Zeeman Transitions in Low Magnetic Field: Dependence of Line Shapes on the Asymmetry Parameter for Spin $\geq 3/2$ Systems *

David Stephenson [a] and John A. S. Smith [b]

[a] Chemistry Dept., Faculty of Natural Sciences, University of the West Indies, St. Augustine, Trinidad, West Indies
[b] Chemistry Dept., King's College, Strand, London WC2R 2LS, U.K.

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Transitions between the Zeeman levels of spin 3/2 systems have been detected in low magnetic fields (ca. 25 mT) via the dynamic solid effect. Transitions are detected at frequencies $\nu_P \pm \nu_Q$, where ν_Q corresponds to the Zeeman splitting of the $\pm 1/2$ and/or the $\pm 3/2$ levels in the small applied field, and ν_P is the proton NMR frequency. Using this approach, the line shape for polycrystalline samples can be recorded with a good signal-to-noise ratio despite the low frequencies involved. Computer calculated line shapes are also presented, which show that the asymmetry parameter can be obtained from the experimental spectra.

Key words: NQR, Zeeman effect, Double resonance, Asymmetry parameter, Solid effect.

Introduction

It has long been a frustration for quadrupole spectroscopists that (in zero field) only one transition frequency can be detected for spin 3/2 nuclei, so that the quadrupole coupling constant and asymmetry parameter (η) cannot be determined uniquely. In theory the powder line shape in the presence of a weak magnetic field should depend (to a small extent) on the asymmetry parameter [1], however because of poor signal-to-noise ratio this is of limited application. Attempts have been made to overcome this problem using double resonance, but extra complications arise due to variation of spin contact in the Zeeman broadened quadrupole line shape [2]. An alternative approach is to use two dimensional nutation spectroscopy, the main disadvantage being the high radio-frequency (RF) power and long pulse lengths needed [3].

In low magnetic field the powder line shape of the Zeeman transitions of quadrupole nuclei is very dependent on the asymmetry parameter, but these occur at very low frequency, are relatively broad and thus difficult, if not impossible, to detect directly. It has been calculated [4] that transitions between the $\pm 1/2$ levels should extend from a reduced frequency of 1 to $2+\eta$ and a peak in the line shape should occur at $2-\eta$ (1 reduced frequency unit $= \gamma_Q B_0/2\pi$).

We show in this paper that it is possible to record these low frequency transitions from polycrystalline samples using the dynamic solid effect and accurately determine the asymmetry parameter.

Usually dynamic solid effect transitions are detected symmetrically placed about the quadrupole resonance frequency [5] at frequencies of $\nu_Q \pm \nu_P$; ν_Q being the frequency of a quadrupole transition, and ν_P the proton resonance frequency in the applied field (B_0). Dynamic solid effect transitions can however also be detected near to the proton frequency at a frequency of $\nu_P \pm \nu_Q$, where ν_Q corresponds to the Zeeman splitting of the $\pm 1/2$ and/or $\pm 3/2$ levels of the quadrupole system. Computer calculations of the solid effect frequencies and transition probabilities show, as expected, that the line shapes depend on the direction and distance of proton dipolar contacts. Despite this complication the marked dependence of line shape on the magnitude of the asymmetry parameter means that this information is retained.

Experimental

The spectra were recorded in a double resonance spectrometer based on mechanical transport of the

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Reprint requests to Dr. D. Stephenson.

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sample [6]. In high field the proton signal was monitored in a field of 0.9438 T. In low field the magnetic field was supplied by a solenoid whose axis was co-linear with the RF coil.

Computer line shape simulations were carried out on a Digital DEC 466D2. To produce the powder line shapes, transition frequencies and probabilities were calculated for at least 400 crystal orientations. The number of data points was increased 64-fold by linear interpolation, and this raw data was multiplied by a Lorentzian of half height width 4 kHz.

1,4-dichlorobenzene (alpha phase monoclinic) and 1,4 dibromobenzene were both obtained from B. D. H., and triphenylbismuth from Koch-Light. All samples were thoroughly ground to a fine powder, before use, to ensure polycrystallinity. All experimental spectra were recorded at room temperature estimated to be between 290 K and 295 K.

Results and Discussion

Figure 1 shows the experimental (upper trace) and calculated line shape (lower trace) for the entire dynamic solid effect spectrum centred on the proton frequency for a polycrystalline sample of 1,4-dichlorobenzene. The strong peak at the line centre is the pure proton transition (centre frequency 1109 kHz at this field strength). The spectrum would be expected to be weak because of the very long proton T_1, but even in this most testing case a spectrum of moderate signal-to-noise was obtained. The spectrum is complicated by the signal from both chlorine isotopes overlapping. Unlike the quadrupole transitions which are at quite different frequencies the Zeeman transitions occur in much the same place, the slight differences being due to the different magnetogyric ratios of the two isotopes. The computer simulated dynamic solid effect (Fig. 1, lower trace) was calculated by first obtaining the Zeeman perturbed energies and wavefunctions by diagonalisation of the quadrupole-Zeeman Hamiltonian. Quadrupole parameters used were $e^2qQ/2h = 30$ MHz (when $e^2qQ/2h \gg \gamma_Q B_0$ the splitting of the $\pm 1/2$ levels is independent of its magnitude), and $\eta = 0.07$ [7]. The dipolar Hamiltonian was then allowed to operate on these mixed wavefunctions. From the wavefunctions that emerge from this second diagonalisation dynamic solid effect transition probabilities can be calculated [8]. The direction and magnitude of the proton dipolar contacts were determined from the crystal structure [9]. One chlorine and the six protons were included in the simulation, and the process carried out for both chlorine isotopes, the two spectra were then combined in the ratio of their natural abundances. The complete spectrum took about one hour of computer time.

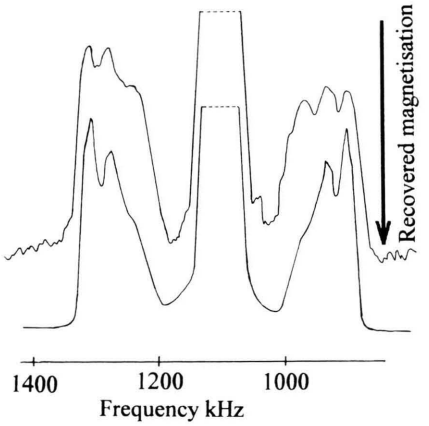

Fig. 1. The entire dynamic solid effect spectrum centred on the proton frequency (1109 kHz) for a polycrystalline sample of 1,4-dichlorobenzene. Upper spectrum experimental, lower calculated.

The differences between the calculated and experimental spectra are due to level crossing in high field (the proton high field frequency and the quadrupole resonance frequency are similar in magnitude), the effect being exacerbated by the very long proton T_1 in high field for this compound. For nuclei with higher resonance frequencies level crossing cannot occur and so this complication is not seen. Experimental and theoretical spectra show peaks at a reduced frequency of $2-\eta$ (either side of the proton frequency) for both isotopes, the same as calculated for the transition detected directly [4]. In order to determine η experiments were performed by scanning more slowly, over a small frequency region around the $2-\eta$ peak, using more modest RF fields (to prevent saturation and hence obtain a spectrum which more accurately reflects the transition probabilities for the system). The average value of six measurements gave an η value of 0.072 (± 0.01) in good agreement with the value of 0.07 from measurements on single crystals [7].

The experiment was repeated for 1,4-dibromobenzene which due to the much higher pure quadrupole transition frequency for both isotopes and the shorter proton T_1 would be expected to give a line shape more faithful to the transition probabilities for the system.

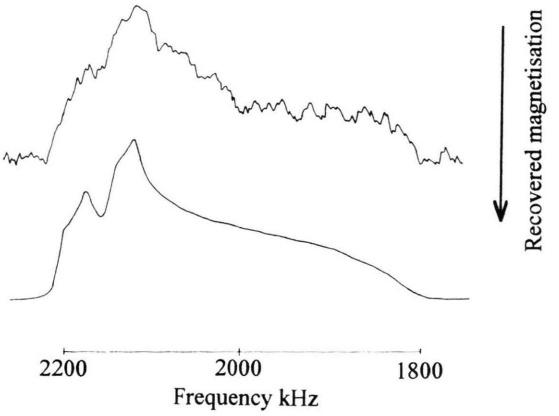

Fig. 2. The experimental (upper) and calculated (lower) dynamic solid effect spectrum of 1,4-dibromobenzene. Only the high frequency side band is shown; the proton resonance frequency is 1425 kHz.

The experimental (upper trace) and calculated (lower trace) high frequency dynamic solid effect line shapes are shown in Figure 2. As was the case for chlorine there is the overlap of signals from two isotopes, however in this case the relative natural abundances are almost the same for the two bromine isotopes. Due to the relatively large magnetogyric ratio of both bromine isotopes the powder line shape covers a large frequency range (ca. 400 kHz) hence the poor signal-to-noise ratio. The high magnetogyric ratio also means that the low frequency solid effect peak cannot easily be recorded. The theoretical spectrum for this compound was calculated in the same way as for 1,4-dichlorobenzene, with appropriate adjustment of the input parameters. A clear peak is seen for the ^{79}Br isotope at a reduced frequency of $2-\eta$. The peak for the larger magnetogyric ratio ^{81}Br isotope is not seen clearly as it occurs at a frequency where the contribution to the line shape from the ^{79}Br isotope is falling. The value of η determined from this spectrum was 0.05 (± 0.03). The larger error reflects the frequency uncertainty in the peak positions due to the poor signal-to-noise ratio. The value obtained from single crystal data of 0.045 [10] falls well within this uncertainty range.

The determination of the dipolar contacts from the crystal structure, and incorporation of these into the Hamiltonian for the system would seem to place a limitation on this technique. In order to see whether this is necessary, or whether it could be assumed that a peak in the spectrum would always occur at a reduced frequency of $2-\eta$, solid effect spectra were calculated for various orientations of a single dipole-dipole contact. The calculated spectra are shown in Fig. 3, the angles Θ and ϕ are the polar angles the vector joining the two nuclei make in the principal axis system of the electric field gradient (EFG) tensor, an η value of 0.2 was used and the quadrupole interaction was taken as being large compared with the Zeeman interaction. Only the high frequency dynamic solid effect peak is shown the low frequency peak is a mirror image of this. Increasing the magnitude of the dipole-dipole interaction caused no change in the shape of the peaks however, as expected, it increased the transition probability. Many of the simulated line shapes show a definite peak, which in all cases occurs at the reduced frequency of $2-\eta$. Only those crystals in which ϕ is close to 90° and/or Θ is close to 0° or 90° is a peak in the powder line shape not seen. In a real sample there will be many dipolar interactions so that it is likely that there will be some orienations for which the powder line shape peaks at a reduced frequency of $2-\eta$.

As an aid to clarity only transitions between the $\pm 1/2$ levels have been used in the calculated spectra shown in Figure 3. The computer simulations show that transitions between the $\pm 3/2$ levels also have significant transition probabilities associated with them. A series of calculated spectra for this transition are shown in Fig. 4 (the same input parameters as in Fig. 3 have been used). Both the high and low frequency dynamic solid effect peaks are shown, and the central proton peak has been suppressed. There is much less angular dependence (of the direction of the dipole-dipole interaction in the EFG frame of reference) than for the $\pm 1/2$ transition. No ϕ dependence is seen and variation of Θ only changes the transition probability, not the line shape. All the lines shapes show two peaks corresponding to the upper lower dynamic solid effect side bands shifted from the central proton peak (not shown) by a reduced frequency of η. So in theory transitions between the $\pm 3/2$ levels could also be used to determine η. In the example chosen the transition probability is not a problem: the calculated spectra in Fig. 4 have been scaled down 400 times as compared with those in Figure 3. The high transition probability can be attributed to the small energy separation of the $\pm 3/2$ levels for some crystal orientations. Because of this small energy separation the peak in the line shape (for small η) normally occurs too close to the central proton peak to be resolved. Increasing the magnetic field does not help as the

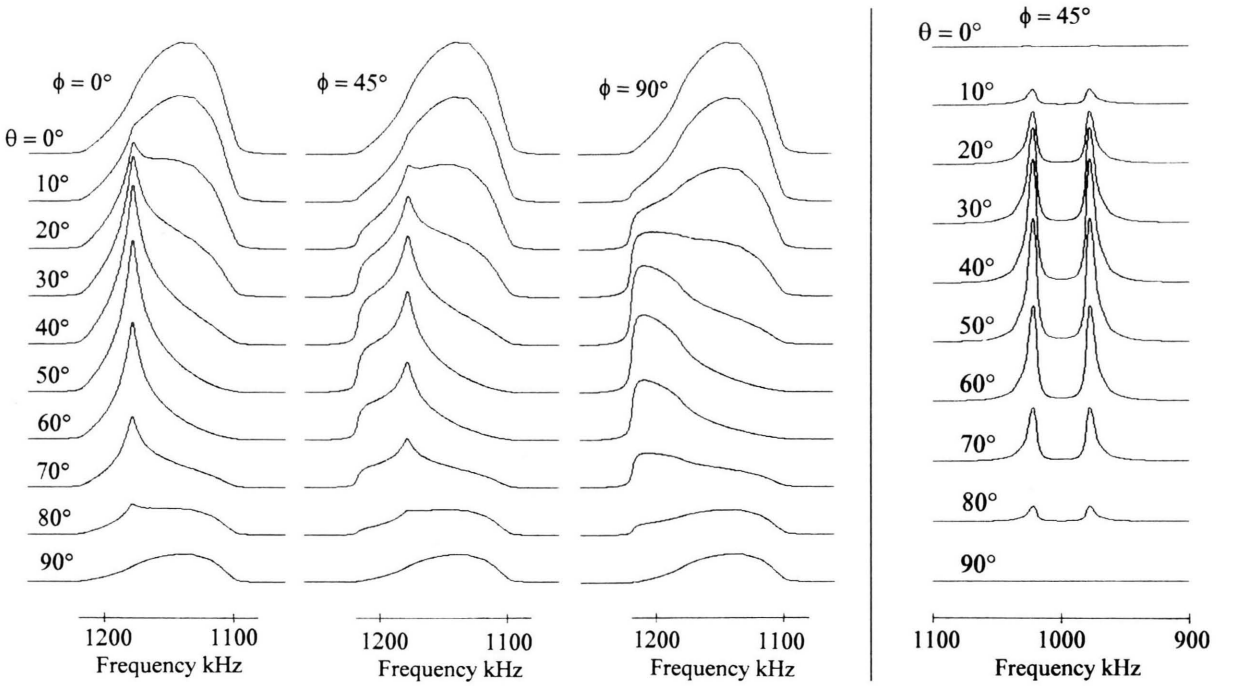

Fig. 3. Calculated dynamic solid effect for transitions between the 1/2 levels of a spin 3/2 nuclei. Θ and ϕ are the polar angles of the vector joining the P and Q nuclei in the principal axes of the EFG tensor. $\nu_P = 1000$ kHz, $\nu_Q = 100$ kHz and $\eta = 0.2$. Only the high frequency solid effect side band is shown (see the left Figure).

Fig. 4. Calculated dynamic solid effect for transitions between the 3/2 levels of a spin 3/2 nuclei. Θ and ϕ are the polar angles of the vector joining the P and Q nuclei in the principal axes of the EFG tensor. $\nu_P = 1000$ kHz, $\nu_Q = 100$ kHz and $\eta = 0.2$. Both solid effect side bands are shown, and the central proton peak has been suppressed. The intensities have been reduced 400 fold as compared with Figure 3.

powder line shape becomes too spread out to be detected easily. It is, however, possible to detect transition between the $\pm 3/2$ levels for nuclei with spin $> 3/2$. Figure 5 (upper trace), shows the full Zeeman spectrum of the ^{209}Bi nucleus (spin 9/2) detected via the dynamic solid effect in the compound triphenylbismuth (only the upper solid effect peak is shown). The peak at 950 kHz is due to transitions between the $\pm 3/2$ levels, the peak occurring at > 1400 kHz is due to double proton flips occurring at twice the proton frequency (2×735 kHz). The transition between the $\pm 3/2$ levels is easier to detect for nuclei with spin $> 3/2$ as the peak in the powder line shape, for a given field strength and magnetogyric ratio, is at higher frequency, and so has a better chance of being resolved from the strong central proton peak. Furthermore, the overall frequency spread of all crystal orientations is much the same as for spin 3/2 nuclei, so excessive broadening is not a problem.

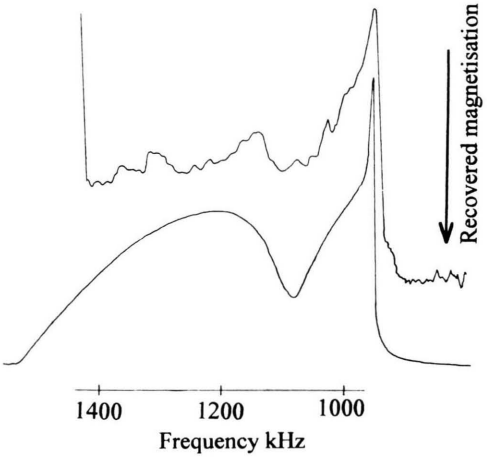

Fig. 5. The experimental (upper) and calculated (lower) dynamic solid effect spectrum of ^{209}Bi ($I = 9/2$) in triphenylbismuth, only the high frequency side band is shown; the proton resonance frequency is 735 kHz.

Figure 5 (lower trace) shows the simulated Zeeman for ^{209}Bi; η has been adjusted to give the best fit to the experimental spectrum which gives $\eta = 0.095\ (\pm 0.002)$, slightly larger than literature value of 0.0875 determined at 77 K [11]. The sharpness of the peak in the powder line shape for this transition allows η to be determined to much higher precision than was the case for transitions between the $\pm 1/2$ levels. To successfully simulate the Zeeman spectrum for this compound it was found to be necessary to use a full solution of the quadrupole-Zeeman Hamiltonian as even when η is small (ca. 0.1) the peak in the powder line shape for transitions between the $\pm 3/2$ levels did not occur at $20\,\eta$, as approximate solutions suggest [12]. Because the simulated spectrum showed close correspondence to the experimental spectrum is was felt unnecessary to add in the effects of dipolar coupling. Dipolar couplings are generally too small to produce frequency shifts: only changes in transition probability. All five Zeeman transitions have been included in the computer simulated spectrum, only transitions between $\pm 1/2$ levels and $\pm 3/2$ levels contribute significantly to the intensity. The low frequency peak is due to transitions between the $\pm 3/2$ levels and the broad hump at higher frequency due to transitions between the $\pm 1/2$ levels; the powder line shape for the latter transition is featureless for this magnitude of η.

This method allows η to be determined without knowledge of the quadrupole transition frequencies (assuming $e^2 q Q/2h \gg \gamma_Q B_0$). Of course the value of η can be obtained directly from the pure quadrupole transitions for nuclei with spin $> 3/2$. However, unlike when pure quadrupole detection is being employed, no searching is required as the position of the Zeeman transitions are known, and can be adjusted by the choice of the magnetic field to suit the RF frequency range available.

Conclusions

Transitions between the $\pm 1/2$ levels of spin 3/2 nuclei in polycrystalline samples of 1,4-dichlorobenzene and 1,4-dibromobenzene have been detected by the dynamic solid effect, and the line shapes used to determine η: the values agree with those from single crystal experiments.

It has been demonstrated that transitions between the $\pm 3/2$ levels can also be detected in this way, and if the peak in the powder line shape can be resolved from the central proton peak, η can be determined to good precision. This has been demonstrated for the spin 9/2 nucleus ^{209}Bi, but should also be possible for spin 3/2 nuclei if η is large (> 0.4).

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