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Abstract

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THE LINE SHAPE OF NUCLEAR MAGNETIC RESONANCE OF ISOLATED GROUPS OF NUCLEI AND INTERMOLECULAR INTERACTION IN A SOLID

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The NMR spectrum of a solid can be readily calculated only for an idealized model, in which it is assumed that the nuclei are arranged in isolated groups and that there is no interaction between these groups. According to this model, spectra have been calculated for isolated groups consisting of 2, 3, and 4 nuclei [1-3]. As a result of the calculations, spectra are obtained that consist of a number of individual narrow lines.

When the calculated spectra are compared with the experimental ones, it turns out that all the lines are broadened owing to interaction between nuclei belonging to different groups. In order to take this broadening into account in calculations of the NMR line shape, it is assumed that each of the lines of the spectrum has a Gaussian shape with a half-width identical for all lines of the spectrum. The half-width of the lines, which depends on the magnitude of the intermolecular interaction, is determined from experiment from the value of the second moment of the NMR line. However, for a three-spin system (methyl group) the experimental line proves to be narrower than that calculated with the aid of such a phenomenological model [2].

Table 1

Substance	S_2, G^2	S_4, G^4	$K = S_4/S_2^2$	Temp., °C
$Be_4O(COOCH_3)_6$	5.30±0.10	140±5	5.00±0.10	160
				62
				20
				−196
CH_3CN	8.50±0.10	228±10	3.15±10	−
CH_3I	9.45±0.07	273±6	3.05±$0.05	

In order to clarify the influence of intermolecular interaction on the NMR line shape of methyl groups at different magnitudes of interaction between individual groups of nuclei, we studied the temperature dependence of the shape and moments of the NMR lines of polycrystalline samples of beryllium oxyacetate $Be_4O(COOCH_3)_6$ and the spectra of methyl iodide CH_3I and acetonitrile CH_3CN at a temperature of −196°.

For recording the spectra and taking account of instrumental functions, the apparatus and relations described previously [6, 7] were used. The experimental results are given in Table 1.

In the compounds investigated, the methyl groups reorient about an axis perpendicular to their plane at temperatures down to −196° [4, 5].

The NMR spectrum of such reorienting groups contains only 3 lines [2] with frequencies γH_0, $\gamma H_0 \pm a(3\cos^2\theta - 1)$ and probabilities 1/2, 1/4, 1/4. Here γ is the gyromagnetic ratio; H_0 is the external magnetic field;

$$\alpha = {}^3/_2\,\mu R^{-3},$$

μ is the magnetic moment; R is the distance between nuclei; θ is the angle between the reorientation axis and the external field H_0.

In the case of a polycrystalline sample, the different orientations of the axes of the individual crystallites are equiprobable. Therefore, in order to obtain the NMR line shape $g(h)$ of such a system under the assumption of Gaussian broadening of each of the spectral components, it is sufficient to average over the solid angle:

$$g(h) = \frac{1}{\sqrt{2\pi}}\left\{\frac{\exp[-h^2/2\beta_1^2]}{2\beta_1} + \frac{1}{4\beta_2}\int_0^1 \left\{\exp\left[-\frac{[h+\alpha(3x^2-1)]^2}{2\beta_2^2}\right] + \exp\left[-\frac{[h-\alpha(3x^2-1)]^2}{2\beta_2^2}\right]\right\} dx\right\}, \tag{1}$$

where h is the distance from the center of the line, $x = \cos\theta$; β_1 and β_2 are the half-widths of, respectively, the central line of the triplet and its side components.

Fig. 1. Dependence of S_4/S_2^2 on S_2.
1–$\beta_1 = \beta_2$; 2–$\beta_1^2 = 4\beta_2^2$; 3–$\beta_1^2 = 1.85\beta_2^2$.
a–$Be_4O(CO-OCH_3)_6$; *b*–CH_3CN; *c*–CHI_3.

The dependences of the second and fourth moments of the NMR line on β_1 and β_2, calculated by us for this model of the line shape, have the form

$$S_2 = {}^2/_5\alpha^2 + (\beta_1^2 + \beta_2^2)/2; \tag{2}$$

$$S_4 = 3\left[{}^8/_{35}\alpha^4 + {}^4/_5\alpha^2\beta_2^2 + (\beta_1^4 + \beta_2^4)/2\right]. \tag{3}$$

Introducing the quantity $S_0 = {}^2/_5\alpha^2$–the second moment of an isolated reorienting methyl group–one can obtain the following expression

Fig. 2. Derivative of the line-shape function for beryllium oxyacetate at 160°, obtained experimentally. Modulation amplitude $2h_m = 1.0$ Oe

Fig. 3. Derivative of the line-shape function (right half), calculated taking into account broadening due to modulation ($2h_m = 1.0$ G)

Figure 1: Fig. 3. Derivative of the line-shape function (right half), calculated taking into account broadening due to modulation ($2h_m = 1.0$ G)

for the ratio of the fourth moment to the square of the second:

$$\frac{S_4}{S_2^2} = \frac{3}{(1+k)^2}\left\{\left(\frac{S_0}{S_2}\right)^2 \frac{4}{7}(6k^2 - 2k - 1) - \frac{S_0}{S_2}\,4k(k-1) + 2(1+k^2)\right\},$$

where $k = \beta_1^2/\beta_2^2$. It is usually assumed ([4,9]) that $\beta_1 = \beta_2$. The dependence of the quantity S_4/S_2^2 on S_2, calculated under this assumption, is shown in Fig. 1, curve 1. The experimental values of the ratio S_4/S_2^2 lie below this curve.

We made the natural assumption that the different lines of the spectrum broaden unequally, i.e., that $\beta_1 \neq \beta_2$. Substitution of the experimental values S_2 and S_4 into (2) and (3) showed that, for beryllium oxalacetate, $\beta_1^2/\beta_2^4 = 4$ over the entire temperature range investigated; i.e., when the intermolecular contribution to the second moment changes by a factor of 10 and the width of each of the lines by a factor of 3, the ratio of the widths of the components of the lines for beryllium oxalacetate remains constant (Fig. 1, curve 2).

Fig. 3. Derivative of the line-shape function (right half), calculated taking into account broadening due to modulation ($2h_m = 1.0$ G)

Calculation of the ratio β_1^2/β_2^2 for CH_3J and CH_3CN gives the same value $\beta_1^2/\beta_2^2 = 1.85$ (Fig. 1, curve 3).

Figure 2 shows the experimentally obtained derivative of the line-shape function for beryllium oxalacetate at a temperature of 160°. Three maxima are clearly visible on the recording curve. Calculation of the derivative of the line-shape function for the methyl group under the assumption that $\beta_1 = \beta_2$, for $S_0 = 6.3$ G^2, gives 2 maxima (8). A calculation carried out under the assumption that $\beta_1^2/\beta_2^2 = 4$ gives 3 maxima (Fig. 3), coinciding in position with the experimental ones. This also confirms the proposed model, which assumes unequal broadening of the different lines of the spectrum.

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Note: Figure translations are in progress. See original paper for figures.