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

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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 $m = 0$.
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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

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**a** 298K, 1000 scans

3.307    3.308    3.309    3.31    3.311    3.312
MHz

**b** 298K , 100 scans

4.6445    4.6455    4.6465    4.6475    4.6485    4.6495
MHz

**c** 77K , 1 scan

3.42    3.421    3.422    3.423    3.424    3.425
MHz

**d** 77K , 1 scan

4.9345    4.9355    4.9365    4.9375    4.9385    4.9395
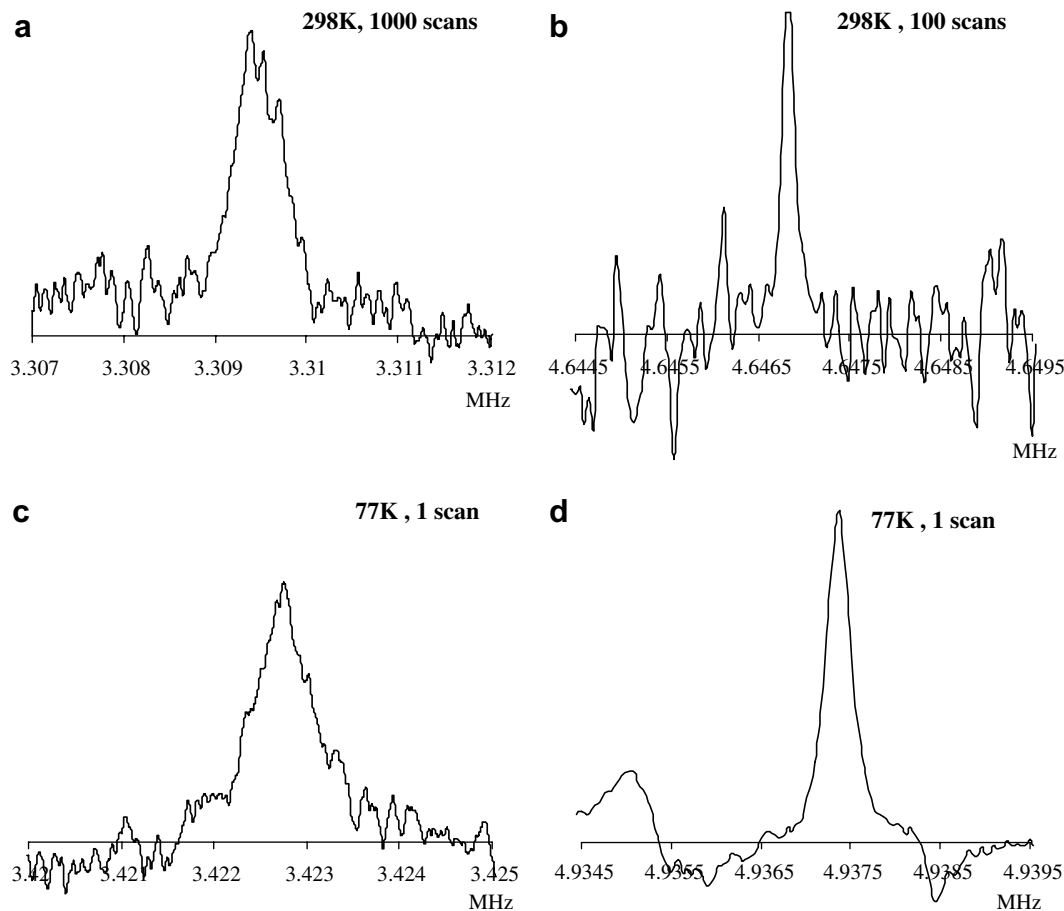MHz

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

$$\begin{pmatrix} p_1 & 0 & 0 \\ 0 & p_0 & 0 \\ 0 & 0 & p_1 \end{pmatrix}.$$
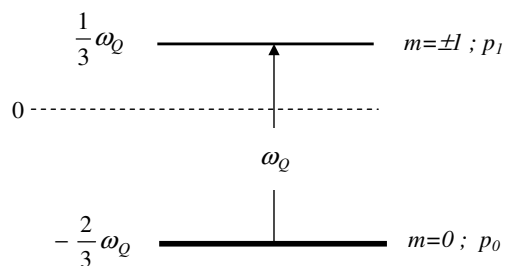
$$\frac{1}{3}\omega_Q \underline{\hspace{3cm}} \quad m=\pm 1 \; ; \; p_1$$

$$0 \dashrightarrow \uparrow \dashrightarrow$$

$$\omega_Q$$

$$-\frac{2}{3}\omega_Q \underline{\hspace{3cm}} \quad m=0 \; ; \; p_0$$

Fig. 2. Schematic representation of the two energy levels involved in the NQR experiment when the field gradient tensor is of axial symmetry. $\omega_Q$ 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:

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

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

ble transition, the intensity of which is thus proportional to $(p_0 - p_1)$. This simple calculation shows that the NQR signal intensity is unambiguously proportional to the difference in populations of the two relevant energy levels, any other factor excluded. By no means, the observed sensitivity enhancement cannot be accounted for by the Boltzmann distribution (at most, a factor of four obtains). Therefore, something else must be put forward.

We can emphasize that, although the final result seems similar, the effect described here has nothing to do with the Haupt effect [7] which arises from the coupling of the spin *angular* momentum with another *angular* momentum, namely the one associated, at very low temperatures, with the tunneling states of a methyl group. This effect is exploited in solid sate NMR, as it can produce, by means of a temperature jump, hyperpolarized spins resulting from a transfer between the rotational tunneling reservoir and the dipolar order [8,9]. It can even be used, in favorable circumstances (i.e. a molecule possessing a methyl group and a nitrogen atom), for obtaining enhanced pure $^{14}N$ NQR spectra by a proton–nitrogen cross-polarization involving adiabatic field-cycling [9].

As a matter of fact, a striking feature of NQR resonances is their strong temperature dependence [5] (which can be of the order of 2 kHz per degree). This arises obviously from an average over molecular vibrations and it is invariably observed that the quadrupolar interaction increases when temperature decreases [10], in relation with the fact that the lowest vibrational energy level becomes more populated. This means that a $T$-jump (i.e. a sudden lowering of temperature) produces a *time dependent* Hamiltonian

$$H_Q(t) = \frac{\omega_Q(t)}{3}(3I_z^2 - 2) \tag{1}$$

This is the usual quadrupolar Hamiltonian for a spin 1 nucleus with an axially symmetric efg tensor: $\omega_Q$ represents the quadrupolar interaction (see Fig. 2), which here becomes time dependent, and $I_z$ the spin operator associated with the spin momentum component along the efg tensor symmetry axis. Thus, the evolution of the spin system is accounted for by the Schrödinger equation

$$H_Q(t)\psi(t) = i\frac{\partial\psi(t)}{\partial t} \tag{2}$$

where $\psi(t)$ is the wave function which can always be written as

$$\psi(t) = c_0(t)|0\rangle + c_1(t)|\pm 1\rangle \tag{3}$$

$|0\rangle$ and $|\pm 1\rangle$ are the eigenvectors associated with the two spin states $m = 0$ and $m = \pm 1$, respectively. Inserting (3) into (2) leads to

$$\frac{dc_0}{dt}|0\rangle + \frac{dc_1}{dt}|\pm 1\rangle = ic_0 H_Q(t)|0\rangle + ic_1 H_Q(t)|\pm 1\rangle \tag{4}$$

For the sake of simplicity, let us assume that the quadrupolar interaction varies linearly with time

$$\langle 0|H_Q(t)|0\rangle = \Omega_Q - at$$
$$\langle \pm 1|H_Q(t)|\pm 1\rangle = \Omega_Q + bt \tag{5}$$

$\Omega_Q$ is the quadrupolar interaction at the lowest temperature; $a$ and $b$ denotes the velocity of its variation concerning the two states of interest ($a, b > 0$ supposed to be independent of $t$ with, in principle, $b = a/2$). This latter assumption is of course an oversimplification aimed at outlining the major trends of the forthcoming calculations.

With these simplified expressions and owing to the fact that $|0\rangle$ and $|\pm 1\rangle$ are orthogonal and normalized, it is easy to solve (4) [11]; we obtain at time $t$

$$c_0(t) \propto \exp\left[-\frac{2i}{3}\left(\Omega_Q - \frac{a}{2}t\right)t\right] \tag{6}$$

$$c_1(t) \propto \exp\left[-\frac{2i}{3}\left(\Omega_Q + \frac{b}{2}t\right)t\right] \tag{7}$$

It is very sure that $c_1(t)$ oscillates very quickly and will not get a definite value because $b$ is positive (see above). Conversely, concerning $c_0(t)$, thanks to the minus sign in (6), it can be noticed that if $a/2t$ tends to $\Omega_Q$, $c_0$ becomes equal to unity and does not exhibit an oscillatory behavior. This amounts to a transition toward the state $|0\rangle$; this is the prerequisite for an overpopulation of the state $m = 0$ and thus for the enhanced lines as experimentally observed.

As far as the general case is concerned (electric field gradient tensor without axial symmetry), we indeed observed the phenomenon for the two high frequency lines of sodium nitrite (lines originating from $m = 0$) but not for the low frequency line ($m = -1 \rightarrow m = 1$). Moreover, this phenomenon does not exist for chlorine NQR (spin 3/2 with $|\pm 1/2\rangle$, $|\pm 3/2\rangle$ sates). Indeed, it can be noticed that the energy corresponding to the state $m = 0$ is negative while the one of the states $|\pm 1\rangle$ is positive (in the case of a spin 3/2, the energies of the two states have the same sign). This sign change indicates that the state $m = 0$ is a "binding" sate which would not be subjected to the usual relaxation processes; it would thus possess a sufficient lifetime for ensuring its preservation, contrary to the states $|\pm 1\rangle$ which would relax rapidly toward Boltzmann distribution. This can be related to the long-lived singlet state observed in nuclear magnetic resonance [12,13]. This could be the clue to the persistent hyperpopulation of the energy level corresponding to $m = 0$ and could explain in which conditions the enhancement of NQR lines occurs.

In summary, we have discovered an experiment by which NQR transitions are enhanced and we have proposed a tentative interpretation to this new phenomenon. We believe that this enhancement could still be improved by finely controlling the sample temperature variation, and in particular by imposing temperature cycles which would sustain this phenomenon.

## Acknowledgment

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