

Double Resonance Detection Using Zero Field Level Crossing*

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Double resonance level crossing detection cannot normally be used to record transitions between the quadrupole Zeeman levels. Neither can it be used if the quadrupole resonance frequency is larger than the proton NMR frequency in high field. A simple variation of the level crossing experiment is demonstrated which allows energy to be efficiently transferred from quadrupole to proton system and hence lead to detection in these two cases. In the case of the quadrupole Zeeman levels it allows transitions between the $\pm \frac{1}{2}$ levels to be detected in a small magnetic field, allowing measurement of the asymmetry parameter (η) for spin 3/2 systems. This is demonstrated for the ^{11}B nucleus in triethanolamine borate. Detection of high frequency quadrupole transitions is demonstrated from which relaxation information is obtained.

Key words: NQR; Asymmetry Parameter; Relaxation; ^{11}B ; ^{35}Cl .

Introduction

For a spin 3/2 nucleus only one transition can be detected in zero field, which means that the 3 non-zero components of the electric field gradient (EFG) tensor (in its principal frame of reference) cannot be determined uniquely. The ability of nuclear quadrupole resonance (NQR) to give a three dimensional picture of the electron density around a nucleus is lost. There have been many attempts to restore this information by applying a small magnetic field to the sample. Traditional NQR spectrometers, however, have poor sensitivity so that the increased frequency spread of the resonance in non-zero field leads to loss of the signal usually before the structure of the line can be observed. With pulsed spectrometers the difficulty of recording large bandwidths consistent with Zeeman broadening is well known. Double resonance detection based on the dynamic solid effect [1] has also been used to tackle this problem. Though this works quite well it has drawbacks: the transition probability of this type of transition falls rapidly with applied field, and the line shape depends not only on the asymmetry parameter (η) but on the direction of dipolar contacts. An alternative approach is to use two dimensional nutation spectroscopy, but high RF powers and long pulses are required [2].

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In this paper we demonstrate a novel variation of double resonance level crossing that can be used to detect, with good signal to noise ratio, transitions of quadrupole systems in non-zero magnetic field. The main advantage of this technique is that the line shapes obtained by level crossing are generally less distorted than those obtained by other double resonance techniques. Therefore it has to be considered the technique of choice when trying to extract line shape sensitive parameters, in particular detection of transitions in a polycrystalline sample between the 1/2 levels of a spin 3/2 system which allows η to be determined [3].

Zero field level crossing also allows high frequency Zeeman broadened quadrupole transitions to be recorded with a good signal to noise ratio.

Experimental

The spectra were recorded on a double resonance spectrometer based on mechanical transport of the sample [4]. In high field the proton signal was monitored in a field of 9438 G. In all experiments the magnetic and RF fields were parallel. Triethanolamine borate (2,8,9-trioxa-5-aza-1-borabicyclo[3.3.3]undecane) was obtained from Aldrich and 1,4-dichlorobenzene (alpha phase monoclinic) from BDH. Both samples were ground to fine powders, before use, to ensure polycrystallinity. Computer line shape simulations were carried out on a Digital DEC 466 D2; 1600 crys-



tal orientations were used and the data were then filled 64-fold to generate the spectrum. Each spectrum took 3 minutes to compute.

The equilibration of spin temperatures in zero field (for half integer spin nuclei) is rapid, so the introduction of an intermediate zero field regime suitable for zero field level crossing can be easily achieved with minimal modification to the double resonance spectrometer. Two solenoids are placed over the transfer tube. The first one supplies the low field used to cause the Zeeman splitting of the quadrupole system whilst the sample is at rest. The second solenoid produces a magnetic field in the opposite direction to the first and is placed a little way along the transfer tube. In the actual experimental arrangement this solenoid was wound directly onto the transfer tube. The second solenoid only contributes to the experiment when the sample is moving between low and high field regimes. The reversed field ensures that the sample goes through zero magnetic field during transfer from low to high field. Neither with the field from the two solenoids in the same direction nor with the second solenoid removed was a signal observed, demonstrating that detection was only by the zero field level crossing route.

Results and Discussion

Detection of Low Frequency Zeeman Transitions

Double resonance level crossing has been used extensively to detect low frequency quadrupole resonance transitions. As the field increases during transfer of the sample from low to high field, cross relaxation can occur between quadrupole and proton spin systems [5]. Zeeman transitions of the quadrupole system cannot be detected using this experimental arrangement. Only in zero field will the splitting of the Zeeman levels of the protons and the quadrupole system be equal and cross relaxation occur. By arranging for the magnetic field felt by the sample to fall to zero during transfer to the high field regime, energy is transferred between the proton and quadrupole levels. So irradiating at a frequency corresponding to the splitting of the 1/2 levels, then dropping the field to zero before monitoring the proton signal in high field, it is found that the recovered proton signal gives an accurate reflection of the line shape for these transitions from which the value of η can be obtained.

An isolated molecule of triethanolamine borate has a three fold axis; this, however, is not retained in the crystal [6]. It may therefore be assumed that η is small but is unlikely to be exactly zero. In a previous study [7] only one ^{10}B transition was detected between the 0 level and the ± 3 levels: insufficient to determine η . However detection of this transition is indicative of a non-zero η (it being forbidden for an axially symmetric EFG). The single transition for the ^{11}B isotope was detected at 620 kHz. When calculating the line shapes, the ^{10}B isotope was considered to make no contribution. This was justified on the basis of the difficulty encountered detecting transitions of this nucleus by other double resonance techniques, its low natural abundance, and the fact that cross relaxation between integer and half integer spin nuclei in zero field is slow [8]. As a further check, the line shape for this isotope in the magnetic field used was generated; it was found to be essentially featureless in the region studied.

The experimental and theoretical line shapes for transitions between the 1/2 levels for ^{11}B are shown in Figure 1. The line shapes show quite clearly that the agreement between experimental and simulated line

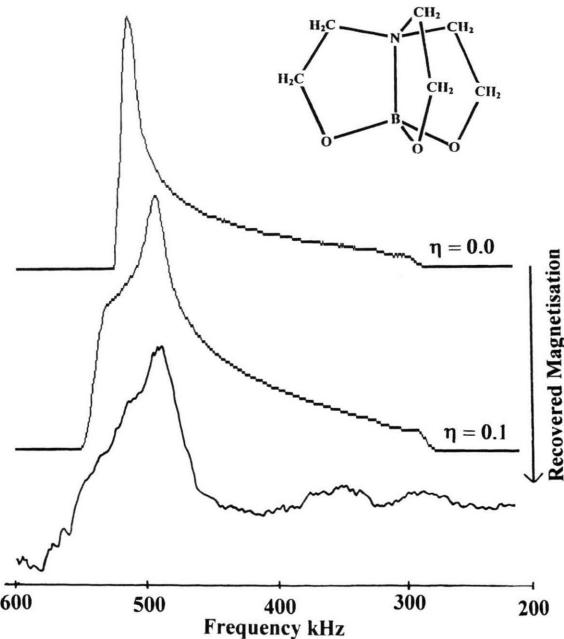


Fig. 1. The zero field level crossing spectra for transitions between the 1/2 levels for the spin 3/2 nucleus ^{11}B in a polycrystalline sample of triethanolamine borate (the applied magnetic field was 216 G). The upper two spectra are calculated for $\eta=0$ (top) and $\eta=0.1$ (middle), lower spectrum experimental.

shapes is very poor for zero η . In particular there is no correspondence in the frequency of the main peak, and the computer generated line shape shows a much sharper maximum. If η is increased, the fit improves; the best fit being at an unexpectedly high value of 0.10 (± 0.02). This seems to indicates that there are quite large interactions between adjacent molecules in the crystal. There is, however, no evidence for ^{14}N having a non-zero η [7, 9]. Another possibility is that the line shapes were distorted due to static disorder in the crystal. An X-ray study [10] has shown extra reflections not expected for the space group ($\text{Pca}2_1$), which could be evidence for this. There is, however, no evidence for this in the ^{14}N resonance measured by cross relaxation [9] or by level crossing [7].

Detection of High Frequency Quadrupole Transitions

If the quadrupole resonance frequency is higher than the proton resonance frequency in high field then level crossing detection of pure quadrupole transitions is not possible. In the case of ^{35}Cl in 1,4-dichlorobenzene (resonance frequency 34.27 MHz), measured using a high field proton frequency of 40 MHz, level crossing is possible for all crystal orientations, but is not experimentally realized due to the short contact time. This is due to the cross relaxation condition occurring when the rate of change of field (with time) is at its largest. So, if a small magnetic field is applied (~ 20 G) thermal mixing type detection is suppressed and no signal is observed at the line centre. Dynamic solid effect signals can still be observed [11], but these are far away from the pure quadrupole transition frequency. If, however, the sample is allowed to experience zero field during transfer, a signal that is proportional to the population difference of the $\pm 1/2$ levels plus the population difference of the $\pm 3/2$ levels is seen at the line centre. So, depending on the quadrupole transition excited, the magnetization stored in the two pairs of levels will either add or subtract. Figure 2 shows the experimental and calculated spectrum of the ^{35}Cl resonance in 1,4-dichlorobenzene. The calculated spectrum assumes that the RF level is sufficient to cause all transitions to be saturated. Like the normal type of level crossing magnetization is stored in the quadrupole levels during irradiation, only being exchanged with the proton system during sample transfer. The implications of this are that the recorded signal will depend on how well the quadrupole levels retain their magnetization. So, by introducing a delay

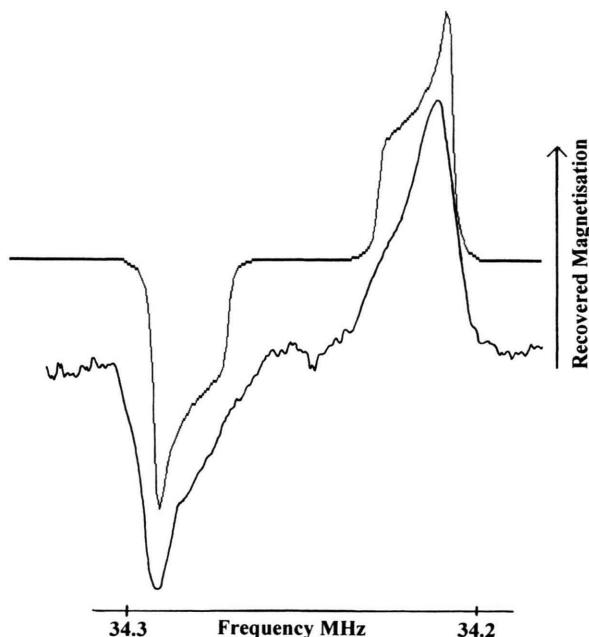


Fig. 2. The zero field level crossing spectrum of a polycrystalline sample of 1,4-dichlorobenzene in a magnetic field of 50 G. Upper spectrum calculated, lower experimental.

between switching off the RF field and sample transfer an estimate of the quadrupole spin-lattice relaxation time can be made. The decay of signal fitted quite well to a single exponential, from which a relaxation time of 150 ms (± 20 ms) was obtained. This value is quite different from the zero field value measured at this temperature of 23 ms [12], and also differs from single crystal measurements in a small magnetic field [13].

A possible explanation is that only the very outer parts of the Zeeman broadened spectrum are retained at delay times longer than 20 ms. The intensity here is provided by crystals in which the principal component of the EFG (q_{zz}) is aligned with the magnetic field. This is the only orientation for which there is no mixing of the $+1/2$ and $-1/2$ wavefunctions. These transitions correspond therefore to almost pure $\Delta m = \pm 2$ transitions. Furthermore relaxation proceeding by a $\Delta m = \pm 1$ process will not affect the zero field level crossing intensity. The most reasonable explanation, therefore, is that $\Delta m \pm 2$ relaxation is slow compared with $\Delta m \pm 1$ relaxation, the relative rates of the two relaxation processes being the reverse of those reported for single crystals [13]. It is, however, consistent with the zero field value if it is assumed that the $\Delta m \pm 1$ relaxation is dominant. This is a reasonable assumption based on the observa-

tion that all crystal orientations for which there is mixing of the 1/2 levels (allowing loss of magnetization by $\Delta m = \pm 1$ processes) disappear from the spectrum if a pre-transfer delay of more than 20 ms is used.

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