INDICATION OF ODD NUMBER OF EQUIVALENT ATOMS IN AN EPR SPECTRUM BY THE FOURIER TRANSFORM

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A numerical criterion is proposed for the indication of odd number of equivalent atoms in an EPR spectrum. Physically, this "oddness" criterion is the relation for the content of negative and positive parts in the imaginary part of the EPR spectrum Fourier transform, provided that the spectrum x-coordinate start is shifted into the spectrum symmetry center. The effect of noise present in the spectrum is analysed and the best limit of Fourier transform for noise effect minimalization is proposed. With even numbers of equivalent atoms in EPR spectrum only, the oddness criterion value for the noiseless spectrum is zero and the deviation from this value is due to the effect of the noise. A criterion value greater than 0.3 indicates the presence of at least one well-resolved component with an odd number of equivalent atoms with spin 1/2 in the spectrum. A value smaller than 0.3 indicates the absence of such a component. However, if this value is greater than 0.1, the presence of either a well-resolved component with a single atom with spin 1 or an ill-resolved component with an odd number of equivalent atoms with spin 1/2 is indicated. Application of the proposed criterion to noise-loaded synthetic EPR spectra is exhibited. The possibility of identifying methyl group splitting by a sharp decrease of the proposed criterion value after the spectrum contraction with the proper splitting constant is demonstrated.

In the analysis of hyperfine structure of linear isotropic EPR spectra, the Fourier transform (FT) of the spectrum has often been used[1 – 7]. With the advent of much more powerful methods[8,9] the FT lost its significance in this respect but nevertheless it can still provide some useful information not directly supplied by other methods. This information regards the presence of an odd number of equivalent atoms. It is the objective of this article to develop this possibility.

THEORETICAL

Fourier Transform Used

FT of EPR spectrum $y(x)$ can be defined as

$$F(y(x)) = Y(s) = \int_{-\infty}^{\infty} y(x)\exp(-i2\pi sx)dx\,, \qquad (1)$$

where s is a new coordinate introduced by FT instead of the coordinate x eliminated by the transform integration. The coordinate x is usually expressed in the magnetic induction units and because the product sx is dimensionless, the s is in inverted units. In this article, in accordance with the SI convention, x will be expressed in millitesla (mT) and s in mT^{-1}. If the coordinate x starts from the spectrum symmetry center and the spectrum has its usual first derivative form then, due to the symmetry of the linear isotropic EPR spectrum, the imaginary part of the spectrum FT, $\mathrm{Im}Y(s)$, contains full FT of this spectrum. With respect to this advantage, only this case will be further considered. Since the symmetry center of EPR spectrum can be easily found[8], the mentioned adjustment with respect to the x-origin poses no problem. The real part of the spectrum FT, $\mathrm{Re}Y(s)$, contains then only the real part of FT of the noise present in the spectrum. This fact can be used for the evaluation of noise present in $\mathrm{Im}Y(s)$ since for random noise both parts of its FT should have equal characteristics.

EPR Spectrum Notation Used

EPR spectrum can be expressed, according to the notation introduced in ref.[8], as being formed from simple multiplet components. This notation will be used throughout this article. Thus, having EPR spectrum $y(x)$ with splitting constants a_i and corresponding spin and equivalent atoms number s_i and n_i, respectively, and peak-to-peak linewidth d, we have in this notation

$$y(x) = \prod_i {}^{*} a_i(s_i,n_i)\mathrm{X}d \,,$$

where $\prod_i^{*}$ means the formal product over all i values and X is the general lineshape descriptor. For the cases where the lineshape influences results, the Lorenz lineshape will be further used and noted as L, and in the case of certain substance spectrum the corresponding atom symbol (e.g. H or N) instead of s_i, can be used. Values of a_i are expressed in mT. Elimination of a splitting from the spectrum by contraction will be expressed by formal division of the spectrum by the corresponding component.

Proposition of the Equivalent Atoms Oddness Criterion

If the number of equivalent atoms in all spectrum components is even (all n_i even) then $\mathrm{Im}Y(s)$ is positive in the whole range of s values. Some n_i being odd, $\mathrm{Im}Y(s)$ contains some negative parts. This fact can be used for the indication of the presence or absence of the odd number of equivalent atoms. As a quantitative numerical criterion for this purpose it is proposed the relation for the content of negative and positive parts in the spectrum FT

$$N(u) = \frac{\int_0^u |\mathrm{Im}Y(s)|\,\mathrm{d}s - \int_0^u \mathrm{Im}Y(s)\mathrm{d}s}{\int_0^u |\mathrm{Im}Y(s)|\,\mathrm{d}s + \int_0^u \mathrm{Im}Y(s)\mathrm{d}s}\,. \tag{2}$$

It can be derived (see Appendix) that for theoretical spectra it holds

$$N(u) = 0 \quad \text{for} \quad y(x) = \prod_i{}^{*}\, a_i(s_i,n_i)\mathrm{X}d \quad \text{and all} \quad n_i \quad \text{even} \tag{3}$$

$$\lim_{(d/a)\to 0} N(\infty) = 1 \quad \text{for} \quad y(x) = a(1/2,n)\mathrm{X}d \quad \text{and odd} \quad n \tag{4}$$

$$\lim_{(d/a)\to 0} N(\infty) = 0.1789789 \quad \text{for} \quad y(x) = a(1,1)\mathrm{X}d \tag{5}$$

$$\lim_{(d/a)\to 0} N(\infty) = 0.0206564 \quad \text{for} \quad y(x) = a(1,3)\mathrm{X}d \tag{6}$$

$$\lim_{n\to\infty} N(u) = 0 \quad \text{for} \quad y(x) = a(1,n)\mathrm{X}d \tag{7}$$

$$N(\infty) = 1 \quad \text{for} \quad y(x) = \text{random noise}\,. \tag{8}$$

The increase in the ratio of the linewidth to the splitting constant, (d/a), will result in a certain change in the $N(u)$ value. This is illustrated in Fig. 1 by the dependence of $N(\infty)$ on (d/a) value for some simple spectra with odd n. Generally, $N(\infty)$ becomes first higher as d/a is increased, goes through a maximum and then decreases to zero. This decrease can be physically ascribed to the loss of multiplet structure resolution. For the well-resolved $a(1,1)\mathrm{L}d$ spectrum the increase of $N(\infty)$ value does not exceed 50%, so that with $N(u)$ value greater than 0.3 a conclusion may be made about the presence of a resolved $a(1/2,n)$ structure with an odd n. The $N(u)$ value in the range from 0.1 to 0.3 indicates either an $a(1,1)$ structure or an ill-resolved $a(1/2,\text{odd } n)$ structure. The $N(\infty)$ value for the $a(1,3)$ structure is in the range of values pertaining usually to noise (see below).

Influence of Noise

The $N(u)$ value for experimental spectra is always distorted due to the presence of noise. Since the effect of random noise increases with increasing value of s, the proper choice of the upper integration limit u for the best $N(u)$ resolution power is necessary. A numerical record of experimental spectra is made by discrete digitalization and due to it the s values are limited by maximal value, s_{max}, corresponding to inverted spectrum digitalization interval. The best u value is therefore always smaller than s_{max}.

To illustrate the noise effect, the dependence of $N(u)$ on u for the spectrum *IIn* from ref.[8] together with the imaginary part of FT of this spectrum is shown in Fig. 2 (FT of the digitalized spectra has been computed using a software FFT procedure on an EC-1033 computer, used in ref.[8]). The spectrum contains all n_i even (see Table I) so that the deviation of $N(u)$ from zero is due to the effect of noise. With respect to the fact that in Re$Y(s)$ only the real part of FT of noise is present and that the imaginary part of FT of noise present in Im$Y(s)$ should have equal characteristics, the signal in Im$Y(s)$ smaller than a double of the signal in Re$Y(s)$ can be regarded as meaningless. The suitable condition for the u determination can have therefore the form

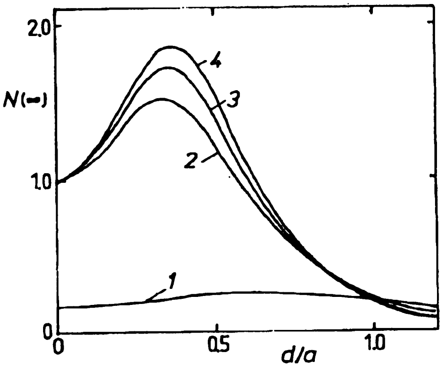

Fig. 1

Dependence of $N(\infty)$ on the ratio d/a for $a(1,1)Ld$ (*1*) and $a(1/2,n)Ld$ spectra with n = 1 (*2*), 3 (*3*), and 5 (*4*).

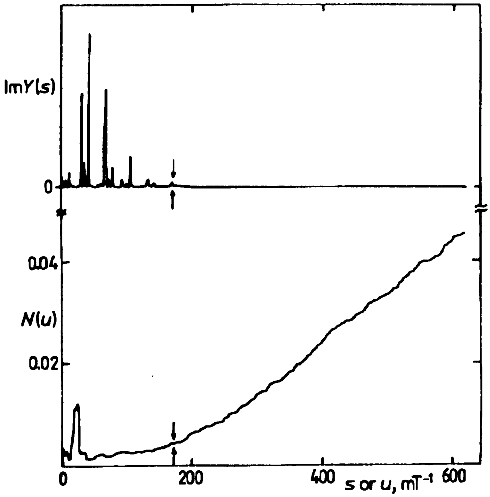

Fig. 2

Imaginary part of Fourier transform of spectrum *IIn* and the dependence of corresponding N(u) on u. Arrows indicate the u value corresponding to condition (9)

$$\max|\mathrm{Im}Y(s)| \;<\; 2\max|\mathrm{Re}Y(s)| \quad \text{for} \quad s \in \langle u, s_{\max}\rangle\,. \tag{9}$$

The u value, corresponding to condition (9) is also shown in Fig. 2. It can be seen that it actually cuts off an unimportant part of $\mathrm{Im}Y(s)$.

It also follows from Fig. 2 that usually $u < s_{\max}/2$. In fact, the interval $\langle s_{\max}/2, s_{\max}\rangle$ corresponds to the fine resolution between original $y(x)$ and $y(x)$ smoothed over doubled digitalization interval. In this part the effect of the noise often prevails and the loss of resolution due to smoothing is usually not important. This fact can be used for the condition for the best u determination in the case of the symmetrized EPR spectrum as is, for example, the spectrum obtained from the contraction[8]. For this case a suitable condition can be

$$\max_{s \in \langle u, s_{\max}/2\rangle}|\mathrm{Im}Y(s)| \;<\; 2\max_{s \in \langle s_{\max}/2, s_{\max}\rangle}|\mathrm{Im}Y(s)| \;. \tag{10}$$

Figure 2 also shows that the noise affects the $N(u)$ value mainly in those parts where the FT is close to zero. Generally, the greater the number of equivalent atoms in EPR spectrum, the greater part is close to zero inside the corresponding FT. It can therefore be expected that even after the described cutting, the effect of noise will increase with an increasing number of equivalent atoms.

Influence of Interaction of Spectrum Components

In spectra with a greater number of components, the interaction of the components influences the $N(u)$ value. Nevertheless, it can be expected that this value roughly ap-

TABLE I
Values of $N(u)$ obtained for some EPR spectra

Spectrum	Composition	$N(u)$
In	0.583 (N) 0.302 (H) 0.233 (H) 0.136 (H) 0.042 (H) 0.029 (H) L0.011 + 13% noise	0.525[a]
IIn	0.105 (N2) 0.181 (H4) 0.029 (H4) L0.008 + 7% noise	0.004[a]
IIIn	0.485 (N4) 0.328 (H12) 0.284 (H12) L0.010 + 7% noise	0.020[a]
IVn	1.090 (H3) 0.625 (H6) 0.170 (H2) L0.020 + 7% noise	1.182[a]
IVn[c]	*IVn*/1.090 (H)	0.012[b]

[a] Condition (9) was used; [b] condition (*10*) was used; [c] contracted *IVn* spectrum.

proaches that for the component with a greater $N(u)$ value. This expectation is based on the fact that the FT of a spectrum is formed by a product of the FT of its individual components. So, for a spectrum with components having only positive FT, the resulting spectrum FT is also only positive, except the noise effect as exhibited above. If one component has negative parts in FT and FT of all others are positive only, the negative parts of the pertaining component remains negative in the spectrum FT, being, as well as the positive part, only modulated by other components. If there is a greater number of components with negative parts in FT, the combination of odd number of negative values gives a negative value, while a combination of an even number of negative values gives a positive value, and at the end the net result is that there prevails the influence of the component giving greater $N(u)$ value.

Conclusions from N(u) Value

On the basis of the above noted reasons, the following rules can be stated. If the $N(u)$ value of the spectrum is greater than 0.3, it can be concluded there is at least one well-resolved component with an odd number of equivalent atoms with spin 1/2 in the spectrum. For $N(u)$ value smaller than 0.3 it can be concluded that all well-resolved components with spin 1/2 have even numbers of equivalent atoms. However, if this value is greater than 0.1, it may be attributed to either a well-resolved component with a single atom with spin 1 or to the component with an odd number of equivalent atoms with spin 1/2 and with the splitting constant comparable with the spectrum linewidth, i.e. to the ill-resolved component (see Fig. 1). If $N(u)$ approaches zero the presence of resolved $a(1/2,\text{odd } n)$ and $a(1,1)$ components is excluded, so that the spectrum can contain only resolved components with an even number of equivalent atoms with spin 1/2 and resolved components with even or higher number of eqivalent atoms with spin 1.

RESULTS

For illustration of practical application of the above conclusions, $N(u)$ values have been obtained for some selected EPR spectra, and the results are given in Table I. Spectra *In*, *IIn* and *IIIn* originate from ref.[8], the spectrum referred to as *IVn* was obtained in the same way. Splitting constants, spins, and numbers of atoms in the *IVn* spectrum correspond to the referred case of a 2,4,6-trimethylphenoxy radical[10]. Obtained $N(u)$ values indeed indicate correctly that in spectrum *In* and *IVn* there are some components with an odd number of equivalent atoms with spin 1/2 while in spectra *IIn* and *IIIn* there are only components with an even number of equivalent atoms. The result for *In* spectrum confirms the expectation that even with high number of components having an odd number of equivalent atoms the $N(u)$ value for the spectrum roughly approaches that for the single component with a greater $N(u)$ value. Comparison of the results for the

IIn and *IIIn* spectra confirms the expectation that the noise effect will increase with an increasing number of equivalent atoms.

The *IVn* spectrum was taken as an example of the important case where the odd number of equivalent atoms is due to the methyl group. From the last row in Table I it is apparent that after contraction of this spectrum by the splitting constant corresponding to the component with an odd number of equivalent atoms, the $N(u)$ value decreases so that it indicates even values of equivalent atoms only in the contracted spectrum. This effect can be used for the identification of splitting constant corresponding to the component with an odd number of equivalent atoms in case of only one such component in the spectrum.

The above results thus confirm that information about the presence or absence of odd number of equivalent atoms, obtained by the application of proposed numerical criterion $N(u)$, suitably supplement the information about splitting constants and spin supplied by advanced methods[8,9].

APPENDIX

Derivation of Eqs (4) – (8) and Fig. 1

The FT of spectra with one splitting constant are

$$F(a(1/2,n)\mathrm{L}d) = \mathrm{i}\, s \cos^n(\pi a s) \exp(-|\pi s d\sqrt{3}|) \qquad (A1)$$

$$F(a(1,n)\mathrm{L}d) = \mathrm{i}\, s\, [1 + 2\cos(2\pi a s)]^n \exp(-|\pi s d\sqrt{3}|)\,. \qquad (A2)$$

With respect to the ratio in $N(u)$, the proportionality factors multiplying $y(x)$ may be omitted. Introducing $as = p$ and $d/a = v$ and taking into account the periodicity of cosine and the fact that the p roots for $(A1)$ are $1/2 + 2j$ and $3/2 + 2j$, we obtain for $a(1/2,\text{odd } n)$

$$N(\infty) = \frac{-\sum\limits_{j=0}^{\infty} \int\limits_{1/2}^{3/2} f_1(j,p,v,n)\mathrm{d}p}{\sum\limits_{j=0}^{\infty} \left[\int\limits_{0}^{1/2} f_1(j,p,v,n)\mathrm{d}p + \int\limits_{3/2}^{2} f_1(j,p,v,n)\mathrm{d}p \right]} =$$

$$= \frac{-\int\limits_{1/2}^{3/2} f_1(p,v,n)\mathrm{d}p}{\left[\int\limits_{0}^{1/2} f_1(p,v,n)\mathrm{d}p + \int\limits_{3/2}^{2} f_1(p,v,n)\mathrm{d}p\right]} , \tag{A3}$$

where

$$f_1(j,p,v,n) = (p + 2j) \cos^n (\pi p) \exp[-\pi(p + 2j)v\sqrt{3}\,]$$

and

$$f_1(p,v,n) = \{p + 2 \exp(-2\pi v\sqrt{3})/[1 - \exp(-2\pi v\sqrt{3})]\} \cos^n (\pi p) \exp(-\pi p v\sqrt{3}) .$$

Similarly for ($A2$) the p roots are $1/3 + j$ and $2/3 + j$ and we obtain for $a(1,\text{odd } n)$

$$N(\infty) = \frac{-\sum\limits_{j=0}^{\infty} \int\limits_{1/3}^{2/3} f_2(j,p,v,n)\mathrm{d}p}{\sum\limits_{j=0}^{\infty} \left[\int\limits_{0}^{1/3} f_2(j,p,v,n)\mathrm{d}p + \int\limits_{2/3}^{1} f_2(j,p,v,n)\mathrm{d}p\right]} =$$

$$= \frac{-\int\limits_{1/3}^{2/3} f_2(p,v,n)\mathrm{d}p}{\left[\int\limits_{0}^{1/3} f_2(p,v,n)\mathrm{d}p + \int\limits_{2/3}^{1} f_2(p,v,n)\mathrm{d}p\right]} , \tag{A4}$$

where

$$f_2(j,p,v,n) = (p + j) [1 + 2 \cos (2\pi p)]^n \exp[-\pi(p + j)v\sqrt{3}\,]$$

and

$$f_2(p,v,n) = \{p + \exp(-\pi v\sqrt{3})/[1 - \exp(-\pi v\sqrt{3})]\} \; [1 + 2 \cos (2\pi p)]^n \exp(-\pi p v\sqrt{3}) .$$

From (*A3*) and (*A4*) then follows that for $a(1/2,\text{odd } n)$

$$\lim_{v \to 0} N(\infty) = \frac{-\int\limits_{1/2}^{3/2} \cos^n(\pi p)\mathrm{d}p}{\left[\int\limits_{0}^{1/2} \cos^n(\pi p)\mathrm{d}p + \int\limits_{3/2}^{2} \cos^n(\pi p)\mathrm{d}p\right]} \qquad (A5)$$

and for $a(1,\text{odd } n)$

$$\lim_{v \to 0} N(\infty) = \frac{-\int\limits_{1/3}^{2/3} [1 + 2\cos(2\pi p)]^n \mathrm{d}p}{\left\{\int\limits_{0}^{1/3} [1 + 2\cos(2\pi p)]^n \mathrm{d}p + \int\limits_{2/3}^{1} [1 + 2\cos(2\pi p)]^n \mathrm{d}p\right\}} \,. \qquad (A6)$$

Enumeration of (*A5*) and (*A6*) results in values given in Eqs (*4*) – (*7*). Figure 1 was computed numerically from Eqs (*A3*) and (*A4*). Equation (*8*) results from equal probability for appearance of positive and negative values in random noise.

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