

^{14}N Quadrupole Resonance line broadening due to the earth magnetic field, occurring only in the case of an axially symmetric electric field gradient tensor

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ABSTRACT

As demonstrated before, the application of a weak static B_0 magnetic field (less than 10 G) may produce definite effects on the ^{14}N Quadrupole Resonance line when the electric field gradient tensor at the nitrogen nucleus level is of axial symmetry. Here, we address more precisely the problem of the relative orientation of the two magnetic fields (the static field and the radio-frequency field of the pure NQR experiment). For a field of 6 G, the evolution of the signal intensity, as a function of this relative orientation, is in very good agreement with the theoretical predictions. There is in particular an intensity loss by a factor of three when going from the parallel configuration to the perpendicular configuration. By contrast, when dealing with a very weak magnetic field (as the earth field, around 0.5 G), this effect drops to ca. 1.5 in the case Hexamethylenetetramine (HMT). This is explained by the fact that the Zeeman shift (due to the very weak magnetic field) becomes comparable to the natural line-width. The latter can therefore be determined by accounting for this competition. Still in the case of HMT, the estimated natural line-width is half the observed line-width. The extra broadening is thus attributed to earth magnetic field. The latter constitutes therefore the main cause of the difference between the natural transverse relaxation time (T_2) and the transverse relaxation time derived from the observed line-width (T_2^*).

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1. Introduction

Although the use of relatively strong static magnetic fields in ^{14}N NQR is relatively common for performing NQDR (Nuclear Quadrupole Double Resonance) experiments with the purpose of taking advantage of NMR proton sensitivity [1], less attention has been paid to the effect of weak static magnetic fields [2–11]. In the solid state, energy levels of nuclear spins greater than 1/2 are split by the so-called quadrupolar interaction which occurs between the nuclear electric quadrupole moment and the electric field gradient (efg) tensor at the considered nucleus. Thus, for observing pure NQR resonances, no magnetic field is in principle needed. However, in the case of ^{14}N NQR, the application of a weak magnetic field (considered as a perturbation) in the course of the NQR experiment has proved to lead to (i) the assignment of the two higher frequency lines (out of three) [9], (ii) the complete determination of the efg tensor from a single line [11]. These

features apply of course to an efg tensor devoid of any symmetry which is thus defined by two parameters and implies three NQR distinct lines. In that case, in accordance with second order perturbation calculations, weak magnetic fields of the order of a hundred Gauss are required. By contrast, when the efg tensor is of axial symmetry (and thus defined by a single parameter), a single transition exists, first order perturbation calculations prevail and very weak magnetic fields (smaller than 10 Gauss) are sufficient for observing definite effects. The latter consist of Zeeman doublets or at least line broadening and signal intensity depending of various experimental parameters including the relative orientation of the static magnetic field B_0 with respect to the radio-frequency field (rf) B_1 of the NQR experiment (in other words, the direction of the NQR probe coil axis) [10]. It is this latter feature which is investigated here with the goal of delineating the role of the earth magnetic field upon the HMT (HexaMethyleneTetramine) line. HMT, a model molecule for NQR, is indeed a highly symmetrical molecule for which the efg tensor at the level of nitrogen atoms is necessarily of axial symmetry. An important (and unexpected) finding of this study will be the broadening of the HMT ^{14}N

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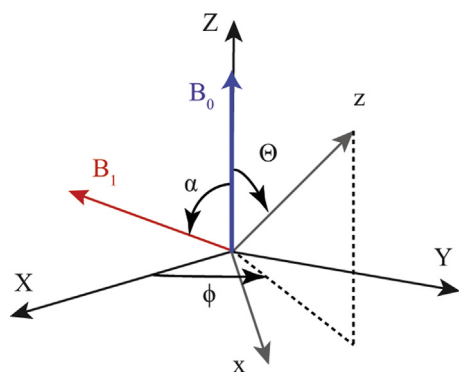


Fig. 1. (X,Y,Z) is a laboratory frame such that the static magnetic field direction (B_0) defines the Z axis, while the direction of the coil generating the radio-frequency field B_1 lies in the (X,Y) plane. z is the symmetry axis of the efg tensor, the orientation of which is defined by the classical polar angles θ and ϕ . Due to the axial symmetry of the efg tensor, the x axis can be chosen anywhere in a plane perpendicular to z . It is assumed here to lie in the plane (Z,z).

Quadrupolar Resonance line induced by the earth magnetic field under standard experimental conditions (that is without any applied static magnetic field).

2. Theory

For an electric field gradient (efg) tensor of axial symmetry, the intensity of the ^{14}N Quadrupolar Resonance signal (peak area in the frequency domain) in the presence of a weak static magnetic field B_0 is given by Eq. (1) [10]. Besides considerations of first-order perturbation calculations, the term “weak” is related to line broadening which precludes, in practice, B_0 values exceeding 6 G. Also, the angular variable θ (see Fig. 1) has been substituted by $u = \cos \theta$.

$$I(\alpha) \propto \int_{-1}^1 \int_0^{2\pi} \sin \left[\beta (u \sin \alpha \cos \phi - \sqrt{1-u^2} \cos \alpha) \right] \times (u \sin \alpha \cos \phi - \sqrt{1-u^2} \cos \alpha) d\phi du \quad (1)$$

where $\beta = \gamma B_1 \tau$ (γ : gyromagnetic ratio; B_1 : amplitude of the radio-frequency – rf – field; τ : duration of the rf pulse) and whereas is the angle between the B_0 and B_1 directions (Fig. 1).

In Eq. (1), $u = \cos \theta$ is directly related to the frequency shift with respect to the pure NQR frequency ($\omega = \gamma B_0 \cos \theta = \omega_0 \cos \theta$) and thus to the line-shape which may include a Zeeman doublet [10]. Consequently, the integration over u (in addition to the integration over ϕ ; see Fig. 1) provides the signal intensity. It can be noticed that this is entirely equivalent to a powder average. In all equations providing the signal intensity, all factors which are frequency independent have been omitted. In practice, data have been normalized according to the maximum intensity.

It must be emphasized that, as far as experimental conditions are concerned, the signal intensity given by Eq. (1) depends solely on the relative orientation of the B_0 and B_1 fields (the angle α) and has nothing to do with the way by which the variation of α is achieved.

Eq. (1) has been established by disregarding the natural line-width of the NQR signal and it is reasonable to consider that the magnetic field has a negligible effect on the NQR signal as long as the frequency shift, $\omega = \gamma B_0 \cos \theta = \omega_0 \cos \theta$, is smaller than the natural line-width $\Delta\omega_{1/2}$ at half-height (unknown since the earth-field produces an extra broadening). Let r be defined as

$$r = \frac{\Delta\omega_{1/2}}{\omega_0} = \frac{\Delta\omega_{1/2}}{\gamma B_0} \quad (2)$$

If u of Eq. (1) happens to be smaller than r , that is, if $r > 1$, no effect of the static magnetic field should be expected (to a first approximation). Conversely, if $r < 1$, the static magnetic field should not have any significant effect on the NQR signal as long as $-r < u < r$. Consequently, in a very general way, Eq. (1) could be substituted by

$$I(\alpha, r) \propto \int_r^1 \int_0^{2\pi} \sin \left[\beta (u \sin \alpha \cos \phi - \sqrt{1-u^2} \cos \alpha) \right] \times (u \sin \alpha \cos \phi - \sqrt{1-u^2} \cos \alpha) d\phi du + \int_{-1}^{-r} \int_0^{2\pi} \sin \left[\beta (u \sin \alpha \cos \phi - \sqrt{1-u^2} \cos \alpha) \right] \times (u \sin \alpha \cos \phi - \sqrt{1-u^2} \cos \alpha) d\phi du \quad (3)$$

r can be derived by fitting experimental intensities against Eq. (3). Of course, when γB_0 is very large with respect to the line-width, r becomes negligibly small and Eq. (1) applies.

In any event, a more accurate value of $\Delta\omega_{1/2}$ can probably be deduced from a fit of experimental line-shapes with a model including a convolution product of the theoretical line-shape (see Eq. (1)) with a Lorentzian function (accounting for the natural line-width). With $w = \omega/\omega_0$ running between $-\infty$ and $+\infty$ and standing for the experimental reduced frequency, the observed signal is given by

$$S(w, \alpha, r) = K \int_{-1}^{+1} F(u) \frac{1}{r^2 + 4(u-w)^2} du \quad (4)$$

with $F(u) = \int_0^{2\pi} \sin [\beta (u \sin \alpha \cos \phi - \sqrt{1-u^2} \cos \alpha)] (u \sin \alpha \cos \phi - \sqrt{1-u^2} \cos \alpha) d\phi$ and where K is a scaling factor. A refined value of r should be derived by fitting the observed peak against Eq. (4), provided that the α and B_0 values have been determined beforehand.

3. Results

Experiments have been carried out with a NQR probe involving a Q-switch design previously described [12]. The rf coil and its associated circuits is included in an assembly which can be oriented so as to vary the relative orientation of the B_0 and B_1 fields (the angle α). This assembly is called a swivel probe in the following and is shown in Fig. 2.

In order to check Eq. (1), a series of experiments were performed with a field of 6 G (so as to minimize earth-field possible effects) delivered by an electromagnet presenting a proper homogeneity over the NQR swivel probe (Fig. 2). Low-power rf pulses were used with $\gamma B_1 \tau = 0.9$ rad (pulse duration: $\tau = 100 \mu\text{s}$). Some typical spectra are shown in Fig. 3.

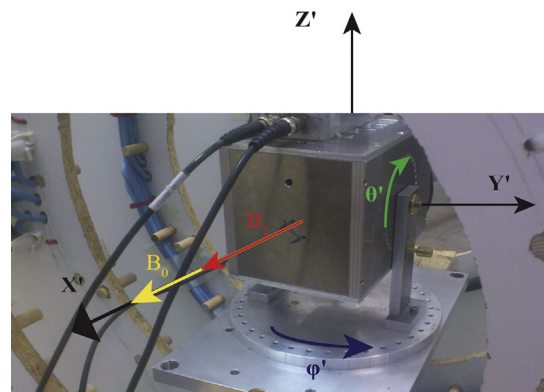


Fig. 2. The swivel NQR probe within an electromagnet. The usual polar angles (θ and ϕ) define the orientation of the B_1 field in the laboratory frame (X', Y', Z').

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