Zeeman NQR Powder Line Shapes for Half Integral Spin Nuclei *

P. J. Bryant and S. Hacobian

Department of Physical Chemistry, The University of Sydney, Sydney, NSW, 2006, Australia

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A polycrystalline material was simulated by assuming a random distribution of small crystalites. The effect of a small applied magnetic field on the NQR lineshape was calculated for half integral spin nuclei ($I = 3/2$, $5/2$, $7/2$ and $9/2$) using a theory based on Toyama's work [11]. The line shapes indicate qualitatively the half width ratios of the upper and lower resonances (e.g. $\Delta\nu_2/\Delta\nu_1$ for $I = 5/2$) and thus enables one to see generally whether the broadening mechanism is mainly due to magnetic or electric effects.

1. General Considerations

Conventionally, the Zeeman effect in NQR has been studied by the variations in the splittings of the resonance of a spin 3/2 system as the orientation of a single crystal was varied in the applied field [1, 2, 3]. Morino and Toyama [4] were the first to show that a distinct effect was also observable in polycrystalline samples. Brooker and Creel [5] and Darville, Gerard and Calende [6] have independently given a full analysis of the problem where the applied magnetic field and the r.f. field were parallel. This has since been extended to other orientations and nuclei [7, 8].

In most polycrystalline samples studied by us so far with multilevel spin systems containing halogen nuclei (e.g. ^{127}I), it has been shown that even for the best and most perfect crystalline samples, electrical broadening effects dominated [9, 10]. As shown in a previous paper [10] with p-diiodobenzene, electrical broadening gives the ratio of 2.0 for the ratio of half widths of the upper and lower ^{127}I lines. It can be qualitatively shown from the calculated line shapes in this paper that the half width NQR line ratio due to magnetic interaction is significantly less than 1.0. In order to observe such magnetic broadening effects almost perfect crystals of p-diiodobenzene had to be obtained but since the compound has a tendency to decompose in heat and light it was not possible to obtain the desired conditions.

Hence, it is proposed to present in the first instance the theoretical prediction of line shapes. To a large extent the theoretical treatment is based on solutions of equations developed by Toyama [11].

2. The Zeeman Perturbation for Half Integral Spin

When a static magnetic field is applied to a nuclear quadrupolar system, the energy levels are determined by solving the secular eqation for the entire perturbed nuclear quadrupolar Hamiltonian $\mathscr{H}$, where

$$\mathscr{H} = H_{\mathrm{Q}} + H_{\mathrm{m}} \,. \tag{1}$$

Here H_{Q} is the pure (unperturbed) nuclear quadrupolar Hamiltonian and H_{m} is that describing the magnetic interaction and is given by

$$H_{\mathrm{m}} = -\gamma \hat{I} \hat{H} , \tag{2}$$

where γ is the magnetogyric ratio and $\hat{I} \hat{H}$ is the scalar product of the nuclear spin and applied magnetic field vectors. In the NQR case, the Zeeman effect is studied with external fields of the order of 100 gauss [1]. The nuclear magnetic dipole-dipole fields are about 1 or 2 gauss and therefore the following perturbation treatment is a valid approximation.

The eigenvalues of the nuclear quadrupolar Hamiltonian for half integral spins with finite asymmetry parameter are given by

$$|\pm m\, Q\rangle = \sum_{m'} a_{\pm m,\, m}\, |m'\rangle \,. \tag{3}$$

The symbol Q used in the above states is taken to mean that they are zero order pure nuclear quadrupolar states. Equation (3) can be seen as two distinct

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Reprint requests to Prof. S. Hacobian, Department of Physical Chemistry, The University of Sydney, Sydney NSW/Australia.

sets in the following:

$$|mQ\rangle = a_{m,1/2}\,|1/2\rangle + a_{m,-3/2}\,|-3/2\rangle + a_{m,5/2}\,|5/2\rangle + \dots, \tag{4.1}$$

$$|-mQ\rangle = a_{-m,-1/2}\,|-1/2\rangle + a_{-m,3/2}\,|3/2\rangle + a_{-m,-5/2}\,|-5/2\rangle + \dots \tag{4.2}$$

with $m = 1/2, 5/2, 9/2,$

$$|mQ\rangle = a_{m,-1/2}\,|-1/2\rangle + a_{m,3/2}\,|3/2\rangle + a_{m,-5/2}\,|-5/2\rangle + \dots, \tag{5.1}$$

and

$$|-mQ\rangle = a_{-m,1/2}\,|1/2\rangle + a_{-m,-3/2}\,|-3/2\rangle + a_{-m,5/2}\,|5/2\rangle + \dots \tag{5.2}$$

for $m = 3/2, 7/2, 11/2.$

From symmetry consideration it is evident that

$a_{m,1/2} = a_{-m,-1/2}$ and $a_{m,-3/2} = a_{-m,3/2}$ and so on. (6)

The Zeeman Hamiltonian H_{M} is given by (7)

$$H_{\mathrm{M}} = -\gamma H\,[I_x \sin\theta\cos\varphi + I_y \sin\theta\sin\varphi + I_z\cos\theta],$$

where H is the magnitude of the applied magnetic field and θ and φ are the polar coordinates of $\hat{H}$ in the nuclear quadrupolar principal axis system. By defining the transition moments (matrix elements of the components of nuclear spins) as

$$\langle \mp mQ|\,\hat{I}_x\,|\pm mQ\rangle = I_{x,m,m}, \tag{8.1}$$

$$\langle \mp mQ|\,\hat{I}_y\,|\pm mQ\rangle = \pm\frac{1}{i}\,I_{y,m,m}, \tag{8.2}$$

$$\langle \pm mQ|\,\hat{I}_z\,|\pm mQ\rangle = \pm I_{z,m,m} \tag{8.3}$$

and

$$\langle \pm (m+1)\,Q|\,\hat{I}_x\,|\pm mQ\rangle = I_{x\,m,m+1}, \tag{8.4}$$

$$\langle \pm (m+1)\,Q|\,\hat{I}_y\,|\pm mQ\rangle = \pm\frac{1}{i}\,I_{y\,m,m+1} \tag{8.5}$$

$$\langle \mp (m+1)\,Q|\,\hat{I}_z\,|mQ\rangle = \pm I_{z\,m,m+1} \tag{8.6}$$

and using the notation of Toyama [11], the matrix elements of the Zeeman Hamiltonian H_{M} between each pair of degenerate states may be expressed as

$$\langle \pm mQ|\,H_{\mathrm{m}}\,|\pm mQ\rangle = \pm\gamma H\cos\theta\, I_{z\,m,m} = \pm M_{m,m} \tag{9}$$

and

$$\begin{aligned}\langle \pm mQ|\,H_{\mathrm{m}}\,|\mp mQ\rangle &= -\gamma H\,[I_{x\,m,m}\sin\theta\cos\varphi \pm i\,I_{y\,m,m}\sin\theta\sin\varphi]\\ &= N_{m,m}.\end{aligned} \tag{10}$$

From these definitions, a typical submatrix of the total Hamiltonian $\mathscr{H}$ for a pair of degenerate states may be constructed thus:

$$\begin{array}{c|cc} & mQ & -mQ \\ \hline mQ & E_{\mathrm{Q}} + M_{m,m} & N^*_{m,m} \\ -mQ & N_{m,m} & E_{\mathrm{Q}} - M_{m,m}, \end{array}$$

where E_{Q} is the energy of the unperturbed state. The roots of the corresponding secular equations for this matrix give the first order energy levels as given by

$$\begin{aligned}E_{\mathrm{m}} &= E_{\mathrm{Q}} \pm [M^2_{m,m} + N_{m,m}\,N^*_{m,m}]^{1/2}\\ &= E_{\mathrm{Q}} \pm \gamma H[I^2_{x\,m,m}\sin^2\theta\cos^2\varphi\\ &\quad + I^2_{y\,m,m}\sin^2\theta\sin^2\varphi + I_{z\,m,m}\cos^2\theta]^{1/2}.\end{aligned} \tag{11}$$

The energy shift of the split levels is therefore expressed as

$$\begin{aligned}E_{\mathrm{m}} = \pm\gamma H[&I^2_{x\,m,m}\sin^2\theta\cos^2\varphi\\ &+ I^2_{y\,m,m}\sin^2\theta\sin^2\varphi + I^2_{z\,m,m}\cos^2\theta]^{1/2}.\end{aligned} \tag{12}$$

Figure 1 shows the splittings and the possible transitions for which $\Delta m = 1$.

In Fig. 1 $|mM\rangle$ denotes the perturbed eigenstate corresponding to $|mQ\rangle$. The frequencies of the inner pair of transitions are given by

$$\nu = \nu_{\mathrm{Q}} \pm \left(\frac{\Delta E_m - \Delta E_{m+1}}{h}\right), \tag{13.1}$$

and the outer transitions occur at

$$\nu = \nu_{\mathrm{Q}} \pm \left(\frac{\Delta E_m + \Delta E_{m+1}}{h}\right), \tag{13.2}$$

where (14)

$$\Delta E_m = E_m - E_{\pm m} \quad\text{and}\quad \Delta E_{m+1} = E_{m+1} - E_{\pm(m+1)}.$$

The dependence of the Zeeman splitting on the orientation of the applied field is given by (12). The dependence on the asymmetry parameter is due to the condition that transition moments are functions of the coefficients of the quadrupolar eigenfunctions in the states $|\pm mQ\rangle$. These in turn are functions of η. When $\eta = 0$, the mixing of the quadrupolar eigenfunctions with $\Delta m = 2$ disappears. In this case, the $\pm m$ degeneracy of the pure nuclear quadrupolar levels is only removed by the magnetic field for the $\pm 1/2$ states. Since only these states are connected by $\Delta m = 1$. Thus only the line corre-

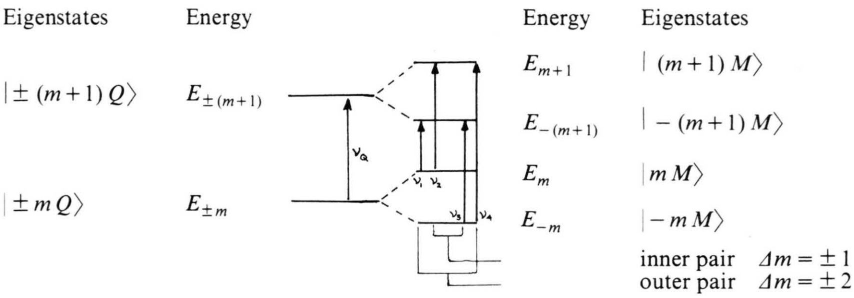

Fig. 1. Zeeman energy levels and transitions.

sponding to a ± 1/2 → ± 3/2 transition will be split into four components. For higher transitions, the outer pair of lines will not be observed.

This feature of the splitting is best examined by a consideration of the intensities of the Zeeman components. These intensities may be calculated using the formulae developed by Toyama [11]. The following analysis is from his paper.

The eigenstates of $\mathscr{H}$ to the zeroth order of $\mathscr{H}$ are given by

$$|mM\rangle = a_m\,|mQ\rangle + b_m\,|-mQ\rangle \tag{15}$$

and

$$|-mM\rangle = -\,b_m^*\,|mQ\rangle + a_m^*\,|-mQ\rangle\,, \tag{16}$$

where the coefficients a_m and b_m, the eigenvalues of H, are defined by

$$\frac{I_{x,m,m}\,H_x}{E_m} = a_m\,b_m^* + a_m^*\,b_m\,, \tag{17}$$

$$\frac{I_{y,m,m}\,H_x}{E_m} = a_m\,b_m^* - a_m^*\,b_m\,, \tag{17.2}$$

$$\frac{I_{z,m,m}\,H_z}{E_m} = a_m\,a_m^* - b_m\,b_m^* \tag{17.3}$$

and the normalization condition

$$a_m\,a_m^* + b_m\,b_m^* = 1\,. \tag{17.4}$$

H_x, H_y and H_z are the magnitudes of the cartesian components of the applied magnetic field $\hat{H}$.

The resultant transition between two eigenstates E' and E'' is allowed for by including the Hamiltonian for the r.f. field. This is denoted by H_{RF}, where

$$H_{\mathrm{RF}} = -\,\gamma\,\hat{I}\,\hat{H}_{\mathrm{R}}\cos 2\pi\nu t\,, \tag{18}$$

where ν is the frequency of the r.f. field $\hat{H}_{\mathrm{R}}$. This expression, together with the expression for the eigenfunction of the Zeeman components is now used to calculate the intensities of the splittings. The well-known formula for the transition probability between the two states E' and E'' is given by

$$W = \hbar^{-2}\,T^2(E', E'')\,g(\nu)\,, \tag{19}$$

where $g(\nu)$ is the spectral distribution function and $T^2(E', E'')$ is the square transition moment. This may be expressed in terms of the r.f. field component in the following manner:

$$T^2(E', E'') = \gamma^2\,|\langle E''|\,\hat{I}\hat{H}_{\mathrm{R}}\,|E'\rangle|^2 \tag{20}$$
$$= \gamma_2 \sum_{i,j=x,y,z} H_{ri}\,H_{rj}\,J_{ij}(E', E'')\,.$$

The intensity parameters $J_{ij}(E', E'')$ are written as

$$J_{ij}(E', E'') = \tfrac{1}{2}\,|\langle E''|\,I_i\,|E'\rangle\langle E'|\,I_j\,|E''\rangle + \langle E''|\,I_j\,|E'\rangle\langle E'|\,I_i\,|E''\rangle|\,. \tag{21}$$

In the following formulae, the positive sign denotes the inner pair and the negative sign outer pair of the Zeeman splittings. Each component of the pair has an equal intensity, and so for the $\Delta m = 1$ transition one need only claculate the following:

$$J_{ij}(+) = J_{ij}(mM,\,(m+1)M) \tag{22.1}$$

and

$$J_{ij}(-) = J_{ij}(mM,\,-(m+1)M)\,. \tag{22.2}$$

These are obtained from the eigenvector of H and the various transition moments defined above. Toyama [11] gives the general solution for both Δm odd and Δm even transitions. Only those appropriate to the $\Delta m - 1$ case are now quoted.

In the following equations $m'' = m' + 1$, and the symbol F is given by

$$F = 1/[(E'_m)\,(E''_m)]: \tag{23}$$

$$J_{xx}(\pm) = \tfrac{1}{2} I^2_{x\,m',m''} [1 \pm F (I_{x\,m',m'}\, I_{x\,m'',m''}\, H^2_x + I_{y\,m',m'}\, I_{y\,m'',m''}\, H^2_y + I_{z\,m',m'}\, I_{z\,m'',m''}\, H^2_z)], \tag{24.1}$$

$$J_{yy}(\pm) = \tfrac{1}{2} I^2_{y\,m',m''} [1 \pm F (-I_{x\,m',m'}\, I_{x\,m'',m''}\, H^2_x - I_{y\,m',m'}\, I_{y\,m'',m''}\, H^2_y + I_{z\,m',m'}\, I_{z\,m'',m''}\, H^2_z)], \tag{24.2}$$

$$J_{zz}(\pm) = \tfrac{1}{2} I^2_{z\,m',m''} [1 \pm F (-I_{x\,m',m'}\, I_{x\,m'',m''}\, H^2_x + I_{y\,m',m'}\, I_{y\,m'',m''}\, H^2_y - I_{z\,m',m'}\, I_{z\,m'',m''}\, H^2_z)], \tag{24.3}$$

$$J_{yz}(\pm) = \tfrac{1}{2} I_{y\,m',m''}\, I_{z\,m',m''} [-I_{y\,m',m'}\, I_{z\,m'',m''} - I_{z\,m',m'}\, I_{y\,m'',m''}]\, F H_y H_z\,, \tag{24.4}$$

$$J_{zx}(\pm) = \tfrac{1}{2} I_{z\,m',m''}\, I_{z\,m',m''} [I_{z\,m',m'}\, I_{x\,m'',m''} - I_{x\,m',m'}\, I_{z\,m'',m''}]\, F H_z H_x\,, \tag{24.5}$$

$$J_{xy}(\pm) = \tfrac{1}{2} I_{x\,m',m''}\, I_{y\,m',m''} [-I_{x\,m',m'}\, I_{y\,m'',m''} + I_{y\,m',m'}\, I_{x\,m'',m''}]\, F H_x H_y\,. \tag{24.6}$$

According to Toyama [11], the expression $I_{i\,m',m''}$ denotes the parameters describing the dependence of the transition upon the i-compound of the r.f. field and $I_{i,m,m}$ as the parameter describing the dependence on the orientation of the applied field.

3. The Zeeman Line Shapes in Polycrystalline Materials

The Zeeman N.Q.R. lineshapes in polycrystalline materials for the half integral spins have been calculated using a computer program based on the above equations. The major steps in this program were the following:

(i) The matrix of the nuclear quadrupole Hamiltonian for a given spin was used as raw data. The eigenvalues and eigenvectors of the matrix were obtained. The coefficients of the quadrupole wave functions $|mQ\rangle$ were equated to the elements of the normalized eigenvectors.

(ii) The transition moments required for evaluation of the intensity parameters were determined.

(iii) A polycrystalline material was simulated by assuming a random distribution of crystallites. Since the frequencies depend on the square of the field components, only angles in the first quadrant need be considered. 100 steps in the polar angles θ and φ were used.

(iv) For each possible orientation, the frequency splittings for both the inner and outer pair of lines were calculated. Since the spectrum is symmetric about ν_Q, only one half of it need be considered. In this case, positive values of E_m were used.

(v) The spectrum was calculated with units of ν_0 where

$$\nu_0 = \nu_H / 2\pi\,. \tag{25}$$

The Larmor frequency, ν_0 was then divided into 30 intervals.

(vi) The transition probability, W, was calculated for a given orientation of the r.f. field in the principal axis system. Experimentally, H was assumed to be parallel to H_{RF} and so the values of θ and φ from above were used.

(vii) A frequency histogram was now built up by placing a number equal to W in the appropriate frequency interval. Some of the resulting frequency distribution for $\eta = 0.0$, 0.5 and 1.0 are displayed in Figure 2. Half of the spectrum only is displayed because this is sufficient to reveal the features of the lineshape.

Several features of the lineshapes in Figure 2 are worthy of comment. Firstly, it was noticed that as spin increases so does the width of the distribution. This effect would appear to be related to the increase in second moments by Biryukov and Berson [12] when $\eta = 0$, only the ν_1 ($\pm 1/2 \rightarrow \pm 3/2$) transition is significantly broadened and possesses distinctive features. The higher transitions are uniformly broadened to a maximum ν_0, the Larmor frequency. This behaviour is expected since as previously mentioned at $\eta = 0$ only the ν_1 line is split into four whereas the outer pair disappears for the higher transitions. There are other differences between the behaviour of the various transitions. For example, for spin 9/2 the transition becomes relatively featureless for $\eta = 1.0$. Experiments to measure η for polycrystalline samples would be best performed on the ν_2 transitions or higher.

Brooker and Creel [5] have shown that for $I = 3/2$ the features or peaks in the line-shape occur at the following critical points $H//x$, $H//y$ and $H//z$,

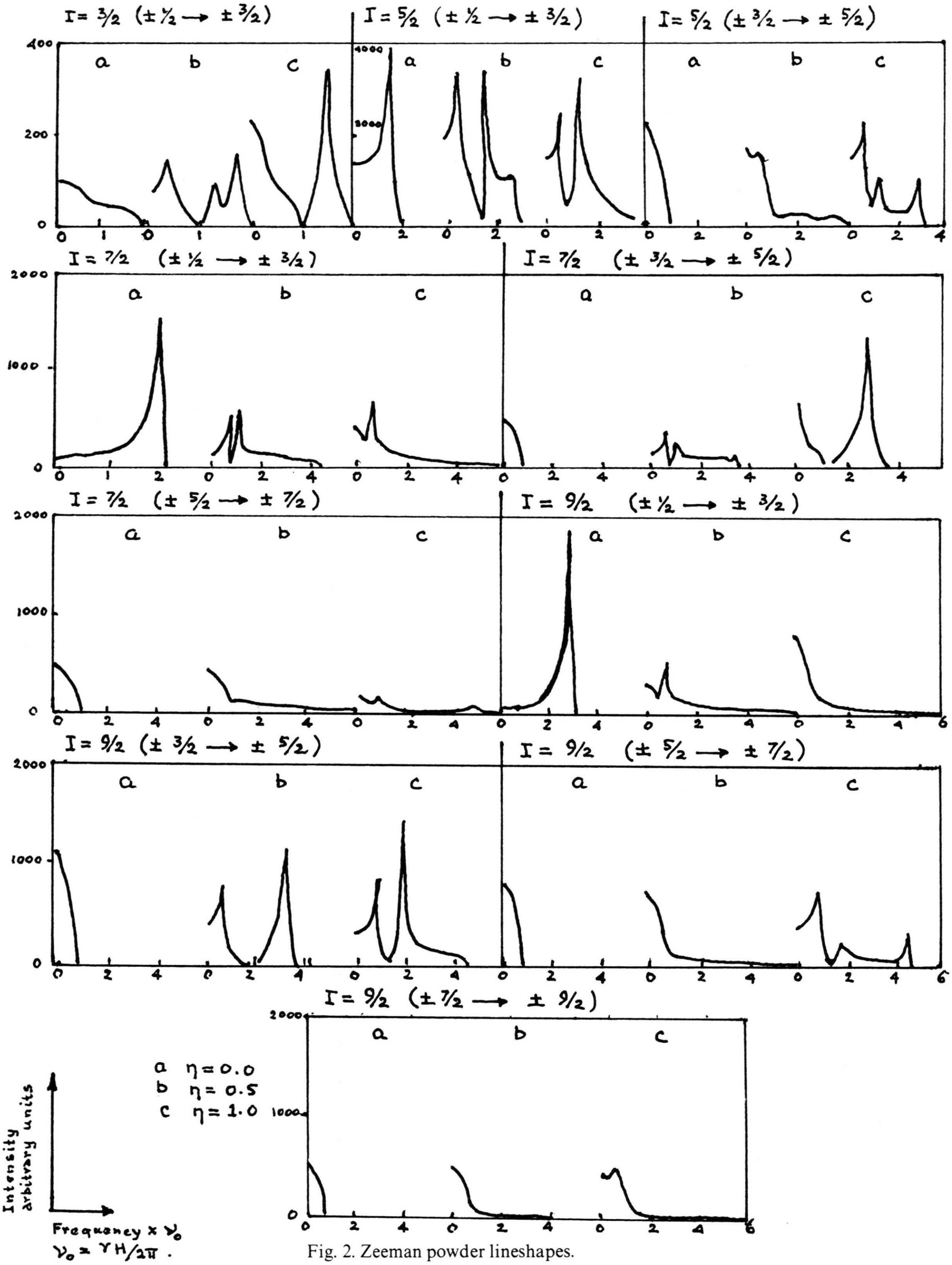

Fig. 2. Zeeman powder lineshapes.

where x, y, z refer to the 1, 2, 3 axes of the principal axes system. The intensity of these peaks increases with increasing η for the higher transition as greater mixing with lower states takes place. As η approaches one, the features for the ν_1 transition appear to collapse toward ν.

In a previous paper [10] it has been shown that for the $I = 5/2$ system the line width ratio $\Delta\nu_2/\Delta\nu_1$ is ideally 2.0 for $\eta = 0$ when only electrical broadening effects were considered. Reference to Fig. 2 clearly shows that qualitatively $\Delta\nu_2/\Delta\nu_1$ is approximately 0.5 for $\eta = 0$ ($I = 5/2$) in the case of pure magnetic broadening. This suggests that Fig. 2 could be qualitatively used as a criterion for determining whether the bonding mechanism is mainly due to electric or magnetic effects.

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