^{1}H-^{14}N Nuclear Quadrupole Double Resonance with Multiple Frequency Sweeps*

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A new highly sensitive ^{1}H-^{14}N nuclear quadrupole double resonance technique is presented which is based on magnetic field cycling and on the application of multiple frequency sweeps of an r.f. magnetic field. The sensitivity and the resolution of the new technique are estimated. Some experimental results obtained by the new technique are presented.

Key words: ^{14}N nuclear quadrupole resonance; Double resonance; Magnetic field cycling; Adiabatic fast passage.

Introduction

^{14}N NQR has proven to be a sensitive technique for the study of the structure and dynamics of molecular solids.

A ^{14}N nucleus has a spin $I = 1$ and thus in zero magnetic field three generally nondegenerate nuclear quadrupole energy levels (Figure 1). None of the transitions between the ^{14}N nuclear quadrupole energy levels is forbidden. The ^{14}N NQR frequencies are rather low – typically between 0 and 4 MHz – and in addition the magnetic dipole moment of a ^{14}N nucleus is small. It is therefore often convenient to measure the ^{14}N NQR frequencies with the ^{1}H-^{14}N nuclear quadrupole double resonance (NQDR) techniques [1–4] which are more sensitive than the direct pulse or cw techniques.

The ^{1}H-^{14}N NQDR techniques are based on magnetic field cycling. A magnetic field cycle is shown in Figure 2. First the sample is left in a high magnetic field B_0 until the temperature T_S of the ^{1}H (proton) spin system reaches the lattice temperature T_L. The proton magnetization is in equilibrium ($T_S = T_L$) equal to $M_0(B_0) = C B_0 / T_L$. Here C is the Curie constant. Then the static magnetic field is adiabatically reduced to a low value B, $B \ll B_0$. The proton spin temperature is immediately after the adiabatic demagnetization

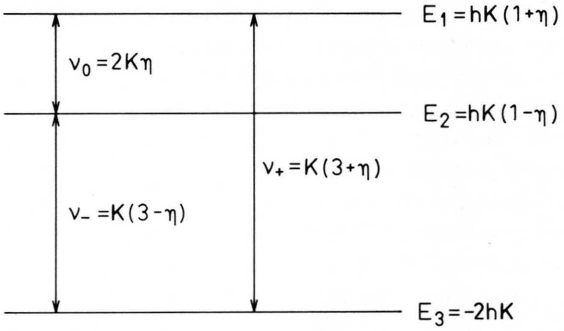

Fig. 1. Energy levels and resonance frequencies of ^{14}N. The constant K, $K = \frac{1}{4}(e Q V_{ZZ}/h)$, is equal to one quarter of the quadrupole coupling constant.

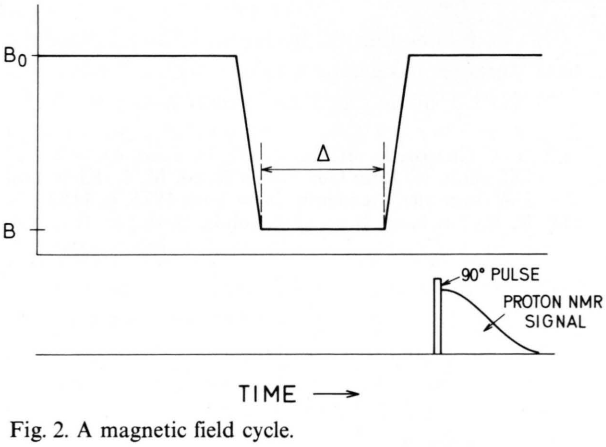

Fig. 2. A magnetic field cycle.

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equal to $T_S = T_L B/B_0$. It is thus by a factor B/B_0 lower than the lattice temperature. The proton magnetization is at the same moment by a factor B_0/B larger than the equilibrium proton magnetization $M_0(B)$, $M_0(B) = CB/T_L$, in the low magnetic field B. The proton magnetization relaxes towards the new equilibrium value $M_0(B)$ with the spin-lattice relaxation time $T_1(B)$. After a time Δ, $\Delta \approx T_1(B)$, the static magnetic field is adiabatically increased to the initial value B_0 and the proton NMR signal S is measured. It is proportional to the remaining proton magnetization, and it decreases with increasing Δ as

$$S(\Delta) \propto \exp(-\Delta/T_1(B)).$$

If during the time spent in the low magnetic field B the ^{14}N nuclear spin system is resonantly coupled to the proton spin system then the relaxation time of the proton spin system may decrease. This happens either if the nitrogens are strongly coupled to the lattice and have thus high spin-lattice relaxation rates or if the nitrogens are affected by a resonant r.f. magnetic field. As a result of the faster relaxation of the proton spin system a lower proton signal is observed at the end of the magnetic field cycle.

In the present paper we briefly describe a new ^{1}H-^{14}N NQDR technique based on magnetic field cycling and on the irradiation of nitrogens with a train of frequency sweeps of an r.f. magnetic field. A more detailed description of the new technique will be published in [5].

Excitation of a Spin System by a Frequency Sweep of an r.f. Magnetic Field

Let us assume that the frequency of an r.f. magnetic field starts to increase at a value which is far below a ^{14}N NQR frequency and then slowly passes the NQR frequency. The question is how do the populations of the nitrogen energy levels change after the sweep is completed, i.e. when the frequency of the r.f. magnetic field is far above the NQR frequency.

The situation is similar to the well known adiabatic fast passage [6] where the frequency ω of the r.f. magnetic field $2B_1 \cos(\omega t)$ is constant whereas the Larmor frequency $\omega_L(t)$ is varied in time by varying the external magnetic field. In this experiment the nuclear magnetization follows the direction of the effective magnetic field $\boldsymbol{B}_{\text{eff}}$.

$$\boldsymbol{B}_{\text{eff}} = (B_1, 0, (\omega_L(t) - \omega)/\gamma), \quad (1)$$

if the adiabatic condition $\mathrm{d}\omega_L/\mathrm{d}t \ll (\gamma B_1)^2$ is fulfilled. Thus if the Larmor frequency starts far from the frequency ω of the r.f. magnetic field, $|\omega_L(0) - \omega| \gg \gamma B_1$, it passes the frequency ω and ends on the other side of ω at a frequency $\omega_L(\infty)$, $|\omega_L(\infty) - \omega| \gg \gamma B_1$, then after the passage the direction of the magnetization as well as the populations of the Zeeman energy levels are inverted.

In our case the electric field gradient (EFG) tensor is constant. Thus the NQR frequencies are constant as well and the passage of an NQR transition with frequency ν_0 is done by the time variation of the frequency $\nu(t)$, $\nu(t) = \nu_0 + \left(\frac{\mathrm{d}\nu}{\mathrm{d}t}\right) t$, of the r.f. magnetic field. The time dependence of the r.f. magnetic field $\boldsymbol{B}_1(t)$ is of the form $\boldsymbol{B}_1(t) = \boldsymbol{B}_1 \cos\left(2\pi\left(\nu_0 t + \frac{1}{2}\left(\frac{\mathrm{d}\nu}{\mathrm{d}t}\right)t^2\right)\right)$. Let us denote the two eigenstates of the quadrupole Hamiltonian separated by $h\nu_0$ as $|a\rangle$ and $|b\rangle$. If a nucleus is prior to the sweep in the state $|a\rangle$ or $|b\rangle$, then the probability P that the nucleus will end after the sweep in the state $|b\rangle$ or $|a\rangle$ can be obtained by numerical solution (5) of the Schrödinger equation

$$i\hbar\, \mathrm{d}|\psi\rangle/\mathrm{d}t = (H_Q - \hbar\gamma \boldsymbol{I}\boldsymbol{B}_1(t))\,|\psi\rangle. \quad (2)$$

The probability P depends on a parameter E,

$$E = 4\pi |\langle a|V|b\rangle|^2/(h^2(\mathrm{d}\nu/\mathrm{d}t)), \quad (3)$$

as shown in Figure 3. Here $V = \gamma \boldsymbol{B}_1 \boldsymbol{I}$ is the perturbation caused by the r.f. magnetic field and $\mathrm{d}\nu/\mathrm{d}t$ is the sweep rate. At low values of E, P increases linearly as $P \propto 0.7\,E$, whereas at large values of E it approaches the value $P = 1$ (adiabatic inversion). P is practically equal to 1 for $E > 3$.

In the case of a system of ^{14}N nuclei irradiated with an r.f. magnetic field of amplitude 2 mT, the frequency of which varies in time with the rate $\mathrm{d}\nu/\mathrm{d}t = 1$ MHz/10 ms, the values of E are for the upper two NQR transitions ($\nu = \nu_+$ and ν_-) equal to $7.2 \cos^2 \alpha_{+,-}$. Here α_+ ($\nu = \nu_+$) is the angle between the X-principal axis of the EFG tensor and the direction of the r.f. magnetic field, whereas α_- is the angle between the Y-principal direction of the EFG tensor and the direction of the r.f. magnetic field. These values of E are not small at all, which demonstrates that an r.f. magnetic field of moderate intensity which sweeps at a decent rate through the ^{14}N NQR spectra significantly changes the populations of the ^{14}N quadrupole energy levels.

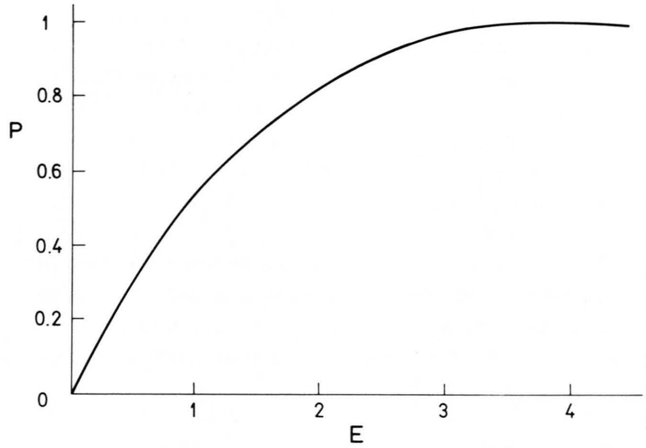

Fig. 3. The probability P to find a nucleus after the frequency sweep in another state than that at the beginning of the frequency sweep as a function of the parameter of the adiabaticity E.

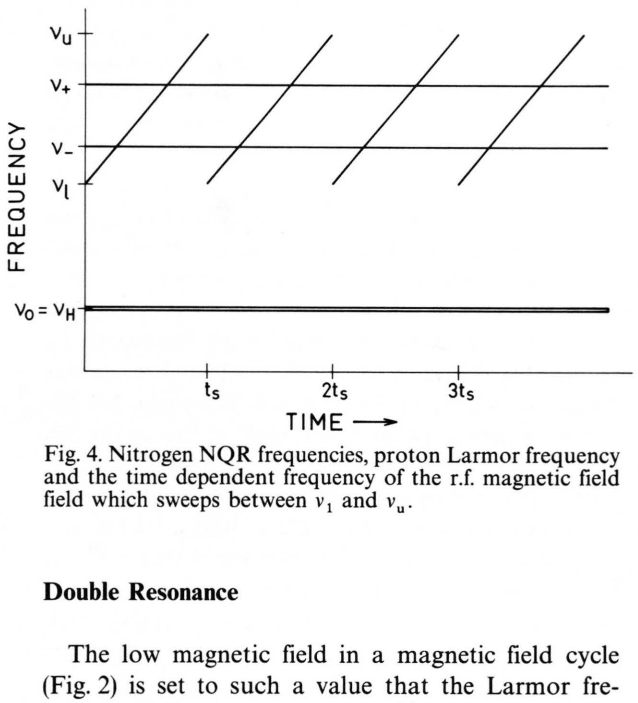

Fig. 4. Nitrogen NQR frequencies, proton Larmor frequency and the time dependent frequency of the r.f. magnetic field field which sweeps between ν_1 and ν_u.

Double Resonance

The low magnetic field in a magnetic field cycle (Fig. 2) is set to such a value that the Larmor frequency ν_L is equal to the lowest ^{14}N NQR frequency ν_0 (Figure 4). The two spin systems are thus resonantly coupled and the proton magnetization relaxes towards the equilibrium value with a common spin-lattice relaxation rate W which depends both on the proton spin-lattice relaxation rate $T_1^{-1}(B)$ and on the nitrogen spin-lattice relaxation rates. If during the time spent in the low static magnetic field B multiple frequency sweeps of an r.f. magnetic field which cover the ^{14}N NQR frequencies ν_+ and ν_- are applied, then the repetitive excitations of the ^{14}N NQR transitions are similar to a fast spin-lattice relaxation of the nitrogens. If for both upper nitrogen NQR transitions the adiabatic conditions are fulfilled ($P=1$), then the apparent nitrogen spin-lattice relaxation rate is approximately t_s^{-1}, where t_s is the sweep time. This appears in the resonantly coupled proton spin system as a relaxation of the proton magnetization towards the value zero with the relaxation rate which is approximately εt_s^{-1}. Here $\varepsilon = N(\mathrm{N})/N(\mathrm{H})$ is the ratio of the number of chemically equivalent nitrogens to the mumber of protons within the unit cell. This additional relaxation of the protons can easily be seen when $\varepsilon t_s^{-1} \geqq T_1^{-1}(B)$, i.e. when $\varepsilon \geqq t_s/T_1(B)$. If for example $t_s = 10$ ms and $T_1(B) = 1$ s then nitrogen signals can easily be seen when $N(\mathrm{N}) \geqq N(\mathrm{H})/100$. In practice the sensitivity is even higher and depends on the signal-to-noise ratio which the proton NMR signal is measured. The sensitivity is mainly limited by the proton spin-lattice relaxation time in the low magnetic field B.

The experimental procedure goes as follows. First the sweep limits ν_1 and ν_u (Fig. 4) are set in such a way that they cover the frequency range in which the ^{14}N NQR frequencies ν_+ and ν_- are expected to be found. The time Δ spent in the low magnetic field is set to a value which is approximately equal to the proton spin-lattice relaxation time in the low magnetic field. Then the magnetic field cycles are repeated at different values of the low magnetic field B. In resonance, i.e. when $\nu_H = \gamma_H B/2\pi = \nu_0$ the proton NMR signal at the end of the magnetic field cycle drops to a lower value. Now the lowest ^{14}N NQR frequency ν_0 is approximately known. The width of the dip in the ν_H-dependence of the proton NMR signal observed around $\nu_H = \nu_0$ is approximately equal to the width of the proton NMR line.

After ν_0 is determined, B is fixed in the center of the dip around $\nu_H = \nu_0$ and the limits of the frequency sweeps are varied. The additional relaxation of the proton system in resonance at $\nu_H = \nu_0$ is observed only when the frequency sweeps cover both frequencies ν_+ and ν_-. If this is not the case, then after a few frequency sweeps a quasiequilibrium population of the nitrogen energy levels is established which is no more affected by the following frequency sweeps. Thus when the lower sweep limit ν_1 passes ν_- or when the upper sweep limit ν_u passes ν_+ then an increase of the proton

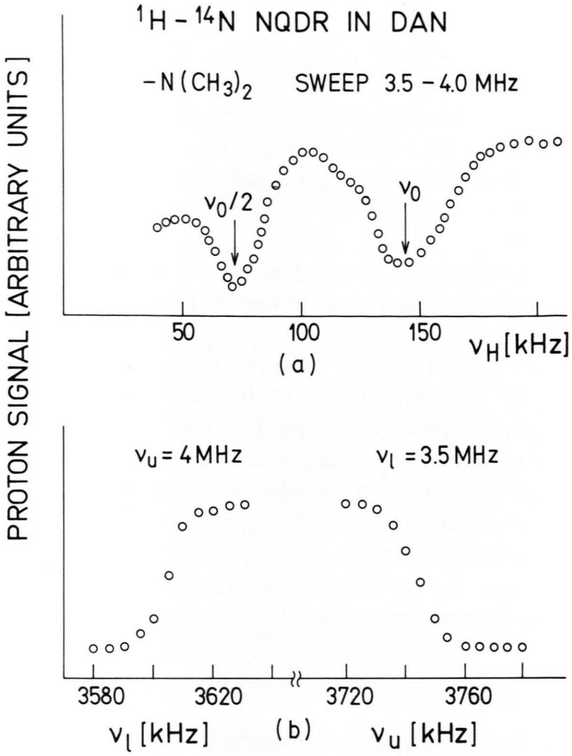

Fig. 5. The determination of the ^{14}N NQR frequencies from the $-N(CH_3)_2$ sites in 4-(N,N-dimethylamino)-3-acetamidonitrobenzene (DAN) with the new technique.

NMR signal at the end of the magnetic field cycle is observed. In such a way the three ^{14}N NQR frequencies are determined, and in addition in the case of complex ^{14}N NQR spectra the NQR lines belonging to the same nitrogen sites can easily be determined.

The resolution of this technique is typically a few kHz. The r.f. magnetic field with the amplitude of approximately 1 mT influences namely the nitrogen NQR transitions already when its frequency is a few kHz shifted from the NQR frequencies. The experiment is also not done in zero magnetic field. The nonzero magnetic field causes broadenings of the nitrogen quadrupole energy levels in polycrystalline samples. The line broadenings are of the order of ν_{LN}^2/ν_Q. Here ν_{LN} is the nitrogen Larmor frequency and ν_Q is a nitrogen NQR frequency. These broadenings are in case of nitrogens resonantly coupled to protons at $\nu_H = \nu_0$ approximately equal to $\nu_0/200$.

As an example of the application of the new technique we present the procedure with which the ^{14}N NQR frequencies from the $C-N(CH_3)_2$ nitrogen sites in 4-(N,N-dimethylamino)-3-acetamidonitrobenzene (DAN) have been measured. The results are shown in Figure 5. The temperature of the sample is 240 K. The parameters of the magnetic field cycles are: $B_0 = 0.8$ T, the proton polarization time in the high magnetic field is 30 s, the time spent in the low magnetic field is $\Delta = 0.3$ s, and the 90° pulse is applied to the sample 0.5 s after the remagnetization is completed. The initial limits of the frequency sweeps are on the basis of the known experimental data for the $-N(CH_3)_2$ group choosen as $\nu_l = 3.5$ MHz and $\nu_u = 4$ MHz. The amplitude B_1 of the r.f. magnetic field was approximately 1 mT. In Fig. 5a two dips are clearly seen in the ν_H-dependence of the proton NMR signal at the end of the magnetic field cycle under the influence of multiple frequency sweeps. No dips are observed without the r.f. irradiation. The dip at $\nu_H = 140$ kHz indeed corresponds to $\nu_H = \nu_0$ whereas the other dip at 70 kHz, which is narrower, corresponds to $\nu_H = \nu_0/2$. At low Larmor frequencies protons absorb energy not only at the Larmor frequency but also at sub-multiples of the Larmor frequency. This is the reason why the dip at $\nu_H = \nu_0/2$ is seen. In Fig. 5b the determination of the upper two nitrogen NQR frequencies by varying the limits of the frequency sweeps is shown. Sharp transitions in the proton NMR signal are observed when the lower sweep limit ν_l passes the frequency 3605 kHz and when the upper sweep limit ν_u passes the frequency 3745 kHz. The ^{14}N NQR frequencies are thus (3745 ± 5) kHz, (3605 ± 5) kHz, and (140 ± 10) kHz. It should be mentioned that in DAN the nitrogen NQR frequencies have been easily observed at a relatively low value of ε, $\varepsilon = N(\mathrm{N})/N(\mathrm{H}) = 1/13$ which demonstrates that the sensitivity of the new technique is high indeed.

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