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BRIEF COMMUNICATIONS

ESTIMATE OF INHOMOGENEOUS LINE BROADENING IN STEADY-STATE MAGNETIC RESONANCE

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We have established relationships between the experimental and theoretical absorption and dispersion line parameters for steady-state magnetic resonance, allowing us to determine both the field characteristics (amplitude of the a.c. magnetic field) and the relaxation characteristics (longitudinal and transverse relaxation times) of the object under study.

Keywords: *magnetic resonance spectroscopy, absorption and dispersion line parameters, detuning from resonance, rf field amplitude, relaxation time, inhomogeneous broadening of a spectral line.*

Introduction. Coherent magnetic spectroscopy of quantum systems are currently widely used in studying the structure and properties of the condensed state of matter. It is subdivided into steady-state and non-steady-state spectroscopy. Steady-state spectroscopy is based on the action of a continuous electromagnetic field on a quantum transition, where the dispersion and absorption signals act as the observable quantities [1, 2]. Non-steady state spectroscopy is based on study of the dynamics of quantum transitions after two-pulse action of coherent electromagnetic radiation on a sample. The observable quantity in this case is the "echo signal" generated at a certain instant of time after the end of the exciting pulse [3]. Among coherent magnetic spectroscopy methods, the most widely used are nuclear magnetic resonance (NMR), electron paramagnetic resonance (EPR), and optical resonance. Most often non-steady-state effects are studied under exact resonance conditions, when the carrier frequency of the pulse matches the central frequency of the quantum transition. Until recently, it was assumed that nonresonant excitation leads to a trivial consequence, namely a reduced effect. However, in addition to this fact, under nonresonant excitation conditions in magnetic materials, as shown in [3], an interesting phenomenon has been observed: the appearance of multiple structure in the nuclear spin echo signal. Nonresonant excitation conditions in the theory [4] were described by dividing the parameter Δ into two terms: $\Delta \to (\Delta - \delta)$, where Δ corresponds to the spread in the frequencies of the spin packets of the inhomogeneously broadened line, $\delta = \omega_n - \omega_0$ is the detuning from resonance, ω_n is the carrier frequency of the electromagnetic field, ω_0 is the central frequency of the quantum transition.

A similar situation also arises in steady-state magnetic resonance, when the dispersion u and absorption υ signals have the form:

$$\frac{u}{M_0} = \frac{\omega_1 \Delta T_2^2}{1 + \Delta^2 T_2^2 + \omega_1^2 T_1 T_2},$$

$$\frac{v}{M_0} = \frac{\omega_1 T_2}{1 + \Delta^2 T_2^2 + \omega_1^2 T_1 T_2},$$

where M_0 is the equilibrium value of the magnetization of the sample; T_1 and T_2 are the energy and phase relaxation times; ω_1 is the Rabi frequency. In these formulas, there is no explicit term for the inhomogeneous broadening δ_n,

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which corresponds to the spread in the Larmor frequencies for the individual spin packets, and the detuning parameter $\delta = \omega_n - \omega_0$. Therefore interpretation of the experimental results is ambiguous; under these conditions, it is difficult to control the degree of detuning of the frequency of the external a.c. magnetic field from resonance. Also in the final step, any observable quantity (in this case, the u and v components) should be averaged over some appropriate distribution function. In magnetic resonance, the experimental line contours are described by form factors in the form of a lorentzian or gaussian distribution or their convolution. It is simplest to choose a lorentzian as the averaging function:

$$G(\Delta) = \frac{\sigma_n}{\pi\,[(\Delta-\delta)^2 + \sigma_n^2]}. \tag{1}$$

The parameter σ_n is the half-width of lorentzian (1), and physically is equivalent to the contribution of inhomogeneous broadening to the resulting line width. Then

$$\left\langle \frac{u}{M_0} \right\rangle = \frac{\sigma_n}{\pi} \int_{-\infty}^{\infty} \frac{\omega_1 \Delta T_2^2}{[1 + \Delta^2 T_2^2 + \omega_1^2 T_1 T_2]} \frac{d\Delta}{[(\Delta-\delta)^2 + \sigma_n^2]},$$

$$\left\langle \frac{v}{M_0} \right\rangle = \frac{\sigma_n}{\pi} \int_{-\infty}^{\infty} \frac{\omega_1 T_2}{[1 + \Delta^2 T_2^2 + \omega_1^2 T_1 T_2]} \frac{d\Delta}{[(\Delta-\delta)^2 + \sigma_n^2]}.$$

Finally:

$$\left\langle \frac{u}{M_0} \right\rangle = \frac{\omega_1 \delta}{\delta^2 + \left(\sigma_n + \sqrt{\frac{1}{T_2^2} + \omega_1^2 \frac{T_1}{T_2}}\right)^2}, \tag{2}$$

$$\left\langle \frac{v}{M_0} \right\rangle = \frac{\omega_1}{T_2} \frac{\sigma_n + \sqrt{\frac{1}{T_2^2} + \omega_1^2 \frac{T_1}{T_2}}}{\sqrt{\frac{1}{T_2^2} + \omega_1^2 \frac{T_1}{T_2}} \left(\delta^2 + \left(\sigma_n + \sqrt{\frac{1}{T_2^2} + \omega_1^2 \frac{T_1}{T_2}}\right)^2\right)}. \tag{3}$$

As a result, we again arrive at a lorentzian line of width $\sigma_0 + \sigma_n$, where $\sigma_0 = \sqrt{\frac{1}{T_2^2} + \omega_1^2 \frac{T_1}{T_2}}$ is equivalent to the contribution of homogeneous broadening to the resulting line width of the quantum transition. (Note that such a procedure is used in [5] for magnetically ordered materials.) Then expressions (2) and (3) take on the more concise form:

$$\left\langle \frac{u}{M_0} \right\rangle = \frac{\delta\omega_1}{\delta^2 + (\sigma_n + \sigma_0)^2}, \tag{4}$$

$$\left\langle \frac{v}{M_0} \right\rangle = \frac{\omega_1}{T_2} \frac{\sigma_n + \sigma_0}{\sigma_0\,(\delta^2 + (\sigma_n + \sigma_0)^2)}. \tag{5}$$

Calculation. Expressions (4) and (5) for the magnetization also separately include the detuning from resonance δ and the inhomogeneous contribution σ_n to the resulting line width. The detuning δ acts as the variable in these expressions.

Let us analyze (4) and (5) with the aim of extracting information about the functional relationships between the measured and analytically obtained parameters of the magnetic resonance signals. For the u component of the mag-

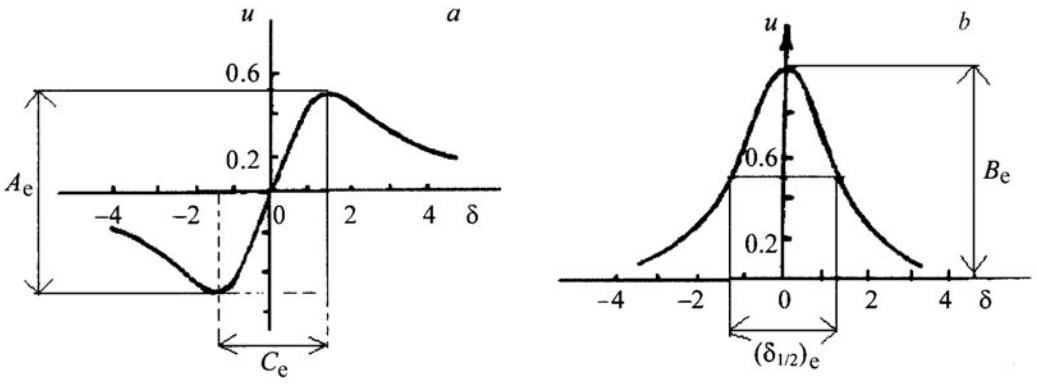

Fig. 1 Magnetic resonance dispersion (a) and absorption (b) signal.

netization, the experimentally determined parameters of the spectrum are twice the magnitude of the peak value (the peak-to-peak amplitude) A_e, which corresponds to the theoretical value of $\omega_1/(\sigma_0 + \sigma_n)$, and also twice the magnitude of the detuning $C_e = \delta_1 - \delta_2$ on either side (the distance along the x-axis between the right-hand and left-hand peaks), equal to its theoretical value $2(\sigma_0 + \sigma_n)$ (Fig. 1a). As a result, we have the functional relationship

$$A_e \times C_e = 2\omega_1 , \tag{6}$$

from which follows the possibility of determining the experimentally important parameter: the amplitude of the external a.c. magnetic field. For $\delta = 0$, the theoretical value of the absorption signal is

$$\left\langle \frac{v}{M_0} \right\rangle = \frac{\omega_1}{T_2} \frac{1}{\sigma_0 (\sigma_n + \sigma_0)} .$$

Let us denote as B_e the corresponding measured amplitude of the absorption signal (Fig. 1b).

For a symmetric line shape, its half-width at half-height $\frac{1}{2}\left\langle \frac{v}{M_0} \right\rangle$ is theoretically equal to $\delta_{1,2} = \pm(\sigma_0 + \sigma_n)/2$ (Fig. 1b), from which the total line width is $\delta_1 - \delta_2 = \sigma_n + \sigma_0$. If we denote the experimentally measured total line width at half-height as $(\delta_{1,2})_e$, then since the theoretical expression for it is $\sigma_n + \sigma_0$, as a result we have the following functional relationship:

$$B_e \times (\delta_{1/2})_e = \omega_1/(\sigma_0 T_2) . \tag{7}$$

As an example of application of the above-indicated procedure, let us consider the experimental magnetic resonance data for diphenyl picryl hydrazyl, for which $T_1 = T_2 = T$ [2]. In this case, the homogeneous contribution to the line width is $\sigma_0 = \sqrt{1/T^2 + \omega_1^2}$. Taking into account (6) and (7), it is not difficult to obtain the formula for the relaxation time:

$$T = \frac{2}{A_e C_e} \sqrt{\frac{A_e^2 C_e^2}{B_e^2 (\delta_{1/2})_e^2} - 1} .$$

Using $(\delta_{1/2})_e = \sigma_n + \sigma_0$, we obtain the expression for the inhomogeneous contribution to the resulting line width:

$$\sigma_n = (\delta_{1/2})_e - \sigma_0 = (\delta_{1/2})_e - A_e C_e \Big/ 2\sqrt{1 - \frac{4B_e^2 (\delta_{1/2})_e^2}{A_e^2 C_e^2}} .$$

The source of the inhomogeneous broadening in the case under consideration may be the inhomogeneity of the external d.c. magnetic field, since due to the fact that the sample has finite dimensions, the d.c. magnetic field has different

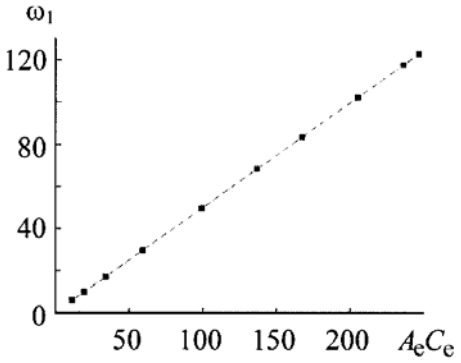

Fig. 2 Amplitude of a.c. rf magnetic field vs. "area" of the dispersion signal.

values over its volume. In the general case, the inhomogeneous broadening is due to inhomogeneities in the sample: the spread in optic axes of the individual crystallites in the polycrystalline material, the static magnetic field created by an adjacent nucleus of a different type at the site where the magnetic moment under study is located, etc.

Thus after averaging the expressions for the steady-state dispersion and absorption components of the magnetization with respect to a lorentzian distribution function, the detuning from resonance δ and the inhomogeneous line width σ_n appear in the expressions, which were not present explicitly before the averaging procedure. The presence of these parameters in the theory allowed us, by comparing the theoretical values with the experimentally determined indices of the spectral line, to obtain functional relationships between them.

In order to illustrate the results obtained, let us make use of the experimental data for A_e and C_e for the diphenyl picryl hydrazyl sample given in [6], and based on these data let us plot the functional dependence $\omega_1 = A_e C_e/2$ (Fig. 2). We see that the amplitude of the a.c. magnetic field varies according to a linear law, which agrees well with the experiment in [6], all the way to saturation of the line. The results obtained are valid for a single symmetric line.

Conclusion. We have established that after averaging the steady-state dispersion and absorption components of the magnetization using a lorentzian distribution function, the detuning from resonance δ and the inhomogeneous line width σ_n appear explicitly in the components. By comparing the theoretical line parameters with their experimental values, we have obtained functional relationships between them, based on which we propose methods for determining the amplitude of the rf field, the relaxation times, and the inhomogeneous line width.

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