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Abstract

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S. N. DOBRYAKOV, Ya. S. LEBEDEV

ANALYSIS OF A SPECTRAL LINE WHOSE SHAPE IS DESCRIBED BY A COMPOSITION OF GAUSSIAN AND LORENTZIAN DISTRIBUTIONS

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1°. The shape of an individual spectral line in the presence of external perturbations is often described by a composition of the Gaussian and Lorentzian distributions (d.) [1,2]

$$A(\omega)=\frac{(8/3\pi^3)^{1/2}}{\Delta\omega_{\mathrm{L}}\Delta\omega_{\mathrm{G}}}\int_{-\infty}^{\infty}\frac{\exp(-2\omega_1^2/\Delta\omega_{\mathrm{G}}^2)\,d\omega_1}{1+4(\omega-\omega_1)^2/3\Delta\omega_{\mathrm{L}}^2},\tag{1}$$

where $\Delta\omega_{\mathrm{L}}$ and $\Delta\omega_{\mathrm{G}}$ are the widths of the Lorentzian and Gaussian lines between the points of maximum slope. The origin is chosen at the center of gravity of the line.

It is known [3] that if the line is described only by a Lorentzian d., then the line shape is Lorentzian and the width between the points of maximum slope is $\Delta\omega_0=\Delta\omega_{\mathrm{L1}}+\Delta\omega_{\mathrm{L2}}$. For Gaussian line distributions the shape is Gaussian, but $\Delta\omega_0=(\Delta\omega_{\mathrm{G1}}^2+\Delta\omega_{\mathrm{G2}}^2)^{1/2}$. It is of interest to obtain the law of addition of line widths for a d. of Gaussian and Lorentzian functions that is closer to experimental conditions (since up to now the line shape (1) has been analyzed only by numerical calculation [4]).

Let us consider the Fourier transform of (1), which has the meaning of the correlation function of the spectrum:

$$F(t)=\int_{-\infty}^{\infty}A(\omega)e^{i\omega t}\,dt=\mathcal{F}_{\mathrm{L}}(t)F_{\mathrm{G}}(t)=$$

$$=\exp\left[-\frac{\sqrt{3}}{2}\Delta\omega_{\mathrm{L}}|t|\right]\exp\left[-\frac{1}{8}\Delta\omega_{\mathrm{G}}^2t^2\right].\tag{1'}$$

In the case of a purely Lorentzian or purely Gaussian distribution function, the spectral width $\Delta\omega$ is related to the characteristic decay time of the correlation function τ by the relation $\Delta\omega \cdot \tau = C$, where C is a coefficient of order unity depending on the method of determining $\Delta\omega$. One may assume that an analogous relation is also valid for the d. (1), i.e., at $t = C_1/\Delta\omega_0$ the exponent in the right-hand side of (1′) must be equal to some constant value C_2. Consequently,

$$\frac{\sqrt{3}}{2}\frac{C_1}{C_2}\frac{\Delta\omega_{\mathrm{L}}}{\Delta\omega_0} + \frac{1}{8}\frac{C_1^2}{C_2}\frac{\Delta\omega_{\mathrm{G}}^2}{\Delta\omega_0^2} = 1,$$

and, taking into account the limiting conditions $\Delta\omega_0 = \Delta\omega_{\mathrm{L}}$ at $\Delta\omega_{\mathrm{G}} = 0$ and $\Delta\omega_0 = \Delta\omega_{\mathrm{G}}$ at $\Delta\omega_{\mathrm{L}} = 0$, we obtain

$$\Delta\omega_{\mathrm{L}}/\Delta\omega_0 + \Delta\omega_{\mathrm{G}}^2/\Delta\omega_0^2 = 1. \tag{2}$$

To check the “semi-intuitive” derivation of equation (2), the equation $A''({}^1/_2\Delta\omega_0) = 0$ was solved numerically, and the dependence between the parameters $\Delta\omega_{\mathrm{L}}/\Delta\omega_0 = \alpha$ and $\Delta\omega_{\mathrm{G}}/\Delta\omega_0 = \beta$ was found. From Table 1 it is seen that the relation $\alpha + \beta^2 = 1$ is satisfied with good accuracy. Obviously, for any-

Table 1

Parameters of the convolution of Gaussian and Lorentzian distributions

$\beta = \Delta\omega_\Gamma/\Delta\omega_0$	$\alpha = \Delta\omega_L/\Delta\omega_0$	$\alpha + \beta^2$	$x_{1/4} = \Delta\omega_{1/4}/\Delta\omega_0$	$x_{1/2}$	$x_{3/4}$	h_Π/h_D
0.000	1.000	1.000	3.441	2.401	1.777	1.299
0.100	0.990	1.000	3.422	2.391	1.772	1.302
0.200	0.960	1.000	3.366	2.363	1.759	1.312
0.300	0.909	0.999	3.276	2.317	1.738	1.327
0.400	0.838	0.998	3.155	2.259	1.712	1.346
0.500	0.747	0.997	3.011	2.194	1.684	1.370
0.600	0.635	0.995	2.857	2.127	1.658	1.396
0.700	0.504	0.994	2.701	2.065	1.633	1.425
0.800	0.355	0.995	2.559	2.009	1.612	1.456
0.900	0.186	0.996	2.438	1.961	1.593	1.488
1.000	0.000	1.000	2.339	1.922	1.577	1.520

an arbitrary number of Lorentzian and Gaussian c.r.’ s, the total width of the spectrum $\Delta\omega_0$ is given by the relation

$$\Delta\omega_0^2 = \Delta\omega_0 \sum_k \Delta\omega_{Lk} + \sum_j \Delta\omega_{\Gamma j}^2.$$

2°. Let us note that $\Delta\omega_L$ and $\Delta\omega_\Gamma$ can be expressed in terms of any independent pair of observed quantities. In particular, it has recently been shown (^{5}) that $\Delta\omega_L$, $\Delta\omega_\Gamma$ can be calculated knowing $\Delta\omega_0$ and $n = M_1/h_\Pi\Delta\omega_0$, where M_1 is the area under the curve, and h_Π is the amplitude of the absorption curve $A(\omega)$.

In practice it is more convenient to use $\Delta\omega_0$ and $x_i = \Delta\omega_i/\Delta\omega_0$ (see Fig. 1), where x_i is determined from $A'(\frac{1}{2}\Delta\omega_i) = iA'(\frac{1}{2}\Delta\omega_0)$ for arbitrary i in the range $0 < i < 1$. Table 1 gives the values of $x_{1/4}$, $x_{1/2}$, $x_{3/4}$ as a function of β (or α). In principle one can calculate x_i for other values of i and construct an anamorphosis of $A(\omega)$ in the coordinates (x_i, β). If the wings of the line are distorted by noise or by overlap with neighboring lines, one can use, as a function of β (or α), the ratio of the amplitude of the first derivative of the absorption signal to the amplitude h_D of the derivative signal of the dispersion $D(\omega)$ at $\omega = 0$. Table 1 gives the values of h_Π/h_D for $0 \le \beta \le 1$, calculated from the formula

Fig. 1. EPR spectrum of the radical 2,2,6,6-methylpiperidone-1-oxyl in benzene. The line shape of each of the three resolved components is a Lorentzian and Gaussian c.r. with $\Delta\omega_L = 0.79$ Oe and $\Delta\omega_\Gamma = 0.89$ Oe; the Gaussian distribution is due to unresolved h.f.s. from 18 protons.

$$h_\Pi/h_D = \frac{2A'(\frac{1}{2}\Delta\omega_0)}{D'(0)} = \frac{\displaystyle\int_0^\infty \exp\left(-\sqrt{3}(1-\beta^2)t - \tfrac{1}{2}\beta^2t^2\right) t\sin t\,dt}{\displaystyle\int_0^\infty \exp\left(-\sqrt{3}(1-\beta^2)t - \tfrac{1}{2}\beta^2t^2\right) t\,dt}.$$

3°. Let us apply equation (2) and the relations obtained in 2° to the analysis of EPR spectra of free radicals with unresolved hyperfine structure. In this case $\Delta\omega_L$ has the meaning of the relaxation width of the spin packet, usually proportional to the concentration of radicals (^{10}), while $\Delta\omega_\Gamma$ is the width of the inhomogeneous distribution of spin packets.

As shown in (^{6}), for N equivalent protons with constant a, $\Delta\omega_\Gamma = a\sqrt{N}$. We generalize this relation to the case of N nonequivalent nuclei with constants a_n and spins I_n. It was found earlier (^{7}) that for

EPR spectrum with hyperfine structure for a Lorentzian shape of the individual components

$$F(t) = F_{\mathrm{L}}(t)\sum_{n=1}^{N}\left(\frac{\sum_{-I_n}^{I_n}\exp(ia_nI_{nz}t)}{2I_n+1}\right),$$

for $(a_nI_n)_{\max}t \ll 1$

$$\sum_{-I_n}^{I_n} \exp(ia_n I_{nz} t)/(2I_n+1) \simeq 1 - \frac{t^2}{6} a_n^2 I_n(I_n+1) \simeq$$

$$\simeq \exp\left\{-\frac{1}{6} a_n^2 I_n(I_n+1) t^2\right\},$$

i.e.,

$$F(t) \simeq \mathscr{F}_{\mathrm{L}}(t) \exp\left\{-\frac{1}{6} t^2 \sum_{n=1}^{N} a_n^2 I_n(I_n+1)\right\}. \tag{3}$$

Relation (3) will be valid for describing practically the entire spectral line if

$$\left(\sum_{n=1}^{N} a_n^2 I_n(I_n+1)\right) \Big/ \left(6(a_n I_n)_{\max}\right)^2 \gg 1.$$

In particular, for approximately equivalent nuclei this corresponds to the condition $N \gg 1$. Comparing (3) with (1′), we find that the contribution to the Gaussian width of the distribution due to unresolved h.f.s. is

$$\Delta\omega_{\mathrm{G}} = \frac{2}{\sqrt{3}} \left(\sum_{n=1}^{N} a_n^2 I_n(I_n+1)\right)^{1/2}. \tag{3'}$$

Equation (3′) is a consequence of the law of large numbers for the variance of the sum of N independent random variables. Direct verification by the atlas $^{(8)}$ showed that, for equivalent nuclei, (3′) is already satisfied at $N \geq 2$ for $a/\Delta\omega_{\mathrm{L}} \leq 0.67$.

4°. As an illustration, we present an analysis of the EPR spectrum of the radical 2,2,6,6-methylpiperidone-1-oxyl in benzene ($N_{\mathrm{H}} = 18$) (see Fig. 1). All three nitrogen components show weak signs of proton h.f.s. For each component of the triplet, $\Delta\omega_0$, $x^1/_4$, $x^1/_2$, $x^3/_4$ were determined; then α, β were found and, by formula (3′), the root-mean-square value of the constant $\bar{a}_n = 0.21$ Oe was calculated for the proton, which agrees satisfactorily with the value $\bar{a}_{\mathrm{H}} = 0.26$ Oe computed from NMR spectra $^{(9)}$.

We also note that $\Delta\omega_{\mathrm{L}}$, $\Delta\omega_{\mathrm{G}}$ can be determined separately by using (2) and saturation experiments, which give $\Delta\omega_{\mathrm{G}}/\Delta\omega_{\mathrm{L}}$, or (2) and the dependence of the line width on concentration $\Delta\omega_0 = \varphi(\Delta\omega_{\mathrm{L}})$ $^{(10)}$.

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Institute of Chemical Physics
Academy of Sciences of the USSR

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