

The Zeeman Effect in Quadrupole Double Resonance Spectra: Dependence of the Line Shapes on the Orientation of the Electric Field Gradient *

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The solid effect spectrum of 1,4-dichlorobenzene was recorded at magnetic field strengths in excess of 50 G; at these field strengths Zeeman structure is seen on the ^{35}Cl resonance. Unlike in single resonance experiments, peaks are asymmetric, and the high frequency and low frequency solid effect peaks have not the same shape. Computer calculation of the solid effect spectrum gives peaks which show the same asymmetry as the experimental spectrum. The simulated line shapes are found to depend on the direction the principal components of the electric field gradient in the crystal framework and indicate that q_{yy} lies in the plane of the benzene ring.

Key words: ^{35}Cl quadrupole resonance, Zeeman effect, Double resonance, Electric field gradient.

Introduction

Systems for which the analysis of dipolar interactions are performed are usually limited to single crystals with a small number of large couplings. In most covalent compounds, coupling is too small to produce significant energy perturbations of the quadrupole levels. The transition probability in solid effect spectra, which rely on dipolar coupling for detection must, however, be influenced by the distance and direction of the coupling nuclei [1].

Solid effect transitions involve simultaneous transitions in two dipolar coupled systems [2], and this is a double resonance method frequently used to detect transition frequencies of quadrupolar nuclei coupled to protons. Normally two solid effect peaks are seen symmetrically placed about the quadrupole resonance frequency, the lower frequency peak being seen at the quadrupole frequency minus the proton frequency ($\nu_Q - \nu_P$), and the higher frequency peak at ($\nu_Q + \nu_P$). Application of a magnetic field to the sample causes

the separation of the two solid effect peaks to increase, and the transition probability to decrease rapidly. Consequently the experiment is usually performed with a very small applied field.

In this paper we demonstrate that solid effect transitions can be detected in magnetic fields in excess of 50 G. At these large fields Zeeman structure can be seen on the peaks, and the shape of the peaks is related to the orientation of the principal components of the electric field gradient (efg).

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. In low field the magnetic field was supplied by a solenoid whose axis was co-linear with the r.f. coil.

The computer simulations were carried out on a Digital Station 425C. The transition frequencies and transition probabilities were computed for 200 crystal orientations. The number of crystal orientations was increased 64-fold by linear interpolation; these raw data were then multiplied by a Lorentzian of half height width 4 kHz to produce the powder spectrum.

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The calculation of the solid effect spectrum containing one dipolar contact took about 15 minutes, that of the 1,4-dichlorobenzene spectrum (with 7 dipolar contacts) took about 4 hours.

1,4-Dichlorobenzene (alpha phase' monoclinic) was supplied by B.D.H. and was ground to a fine powder to ensure polycrystallinity.

Results and Discussion

The Hamiltonian used to calculate the solid effect spectrum comprised three interactions: quadrupole, Zeeman and dipole. Due to the relatively small dipole interactions it was found to be necessary (and justified) to treat this interaction separately from the other two. The quadrupole-Zeeman Hamiltonian matrix [4] was first calculated and diagonalised to give the Zeeman perturbed energies and wavefunctions, the wavefunctions obtained were operated on by the dipole Hamiltonian and a second diagonalisation performed, the tolerances in the computer procedure being adjusted to allow for the small (but significant) off-diagonal elements. The dipolar Hamiltonian was of the form [1]

$$\hat{H}_{dd} = S(A + B + C + D + E + F), \quad (1)$$

$$S = \frac{\gamma_P \gamma_Q \hbar^2 \mu_0}{16 \pi^3 r^3} \quad (\text{the dipole-dipole interaction in frequency units}), \quad (2)$$

$$A = \hat{I}_{Qz} \hat{I}_{Pz} (3 \cos x \cos y - \cos z), \quad (3)$$

$$B = -0.25(\hat{I}_{Q+} \hat{I}_{P-} + \hat{I}_{Q-} \hat{I}_{P+}) (3 \cos x \cos y - \cos z). \quad (4)$$

x is the angle between the principal component of the electric field gradient (q_{zz}) and the vector joining the two nuclei (P-Q vector), y is the angle between the magnetic field and the P-Q vector, z the angle between q_{zz} and the magnetic field and r the distance between the two nuclei.

All the other terms (C , D , E , and F) are assumed to be averaged to zero by the rapid and dissimilar precession frequencies of the two nuclei.

The simulated line shapes for the solid effect in the presence of one proton-quadrupole dipolar contact are shown in Figure 1. The quadrupole parameters used are those for 1,4-dichlorobenzene ($e^2 Q q / 2 \hbar = 34\,240$ kHz, $\eta = 0.07$ [5]), $S = 500$ Hz (2), applied field 50 G. The angles θ and ϕ are the polar angles of the P-Q vector in the efg frame of reference. Only the

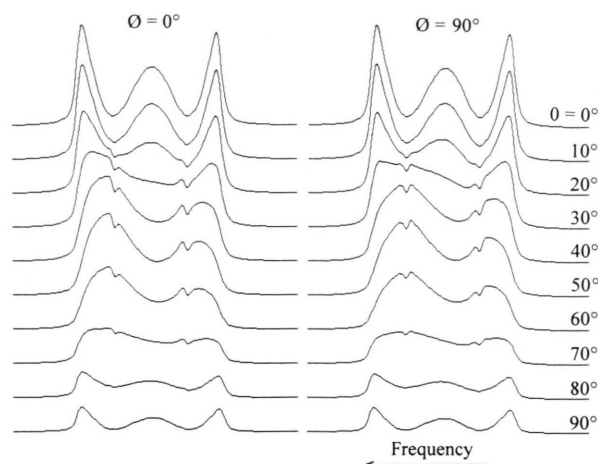


Fig. 1. Calculated solid effect powder spectrum for a spin 3/2 nucleus coupled to a single proton, S (equation (2)) = 500 Hz, $e^2 Q q / 2 \hbar = 34\,240$ kHz, $\eta = 0.07$, θ and ϕ are the polar angles of the vector joining the two nuclei in the efg coordinate system.

lower frequency solid effect is shown (in positive enhancement); the higher frequency peaks are a mirror image of these. This mirror image relationship implies that the transition probabilities within the Zeeman perturbed quadrupole levels are quite different for both peaks. For values of $\theta = 0^\circ$ and 90° the lineshapes have a centre of symmetry, for all angles in between the peaks show varying degrees of asymmetry. As would be expected in view of the small value of η , the variation of the line shape with the angle ϕ is quite small. It should be noted that the line shapes also depend on the size of the dipolar coupling and the strength of the magnetic field, however qualitatively the shapes and in particular the asymmetry are remarkably persistent on variation of the input parameters.

The experimental upper and lower solid effect peaks for polycrystalline 1,4-dichlorobenzene are shown in Figure 2a. As is usual for solid effect spectra recorded at high frequencies, the low frequency peak is seen as an enhancement of the proton signal, when monitored in high field, and the high frequency peak is seen as a loss of proton signal. The centres of the upper and lower solid effect peaks are separated by about 425 kHz. Because of the high field (ca. 50 G) Zeeman structure is seen on the peaks, and both show a high asymmetry. The two peaks are almost the mirror image of each other.

The computer simulated spectra are shown in Figs. 2b and 2c. The size and direction of the chlorine proton dipole-dipole interactions were determined

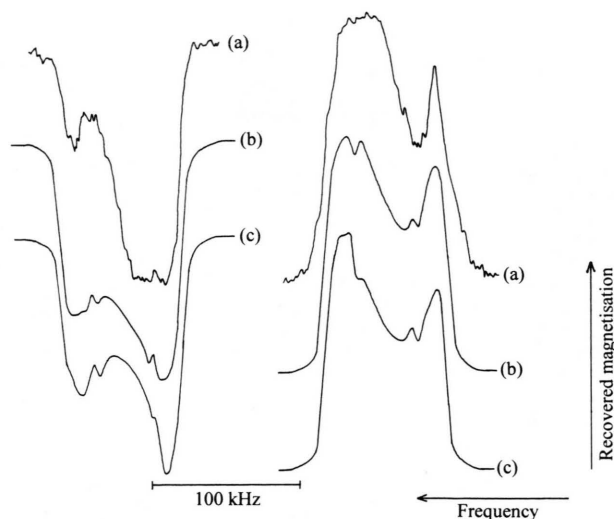


Fig. 2. Experimental and calculated solid effect spectra
 (a) experimental spectrum of polycrystalline 1,4-dichlorobenzene,
 (b) calculated spectrum with q_{yy} in the plane of the benzene ring,
 (c) calculated spectrum with q_{yy} perpendicular to the plane of the ring.

from the crystal structure [6]. Because of the large dependence of dipole-dipole interactions on inter-nuclear separation, only a small number of contacts need be incorporated into the fit. For 1,4-dichlorobenzene about 90% of the solid effect intensity comes from three proton dipolar contacts to each chlorine. Two of the contacts are intramolecular from the two

ortho protons $S=510$ Hz (2), and there is one inter-molecular contact $S=650$ Hz. In each case the proton was also considered to be strongly dipolar coupled to its ortho neighbour. So the final simulation contained 7 nuclei (one chlorine and six protons). The principal component of the efg q_{zz} was assumed to lie along the carbon chlorine bond, and two simulations were carried out, one with q_{yy} in the plane of the benzene ring and the other with q_{yy} perpendicular to it. The results are shown in Figs. 2b and 2c. A rather better fit is obtained for q_{yy} in the plane (Fig. 2b), particularly the inner halves of the lines which have a reduced intensity for q_{yy} perpendicular to the ring. Notice that for both the calculated and experimental spectra the two solid effect peaks do not show mirror symmetry. This has been brought about by the strong coupling between ortho protons. The calculated transition probabilities for these double spin flips in a field of 50 G are some five orders of magnitude lower than chlorine quadrupole transitions (these are also calculated in the program but show no dipolar coupling effects). Three spin flips (at a frequency of $\nu_Q \pm 2\nu_P$) are also predicted but have calculated transition probabilities 16 orders of magnitude smaller than single flips, and so would not be expected to be detected experimentally.

In an attempt to reduce the differences between the experimental and calculated line shapes, q_{zz} was moved by 5° in the direction of the strong intermolecular dipolar interaction. A corresponding improvement was seen, but the fit was still not perfect.

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