Time Domain Zero Field NMR and NQR*

A. Bielecki, D. B. Zax, A. M. Thayer, J. M. Millar, and A. Pines
Department of Chemistry, University of California, and Materials and Molecular Research Division, Lawrence Berkeley Laboratory, Berkeley, California 94720

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Field cycling methods are described for the time domain measurement of nuclear quadrupolar and dipolar spectra in zero applied field. Since these techniques do not involve irradiation in zero field, they offer significant advantages in terms of resolution, sensitivity at low frequency, and the accessible range of spin lattice relaxation times. Sample data are shown which illustrate the high sensitivity and resolution attainable. Comparison is made to other field cycling methods, and an outline of basic instrumental requirements is given.

Introduction

Time domain field cycling techniques have recently been applied to zero field studies involving nuclear quadrupolar and dipolar interactions in a number of polycrystalline materials [1, 2]. Such techniques are time domain analogs of the frequency domain, field cycling methods of Ramsey and Pound, Anderson, Redfield, Hahn, and others [3–7]. They are as well quite similar to the time domain, low field NMR method of Strombotne and Hahn [8].

Figure 1 (a) shows the basic experiment in an idealized form. The field cycle consists of three periods, associated respectively with preparation, evolution, and detection. In the first period, a field is applied for long enough ($\tau \gg T_1$) to magnetize the nuclear spins. Then the field is suddenly switched to zero to initiate the evolution interval. In zero field, magnetization is not a stable form of spin order, and evolves at the natural frequencies of the spin system. The field is suddenly switched on after some time, at which point the magnetization ceases to evolve and may be measured in the final period by high field NMR methods. In a single field cycle, the magnetization observed corresponds only to a single value (the terminal value) of the zero field time. To determine how the magnetization varies as a function of time, the field cycle is repeated with regularly incremented lengths of the zero field interval, and thus the evolution and decay of the magnetization is measured point by point. The Fourier transform of that magnetization function is equivalent to the zero field absorption spectrum.

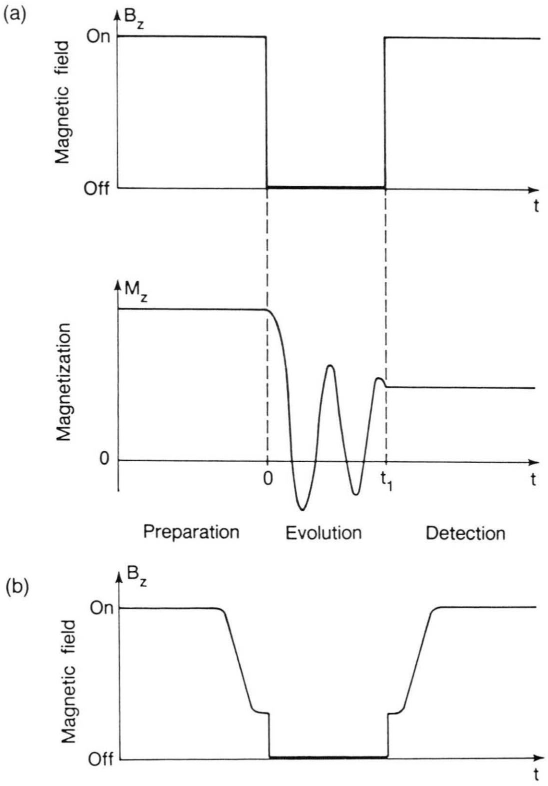

Fig. 1. (a) Idealized timing diagram for the basic time domain field cycling experiment. (b) Modified field cycle which is more feasible when the fields used for preparation and detection are large.

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Reprint requests to Dr. A. Bielecki, Department of Chemistry, University of California, Berkeley, California 94720, USA.

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In many cases, this time domain method holds certain advantages over frequency domain methods. Since it involves no irradiation in zero field, power broadening is not a problem; hence the resolution is limited only by dipolar broadening, spin-lattice relaxation, and sample inhomogeneity, and not by instrumental effects. In deuterium NQR experiments, for example, we often observe signals with linewidths of a few hundred Hertz. A further consequence of having no zero field irradiation is that the field cycles can be very short. Thus samples with relatively short T_1's (down to ~ 0.3 s, at present) are accessible. As well, the sensitivity is uniform across the spectrum, not falling off at low frequencies as in frequency domain experiments. These time domain experiments do not require the presence of abundant spin 1/2 nuclei in quadrupolar studies. Furthermore, time domain experiments can be made to selectively excite zero field coherences of one nuclear species and not another [2]. In indirect detection NQR experiments, where the spectrum of one species (e.g. ^{2}D) is obtained by observation of a second species (e.g. ^{1}H), this proves quite helpful in suppressing the zero field response of the detected species. In practice, these advantages are most important in studies at low frequencies (particularly for $f \lesssim 200$ kHz). Thus the time domain techniques of this work complement the frequency domain methods which work best at higher frequencies.

Instrumental Considerations [9]

In the field cycle depicted in Fig. 1 (a), the field transitions occur in a time short compared to the characteristic periods (i.e. $1/\omega$) of the zero field nuclear evolution, which are typically a few microseconds. These transitions are sudden in the quantum mechanical sense, so magnetization created in high field remains magnetization in zero field. The fields applied for preparation and detection must be relatively large, $\gtrsim 1$ Tesla, and uniform, to obtain good sensitivity. As it is difficult to switch such large fields in a few microseconds, the alternative field cycling scheme shown in Fig. 1 (b) proves useful. Here the field transitions are accomplished in two steps. The field is shifted relatively slowly between the high field level and an intermediate field (by mechanical shuttling of the sample in ~ 0.15 s in our apparatus). The transition time in this slow step is subject only to the constraint that it must be much less than the spin-lattice relaxation time T_1, or otherwise a large fraction of the signal magnetization is lost. Between the intermediate field and zero, the field shift is sudden in the sense outlined above. In our apparatus, this transition is accomplished in ~ 1 µs with a small electromagnet coil.

There is an additional requirement on the intermediate field. It must be large enough that the nuclear Zeeman interaction is stronger than the local interactions, so that the primary form of spin order in the intermediate field is magnetization. For example, in studies of deuterium NQR, an intermediate field of about 300 Gauss is satisfactory.

Zero Field NQR

Figure 2 at the top shows the time domain pure NQR signal of the ^{2}D nuclei in a polycrystalline sample of perdeuterated 1,4-dimethoxybenzene. The Fourier transform of that signal gives the spectrum, shown at the bottom of Figure 2. The group of peaks around 35 kHz corresponds to the methyl group, and the small splittings there are due in part to the dipolar couplings between the methyl deuterons. Four peaks are resolved around 135 kHz. These are the ν_- and ν_+ peaks of the two inequivalent aromatic ring ^{2}D sites. Near zero frequency, the ν_0 peaks of the aromatic sites are observed, and additionally a cluster of peaks associated with the methyl group. The ν_0 peaks, which are important in assigning the higher frequency lines to specific sites, are only rarely observed in frequency domain studies of spin 1 nuclei [10], and never at such low frequencies.

Zero Field NMR

In the zero field NMR of spin 1/2 nuclei, the spectra tend to be broad, and in the spectral analysis the ability to model and calculate the intensities in addition to frequencies is essential. With the field cycle of Fig. 1, the initial condition is so well characterized that the intensity distribution is easily calculated.

Figure 3 shows the zero field proton spectrum of 1,2,3,4-tetrachloronaphthalene-bis(hexachlorocyclo-

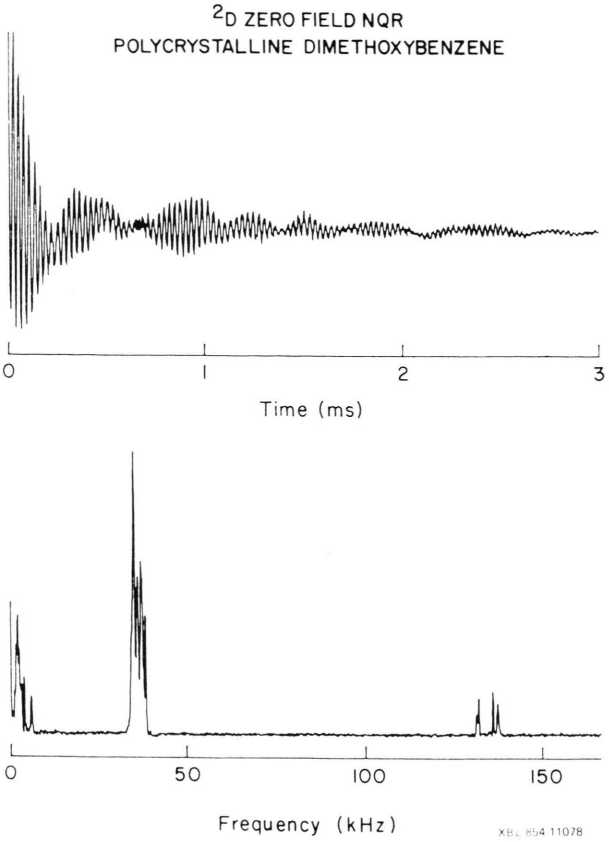

Fig. 2. At top, the ^2D NQR signal of 1,4-dimethoxybenzene-d_{10}, as obtained in the time domain. At bottom, its Fourier transform, the pure NQR spectrum. Note the sensitivity at low frequency and the high resolution.

pentadiene)adduct. The four protons are influenced primarily by their mutual dipolar couplings, which are sensitive to the molecular geometry. Figure 4 shows spectra generated by computer simulations based on hypothetical arrangements of the protons about the central ring of the structure. By comparing the experimental spectrum with the simulated patterns, the structure can be accurately determined. The structures represented in the right column of Fig. 4 differ only in the molecular conformation, and yet give distinctly different spectra. The simulation at the bottom right in Fig. 4 provides the best fit to the actual spectrum.

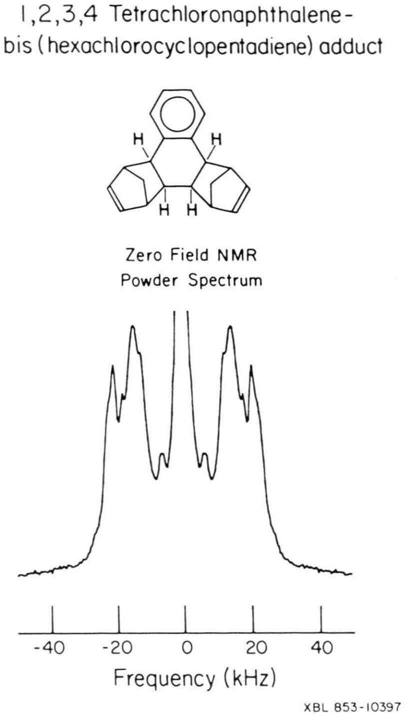

Fig. 3. At bottom, the ^1H pure dipolar spectrum of the compound shown at top. Dipolar spectra are plotted on both sides of zero frequency by convention.

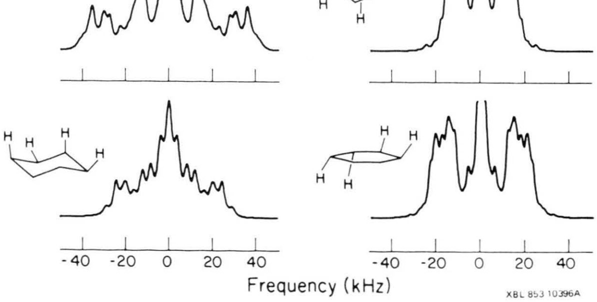

Fig. 4. Simulated dipolar spectra for hypothetical arrangements of the protons in 1,2,3,4-tetrachloronaphthalene-bis(hexachlorocyclopentadiene)adduct. The one at the bottom right best matches the experimental spectrum (Figure 3).

Pulsed Field Cycling and Indirect Detection [2]

An alternative time domain field cycling scheme is illustrated in Figure 5. Here the preparation and

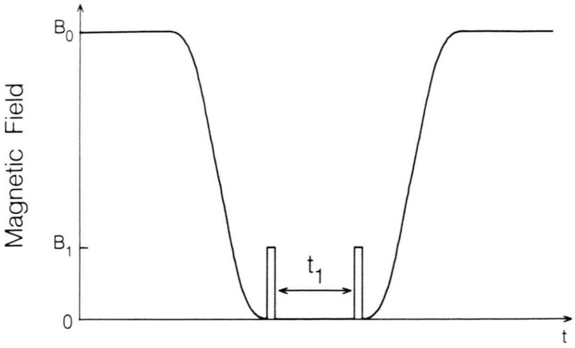

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Fig. 5. Modified field cycle employing dc field pulsing in zero field to create and monitor coherently evolving spin states. The adiabatic field transitions to and from zero field facilitate indirect detection when two or more nuclear spin species are near to each other.

detection intervals include adiabatic field shifts to and from zero field. During the zero field interval, coherent evolution of the spin order is initiated by the application of a short dc field pulse. That pulse is strong enough that it transforms the stationary spin order created in the adiabatic cycle (i.e. populations) into coherences, which are allowed to evolve for a time t_1. Then the coherences are transformed back into stationary states by a second dc pulse followed by the adiabatic remagnetization, after which the high field signal is probed. This method has a practical advantage over the sudden field switching scheme of Fig. 1; if electromagnets are used for the pulsing and switching, the pulsed scheme appears to be more feasible since the demands placed on the electronics are of relatively short duration.

For systems of quadrupolar nuclei near spin 1/2 nuclei (Q-I systems), adiabatic demagnetization permits the transfer of spin order from the I spins to the Q spins. Similarly, information about the evolved Q state can be communicated back to the I spins for indirect detection in high field. This is analogous to common techniques in frequency domain field cycling studies [5–7]. Indirect detection via protons offers several advantages related to the convenience and efficiency of the high field detection. Usually the measurement of proton NMR signals demands less of the rf hardware, as compared to NMR measurements of quadrupolar nuclei. The larger magnetic moment of the proton brings about a large gain in the signal to noise ratio. Also in some cases indirect detection allows zero field measurements of nuclei with T_1's too short or inconveniently long for other field cycling methods.

As an example, Fig. 6 shows the ^{14}N pure NQR spectrum of ammonium sulfate, measured by observation of the protons, using the method of pulsed field cycling with indirect detection. Two sets of ν_0, ν_-, and ν_+ transitions are well resolved, indicating that there are two inequivalent types of ammonium sites. Ordinarily the low frequency lines would be obscured by the proton zero field signal, which occurs in a broad band from 0 to ~40 kHz. Here the proton signal is greatly reduced by the proper choice of pulse angle. The amplitude and duration of the dc pulses are chosen so that ideally the proton spins are rotated by a multiple of 2π radians, and thus left unaffected by the pulses. The pulse rotation angle is proportional to the gyromagnetic ratio, so the ^{14}N spins are subject to something less than a full rotation, and evolution in zero field is thus initiated. This technique has been applied also in a number of studies involving ^{2}D NQR in isotopically enriched compounds.

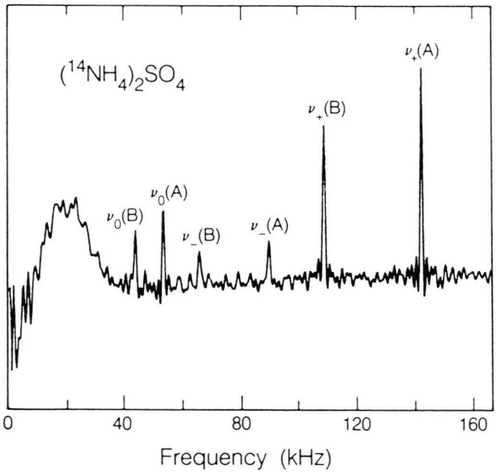

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Fig. 6. ^{14}N spectrum of ammonium sulfate measured by the pulsed field cycling method outlined in Fig. 5, with indirect detection through the protons. The proton signal (below 40 kHz) is somewhat suppressed by selecting pulse lengths corresponding to $2\pi n$ rotations for the proton spins.

Acknowledgements

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