Journal of Magnetic Resonance **150,** 132–136 (2001)
doi:10.1006/jmre.2001.2333, available online at http://www.idealibrary.com on

Solid State Proton Imaging Detected by Quadrupole Resonance

J. Perlo, F. Casanova, H. Robert,[1] and D. J. Pusiol

Facultad de Matemática, Astronomía, y Física, Universidad Nacional de Córdoba, Ciudad Universitaria, 5000 Córdoba, Argentina

Received September 11, 2000; revised March 26, 2001

A double resonance method for imaging of solid materials containing quadrupole nuclei via the coupled protons is reported. The technique uses a static field gradient to encode the position on the protons and the method of double resonance spin-echo to detect the occurrence of proton resonances by affecting the zero-field echo signal from the quadrupole system. The double resonance imaging method offers the advantages of higher spatial resolution and straightforward image reconstruction for powder samples compared with rotating-frame and Zeeman-perturbated nuclear quadrupole resonance encoding techniques.

Key Words: **solid state imaging; nuclear quadrupole resonance; spatially resolved NQR spectroscopy; NQR imaging.**

INTRODUCTION

In NMR imaging in rigid solids it is particularly difficult to achieve high spatial resolution. Because of its high gyromagnetic ratio, the protons, which are the most sensitive nuclei, experience large dipolar interaction. It is necessary to apply Zeeman field gradients large enough to spread the ^{1}H spectrum beyond the dipolar-broadened linewidth. Various approaches to obtain proton images in solids have been employed with different degrees of success (see for example (*1, 2*)).

In many solids containing nuclei with an effective strong quadrupole interaction, the zero-field nuclear quadrupole resonance (NQR) can easily be observed in single crystals as well as in powder samples. NQR images are generated by either the rotating-frame technique based on the application of radiofrequency field gradients (*3*) or the Zeeman-perturbated method using static magnetic field gradients (*4*). Several rotating-frame NQR imaging (ρ-NQRI) techniques (*5–7*) have been developed for one- and two-dimensional imaging and the spatial resolution with cm scale objects is of the order of millimeters. Because quadrupole nuclei have small gyromagnetic ratio compared with protons, higher resolution in ρ-NQRI demands very high radiofrequency power that makes microscopic resolution a practical impossibility.

In some quadrupole systems with half-integral spins, which do not couple appreciably among themselves, the lifetime of the transverse coherence is limited by the strong dipolar interaction with nearby protons. As demonstrated by Herzog and Hahn (*8*), the method of double irradiation can be used as a means of detecting the resonance of the spins *I* by affecting the echo signal of the spins *S*. The method has been applied on a polycrystalline sample of paradichlorobenzene, the spin *I* being the protons and the observed spin *S* that of ^{35}Cl. A small static magnetic field is applied to the solid and low-frequency irradiation of the proton system during the NQR experiment affects the echo signal of the quadrupole nuclei. The occurrence of a proton resonance can then be measured by observing the effect on the quadrupole echo of chlorine.

The solid state imaging experiment reported in this paper uses a small static magnetic field gradient to spread the proton Zeeman resonances in paradichlorobenzene. The ^{35}Cl resonance is used as a means of detecting the resonance of the protons. By sweeping the irradiation frequency on the ^{1}H system, the occurrence of the proton resonances at different positions in the solid is detected. Therefore, a high-resolution profile of the polycrystalline object is reconstructed from changes in the quadrupole echo's amplitude. With the double resonance imaging (DRI) method we exploit the large gyromagnetic ratio of protons to achieve high spatial resolution with small magnetic field gradients and the signal from large quadrupole splitting of chlorine as an indicator of proton resonance for higher sensitivity. Unlike the previously published quadrupole imaging method, i.e., ρ-NQRI and Zeeman-perturbated techniques, with the double-irradiation technique a one-dimensional projection of the object is directly constructed from changes in the echo's amplitudes. Therefore, no special deconvolution methods are needed to reconstruct spatial distribution with powder objects. Submillimeter spatial resolution was achieved with this technique, yielding significant improvement in spatial resolution compared with the ρ-NQRI method.

DOUBLE RESONANCE IMAGING METHOD

For the double resonance technique, a weak static magnetic field B_0 is applied to define a resonance frequency ν_{H} for the proton system. During continuous wave (CW) irradiation or stirring at the proton resonance frequency, the chlorine echo signal is detected at the transition frequency ν_{Q} of the quadrupole splitting

---

[1] Present address: Quantum Magnetics, 7740 Kenamar Court, San Diego, CA 92121.

by using the Carr–Purcell single-echo pulse sequence. The fast reorientation of protons driven by the CW irradiation leads to an effective average of the local field at the quadrupole nucleus positions, increasing the spin–spin time decay constant T_2. A theoretical description of the line narrowing technique by double frequency irradiation is given in Refs. (*8*, *9*). In this section, we describe the application of the nuclear magnetic quadrupole double resonance suggested by Herzog and Hahn (*8*) for spatial localization in solids.

Let the ^{35}Cl echo amplitude E_0 observed in a two-pulse experiment be expressed as $E_0 = \exp(-2\tau/T_2)$, where $(1/T_2)$ is the second moment of the S spins due to all species of nuclear neighbors

$$\frac{1}{T_2} = \frac{1}{T_2^{SS}} + \frac{1}{T_2^{IS}}, \qquad [1]$$

and T_2^{PS} $(P = S, I)$ is the contribution of spins P to the second moment of S spins. The chlorine echo amplitude can then be expressed as $E_0 = E_{SS}E_{IS}$, where $E_{PS} = \exp(-2\tau/T_2^{PS})$ for $P = I, S$. In our experiments, we found that E_{IS} can be approximately described as a gaussian function of the frequency difference from exact proton resonance $\Delta\nu = \nu_{\mathrm{H}} - \nu_0$,

$$E_{IS}(\Delta\nu) = \exp\left(-\frac{\Delta\nu^2}{2\sigma_{IS}^2}2\tau\right) + E_{IS}(0). \qquad [2]$$

$E_{IS}(0)$ is the static contribution to the echo decay of S spins due to the local field of spins I when the proton stirring is far from resonance. σ_{IS} is the width of the double resonance line and it is a function of the magnitude B_2 of the double resonance perturbing RF field.

To achieve spatial localization of protons, a static magnetic field gradient G_0 is superimposed to the weak static field to make the Larmor frequency spatially dependent, $\nu_{\mathrm{H}}(z) = \gamma_{\mathrm{H}}(G_0 Z + B_0)$. The double resonance line

$$E_0(\Delta z) = E_{SS}\left[\exp\left(-\left(\frac{\gamma_{\mathrm{H}} G_0 \Delta z}{\sigma_{IS}}\right)^2 \tau\right) + E_{IS}(0)\right] \qquad [3]$$

is a function of the spatial coordinate $\Delta z = z - z_0$, where z_0 is the position at which the resonance condition $\nu_{\mathrm{H}} = \nu_{\mathrm{H}}(z_0)$ is fulfilled. Since the decrease of the second moment of the quadrupole system induced by the stirring vanishes far off resonance, the change of the quadrupole echo's amplitude due to the lengthening of T_2 indicates the resonance of protons contained in the slice centered at z_0. The net echo signal amplitude is then given by an integral over the normalized spin density function $\rho(z)$,

$$E_0(z_0) = E_{SS}\left[\int_{-\infty}^{\infty} dz\rho(z) \times \exp\left(-\left(\frac{\gamma_{\mathrm{H}} G_0 \Delta z}{\sigma_{IS}}\right)^2 \tau\right) + E_{IS}(0)\right]. \qquad [4]$$

The quadrupole echo amplitude is a convolution of the spatial distribution of spins $\rho(z)$ with the point response function or double resonance lineshape E_{IS}. To map a one-dimensional density profile, the irradiation frequency ν_{H}—or equivalently the static field B_0—is changed in successive experiments to move the resonance condition to various slices along the axis defined by G_0. Measuring the echo's amplitude as a function of position z_0 of the selected slice, a 1D spin density profile along the magnetic field gradient direction is obtained.

For a given strength of the encoding field gradient, G_0, the spatial resolution Δz_{r} of the DRI technique is determined by the width at half the height of the gaussian function and it is given by

$$\Delta z_{\mathrm{r}} = \sqrt{\frac{\ln 2}{\tau}}\frac{\sigma_{IS}}{\gamma_{\mathrm{H}} G_0}. \qquad [5]$$

Therefore, the width of the selected slice depends on the linewidth σ_{IS} of the double resonance spectrum, which varies with the magnitude B_2 of the low-frequency irradiation field and the interval τ of the quadrupole spin-echo sequence. The optimization of these parameters was done experimentally as discussed in the next section.

EXPERIMENTAL SETUP

Figure 1 shows a drawing of the double resonance probehead built for the implementation of the described technique. Two coils, 75 mm in diameter and separated by 55 mm, in an anti-Helmholtz configuration provide an approximately constant magnetic field gradient at the position of the test object. The proton irradiation frequency was $\nu_{\mathrm{H}} = 90$ KHz, and the scanning of the on-resonance slice position was performed through the variation of the currents i_1 and i_2 on each coil. To keep the spatial

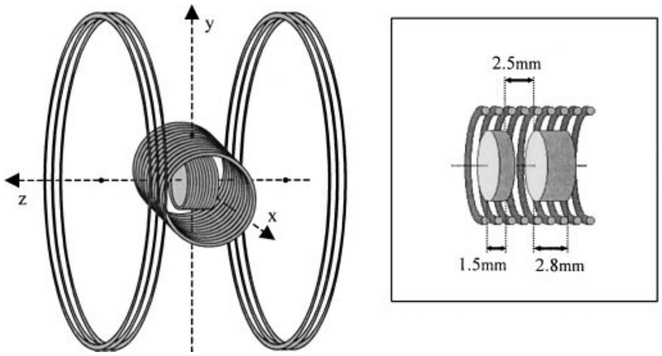

FIG. 1. Double resonance probehead schematics drawn in perspective. Two coils of 75-mm diameter separated by 55 mm generates a static magnetic field gradient to label the position of protons in the solid. A solenoidal coil, 30 mm in diameter and 35 mm long, perpendicular to the Zeeman coils provides the proton irradiation field B_2 at low frequencies. A solenoidal coil 12 mm in diameter and 13 mm long tuned at 34.266 MHz, perpendicular to the direction of the other coils, was used to transmit and detect at the frequency of the ^{35}Cl quadrupole transition. The test object consists of two cylinders of powder paradichlorobenzene of 10-mm diameter and 2.8- and 1.5-mm thickness, with a plastic spacer of the same diameter and 2.5-mm thickness.

resolution constant, the current through the coils was adjusted according to $i_1 = i + n\Delta i$ and $i_2 = i - n\Delta i$, so that the total current was constant. The strength of the total magnetic field along the axis of the coils can be written as

$$B_0(z) = \frac{N\mu_0}{2r}\left[i\left(\frac{1}{(1+((z+d/2)/r)^2)^{\frac{3}{2}}} - \frac{1}{(1+((z-d/2)/r)^2)^{\frac{3}{2}}}\right) + n\Delta i\left(\frac{1}{(1+((z+d/2)/r)^2)^{\frac{3}{2}}} + \frac{1}{(1+((z-d/2)/r)^2)^{\frac{3}{2}}}\right)\right],$$

where r is the coil radius, d is the separation between coils, and z is the coordinate along the axis with $z = 0$ at the center of the coil array. The static magnetic field can then be described by the series

$$B_0(z) = \frac{N\mu_0}{2r}\left[1.05 n\Delta i\left(1 + 0.72\left(\frac{z}{r}\right)^2\right) + 1.48 i\left(\frac{z}{r}\right)\left(1 + 0.3\left(\frac{z}{r}\right)^2\right)\right] \qquad [6]$$

to third order in the parameter (z/r). In our experiments $(z/r) < 0.1$ and numerical evaluation of the coefficients in last equation shows that the departure from a constant gradient is less than 1% over the region of the object. Therefore, it is possible to write the magnetic field produced by this coil as $B_0(z) = Aiz + Bn\Delta i$. The total current i determines the strength of the static gradient, and $n\Delta i$ determines the linear increment in the spatial coordinate of the point where the resonance condition is fulfilled.

To avoid heating of the object, which leads to an undesirable shift of the quadrupole resonance, the gradient coils were switched on 10 ms before running the spin-echo sequence and switched off during the waiting time between experiments. A time interval of 10 ms assures equilibrium for the proton system before running detection of the ^{35}Cl echo signal.

A solenoidal coil, 30 mm in diameter and 35 mm long, perpendicular to the Zeeman coils provides the proton irradiation field at low frequencies. This coil was tuned at the proton working frequency by a series capacitance to obtain a low input impedance suited to be driven by an audio amplifier. NQR signals were generated and detected by means of a solenoid coil 12 mm in diameter and 13 mm long. The NQR resonant circuit was tuned at 34.266 MHz, the ^{35}Cl quadrupole transition frequency for the solid at room temperature. The pulse widths in the single spin-echo sequence were optimized to give the maximum echo amplitude without stirring of the protons. The resulting widths were 8 and 16 μs for the preparatory and refocusing pulses, respectively.

EXPERIMENTAL RESULTS

Spatial resolution Δz_r of the DRI technique is determined by the width σ_{IS} of the double resonance line E_{IS}. We determined the spatial selectivity of the described encoding technique by studying the dependence of the points response function E_{IS} with both the time interval τ between pulses and the strength of the proton irradiation field B_2 using a powder sample. To measure the shape of the double resonance line we acquired the NQR echo's amplitudes as a function of Zeeman field strength B_0 with a constant proton irradiation frequency $\nu_H =$ 90 kHz.

First, we study the dependence of the decoupling with the amplitude of B_2 field. Figure 2 shows the echo's amplitude plotted as a function of the B_2 intensity with $\tau = 1$ ms. A first maximum occurs at $B_2 = 8$ G, resulting in an increment of T_2 from 0.6 to 2.2 ms. The longest T_2 value of 3.5 ms is achieved for a B_2 intensity of about 25 G and remains almost constant up to the highest audio field amplitude applied in our experiment. The maximum sensitivity with the double-irradiation technique is achieved with B_2 higher than 25 G that gives the longest T_2 value. However, the width of the double resonance line with $B_2 = 25$ G is larger than the linewidth resulting with the parameter for the first maximum $B_2 = 8$ G. The double resonance spectra with B_2 at 8 and 25 G are compared in Fig. 3. The narrower double resonance line for the lower B_2 is apparent in Fig. 3 and the intensity of the B_2 field in the localization experiments was set at 8 G to achieve higher spatial resolution.

We made no attempt to explain the behavior of chlorine transverse relaxation with the parameters of the decoupling technique. It should be pointed out that the highest intensity of the B_2 field applied in the experiment shown in Figs. 2 and 3 is higher than the magnitude of the static magnetic field B_0. In

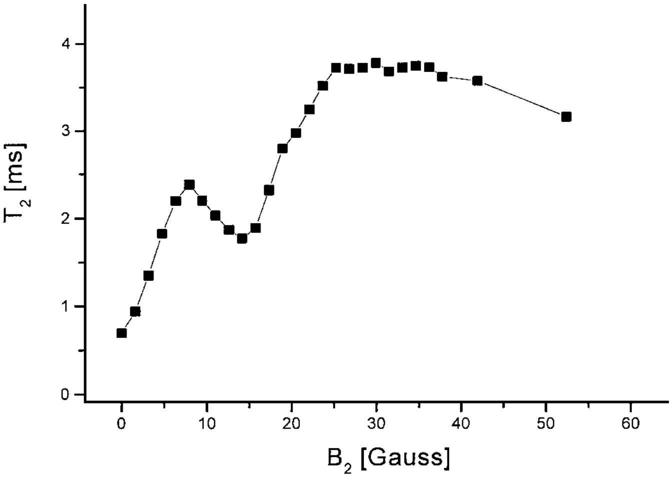

FIG. 2. Dependence of the chlorine T_2 lengthening with the amplitude of the proton irradiation field B_2. The powder object was placed in a uniform static field and on-resonance proton irradiation was performed at 90 kHz. The separation τ between pulses in the single-echo pulse sequence was 1 ms.

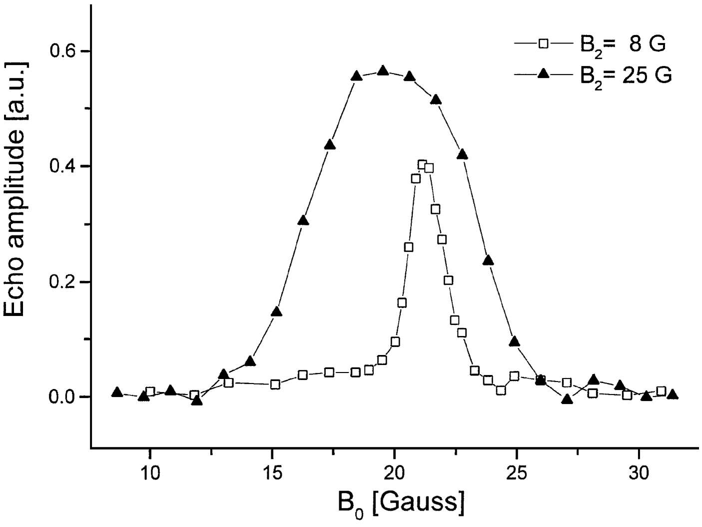

FIG. 3. Double resonance spectra for two different B_2 amplitudes, 8 and 25 G, obtained with a $\tau = 1$ ms and applying a B_0 at which the resonance is fulfilled at 90 kHz. The narrower double resonance line at $B_2 = 8$ G yields better spatial resolution in the localization experiments.

Ref. (*8*) the double resonance in solids is described for weak CW RF excitation. Therefore, it might be possible to analyze the lengthening of ^{35}Cl spin-echo envelope by using the theory of RF photon dressing (*10*).

Figure 4 shows a set of double resonance spectra for different values of τ with $B_2 = 8$ G. The horizontal offset at short τ values is the echo amplitude without low-frequency irradiation of the protons. The linewidth decreases as the time τ between the RF pulses increases as expected from the discussion in the previous section. Thus, the spatial resolution is better for longer τ. On the other hand, the signal-to-noise ratio decreases when τ increases because of transverse relaxation. Then, the optimum τ value results as a trade-off between spatial resolution and sensitivity. We choose $\tau = 1.8$ ms and $B_2 = 8$ G as the optimum parameters to obtain high spatial resolution with no significant degradation in sensitivity.

The test object for the localization experiments consists of two cylinders of powder paradichlorobenzene of 10 mm in diameter and 2.8 and 1.5 mm thickness separated by a plastic disk of the same diameter and 2.5 mm thickness (Fig. 1). The object was placed at the center of the radiofrequency coils as shown in Fig. 1. The currents through the coils were adjusted to give a static field gradient of $G_0 = 20$ G/cm. The expected spatial resolution with our experimental conditions was about 0.5 mm.

Figure 5 shows a one-dimensional density profile of the two-disk object acquired with the DRI technique. To construct the spatial profile we acquired the ^{35}Cl echo amplitude as a function of the slice position. The currents through the coils were adjusted to give a spatial displacement of the selected slice of 200 μm between experiments. To increase the signal-to-noise ratio, 200 echoes were accumulated with a recycle delay of 500 ms for every position of the selected slice. The resulting spatial resolution in the profile shown in Fig. 5 agrees with the calculated value.

To compare the resulting spatial resolution of the DRI method with previously published localization techniques, we show in Fig. 6 a one-dimensional quadrupole nuclear density of the same object recorded by the rapid rotating frame NQR technique (*4*). The encoding RF gradient was produced by a three-turn surface coil 24 mm in diameter driven by a power amplifier Kalmus LP 1000. The measured RF gradient strength was approximately 30 G/cm at the position of the object. The nutation signal was

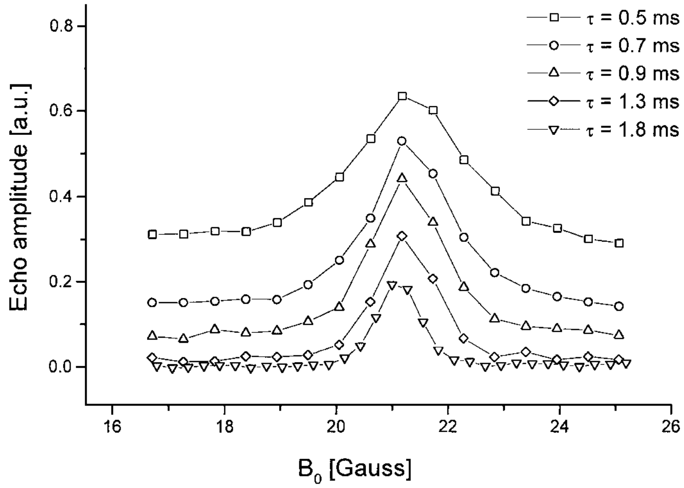

FIG. 4. Double resonance lineshapes for paradichlorobenzene obtained at different τ values. The linewidth decreases as the time interval τ increases, and then the resolution under a static gradient is better for longer τ. For these experiments the proton irradiation frequency was fixed at 90 kHz and B_0 amplitude was varied to shift the proton line off resonance. The amplitude B_2 of the irradiation field is 8 G.

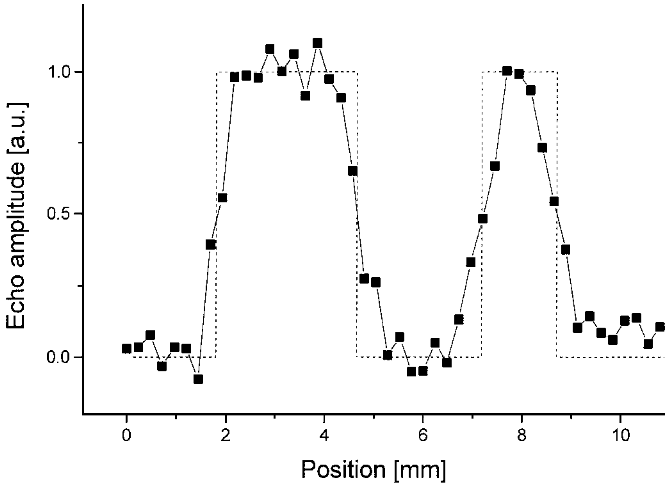

FIG. 5. Spin density profile of the two-disk object shown in Fig. 1 applying a $G_0 = 20$ G/cm. Echo amplitudes were acquired by changing the slice position in steps of 200 μm and 200 echoes were accumulated every 500 ms. Spatial resolution evaluated from the profile is about 0.5 mm, which agrees with the calculated value.

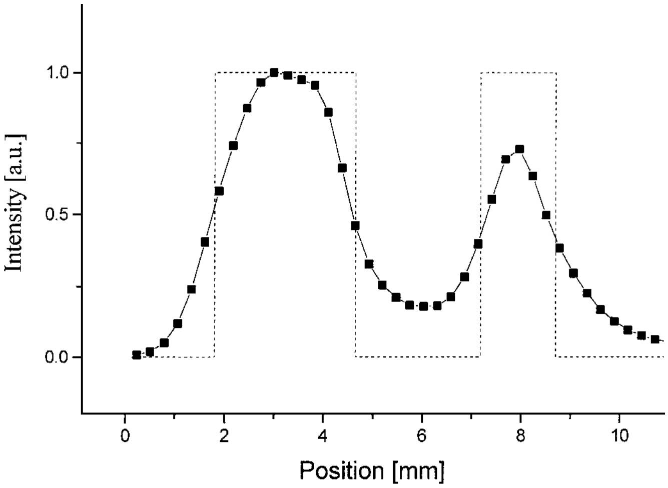

FIG. 6. Spin density projection recorded by the rapid rotating frame NQR technique and reconstructed by the maximum entropy method of the two-disk object. The strength of the applied RF gradient was 30 G/cm and 200 scans were averaged. The resulting spatial resolution in this experiment is about 2.5 mm.

acquired with a train of 64 RF pulses and 15 μs width separated by acquisition windows of 40 μs, and 200 scans were averaged for increased signal-to-noise ratio. The reconstruction of the one-dimensional profile was performed by the maximum-entropy method to remove the powder distribution of nutation frequencies that distort the image from the profile (*11*). As the same surface coil was used for signal detection, adequate B_1 field correction was applied in the spatial dimension to compensate for the spatial dependence of sensitivity.

CONCLUDING REMARKS

The nuclear magnetic quadrupole resonance imaging technique described in this paper is applicable when relaxation of quadrupole nuclei is caused by local magnetic field fluctuations which arise from neighboring unlike spins. It offers a number of advantages over previously developed spatial localization methods for quadrupole systems. Because the spatial encoding is performed using the proton system, the larger gyromagnetic ratio leads to significant improvement in spatial resolution compared with rotating-frame NQR imaging methods. The experimental results reported in this paper show a spatial resolution of the order of 0.5 mm for the double resonance imaging method and 2.5 mm for the ρ-NQRI technique.

Unlike the previously reported NQR imaging techniques, i.e., Zeeman-perturbated and rotating-frame imaging, reconstruction of spatial information with the double resonance localization method is straightforward. There is no need for special reconstruction algorithms to take into account the powder distribution on the encoding gradients. As a static field gradient is used for spatial encoding, a higher uniformity of the gradients can be achieved compared with the RF gradients over a similar volume, thus reducing image distortion.

A number of modifications to the proposed double resonance method can be conceived to increase sensitivity and reduce data acquisition time. For example, by switching off the static field gradient at the maximum of the chlorine echo, a zero-field quadrupole signal can be acquired given higher sensitivity and access to the full spectroscopic information of the quadrupole resonance in a manner similar to the two-dimensional ρ-NQRI technique. Implementing a pulsed proton decoupling method, instead of the CW technique suggested in this paper, would open the possibility of single-shoot one-dimensional localization by the double resonance approach. This work is in progress in our laboratory.

ACKNOWLEDGMENTS

We thank the National Agency of Science and Technique (ANPCYT) and the National and Provincial Research Councils (CONICET and CONICOR) for financial support. F.C. thanks CONICET for a Research Fellowship.

REFERENCES

1. P. T. Callaghan, "Principles of NMR Spectroscopy," Clarendon Press, Oxford, 1991.
2. J. B. Miller, *Prog. NMR Spectrosc.* **33,** 273 (1998).
3. E. Rommel, P. Nickel, R. Kimmich, and D. Pusiol, *J. Magn. Reson.* **91,** 630 (1991).
4. S. Matsui, K. Kose, and T. Inouye, *J. Magn. Reson.* **88,** 186 (1990).
5. H. Robert, A. Minuzzi, and D. Pusiol, *J. Magn. Reson. A* **118,** 189 (1996).
6. H. Robert and D. Pusiol, *J. Magn. Reson.* **127,** 109 (1997).
7. E. Rommel, D. Pusiol, P. Nickel, and R. Kimmich, *Meas. Sci. Technol.* **2,** 866 (1991).
8. B. Herzog and E. L. Hahn, *Phys. Rev.* **103,** 148 (1956).
9. A. Abragam, "The Principles of Nuclear Magnetism," Clarendon Press, Oxford, 1961.
10. T. Ito and T. Hashi, *J. Mol. Struct.* **58,** 389 (1980).
11. H. Robert, D. Pusiol, E. Rommel, and R. Kimmich, *Z. Naturforsch.* **49a,** 35 (1994).