nuclear quadrupole resonance; Nitrogen-14; Sensitivity enhancement; Temperature jump

There is currently a widely accepted interest in nitrogen-14 pure nuclear quadrupole resonance (NQR) because this technique is potentially invaluable for detecting and characterizing unambiguously compounds containing nitrogen atoms, such as explosives and drugs [1]. Limited to solid state, this magnetic resonance experiment is however hampered by a poor sensitivity due to low resonance frequencies (in the 5 kHz–6 MHz range). Indeed, much effort is presently made for circumventing this inconvenient as illustrated by recent papers which combine proton NMR (nuclear magnetic resonance) at low magnetic field and nitrogen-14 NQR [2] in order to transfer proton polarization to nitrogen. This poor sensitivity arises from a weak population difference between the states connected by the NQR transition. This population difference stems from Boltzmann distribution, provided that the system has been at thermal equilibrium for some time prior to the NQR measurement. We wish to demonstrate here that this is not so in non-equilibrium conditions, as experimentally assessed by the dramatic increase of the NQR signal when going rapidly from ambient temperature to liquid nitrogen temperature (Fig. 1).

The actual experiment proceeds as follows: 0.3 g of powder is inserted into a 5 mm o.d. NMR tube of 5 cm height which is subsequently sealed. This small size has been chosen in order to minimize temperature variations within the sample. The NQR probe (previously described [3]) is kept at ambient temperature. The sample is plunged into a Dewar containing liquid nitrogen for some tens of seconds (T-jump), then rapidly positioned in the probe while the spectrometer is running (radio-frequency pulses followed by signal acquisition). An enhanced signal as the ones in Fig. 1 is observed at *each* scan for roughly one minute while pulsing every second. The relatively long T_1 (longitudinal relaxation time) values at 77 K (17 s for HMT [4] and 5 s for sodium nitrite [5]) should not affect the observed signals in spite of a fast repetition rate, as shown in a previous work [6]. When the signal has disappeared (not because of T_1 but because the sample temperature has increased in such a way that the NQR signal is no longer visible in the selected spectral window), the experiment can be repeated and proved to be perfectly reproducible. Because of technical limitations, we have been unable to obtain

* Corresponding author. Fax: +33 3 83 68 43 47.
E-mail address: Daniel.Canet@rmn.uhp-nancy.fr (D. Canet).

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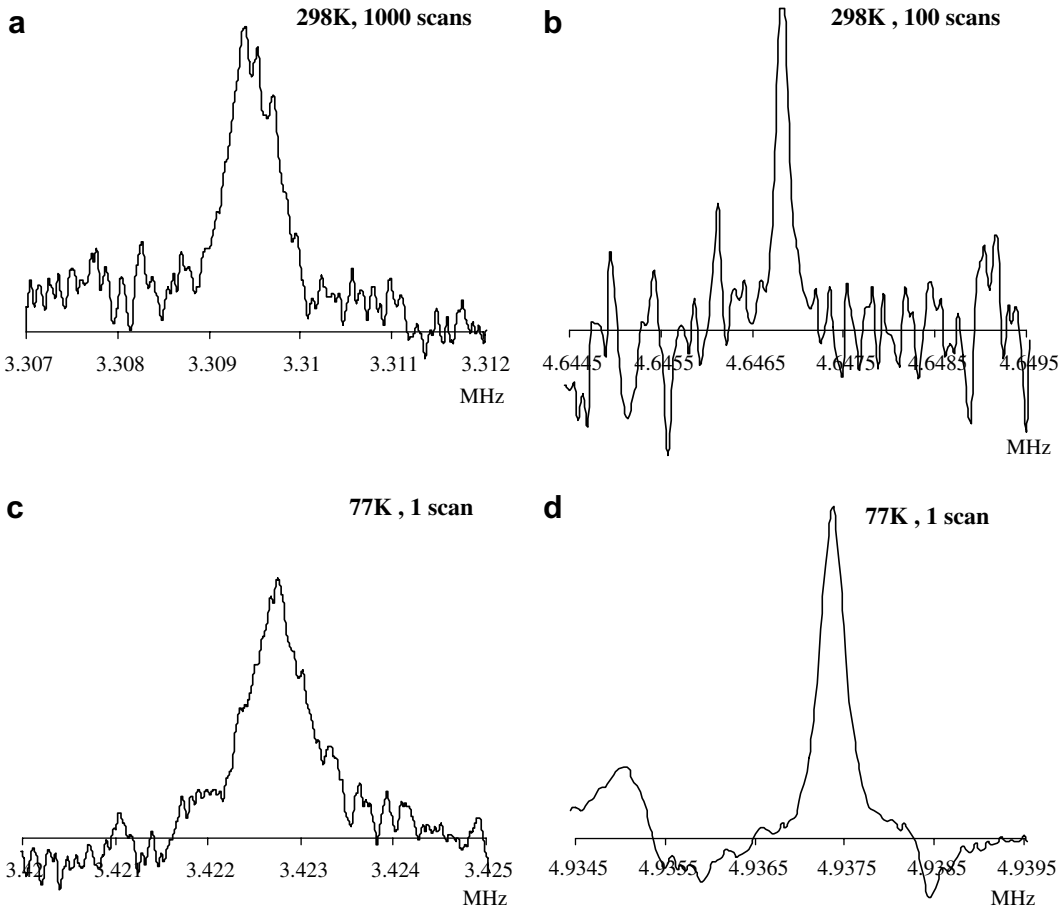

Fig. 1. Comparison of ^{14}N NQR spectra at ambient and nitrogen liquid temperatures (after a T-jump from 298 to 77 K). Oscillations in the 77 K spectrum are due to zones of the sample where the temperature is not exactly the one corresponding to the main peak. Left: hexamethyltetramine (electric field gradient tensor of axial symmetry). Right: sodium nitrite line of highest frequency (general case).

equilibrium spectra at 77 K so that T-jump spectra are compared with ambient temperature spectra.

It can be noticed that no such enhancement occurs when the sample is immersed in liquid nitrogen for a long time. Conversely, if liquid nitrogen is continuously injected so as to counteract temperature increase, one observes a sort of stabilization of the phenomenon which can last for very long periods.

In order to understand more easily this phenomenon, let us start with a system for which the electric field gradient (efg) tensor at the level of the nitrogen nucleus is of axial symmetry. In that case and as nitrogen-14 is a nucleus of spin $I = 1$, the quadrupolar interaction (between the nuclear quadrupole moment and the efg) leads to only two energy levels. If we denote by m the quantum number characterizing the spin state, the lower level is associated with $m = 0$, whereas the upper level is associated with $m = \pm 1$. We shall also denote by p_0 and p_1 the populations of these two levels (Fig. 2), so that the density matrix (constructed on the basis $|1\rangle, |0\rangle, |-1\rangle$) can be written as

$$\begin{pmatrix} p_1 & 0 & 0 \\ 0 & p_0 & 0 \\ 0 & 0 & p_1 \end{pmatrix}.$$

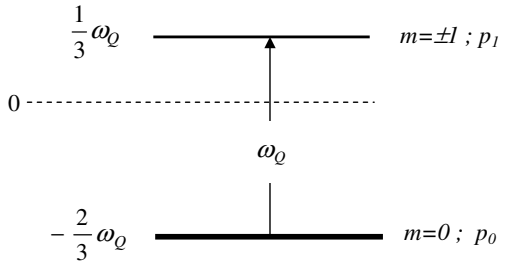

Fig. 2. Schematic representation of the two energy levels involved in the NQR experiment when the field gradient tensor is of axial symmetry. ω_Q is the resonance frequency.

Using a procedure recently published [3], we can easily calculate the density matrix which results from the application of a radio-frequency pulse:

$$\begin{pmatrix} p_1 & 0 & 0 \\ 0 & p_0 \cos^2\alpha + p_1 \sin^2\alpha & -\mathrm{i}\sin\alpha\cos\alpha(p_0 - p_1) \\ 0 & \mathrm{i}\sin\alpha\cos\alpha(p_0 - p_1) & p_0 \sin^2\alpha + p_1 \cos^2\alpha \end{pmatrix},$$

α being a sort of flip angle ($\alpha = \gamma B_1 \tau$; γ: gyromagnetic ratio, B_1: amplitude of the radio-frequency field, τ: pulse duration). The off-diagonal elements correspond to the observa-