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A Modified Method of Discrete Fourier Transform Application to Electron Spin Resonance Spectral Data

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Synopsis. With the development of signal processing techniques, the spectral data obtained from analytical instruments have been collected and searched with the aid of a digital computer. Recognition of the spectrum as a wave pattern is adequate in such situations. The previous study[1] demonstrated signal processing based on this idea, involving the discrete Fourier transform (DFT) applied to ESR spectral data, and the advantages of this method with respect to memory capacity and searching speed. In that study, however, the spectral data were limited to symmetrical traces from organic free radicals in solution, in which case the ESR spectra exhibit isotropic hyperfine structure. This paper describes some modifications of the method rendering it applicable to asymmetrical traces, thus, for general use.

Modification of the Procedure

For the ESR spectral data, which are considered as a time series, values of $f(nT)$ $(0 \leq n \leq N-1)$ consisting of N samples, the discrete Fourier transform (DFT), $F(k\Omega)$ $(0 \leq k \leq N-1)$, may be calculated using the Fourier processing algorithm. The notation and details of formulation are the same as in a previous paper.[1]

Mathematically, $f(nT)$ and $F(k\Omega)$ are complex numbers, but for an actual DFT sequence, the real part of $F(k\Omega)$ is even and the imaginary part is odd due to the nature of the DFT,[2] since the values of $f(nT)$ are real numbers as obtained from experiment. In a method presented previously,[1] only the imaginary parts of $F(k\Omega)$ appear due to the nature of the symmetrical ESR pattern, and these are stored in the file. The present method, which is intended for application to asymmetrical patterns, however, requires both the real and imaginary parts of the DFT terms in addition to the k-values. This requires 50% more storage than the previous method.

For the file search, the known DFT, $P(k\Omega)$, and the unknown DFT, $Q(k\Omega)$, are treated in an expression for the absolute value and the argument,

$$\left.\begin{array}{ll} \text{known:} & P(k\Omega) = |P_k| \exp(ip_k) \\ \text{unknown:} & Q(k\Omega) = |Q_k| \exp(iq_k) \end{array}\right\}, \quad (1)$$

although the comparison procedure should be modified.

For the shift between the known and unknown traces, the absolute values, $|P_k|$ and $|Q_k|$, may be directly compared, since the absolute values of the DFT are invariant for the shifted traces.

On the other hand, the argument cannot be compared as it is. The comparison procedure is modified by utilizing the relationship that the shift in the time domain results in rotation of the argument in the frequency domain. In other words, the difference in argument angles due to the shift is linearly related to the difference in the magnetic fields to the order k, if the microwave frequency is assumed to remain unchanged. The arguments for unknown data are modified in the following manner:

$$\left.\begin{array}{l} q'_k = q_k - (k/k_{max})(q_{k_{max}} - p_{k_{max}}),\ k_{max} \neq 0 \\ q'_{k_{max}} = p_{k_{max}} \end{array}\right\}. \quad (2)$$

These equations indicate that the DFT arguments are rotated proportionally to the k/k_{max} ratio, so that the argument for an unknown k_{max} th DFT becomes equal to that for the known. Then, the modified argument q'_k can be compared with the standard argument p_k.

Results and Discussion

The applicability of the modified method was tested on asymmetrical ESR spectra. The hyperfine structure of the dialkyldithiocarbamate complex in solution is asymmetrical, because the line widths are dependent on the magnetic quantum number, m_I, of the central metal nucleus due to insufficient averaging for the anisotropy.[3,4]

The examples of ESR spectra were measured on diethyldithiocarbamate of Cu(II) in toluene under different conditions, such as for different signal heights, shifts, and signal-to-noise ratios. Traces 1a and 2a in Fig. 1 are taken as examples of known and unknown spectra, respectively.

The number of sampling points, N, is 512, since N should be a power of 2 for fast Fourier transform computation.[2] The DFT waveforms obtained are shown

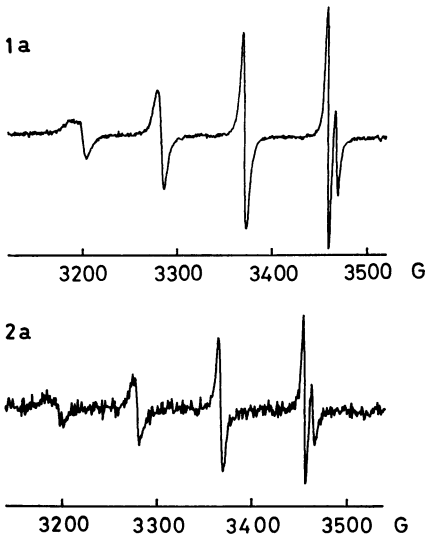

Fig. 1. Original spectral traces of Cu(II) diethyldithiocarbamate. 1a and 2a, assumed as known and unknown, are contrasted in respect of signal height, shift, and S/N ratio.

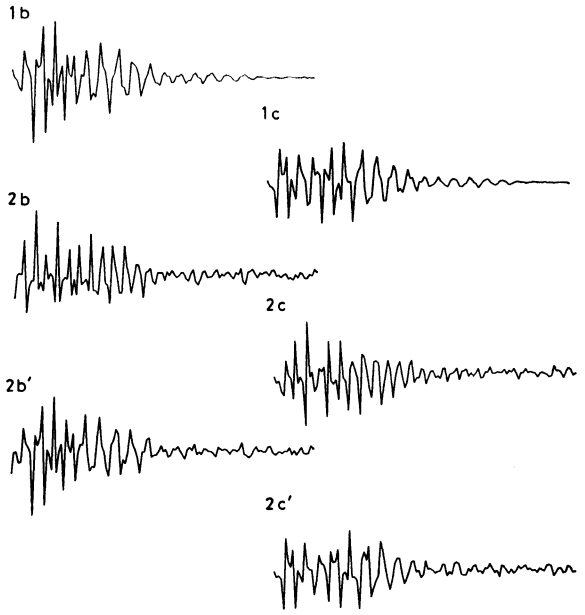

Fig. 2. DFT plots corresponding to 1a and 2a. 1b, 2b, and 2b′ are real-part plots and 1c, 2c, and 2c′ are imaginary-part plots. 2b′ and 2c′ are modified DFT plots.

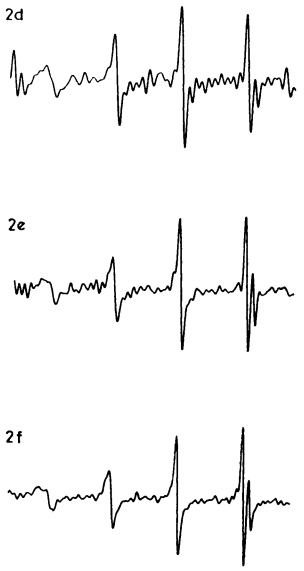

Fig. 3. The reproduced traces by inverse Fourier transform on modified DFT's 2b′ and 2c′. 2d, 2e, and 2f are transformed from 20, 40, and 60 DFT terms in the largest order, respectively.

in Fig. 2. Plots 1b and 1c are the real and imaginary parts, respectively, corresponding to 1a, and plots 2b and 2c the real and imaginary parts, respectively, corresponding to 2a. As comparisons between 1b and 2b, and between 1c and 2c indicate, these are completely different.

To obtain the unknown argument, q'_k, in Eq. 2, a problem arises from multi-valued arctangent function. Although the argument should change linearly with the magnetic field, the actual angle may differ by 2π radians.

Moreover, since the argument, p_k, is computed using the FORTRAN statement, "ATAN2(AIMAG(P(K)), REAL(P(K)))", p_k will fall within the range $-\pi$ to π. Such angles were corrected using the fact that the advanced trace shift corresponding to greater magnetic field results in a gain of the argument, as was discussed previously.[1)]

In comparing known and unknown data for search, another problem occurs: when angle p_k is near π or $-\pi$ radians, the comparison may be unsuccessfull because of deviation errors and the discontinuity of the arctangent function in these regions. For this reason, the DFT are returned as real and imaginary numbers. Therefore, the parameters obtained for the unknown data can be compared with those for the standard data.

Modified DFT plots for the unknown trace, 2a, are shown as 2b′ and 2c′ in Fig. 2. It is seen that 2b′ is almost identical with 1b, and, similarly, 2c′ with 1c, although small differences are present.

The inverse Fourier transform using some of the largest terms may reproduce the original pattern as described previously.[1)] This is demonstrated for the largest twenty, forty, and sixty DFT terms in Fig. 3. Fairly good reproduction is realized for sixty terms, but the number of terms required for an asymmetrical trace is greater than that for a symmetrical trace. The symmetrical wave pattern would be more sinusoidal, requiring fewer DFT terms. On the other hand, an asymmetrical wave pattern, being composed of higher DFT terms, might be less favorable to Fourier processing. Fourier processing, however, might still be effective with respect to data normalization for search and with a reduction of computer memory compared with the storage of original spectral values. It is believed that the present method may be applicable, in general, to analytical spectral data, as well as ESR data.

References

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