

Zero field NMR and NQR with selective pulses and indirect detection

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Zero field NMR and NQR spectra are obtained by the application of dc magnetic field pulses to a demagnetized sample. Pulsed dc fields allow for selective excitation of isotopic species and provide a means for coherent manipulation of the spin system in zero field. Using these selective pulses and level crossing techniques, indirect detection of a quadrupolar nucleus may be accomplished via protons without obtaining the proton background signal in the NQR spectrum. Experimental results from a variety of ^1H , ^2H , and ^{14}N homo- and heteronuclear systems are presented as an illustration of these techniques.

INTRODUCTION

Time domain zero field techniques have recently been applied to polycrystalline solids,¹ extending the field cycling experiments of Hahn *et al.*² and others.³⁻⁶ In the original zero field experiment, evolution was initiated by sudden field switching. In this paper we introduce a variation which relies on the pulsed application of a dc magnetic field after demagnetization to initiate evolution in zero field. This pulsed method can be used to selectively irradiate isotopic species (e.g., protons and deuterons) in zero field and can also be adapted to exploit the advantages of indirect detection for sensitivity enhancement and extended ranges of relaxation times. The pulsed method also greatly enhances the ability of the experimentalist to coherently manipulate the spin system and allows application of composite and multiple pulse techniques to zero field experiments.

First, we briefly describe the original zero field experiment. The sudden switched version, Fig. 1, is performed by shuttling a sample from a large polarizing field B_0 to a collinear intermediate field B_i which is then switched off suddenly to initiate evolution under the zero field Hamiltonian. The spin eigenfunctions in the field B_i differ from those in zero field; thus, when B_i is suddenly switched off, the system which was originally in high field eigenstates will evolve under the zero field Hamiltonian. After an evolution period t_1 , B_i is suddenly switched on and the sample shuttled back to high field where evolution during t_1 is probed at a later time as in two-dimensional NMR.⁷ The z component of the magnetization at time t_1 is measured using pulsed spin locking⁸ or for quadrupolar systems, multiple echoes, to enhance the detection sensitivity. The integral of this signal is recorded as a function of t_1 forming an interferogram which when Fourier transformed yields the zero field spectrum.

Now, consider a case in which the spin system consists of two isotopic species, e.g., protons and deuterons. The sudden experiment initiates evolution for all spin species, as long as the spin interaction with the switching field is large compared with zero field interactions, i.e., dipolar and quadrupolar interactions. Thus any evolution of the spin system present in the detected signal will produce a zero field spectrum containing both dipolar and quadrupolar frequencies. Even if the deuteron evolution could be detected through the protons, it may often be obscured by the signal from the

protons, which can occur over all or part of the range of 0–50 kHz. It is thus worth considering pulsed experiments on completely demagnetized states⁹ which are better suited for indirect detection experiments as level crossings will occur during the field cycle.

EFFECTS OF dc PULSED MAGNETIC FIELDS

Neglecting the heteronuclear dipolar coupling between a system of protons and deuterons, the density operator for a system demagnetized from high field to zero field can be written in the molecular frame as

$$\rho_M(0) = \rho_I + \rho_S, \quad (1)$$

where

$$[\rho_M(0), \mathcal{H}_{ZF}] = 0 \quad (2)$$

and I and S correspond to the protons and deuterons, respectively, and \mathcal{H}_{ZF} is the pure dipolar Hamiltonian for protons and the quadrupolar Hamiltonian for deuterons in zero field. It will be necessary to evaluate the effect of applied dc pulses in a fixed laboratory frame where the density operator ρ becomes

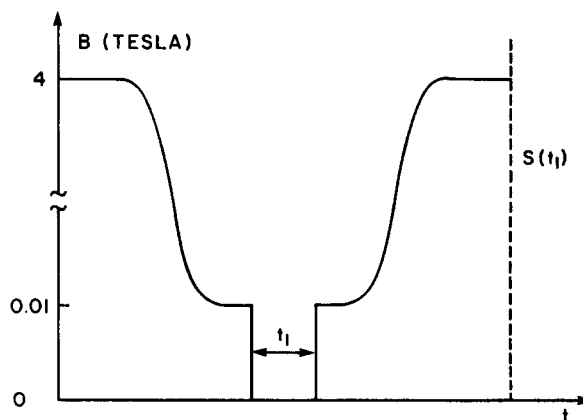


FIG. 1. Field cycle for the sudden zero field experiment. The sample is shuttled adiabatically from the magnetic field B_0 to an intermediate field B_i , illustrated here as 0.01 T. Sudden removal of the intermediate field initiates zero field evolution for a time t_1 after which B_i is reapplied and the sample is returned to high field. The magnetization is detected for regularly incremented values of t_1 forming the interferogram $S(t_1)$ which when Fourier transformed produces the zero field spectrum.

$$\rho_L(0) = R(\alpha, \beta, \gamma)^{-1} \rho_M(0) R(\alpha, \beta, \gamma), \quad (3)$$

where $R(\alpha, \beta, \gamma)$ is the rotation operator relating the lab to the molecular axes in terms of the Euler angles α , β , and γ . A similar expression transforms the zero field Hamiltonian into the laboratory frame:

$$\mathcal{H}_{ZF}^L = R(\alpha, \beta, \gamma)^{-1} \mathcal{H}_{ZF} R(\alpha, \beta, \gamma). \quad (4)$$

At time $t = 0$, consider the application of a dc pulsed magnetic field which is turned on for a time τ . The density operator $\rho_L(\tau)$ is then written

$$\rho_L(\tau) = \exp(-i\mathcal{H}_{dc}\tau)\rho_L(0)\exp(i\mathcal{H}_{dc}\tau).$$

Choosing the laboratory z axis parallel to the pulsed dc field, then

$$\rho_L(\tau) = \exp(-i\gamma_I I_z B_{dc}\tau)\rho_{IL}\exp(i\gamma_I I_z B_{dc}\tau) + \exp(-i\gamma_S S_z B_{dc}\tau)\rho_{SL}\exp(i\gamma_S S_z B_{dc}\tau), \quad (5)$$

where $\mathcal{H}_{dc} = [\gamma_I I_z + \gamma_S S_z] B_{dc}$ and describes the dc pulsed field, such that pulse angles of $\theta_I = \gamma_I B_{dc}\tau$ and $\theta_S = \gamma_S B_{dc}\tau$ may be defined, and we have assumed $|\mathcal{H}_{dc}| \gg |\mathcal{H}_{ZF}|$. (6)

Since the effective pulse angle is different for the protons and deuterons, it allows a selective means for their manipula-

tion since \mathcal{H}_{dc} depends on their gyromagnetic ratios. In general, the effect of a pulse depends on the relative orientation of the spin system and field; however, for any particular species a 2π pulse given by $\theta = \gamma B_{dc}\tau$ will leave the density operator unchanged.

As a simple test of these ideas consider the following experiment [Fig. 2(a)] performed on the protons in polycrystalline $\text{Ba}(\text{ClO}_3)_2 \cdot \text{H}_2\text{O}$. The sample, initially in high field, is shuttled to zero field where it is subjected to a single dc pulse of varying length, then shuttled back to high field where its proton pulsed spin locking signal is recorded. The high field signal for a pulse of length τ is given by

$$S(\tau) = \text{Tr}[\rho_L(0)\exp(-i\mathcal{H}_{dc}\tau)\rho_L(0)\exp(i\mathcal{H}_{dc}\tau)]. \quad (7)$$

For a powder sample, Eq. (7) must be averaged over all possible orientations, i.e., over all α , β , and γ of Eq. (3).

Figure 2(b) shows that the experimental response is periodic and that the signal magnitude for $\theta = 2\pi$ is nearly equal to that for $\theta = 0$. This experimental result is for a dipolar system consisting of nearly isolated water molecules but the same behavior has been observed in deuterium systems. Assuming isolated ^1H spin pairs and that a single spin temperature describes the demagnetized states,

$$\rho_M(0) = \beta_D \mathcal{H}_D$$

and performing the integration over the presumed powder distribution, the signal function calculated from Eq. (7) is

$$S(\tau) = 1/5 [1 + 2 \cos(\gamma_I B_{dc}\tau) + 2 \cos 2(\gamma_I B_{dc}\tau)] S(\tau = 0). \quad (8)$$

This agrees with the experimental results showing local maxima at $n\pi$, but predicts no signal decay. The decay may be explained by the inhomogeneity of the pulsed fields together with evolution and relaxation which occurs during the dc pulse. Inhomogeneous pulsed fields indeed result in a more severe damping effect on the observed signal. Evidence for evolution under the internal Hamiltonian during the dc pulse may be seen in quadrupolar systems in which the damping effect is more pronounced as the condition presented in Eq. (6) is not stringently met.

In what follows, we deal with two situations arising from the above considerations. First, in a homonuclear system one can initiate evolution under the zero field Hamiltonian by simply pulsing a system which is initially in a stationary (diagonal) state in zero field, as consistent with Eq. (2). Secondly in a heteronuclear system, by using a pulsed field which acts as an identity rotation for one spin species it is possible to effectively rotate that part of the total density matrix corresponding to only one and not the other species. Thus in a system of deuterons and protons one should be able to selectively excite and induce evolution for the deuterons since the deuteron-proton dipolar coupling is essentially quenched in zero field.¹⁰ Similarly, a 2π pulse for protons is a $\pi/2$ pulse for ^{13}C in heteronuclear zero field NMR.¹¹ Clearly, such selective pulses can be applied to spin decoupling in zero field.

PULSED ZERO FIELD DETECTION

To apply dc magnetic field pulses in obtaining zero field spectra, many schemes are possible. Two simple examples of

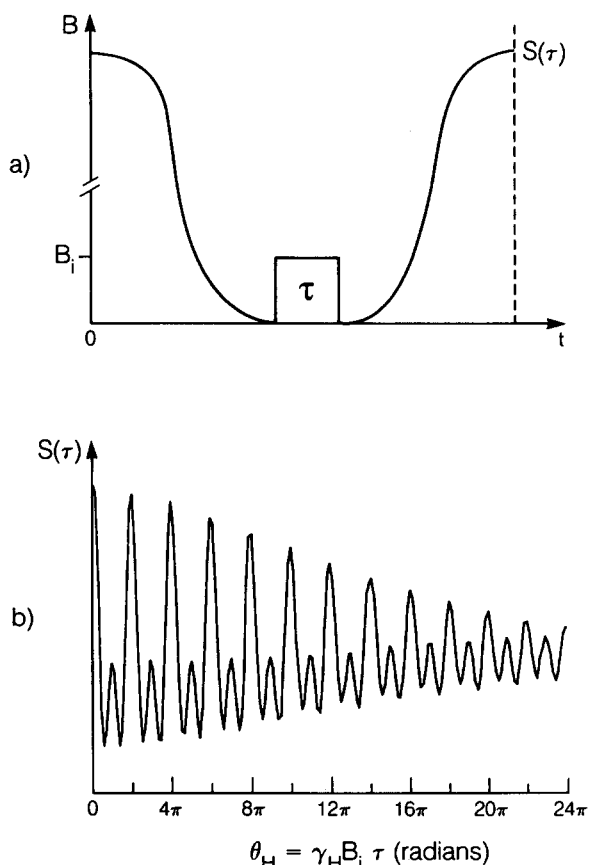


FIG. 2. Field cycle for application of a single dc magnetic field pulse (a) and high field magnetization as a function of dc pulse length (b). The pulse angle is given by $\theta = \gamma_H B_{dc}\tau$ where τ is on the order of a few μs and $B_{dc} \gg B_{\text{local}}$. The magnitude of the proton magnetization from a sample of $\text{Ba}(\text{ClO}_3)_2 \cdot \text{H}_2\text{O}$ is detected as a function of the dc pulse applied after demagnetizing the sample to zero field. The detected signal is periodic as given by Eq. (8) and after a 2π pulse the magnetization is nearly equal to its initial value. The damping may be attributed to imperfections in pulsed field homogeneity and amplitude.

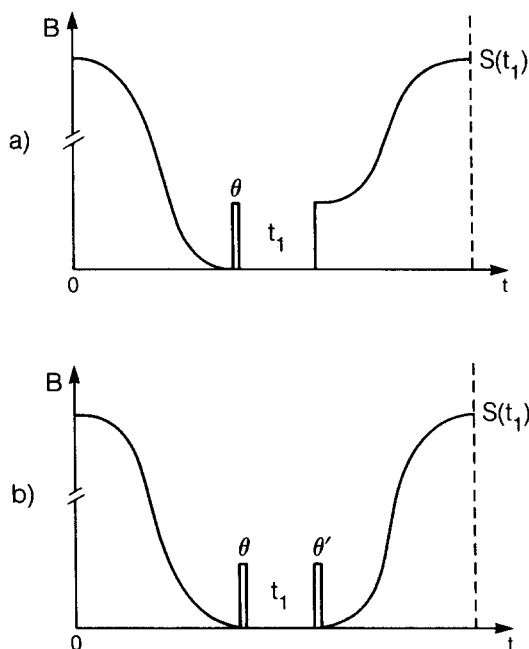


FIG. 3. Schematics of the field cycles used for pulsed zero field NMR and NQR. The sample is demagnetized by removal of the sample to a region of zero applied magnetic field. The spin system after demagnetization is in eigenstates of the zero field Hamiltonian and evolution may be initiated by the application of the first dc pulsed field (θ). After the evolution period t_1 , which is incremented in successive field cycles, evolution is terminated by the application of a suddenly switched magnetic field as in (a) or by a second dc pulse (θ') as in (b). The sample is then remagnetized and the high field signal is recorded.

the field cycles and pulse sequences are shown in Fig. 3. After demagnetization to zero field the reduced density matrix is diagonal in the zero field basis set and therefore is proportional to second rank tensors only. The form of the initial state in zero field will depend on the dynamics of the demagnetization. This aspect will be treated in detail in a later paper.¹² The initial dc pulse results in off-diagonal terms which evolve for a time t_1 under the zero field Hamiltonian. Detection of the zero field evolution may be accomplished by application of a suddenly switched field in the same direction as the first pulse (in this case, z) and remagnetization to high field where the z component of the magnetization is sampled as described above. This field cycle is illustrated in Fig. 3(a) and the high field signal is formally given by

$$S(t_1) = \text{Tr} [I_z \exp(-i\mathcal{H}_{ZF}^L t_1) \exp(-i\theta I_z) \rho_L(0) \times \exp(i\theta I_z) \exp(i\mathcal{H}_{ZF}^L t_1)], \quad (9)$$

where for simplicity we are considering a homonuclear system of spins, I , where I refers to any isotopic species. This is analogous to directly detected magnetization in a pulsed NQR experiment where the signal is sinusoidal and begins with zero intensity. This is due to the orthogonality of second rank (the initial density matrix) and first rank tensors (the detected operator). Alternatively, to detect zero field evolution a second pulse applied after the t_1 period will return a portion of the off-diagonal elements to the diagonal. Upon remagnetization these population differences are measurable by standard high field pulse sequences. In these ex-

periments it is not possible to find pulse angles which excite complete evolution for all crystallite orientations. Thus the signal is necessarily somewhat reduced from the previously described experiment (Fig. 1), as only a portion of the total spin order evolves in zero field. Figure 3(b) illustrates this field cycle and zero field pulse sequence, and the high field signal is now given by

$$S(t_1) = \text{Tr} [\rho_L(0) \exp(-i\theta' I_z) \exp(-i\mathcal{H}_{ZF}^L t_1) \exp(-i\theta I_z) \times \rho_L(0) \exp(i\theta I_z) \exp(i\mathcal{H}_{ZF}^L t_1) \exp(i\theta' I_z)]. \quad (10)$$

Figures 4(a) and 4(b) illustrate our results for the sudden transition field cycle (as seen in Fig. 1), and the demagnetization and pulsed direct detection zero field experiments [Fig. 3(b)] done on perdeuterated 1,4-dimethoxybenzene. As expected, the frequencies obtained in both are identical and the linewidths agree within experimental error. Comparison of

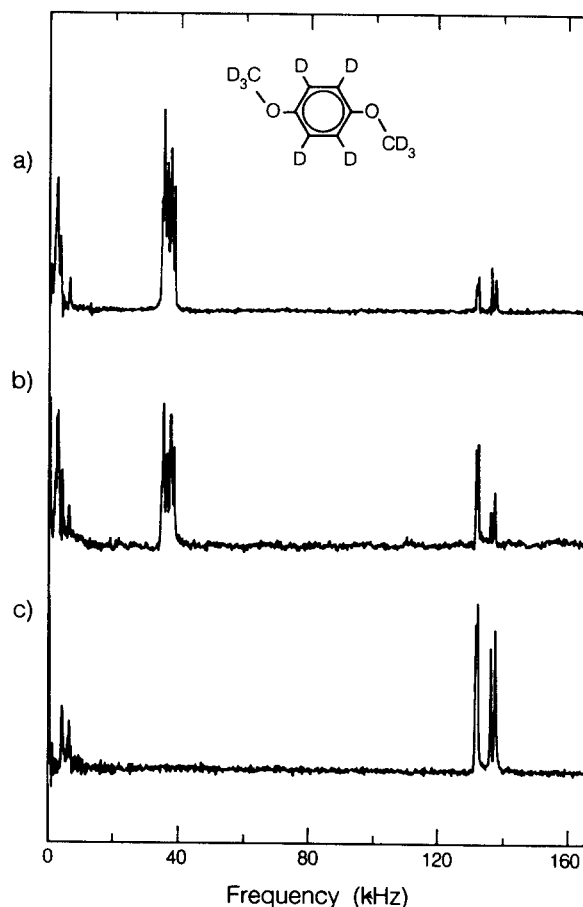


FIG. 4. Zero field NQR spectra of 1,4-dimethoxybenzene ($\text{CH}_3\text{OC}_6\text{H}_4\text{OCH}_3$). (a) Sudden transition zero field spectrum of perdeuterated dimethoxybenzene obtained using the field cycle described in Fig. 1. Peaks at frequencies corresponding to the methyl and aromatic deuterons are resolved. (b) Pulsed direct detection zero field spectrum of perdeuterated dimethoxybenzene obtained using the field cycle of Fig. 3(b). As the magnitude of the observed magnetization is dependent on the dc pulse lengths used, peak intensities are now scaled differently with respect to (a). Relaxation effects occurring during the different length field cycles in the sudden and pulsed experiments are manifested in the different relative methyl and aromatic signal intensities of (a) and (b). (c) Indirect detection via protons of the deuterium NQR spectrum in 60%–70% aromatic deuterated 1,4-dimethoxybenzene. (Note that in this sample the methyl groups were not deuterated.) Clearly resolved ν_+ , ν_- , and ν_0 transitions are observed with no evidence of proton signal. Signal-to-noise for the aromatic deuterons is improved relative to the sudden and pulsed zero field methods.

the two experiments is reasonably straightforward, but we defer this to a later section.

INDIRECT DETECTION WITH SELECTIVE PULSES

Above we have shown that dc pulses can initiate zero field evolution and from Eq. (5) that this evolution can be made selective. All that is required for an indirect detection experiment is that the time evolution of the quadrupolar system be communicated to the protons.

We consider a spin system of deuterons and protons and the indirect detection by level crossing principles of Hahn *et al.*² During the demagnetization of the sample in the field cycle of Fig. 3(b), successive crossings occur between the proton and deuteron energy levels resulting in enhanced order in the deuteron system. After the evolution period and second pulse, remagnetization of the sample will bring about the same level crossings, though in reverse order. The high field magnetization of such protons is then modulated at the NQR frequencies of the deuterons thus contacted.

Using dc pulses that are multiples of 2π for the protons in the field cycle of Fig. 3(b) (i.e., $\theta = \gamma_S B_{dc} \tau$ for the deuterons), we obtain the zero field spectrum of 60%–70% deuterated 1,4-dimethoxybenzene- d_4 ($\text{CH}_3\text{OC}_6\text{D}_4\text{OCH}_3$) shown in Fig. 4(c). No signal is observed due to the protons, only the characteristic ν_+ , ν_- , and ν_0 lines due to the two crystallographically inequivalent aromatic deuterons.^{1,13}

The experimental results for the dimethoxybenzene samples shown in Fig. 4 allow for comparison of the signal-to-noise obtained in each of the different versions of the experiment. The length of each FID is roughly equal and the dwell time is equal for these three experiments. The pulsed direct detection [Fig. 4(b)] and the sudden [Fig. 4(a)] versions used 4 and 3 times as many signal averages, respectively, as the indirect detection version [Fig. 4(c)]. Thus the aromatic signal-to-noise obtained via the indirect method is at least twice as good as in the others. Our studies of partially deuterated diethylterephthalate and its perdeuterated analog provide further agreement with this result. Of course, the method requires that the dipolar coupling between deuterons and protons be sufficient to allow efficient spin diffusion during the field cycle, so protons spatially distant from a deuteron would be expected to provide less efficient polarization transfer.

Arbitrary pulse lengths will produce proton signal in heteronuclear systems which can obscure low frequency (< 50 kHz) ^2H lines. Figure 5 demonstrates this point in a series of indirectly detected zero field NQR spectra of diethylterephthalate- d_4 ($\text{CH}_3\text{CD}_2\text{CO}_2\text{C}_6\text{H}_4\text{CO}_2\text{CD}_2\text{CH}_3$) obtained by the method outlined above. Proton signal is clearly visible in those spectra where the $n \times 2\pi$ condition is not met for the protons, but is eliminated with two $n \times 2\pi$ dc pulses. A further advantage of the initial selective 2π pulse on the protons is that the density operator ρ_I undergoes no t_1 dependent evolution; therefore, the dynamics of the level crossing should be sensitive only to deuterium evolution. Diethylterephthalate contains two crystallographically inequivalent methylene deuterons since the methyl–methylene bond is tilted out of the plane of the $-\text{CO}_2\text{C}_6\text{H}_4\text{CO}_2-$ moiety¹⁴ thus producing the six line spectra for two uncoupled qua-

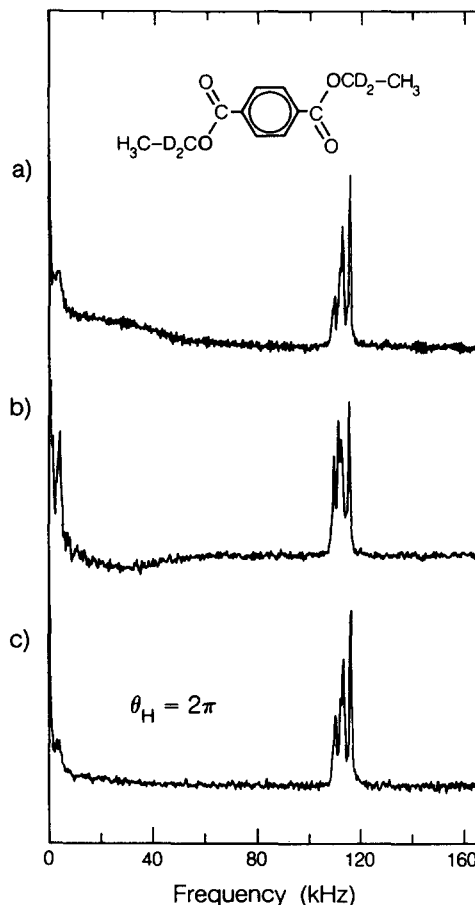


FIG. 5. Indirect detection zero field NQR spectra of diethylterephthalate- d_4 ($\text{CH}_3\text{CD}_2\text{CO}_2\text{C}_6\text{H}_4\text{CO}_2\text{CD}_2\text{CH}_3$). (a) dc pulses used which do not satisfy the $n \times 2\pi$ criterion for the protons, thus signal due to both proton and deuteron evolution is observed. The proton signal appears as a broad hump below 50 kHz. (b) Same as (a) except that dc pulses now used cause the proton signal to appear inverted relative to the deuteron signal. (c) dc pulses equal to $n \times 2\pi$ allow for selective detection of only the deuterium NQR spectrum. Low frequency lines can be clearly resolved with no interfering signal from proton evolution or absorption. Three lines may be assigned to each of two crystallographically inequivalent methylene deuterons. Calculated values of $(e^2qQ)/h$ and η from the observed frequencies are A: $(e^2qQ)/h = 153.1$ kHz, $\eta = 0.051$; B: $(e^2qQ)/h = 149.8$ kHz, $\eta = 0.039$.

drupolar nuclei with nonzero η . The magnitude of the observed signal depends upon the pulse lengths used, therefore the relative peak intensities are scaled differently in the spectra of Fig. 5.

Although the use of selective pulses and indirect detection has thus far been presented as a method of obtaining deuterium NQR spectra, the principles are entirely general and can be applied to any system in which there is sufficient contact between the observed and detected nuclei. As an example, we present a preliminary ^{14}N zero field NQR spectrum obtained from a sample of polycrystalline ammonium sulfate shown in Fig. 6, obtained by the sequence in Fig. 3(b) with indirect detection by protons. All six lines are resolved for the ν_+ , ν_- , and ν_0 transitions of the two inequivalent ^{14}N sites and yield values of $(e^2qQ)/h$ and η in agreement with single crystal results¹⁵ and other field cycling experiments in which the ν_0 lines do not appear.¹⁶ Under other conditions the proton signal would obscure the low frequency lines but here the use of the selective 2π pulses for the protons greatly

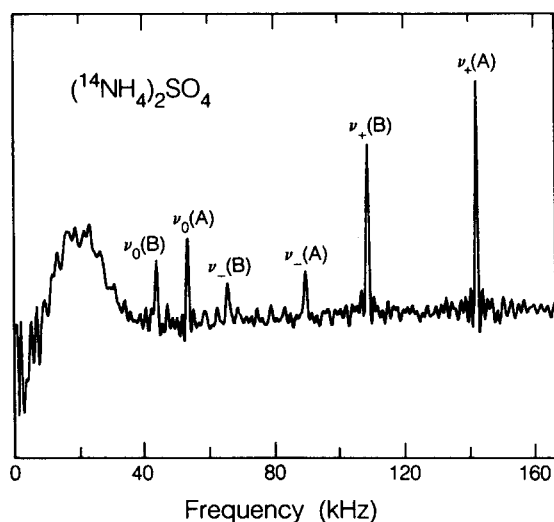


FIG. 6. Indirectly detected pulsed zero field ^{14}N NQR spectrum of $(\text{NH}_4)_2\text{SO}_4$ with selective 2π pulses for the protons. Peaks corresponding to two inequivalent sites are labeled A and B. Residual proton signal appears below 40 kHz but has been reduced enough to allow for resolution of the ^{14}N NQR lines. From the frequencies observed at room temperature, $(e^2qQ)/h$ and η can be calculated. Site A: $(e^2qQ)/h = 154.5$ kHz, $\eta = 0.688$, Site B: $(e^2qQ)/h = 115.9$ kHz, $\eta = 0.747$. (At 296.1 K, Batchelder and Ragle (Ref. 16) give values of I: $(e^2qQ)/h = 154.53$ kHz, $\eta = 0.684$; II: $(e^2qQ)/h = 115.71$ kHz, $\eta = 0.749$.)

reduces their contribution to the signal. Compensation for the inhomogeneity of the dc pulsed fields should provide increased discrimination against the proton signal.

SUMMARY

We have demonstrated two variations of the time domain zero field experiment which are performed by simply pulsing a sample demagnetized to zero field and that selective NQR spectra may be obtained which offer the sensitivity advantage of indirect detection. The initial density operator need not be proportional to I_z in the variations presented here, so spin systems can be probed under a wider variety of conditions. Perhaps most important is that this work can be extended in experiments where one manipulates the spin system with pulse sequences analogous to those used in high field. Composite pulses¹⁷ should be applicable to the problem of inhomogeneity of the pulsed dc field, as well as to multiple pulse experiments and spin decoupling in zero field.

In addition, we note that the indirect detection experiment depends more on the relaxation times of the protons than those of the deuterons. This can be of utility when the deuteron T_1 is inconveniently long, or when T_{1Q} is inconveniently short. As long as the ^2H T_{1Q} is on the same order as the zero field time period, one can conceivably obtain the deuterium spectrum via the protons.

The dc pulsed variation of the zero field experiment allows for detection of NQR spectra without loss of informa-

tion due to the proton background which is not normally the case with frequency domain techniques. Quadrupolar nuclei with small coupling constants are readily observed and resolution of ν_0 lines for spin $I = 1$ systems permit spectral interpretation which is usually done with the help of double transition frequencies and a knowledge of crystal structure.^{18,19} The experiments were conducted on a home-built zero field spectrometer²⁰ with demagnetization times on the order of 100 ms and pulsed dc fields of 30–500 G for times of 1 μs to a few hundred ms.

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¹D. P. Weitekamp, A. Bielecki, D. Zax, K. Zilm, and A. Pines, *Phys. Rev. Lett.* **50**, 1807 (1983); A. Bielecki, J. B. Murdoch, D. P. Weitekamp, D. B. Zax, K. W. Zilm, H. Zimmermann, and A. Pines, *J. Chem. Phys.* **80**, 2232 (1984).

²J. C. Koo, Ph.D. thesis, University of California, Berkeley, CA (unpublished); J. C. Koo and Y. N. Hsieh, *Chem. Phys. Lett.* **9**, 238 (1971); R. L. Strombotne and E. L. Hahn, *Phys. Rev.* **133**, A 1616 (1964); R. E. Slusher and E. L. Hahn, *Phys. Rev.* **166**, 332 (1968).

³D. T. Edmonds, *Phys. Rep.* **29**, 233 (1977); D. T. Edmonds, *Int. Rev. Phys. Chem.* **2**, 103 (1982).

⁴A. G. Redfield, *Phys. Rev.* **130**, 589 (1963).

⁵T. L. Brown, L. G. Butler, D. Y. Curtin, Y. Hiyama, I. C. Paul, and R. B. Wilson, *J. Am. Chem. Soc.* **104**, 1172 (1982).

⁶J. W. Clymer and J. L. Ragle, *J. Chem. Phys.* **77**, 4366 (1982).

⁷W. P. Aue, E. Bartholdi, and R. R. Ernst, *J. Chem. Phys.* **64**, 2229 (1976).

⁸E. D. Ostroff and J. S. Waugh, *Phys. Rev. Lett.* **16**, 1097 (1966); W. K. Rhim, D. P. Burum, and D. D. Elleman, *ibid.* **37**, 1764 (1976); D. Suwelack and J. S. Waugh, *Phys. Rev. B* **22**, 5110 (1980); M. Matti Maricq, *Phys. Rev. B* **25**, 6622 (1982).

⁹A. G. Anderson, *Phys. Rev.* **115**, 863 (1959); A. G. Anderson and S. R. Hartmann, *ibid.* **128**, 2023 (1962); V. S. Grechishkin, V. P. Anferov, and N. Ja. Sinjavsky, *Adv. Nucl. Quad. Reson.* **5**, 1 (1983).

¹⁰G. W. Leppelmeier and E. L. Hahn, *Phys. Rev.* **141**, 724 (1966); S. Vega, *Adv. Magn. Reson.* **6**, 259 (1973).

¹¹D. B. Zax, A. Bielecki, K. W. Zilm, and A. Pines, *Chem. Phys. Lett.* **106**, 550 (1984).

¹²J. M. Millar, A. M. Thayer, A. Bielecki, D. B. Zax, and A. Pines (in preparation).

¹³T. H. Goodwin, M. Przybylska, and J. M. Robertsen, *Acta Crystallogr.* **3**, 279 (1950).

¹⁴M. Bailey, *Acta Crystallogr.* **2**, 120 (1949).

¹⁵R. Blinc, M. Mali, R. Osredkar, A. Prelesnik, J. Seliger, and I. Zupanic, *Chem. Phys. Lett.* **14**, 49 (1972).

¹⁶L. S. Batchelder and J. L. Ragle, *J. Magn. Reson.* **37**, 469 (1980).

¹⁷M. H. Levitt and R. Freeman, *J. Magn. Reson.* **43**, 65 (1981).

¹⁸D. T. Edmonds and A. A. L. White, *J. Magn. Reson.* **31**, 149 (1978).

¹⁹R. O. Day, N. Hadipour, and J. L. Ragle, *J. Magn. Reson.* **57**, 369 (1984).

²⁰A. Bielecki, D. B. Zax, K. W. Zilm, and A. Pines (in preparation).