

TWO-DIMENSIONAL ZERO-FIELD NMR AND NQR

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Correlations between quadrupolar frequencies in a spin $I = 1$ system are determined through a two-dimensional version of the zero-field NMR experiment. Results presented on a selectively deuterated polycrystalline solid illustrate this for the quadrupolar lines corresponding to inequivalent deuterium sites.

1. Introduction

Two-dimensional NMR methods involve recording the NMR signal as a function of two time variables with subsequent transformation to produce a spectrum described by two frequency variables [1,2]. Applications of these experiments are generally to weakly coupled liquids and the frequencies observed depend upon the specific excitation pulse sequence used. Common examples are those which show correlations between chemical shifts and scalar couplings [3], between different chemical shifts [1,2,4] exchanging or cross relaxing dipolar coupled nuclei [5], and multiple quantum transitions [2]. By measuring the connectivities between spectral transitions, a determination of structure, conformation, dynamics or assignment of an otherwise intractable one-dimensional spectrum is possible.

In zero-field NMR and NQR, dipolar and quadrupolar interactions in the absence of an applied magnetic field are observed [6]. These experiments yield well-resolved, sharp line spectra in polycrystalline solids. In zero field, quadrupolar frequencies label specific chemical sites while dipolar couplings should induce connectivities between zero-field transitions of neighboring spins. In this communication, we demonstrate the principles of two-dimensional NMR to the detec-

tion of quadrupolar nuclei in zero applied magnetic field. Through a combination of these techniques, the connectivities in the NQR transitions of a spin $I = 1$ nucleus are shown.

2. Zero-field NQR spectra

A spin $I = 1$ quadrupolar nucleus, such as deuterium, has three energy levels in zero field [7]. For a non-axially symmetric electric field gradient, these levels are non-degenerate linear combinations of the high field states. The allowed transitions are labeled ν_0 , ν_- and ν_+ , in order of increasing frequency. The dependence of these frequencies on quadrupole coupling constants (e^2qQ/h) and asymmetry parameter (η) are given by [7]:

$$\nu_+ = (3 + \eta)K, \quad \nu_- = (3 - \eta)K, \quad \nu_0 = 2\eta K = \nu_+ - \nu_-,$$

in which $K = e^2qQ/4h$ for $I = 1$. Values of η and e^2qQ/h , which are descriptive of a quadrupolar system, may be calculated for a given chemical site assuming that the pair of corresponding ν_- and ν_+ lines is distinguishable. If there are two or more inequivalent sites, the NQR spectrum will consist of a superposition of six or more lines. Therefore, resolution of the difference frequency ν_0 lines at very low frequencies is essential in assigning the one-dimensional spectrum.

The one-dimensional zero-field NQR spectrum of the methylene group of polycrystalline diethyltereph-

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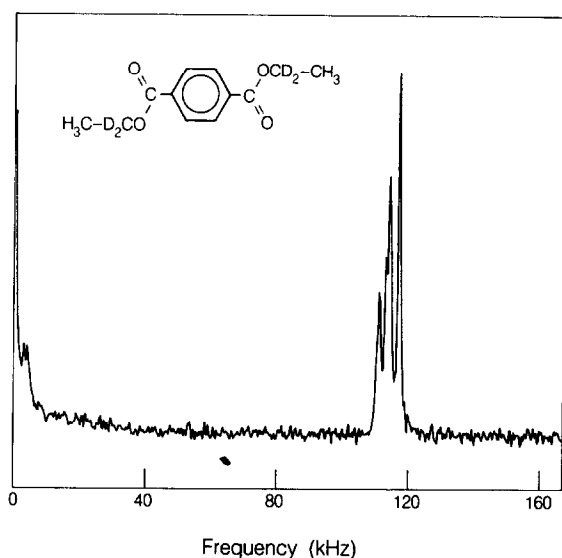


Fig. 1. One-dimensional zero-field deuterium NQR spectrum of selectively deuterated diethylterephthalate- d_4 . The spectrum was detected indirectly via $^1\text{H}-^2\text{H}$ level crossings. Six lines are resolved corresponding to the $\nu_0/\nu_-/\nu_+$ transitions of two inequivalent methylene deuterons. Through the use of the low-frequency ν_0 lines, combinations of peaks may be assigned as the ν_-/ν_+ pair corresponding to a single quadrupolar site.

thalate is shown in fig. 1. The spectrum was obtained using the selective indirect detection method which has been described in detail elsewhere [8]. Essentially this experiment involves using the $^1\text{H}-^2\text{H}$ level crossings which occur as a consequence of the field cycle to polarize and detect the NQR spectrum [9]. Pulsed dc fields, chosen to act as rotations of $2\pi n$ radians for the protons, are used to selectively excite the zero-field evolution of only the deuterons. The two deuterons of a particular methylene group are inequivalent resulting in the six-line spectrum. The low-frequency lines are resolved and allow for calculation of quadrupole coupling constants and asymmetry parameters for the inequivalent sites. If more sites were present, it becomes evident that overlapping lines would make assignment difficult.

3. Two-dimensional zero-field experiment

The correlations between the NQR frequencies can also be observed by probing the connectivities in the

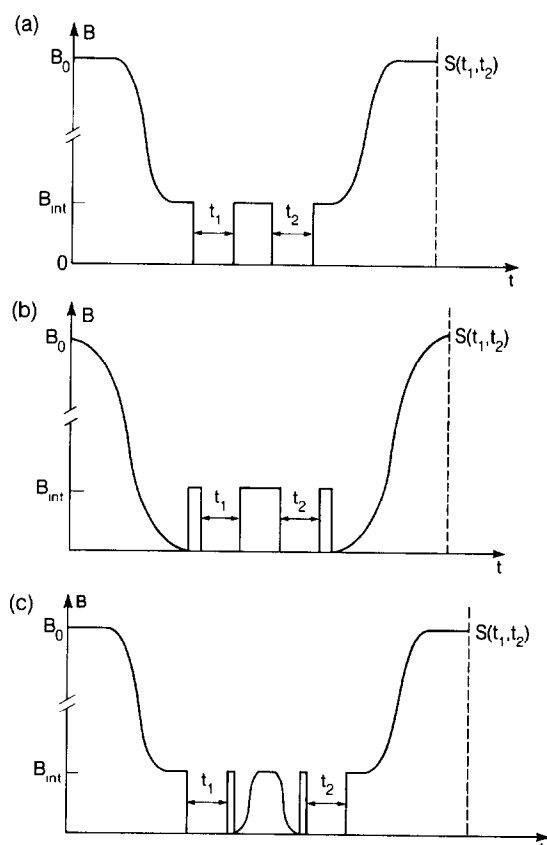


Fig. 2. Field cycles for two-dimensional zero-field experiments. (a) The sample is demagnetized to an intermediate field, B_{int} , which is switched off suddenly to initiate evolution in zero field. The evolution period is divided into two time periods, t_1 and t_2 , by reapplication of the field. If the dc field is applied as a brief pulse, it will act as a rotation on the spin system and mix coherences. Evolution then continues for t_2 and is terminated with a sudden reapplication of the intermediate field and remagnetization to high field. The signal is sampled as a function of the independently incremented time variables. If the applied field is longer in duration, $\approx 0.5-1$ ms correlations between dipolar coupled groups of spins should develop. (b) Using demagnetization to zero field, indirect detection of the zero-field NQR spectrum is possible. The short pulsed dc magnetic fields are used to initiate zero-field evolution for t_1 , to mix coherences as in (a), and to terminate evolution after t_2 . Remagnetization after the zero-field period again provides for the $^1\text{H}-^2\text{H}$ level crossings and the detection of the signal in high field. (c) The preparation of the spin system and t_1 evolution period are identical to that shown in (a). Applying a brief dc pulsed field will effectively store the magnetization, and prevent the decay of coherences under the applied field. Cycling the field slowly to an intermediate level show provide for cross relaxation between groups of spins. Evolution is re-initiated for t_2 by a second dc pulse then halted and detected in the same manner as in (a) and (b).

spin $I = 1$ manifold through a two-dimensional version of the field cycle. The simplest form of the field cycle, in which the zero-field interval is divided in half, is shown in fig. 2a. The sample is demagnetized to an intermediate field, B_{int} , which is switched off suddenly to initiate evolution. The system evolves under the quadrupolar Hamiltonian for the time t_1 . Application of a short dc pulsed field will transfer coherence between the energy levels of the spin 1 system. Evolution in zero field continues after the pulse for a time, t_2 . Reapplication of the field and remagnetization provides for sampling of the magnetization in high field. In successive field cycles, the zero-field periods are incremented independently to produce a time domain signal as a function of t_1 and t_2 which when Fourier transformed produces the two-dimensional zero-field spectrum.

Other initial conditions are also possible in this experiment. In actual practice, for the increase in sensitivity and potentially shorter ^1H T_1 relaxation times, the signal can be detected indirectly via the protons as described previously. The field cycle of fig. 2b uses demagnetization to zero field followed by pulsed dc magnetic fields to initiate and terminate zero-field evolution (rather than the sudden transition of B_{int}). Of course, the behavior of the spin system has the same dependence on the natural quadrupolar frequencies, as in the version with sudden transitions in the intermediate field, although now the intensities of the spectrum will also be a function of the initial and final dc pulse angles and the dynamics of the level crossings. A short dc pulsed field can be applied to mix coherences in the same manner as in fig. 2a.

In addition to observing quadrupolar frequencies, connectivities between dipolar coupled groups of spins might also be established by altering the mixing period of the experimental field cycle. Assuming a deuteron-deuteron dipolar coupling of $\nu_D \approx 1$ kHz, application of an intermediate field, as in fig. 2a, for ≈ 1 ms ($\approx 1/\nu_D$) or longer should allow a coherence transfer between dipolar coupled spins. Thus correlations based on spatial proximity can also be developed. In cases where the coherences do not persist for longer than a few milliseconds, signal might be conserved if the evolving magnetization is stored as populations by application of a dc pulse as shown in fig. 2c. Thus the decay is now described by a time constant related to T_{1z} which is expected to be longer than the decay of

the coherences in solids. By slowly cycling the field to an intermediate value, the energy levels of inequivalent deuterons may be brought into contact. This is similar to the signal enhancement approach via repeated level crossings used in frequency domain double-resonance NQR experiments [10].

As an experimental verification of the applicability of these field cycles, the two-dimensional zero-field spectrum of the high-frequency ν_- and ν_+ lines of the same methylene sites in polycrystalline diethylterephthalate- d_4 is shown in fig. 3. The field cycle of fig. 2b was employed to indirectly and selectively detect only the deuterium NQR signal with all dc pulse angles equal to multiples of 2π for the protons. A mixing

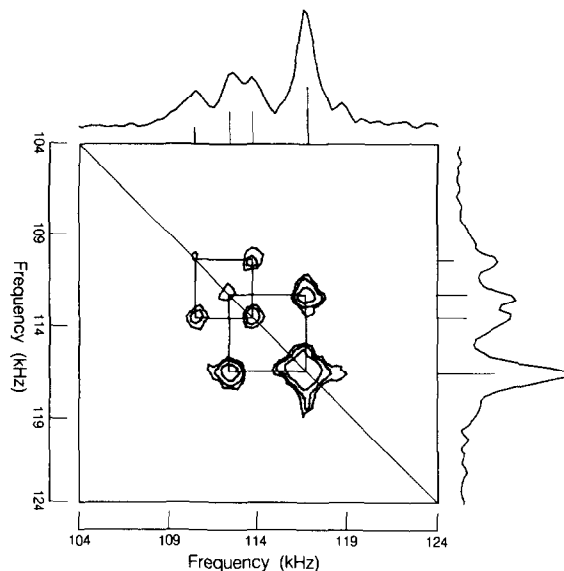


Fig. 3. Two-dimensional zero-field NQR spectrum of the high-frequency ν_-/ν_+ transitions of polycrystalline diethylterephthalate- d_4 . The spectrum was obtained through indirectly detecting the ^2H signal via the protons as described in fig. 2b. By using pulses which were multiples of 2π for the protons, selective excitation of only the quadrupolar transitions is possible. The transfer of coherence between states in the spin $I = 1$ manifold was produced with a short dc pulsed field (about a few hundred gauss) corresponding to a ^2H pulse angle of approximately 165° as described in the text. Diagonal peaks along the $\nu_1 = \nu_2$ line correspond to the one-dimensional spectra as shown in the projections. The peak positions of the one-dimensional spectrum are indicated by the stick spectra. Cross peaks indicate correlations between the ν_+ and ν_- transitions of an individual deuteron site. The connectivities are illustrated by the connecting lines.

pulse of $3 \times 2\pi$ radians for the protons is approximately a 165° deuteron pulse which is close to the 180° pulse predicted to give maximum intensity in the cross peaks [11]. The diagonal peaks fall along the $\nu_1 = \nu_2$ line and reproduce the one-dimensional spectrum. Off-diagonal peaks correspond to the ν_-/ν_+ connectivities in the spin $I = 1$ manifold and are illustrated by the connecting lines. One connected pair of lines belongs to one deuteron of the CD_2 group and the second pair belongs to the other inequivalent deuteron.

4. Summary

NQR transitions in frequency domain experiments are often assigned on the basis of weakly allowed double transition peaks [12], double irradiation of two NQR lines [10], or by the shift in frequencies due to application of a low field [13] since the low-frequency lines are often obscured or unobserved [10]. Time domain techniques [6] have the low-frequency detection capabilities, resolution and selectivity to assign transitions on the basis of ν_0 lines. All of these approaches are plagued by the problem of increased complexity of the spectrum with increasing numbers of quadrupolar sites. Two-dimensional zero-field NMR experiments can address many of these problems by utilizing the cross-peak correlations to determine connectivities. A large variety of experimental conditions, produced with different field cycles, can be envisioned with the use of pulsed magnetic fields to manipulate the spins in zero field.

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