METHOD OF CORRECTING ESR LINE SHAPES

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It is well known that there is a discrepancy between signal intensity and accuracy of reproduction of signal line shapes in the ESR registration (phase-sensitive detection). The discrepancy is due to modulation of a magnetic field during registration. With a higher modulation amplitude, not only the amplitude but also distortions of the signal increase. Therefore when a signal-to-noise ration is low, it is necessary to use large modulation amplitudes. Numerous attempts have been made to overcome the distortion problem. A radical solution is to avoid using magnetic field modulation and employ other approaches, such as impulse methods [1] or the so-called "non-modification registration" described in [2]. However, this can be done with the aid of special devices other than phase-sensitive detection system. Among the studies using the modulation approach the work of G.V.H.Wilson [3] who established applying the Fourier analysis is particular interest the dependence of a signal amplitude on a signal true resonance line shape and on an amplitude of a magnetic field modulation. The work reported methods of correcting NMR and ESR line shapes, as well as their applications and limitations. The present study extends further one method for determination of true shapes using the Fourier coefficients, describing two methods for line shape correction of complicated spectra applicable for any modulation amplitudes. The proposed methods do not induce additional distortions.

Basic ti the present study was the dependence of the amplitude of modulated signal $F_n(t) = F\left(H(t) + H_m \cdot \cos(f_m t)\right)$ on the true shape line of absorption signal $F(H)$ and on

the modulation amplitude during a linear sweep of the magnetic field $H(t)$. In the Fourier analysis, this dependence can be expressed as:

$$\tilde{F}_m(f) = \sum_{k=-\infty}^{k=\infty} \mu_k i^k J_k\left(2\pi H_m \cdot (f - kf_m)\right) \cdot \tilde{F}(f - kf_m). \tag{1}$$

Here, line shapes of the modulated signal are obtained by summation of harmonics of the modulation frequency; H_m, f_m — amplitude and frequency of the magnetic field modulation, respectively; $\tilde{F}$ — the Fourier representation of the true line shape; J_k — the Bessel function of the first kind of k order; $\mu_k = \begin{cases} 1, k = 0 \\ 2, k \geq 1 \end{cases}$.

Each k Fourier term is a product of the Fourier representation of the true line shape by the Bessel function of the 1st kind of k order. Correction reported in [1] is carried out by simple division of coefficients of modulated line shapes by the Bessel function. However, the division is complicated due to thr oscillatory nature of the Bessel function. The number of zero points of the Bessel function is determined by the modulation amplitude: at the optimal modulation amplitude (when the signal is maximal) there may be 5–7 zero points. Consequently, it is impossible to restrict correction of coefficients to one or two zero points, as suggested in [1], because the accuracy is determined by the neglected coefficients. These difficulties in correction can be resolved by obtaining the Fourier Coefficients in zero region by means of some independent methods. This can be done by 1) detection of at least two signals with different modulation amplitudes and 2) detection of no less than two harmonics of the modulation frequency. It is obvious that changing the modulation amplitude we will shift the position of zero points and unknown coefficients can be easily derived. This is also possible for detection at different orders never coincide. With these methods of detection, the true line shapes are calculated applying the maximum likelihood method [4].

Likelihood function is defined as joint probability density of sample distribution S_j (detected spectrum at point j). Assuming that values S_j have normal distribution with a mean Fm_j and standard deviation σ_j, we have the likelihood function as:

$$L(S_j, F) = \exp - \left\{ \sum_{j=1}^{N} \left(S_j - Fm_j(F_j)\right)^2 \sigma_j^{-1} \right\} \tag{2}$$

where j is a point of detection; Fm_j is the value of modulated signal at j; and F_j — true line shapes at j.

In order to get the true line shapes as a function of the modulated signal, a set of the likelihood equations should be solved:

$$\partial \log L / \partial F = 0 \tag{3}$$

If two signals (S^1 and S^2) are detected with modulation amplitudes H_{m1} and H_{m2}, the solution for Eq.(3) in the Fourier representation is

$$\begin{aligned} \tilde{F}_j = -i/2 \left\{ \tilde{S}_j^1 \cdot J_1(H_{m1}/H_p \cdot 2\pi j T_p) + \tilde{S}_j^2 \cdot J_1(H_{m2}/H_p \cdot 2\pi j T_p) \right\} \times \\ \times \left\{ J_1^2(H_{m1}/H_p \cdot 2\pi j T_p) + J_1^2 \cdot J_1(H_{m2}/H_p \cdot 2\pi j T_p) \right\}^{-1}. \end{aligned} \tag{4}$$

For detection at k_1 and k_2 harmonics (S^{k1}, S^{k2}), the solution will be

$$\tilde{F}_j = \sum_{k=k_1,k_2} \tilde{S}^k \mu_k \cdot i^k J_k(H_m/H_p 2\pi j T_p) \left\{ \sum_{k=k_1,k} (\mu_k \cdot J_k(H_m/H_p 2\pi j T_p))^2 \right\}^{-1}. \qquad (5)$$

Since the denominator in eq.(4)–(5) is not equal to 0 in any finite region, correction with these equations does not set a limit to the modulation amplitude H_m.

However, the method using eq.(4) is disadvantageous in that the recordings should be carried out at different timing and with various modulation amplitudes, which requires twice as long period for detection. For this reason, another method based on eq.(5) was employed. In this case, synchronous recordings at various harmonics can be readily performed.

Recordings of the spectra were carried out on a ESR spectrometer allowing a simultaneous detection at four harmonics. As a sample, 10^{-3} mmol/l diphenylpicrylhydrosyn (DPPH) in dioxan solution was used. Recordings were done with the magnetic field sweep $H_p = 140$ gs, scan time $T_p = 25$ ms, modulation amplitude $H_m = 7$ gs, modulation frequency $f_m = 10$ kHz, the number of cycle accumulation $N = 100$. In these conditions, there are four zero points of the Bessel function un the region of interest. Fig.1 shows a DPPH signal at the output of the low pass filter ($\tau = 2 \cdot 10^{-5}$ sec) attached to the amplifier output connected with the micro wave detector, and Fig.2 gives its Fourier representation. The ESR non-distored spectrum was determined by applying eq.(5) and calculations were done for the second and third harmonics of the modulation frequency. For connection, the following expression was used:

$$\tilde{F}(j) = -i\{\tilde{S}^2(j)\ J_2(H_m/H_p \cdot 2\pi j T_p) + i\tilde{S}^3(j) \cdot J_3(H_m/H_p \cdot 2\pi j T_p)\} \times \qquad (6)$$
$$\times \{J_2^2(H_m/H_p \cdot 2\pi j T_p) + J_3^2(H_m/H_p \cdot 2\pi j T_p)\}^{-1}.$$

where $\tilde{S}^k(j) = \tilde{F}_m(j + kf_m)$. The true line shape of the (detected) modulation signal is derived as an inverse Fourier transform of $\tilde{F}_j$, i.e.

$$F_{\text{true}} = \text{Fur}^{-1}\left\{\tilde{\text{F}}_\text{j}\right\}.$$

Fig.3 shows true line shapes of the ESR PDDH signal in dioxan.

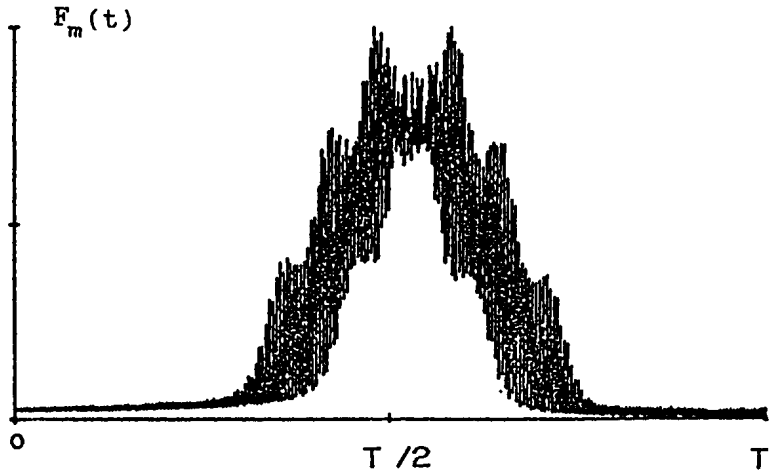

Fig.1. ESR signal of DPPH in dioxan at output of low pass filter

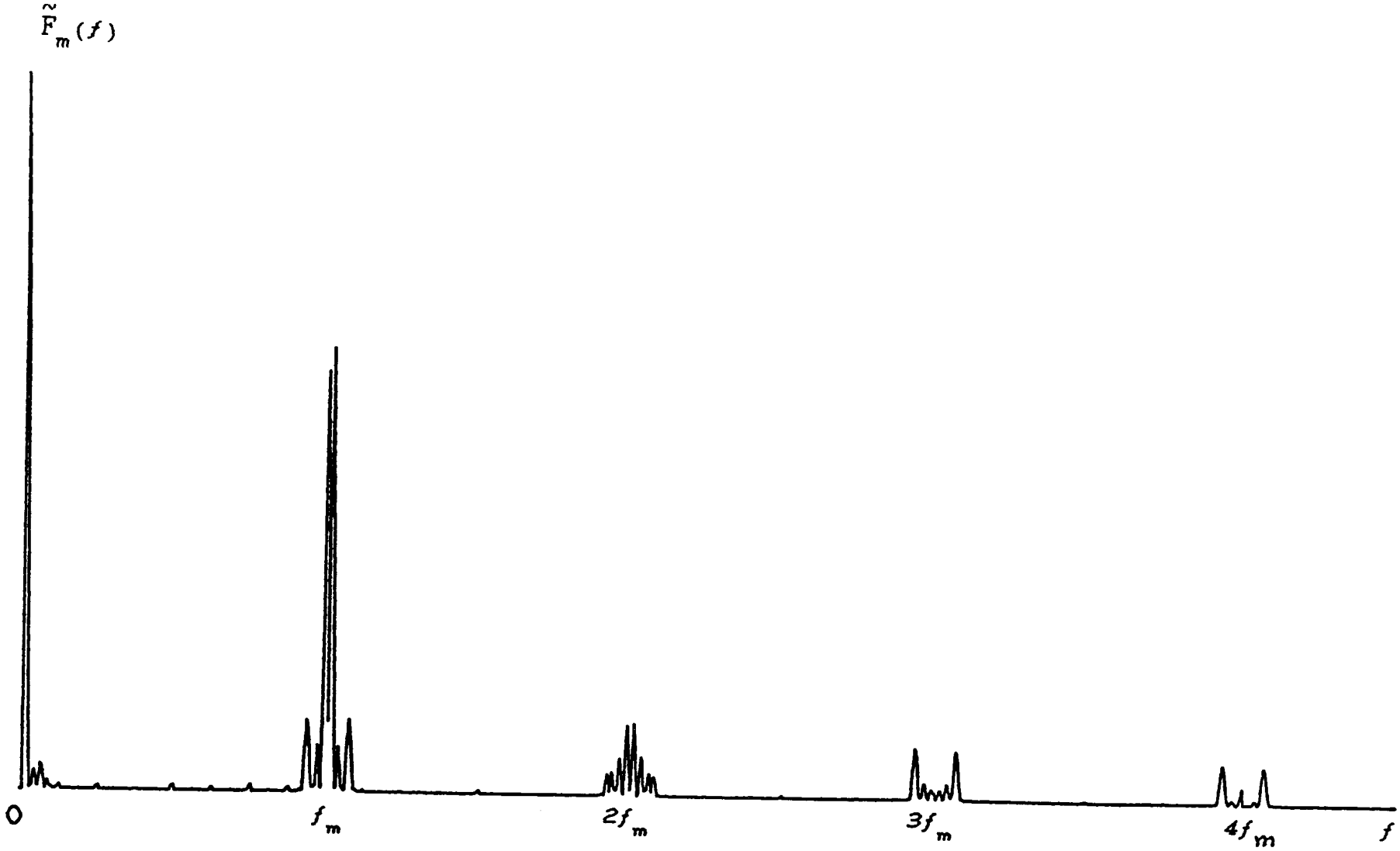

Fig.2. Fourier representation of the ESR signal of DPPH in dioxan

Two methods for correcting true line shapes, based on the general representation of the modulation signal, are proposed. The methods do not induce additional distortions, are fast and accurate, and give good results.

The first method involves detection of two signals at various modulation amplitudes. It requires additional time for recordings and knowledge of the H_m value with an accuracy no less than 0.001.

The second method consists in detection of the modulation frequency at two harmonics. Recordings take no more time than the conventional phase-sensitive detection. The accuracy of the modulation amplitude H_m is about 2%. Both methods are applicable for any line shapes and any modulation amplitude.

The experimentally detected signal DPPH has no more modulation distortions. Signal-to-noise ratios for a DPPH signal detected by these and conventional methods are close.

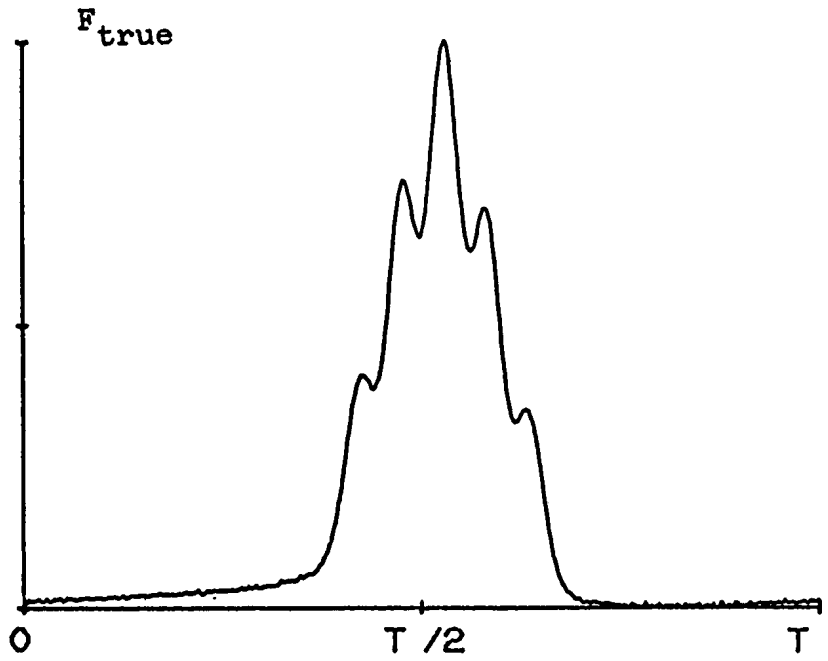

Fig.3. True line shapes of ESR signal of DPPH in dioxan

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