Low Frequency NQR using Double Contact Cross-relaxation

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A cross-relaxation technique is described which involves two spin contacts per double resonance cycle. The result is an improvement in signal to noise ratio particularly at low frequencies. Experimental spectra and analyses are presented: ^{14}N in ammonium sulphate showing that the technique gives essentially the same information as previous studies; ^{14}N in ammonium dichromate determining e^2Qq/h as (76±3) kHz and η = 0.84±.04; ^{7}Li in lithium acetylacetonate for which the spectrum (corrected for Zeeman distortion) yields e^2Qq/h = (152 ±5) kHz and η = .5 ±.2. Calculated spectra are presented to demonstrate the η dependence of the line shapes for ^{7}Li.

Key words: NQR; ^{14}N; ^{7}Li; Low Frequency; Double Resonance.

Introduction

Recording low frequency NQR signals presents various difficulties: single resonance techniques are limited by the unfavourable Boltzmann factor. Double resonance methods, using protons as the detector nucleus, also have drawbacks: radiative methods can result in direct excitation of the proton dipolar absorption edge; keeping circuits tuned over a large dynamic range is problematic; non-radiative double resonance techniques often fail at low frequencies due to short proton relaxation times.

An alternative approach to the problem that has proved to be successful is zero field FTNQR [1]. In this paper we present two-contact double resonance cross-relaxation spectroscopy, a less experimentally demanding technique than zero field FTNQR. It can also detect low frequency transitions, but unlike zero field FTNQR, can equally be applied to higher frequency measurements (provided the Zeeman broadening of the quadrupole system is not too large). We have previously shown that this technique can be used to detect transitions around 1 MHz in nitrobenzoic acids [2]. Here we give details of the experimental arrangement and show that the technique can be extended to detect transitions in the tens of kHz range. It is a non-radiative technique which relies on a long quadrupole relaxation time (> 1 s) rather than a long low field proton relaxation time. Surprisingly, quadrupole relaxation times are often quite long for low frequency transitions. It is however only applicable to nuclei with relatively high abundance, the signal strength depending on the heat capacity of Q spins. As with other double resonance techniques based on cross-relaxation, Zeeman broadening can be a problem but at low frequencies it is usually not significant.

Experimental

The spectra were recorded on a double resonance spectrometer based on mechanical transport of the sample [3]. In high field the proton signal was monitored in a field of 9438 G. The variable cross-relaxation field was supplied by a solenoid wound directly onto the transfer tube. The solenoid was terminated before the end of the tube so that when the sample is at rest at the end of the tube it experiences zero field. A cross-relaxation condition is realized only during sample transfer. The contact proved to be sufficiently long for effective spin contact to take place. This is not unexpected as double resonance

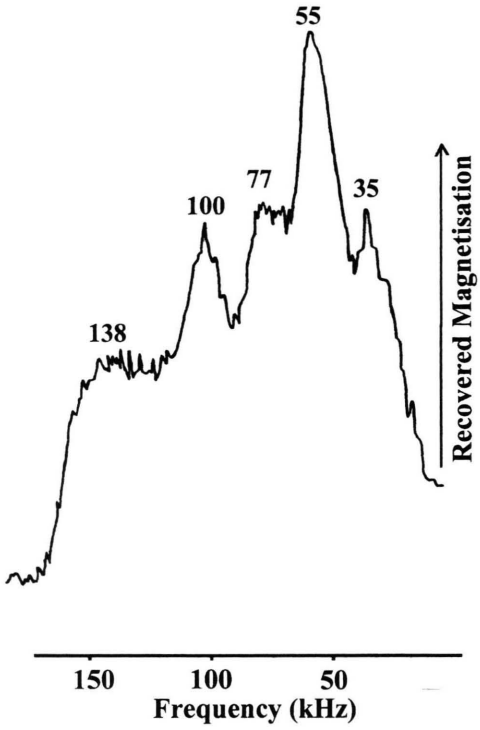

Fig. 1. Double contact cross-relaxation spectrum of ammonium sulphate. The position (in kHz) of the features in the spectrum are indicated. The sample was left to relax in high field for 10 s and the time spent in zero field was 0.5 s.

level-crossing [4] uses a much shorter contact time and usually achieves good polarization transfer.

High field line width measurements were carried out using a Bruker DRX 400 spectrometer.

Results and Discussion

In the usual form of the double resonance detection, using cross-relaxation, a small applied magnetic field brings two levels of the quadrupole energy level system into contact with the proton Zeeman levels. Rapid equilibration of the energy of the two pairs of levels occurs. Relaxation with the two levels still in thermal contact then takes place. In this variation of the technique the spin systems are only brought into contact for a time sufficient to achieve energy equilibration. The two systems are then isolated by changing the magnetic field. Any non-matching field could be used. A r.f. field is then applied at the proton resonance frequency equalizing the population of the proton levels. For experimental simplicity the field

Table 1. Quadrupole coupling constants and asymmetry parameters for ^{14}N in ammonium sulphate: the results obtained using double contact cross-relaxation and for comparison data from two previous studies.

Nitrogen site	e^2Qq/h (kHz)	η	Reference
N(a)	153± 5	0.62±.1	this work
N(b)	115± 5	0.82±.1	this work
N(a)	154.5	0.688	[1]
N(b)	115.9	0.747	[1]
N(a)	154.5	0.686	[7]
N(b)	115.7	0.749	[7]

was dropped to zero and low power r.f. applied within the proton dipolar edge (at 3 kHz). Following this the original strength of static field is again applied. Much of the polarization stored in the quadrupole levels remains and is transferred back to the protons. Finally, to complete the double resonance cycle, the sample is returned to high field where the proton polarization is measured. So if the cross-relaxation field matches the proton levels to that of a pair of quadrupole levels an enhanced proton signal is detected at the end of this cycle. If this condition is not satisfied a zero signal results. This has the distinct advantage that a small change from zero rather than a small change in a large signal is to be detected.

As a test of the utility of the technique we show it applied to ^{14}N in ammonium sulphate, a system which has been previously studied by zero field FTNQR [1]. The spectrum obtained from 0 to 180 kHz is shown in Figure 1.

Some problems were experienced with this test sample: there are two inequivalent nitrogens in the unit cell giving rise to six transitions below 150 kHz; the proton-proton dipolar coupling within the ammonium group is strong, enabling cross-relaxation to occur over quite a large frequency range hence giving a large natural line width to the resonances detected. To facilitate analysis the proton resonance in high field (400 MHz) was measured. This showed that the dipolar coupling constant was about 10 kHz (a considerable reduction from the value calculated based on the molecular geometry of 25 kHz). This reduction is caused by motion of ammonium groups; an effect that is well documented [5]. The high field NMR of the solid also showed that the proton line was essentially featureless consisting of a broad flat topped peak, the plateau of the peak extending between ±10 kHz from the isotropic chemical shift and the half height width was 36 kHz. Calculations based on this value

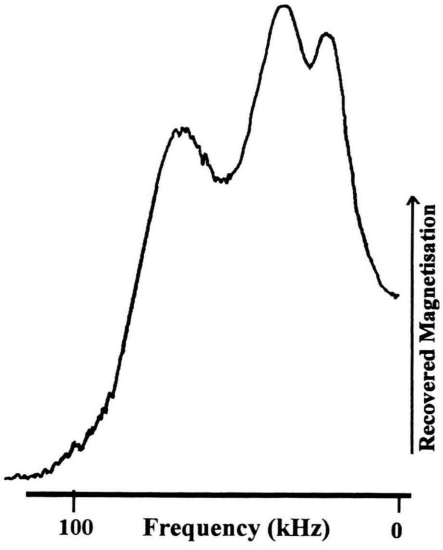

Fig. 2. Double contact cross-relaxation spectrum of ammonium dichromate. The sample was left to relax in high field for 10 s and the time spent in zero field was 0.5 s.

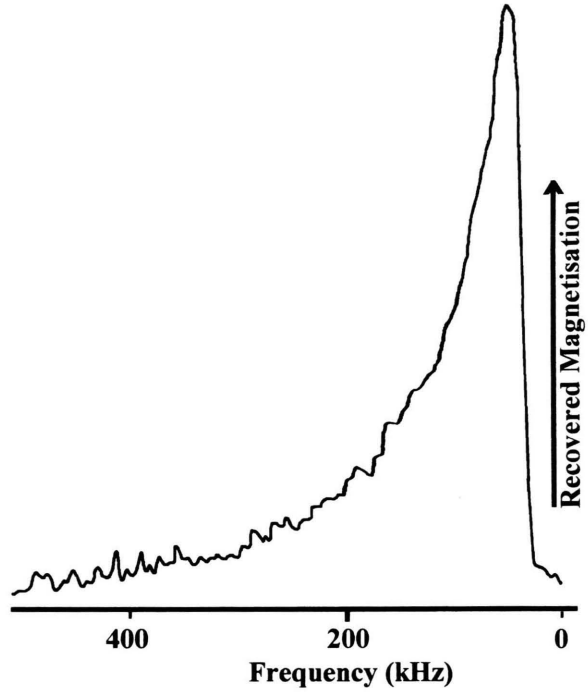

Fig. 3. Double contact cross-relaxation spectrum of lithium acetylacetonate. The sample was left to relax in high field for 20 s and the time spent in zero field was 1 s.

of dipolar coupling were carried out to determine the line shape expected in low field. It was assumed that the only significant dipolar contacts were those of the four protons bound to nitrogen. Using the untruncated dipolar Hamiltonian, separate spectra were calculated for 200 crystal orientations, and the data combined to give a spectrum [6]. The calculated line shapes showed that there was very little deviation from the high field line shape down to a proton resonance frequency of 25 kHz. At this point asymmetry became noticeable.

So the double contact cross-relaxation spectrum of ammonium sulphate can be understood on the basis of a trapezoidal detecting envelope. Unfortunately this leads to some overlap. The sharp peaks at 55 and 100 kHz and the shoulder at 77 kHz are due to the detecting envelope overlapping two nitrogen transitions. A single isolated peak would not be expected to be so sharp. Furthermore the overlapping resonances must stem from different nitrogen sites to produce such an enhancement of the signal. A rough estimate can be made of the separation of the two resonances contributing to each of these peaks based on their sharpness. The sharp peaks at 55 and 100 kHz are estimated to be the result of two peaks 20 kHz apart and for the shoulder at 77 kHz a separation of 30 kHz was determined. Combining this information gives the results shown in Table 1. The table also shows, for comparison, data from the most reliable previous studies [1, 7]. The calculation of the quadrupole coupling and asymmetry parameter are based on the ν_+ and ν_- lines as some frequency shift of the ν_0 lines occurs due to stray fields from the main magnet. Results are in agreement with those from the previous studies but the error associated with this determination is larger due to the overlap experienced in the spectrum.

Figure 2 shows the spectrum obtained for ammonium dichromate. In this case only 3 lines are seen corresponding to one nitrogen site in the unit cell. Measurements of the proton line width in high field show that the dipolar coupling is smaller than that of the sulphate at 7.5 kHz. The ν_0 and ν_- lines are at such low frequency that stray field from the main magnet is causing the cross-relaxation condition to be realized at a lower applied field than expected. Because of the experimental arrangement the direction of the stray field from the main magnet is at right angles to that of the cross-relaxation solenoid. If this information is combined with the necessity that the transition frequencies be additive then the corrected

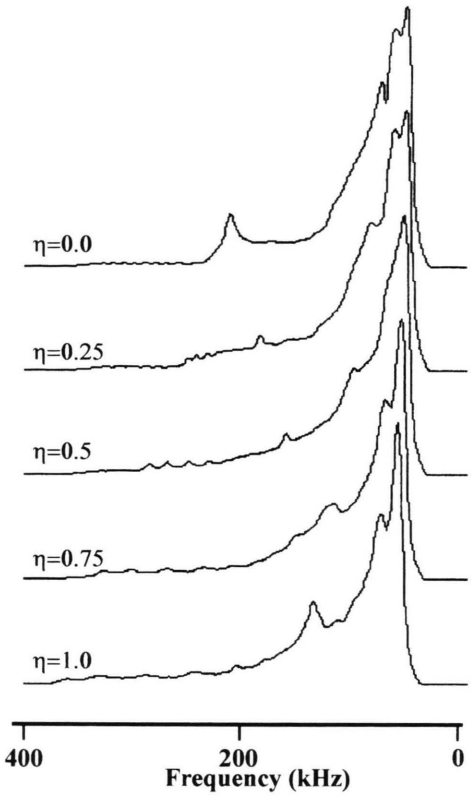

Fig. 4. Calculated spectra for ^{7}Li using e^2Qq/h = 152 kHz and η = 0 to 1 in steps of 0.25. 100 crystal orientations were used. The data were filled 64-fold and compiled into a spectrum using 1 kHz steps. The final spectrum was smoothed using a Lorentzian with a half height width of 3 kHz.

frequencies obtained are 33, 41, and 73 kHz. This gives a quadrupole coupling constant of (76 ±3) kHz and an asymmetry parameter of 0.84 ±.04.

Figure 3 shows the two contact cross-relaxation spectrum for a half-integer spin nucleus – ^{7}Li in lithium acetylacetonate. Integer spins, except zero η cases, show very little Zeeman broadening. However, half-integer spins show Zeeman broadening even in small magnetic fields. Furthermore, the non-uniform magnetic field across the spectrum causes distortion of the line shape. ^{7}Li has a relatively large magnetogyric ratio so its spectrum shows an extreme example of Zeeman broadening and distortion. Line shape calculations using e^2Qq/h = 152 kHz and η = 0 to 1 in steps of 0.25 are shown in Figure 4. The spectra were calculated using a method previously described [7]. The calculated cross-relaxation spectra show some η dependence, the best fit to experiment was with a quadrupole coupling constant of 152 ±5 kHz and η = 0.5 ±0.2. For both low and high values of the asymmetry parameter extra peaks would be expected to be resolved. No contribution is expected for the other isotope of lithium (^{6}Li) due to its low natural abundance, the strength of the signal depending on the heat capacity of the Q spins.

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