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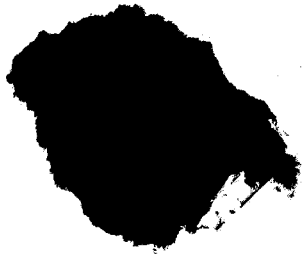
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Least Squares Curve Fitting of EPR Spectra

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Abstract

A computer program is described which uses least squares curve fitting for the analysis of electron paramagnetic resonance spectra in solution. The relevant spectroscopic constants are directly determined and their accuracy may be improved by one order of magnitude over that which is obtained from following the usual procedure. In addition, the program gives reliable intensities and works equally well in cases of incompletely resolved absorption lines. The digital apparatus which facilitates the acquisition and subsequent handling of the numerical data for a spectrum is discussed. Finally, two examples are shown to illustrate the great potential of this method for analyzing spectra. It should be easy to adapt this procedure to similar problems in other branches of spectroscopy.

Introduction

The recording of a spectrum is only the first step towards the final aim of the evaluation of the spectroscopic constants. A tedious and often complicated analysis must be done in order to extract this information from the recorded spectrum. Generally speaking, it is a problem of reducing the amount of data to a few relevant constants (1). The traditional form of this analysis of molecular spectra normally uses a very limited amount of the available data. The usual effort is concentrated toward finding the resonance frequency or field, and possibly the intensity of an absorption line, in the regions of maximum signal. But the steep ascent and descent of the signal carries as much valuable information as does the central part. This conventional method of analysis obviously becomes difficult, if incompletely resolved absorption lines are encountered. Serious errors may result, if only apparent maxima are measured since they may be shifted up to one half width from the true centers. In addition, intensity measurements are extremely difficult with this approach, and intensities are therefore often omitted. Further problems arise if the spectra have a low signal-to-noise ratio.

In order to improve the accuracy and to simplify the analysis, some mathematical procedure should be used. Such a procedure should give directly the relevant constants of the spectrum. Furthermore, it should take the complete spectrum into account. Least squares curve fitting is a powerful method which can be used in such a procedure. It is not subject to obvious personal prejudices, which can easily happen in the simple form of analysis, but of course it is still subject to program judgments.

Application of this type of mathematical treatment to the measured spectrum usually requires that extensive numerical data be fed into a computer. Careful consideration must be given to the instrumentation to facilitate the subsequent computer calculations. The usual graphical analogue recording of the spectrum is not suitable. The full accuracy of the data should be retained so that it should be directly measured in digital form and recorded on one of the standard means of input to a computer (paper tape, punched cards or magnetic tape). On-line operation is also possible, but least squares analysis requires a very large number of machine operations and this kind of treatment is best done on the largest possible computer. Since on-line operation is normally performed with small computers we have chosen to operate off-line and with magnetic tape recording because of its speed and high recording density.

One tentative use of this procedure had already given promising results (2) for microwave spectra. In this paper we show some applications of the least squares curve fitting technique to the analysis of epr spectra. We will give a description of the apparatus, then the mathematical and computational procedure and finally two examples.

Apparatus

A Varian epr spectrometer (Model V4502 with a V3400 9 inch magnet and a Fieldial Unit V-FR2503) with 100 kc/sec modulation was used for the measurements and recording of the spectra. The digital instruments attached to it consisted of an electronic counter (Hewlett-Packard, Model 5245L), a digital voltmeter (Honeywell-EI Multimeter, Model 630S), an output control unit (Honeywell-EI, Model 825), and an incremental tape recorder

(Kennedy, Model 1400). These instruments constitute a Honeywell-EI Automatic Data Logging System Model S6114. This system was designed to have the features of simultaneous integration in both the frequency and voltage channels. The voltmeter was also chosen because of its zero cross-over error and guarded differential input.

The output of the spectrometer was fed to the digital voltmeter. Two modes of operation are possible to measure the field sweep. The first mode is suitable for broad field coverage and uses the voltage from the X-axis potentiometer coupled to the Fieldial sweep unit which is proportional to the field sweep. The voltage is transferred to a frequency through a voltage-to-frequency converter (Vidar, Model 240) and is measured by the electronic counter. In the second mode, the frequency of an nmr magnetometer which is locked in to the magnetic field is directly counted.

The binary coded decimal (BCD) outputs from the voltmeter and the counter are sent to the output control, a device which converts the parallel-entered data from both sources into computer-compatible codes in a bit-parallel, serial-by-character format suitable for driving the incremental tape recorder. An additional duty of the output control is to coordinate the data flow from both sources. The system is capable of measuring a frequency and a voltage simultaneously and recording the results on the magnetic tape as a word six times per second. This word consists of a word separator code, 7 digits from the counter with a 0.1 sec gate time, the sign of the voltage and 5 digits from the voltmeter. The system performed well and efficiently collected the numerical data for subsequent computer handling.

Mathematical Procedure

The mathematical procedure of least squares curve fitting to an epr spectrum was designed for the case of a transition-metal ion complex in a liquid solution, but it may readily be adapted to related problems. In constructing a mathematical procedure one must consider the possibility of using an analytical function to describe the spectrum, which can reduce the computational effort and speed up the numerical calculations. The line shapes of the individual absorption lines are generally close to the Lorentzian, as a function of the magnetic field H

$$L(H) = I\delta/\pi [(H_m - H)^2 + \delta^2]$$

where I is the integrated intensity, δ the half width and H_m the center of the line. This line shape is only correct if confirmed by experiment and if the dispersion signal is carefully rejected in the microwave bridge. Such an assumption was verified experimentally so that an analytical procedure could be used for the least-squares fit (3). The epr spectrum was displayed as the first derivative of the absorption, as it is usually recorded. The curve fitting program needed therefore the derivative of the Lorentzian as a basic line shape function. Two different points of view were taken to specify the relevant spectroscopic constants. The spectrum was considered as either consisting of a number of individual absorption lines, each of which had a different line center H_m , intensity I_m and half width δ_m , or as arising from several similar complexes each with a spectrum split into hyperfine components due to one nucleus with spin I. The line centers of each complex were determined

according to a second-order Hamiltonian

$$H_{mk} = H_k - a_k m_I - a_k^2 [I(I+1) - m_I^2]/2H_k.$$

with a resonance field H_k and a hyperfine coupling constant a_k and with different half widths δ_{mk} but with equal integrated intensities I_{mk} for each hyperfine component. These sets of relevant constants are suggested both from theoretical considerations and by experiment. In addition to these spectroscopic constants two quantities were introduced to describe a base line shift S and a linear base line drift D . The functional dependence of the spectrum is a sum over the different complexes and the hyperfine components of derivatives of the Lorentzian with the relevant spectroscopic constants as parameters, so that we can write

$$L'(H) = \sum_k \sum_{m=-I}^I 2I_{mk} \delta_{mk} (H_{mk} - H) / \pi [(H_{mk} - H)^2 + \delta_{mk}^2]^2 + S + DH.$$

This is a nonlinear function of the parameters to be determined through the least squares fit. The problem was linearized using the analytical partial derivatives of the function $L'(H)$ for all the parameters. A reasonable estimate for the parameters must be given to start the least square curve fitting.

Since the number of data points recorded for one spectrum greatly exceeded the amount necessary for a least squares fit, the direct use of all these data would increase the computation time without gaining proportionate accuracy. A program was written which reads the information from the tape, checks it and calculates a convenient but still large number of data points by smoothing over several original points with a second order polynomial (4). This smoothing must be applied carefully as it tends to

broaden the absorption lines. Then the contribution of each point of the smoothed data to the normal equations is calculated by our least square fitting program (5). This approach was chosen to save storage room in the computer and to decrease the turn around time. The normal equations are solved and the corrections for the parameters found. Due to the nonlinearities of the line shape function, this procedure must be reiterated until the sum of the squares of the deviations becomes stable. It may sometimes happen that a better solution may be found by changing the input parameters. Such a condition is clearly shown by a bad fit with the calculated function. The least squares procedure itself does not guarantee to always find the best possible solution. For this reason we always examine the fit with a graphical display. Towards the end of the iterations, oscillatory behavior was observed in some runs. This was observed if the determinant of the normal equations is small. By reducing the calculated corrections for the critical parameters by an appropriate factor, this difficulty could be suppressed but a slightly slower convergence resulted. The standard deviations of the parameters are calculated for the final parameters in order to give some estimate of their accuracy and reliability. If 500 smoothed data points were selected, a typical least squares solution was found in 30 seconds of CDC 6600 central processor time if 20 parameters were adjusted.

Applications to EPR Spectra

Specific applications of this program will be discussed below. The first example deals with the spectra of a mixture of three different vanadyl complexes in chemical equilibrium. Main emphasis here was placed

on the determination of the relative intensities in this mixture. Since the hyperfine coupling constants and g values for analogous complexes are within close limits, the absorption lines for different complexes are largely overlapping even in the derivative presentation. A visual analysis of these spectra can give only rough estimates of the relative intensities, and even coupling constants and g values are difficult to obtain. A typical result of the computer analysis of this kind of spectra is shown in Figure 1. The crosses present only part of the measured and smoothed data points. The calculated curve fits the measured spectrum very well. At the bottom of this Figure, the magnified difference between calculated and measured points shows certain small but systematic errors. Part of these deviations can be explained by a small dispersion signal. A critical point of the analysis was the linearity of the field sweep and various types of methods were used to correct the X-axis signal. Both the X-axis corrections and removal of dispersion have been improved since this Figure was prepared. The most interesting results from the analysis were the intensity measurements. From different runs of the same spectrum it was concluded that the relative intensities determined with the least squares program are reliable to approximately one percent of the sum. The g values and hyperfine coupling constants are obtained with very good accuracy, and they easily show, for example, a systematic dependence on temperature for a single vanadyl species. This method of analysis of epr spectra will have many applications in the investigation of equilibrium constants for transition metal complexes and for their thermodynamical properties. The results for a series of vanadyl complexes will be published separately.

The second case is an example of the capabilities of this least squares program for the analysis of very poorly resolved spectra. The spectrum of an aqueous copper solution is shown in Figure 2. The crosses represent one third of the smoothed data points used for the least squares fit. The calculated spectrum gives a particularly good fit to the observed spectrum as may be seen from the enlarged scale for the errors in this spectrum. The crucial point here was the determination of the two spectroscopic constants and especially the line widths for the four hyperfine components. It is obvious that a conventional analysis could give only crude estimates, particularly for the line widths. The least squares program yielded line width values which are accurate to better than one percent. This feature opens the door for many interesting investigations.

A similar program has been written for the analysis of organic radical spectra. In this work it is necessary to use a locked-in nmr field measuring system. This program has, for example, been used on a radical with almost completely resolved hyperfine components and line widths near 0.2 gauss. The least squares coupling constants are accurate to 0.002 gauss which is close to the ability of our nmr system to follow the magnetic field. There are also obvious advantages to the use of least squares techniques for organic radical spectra.

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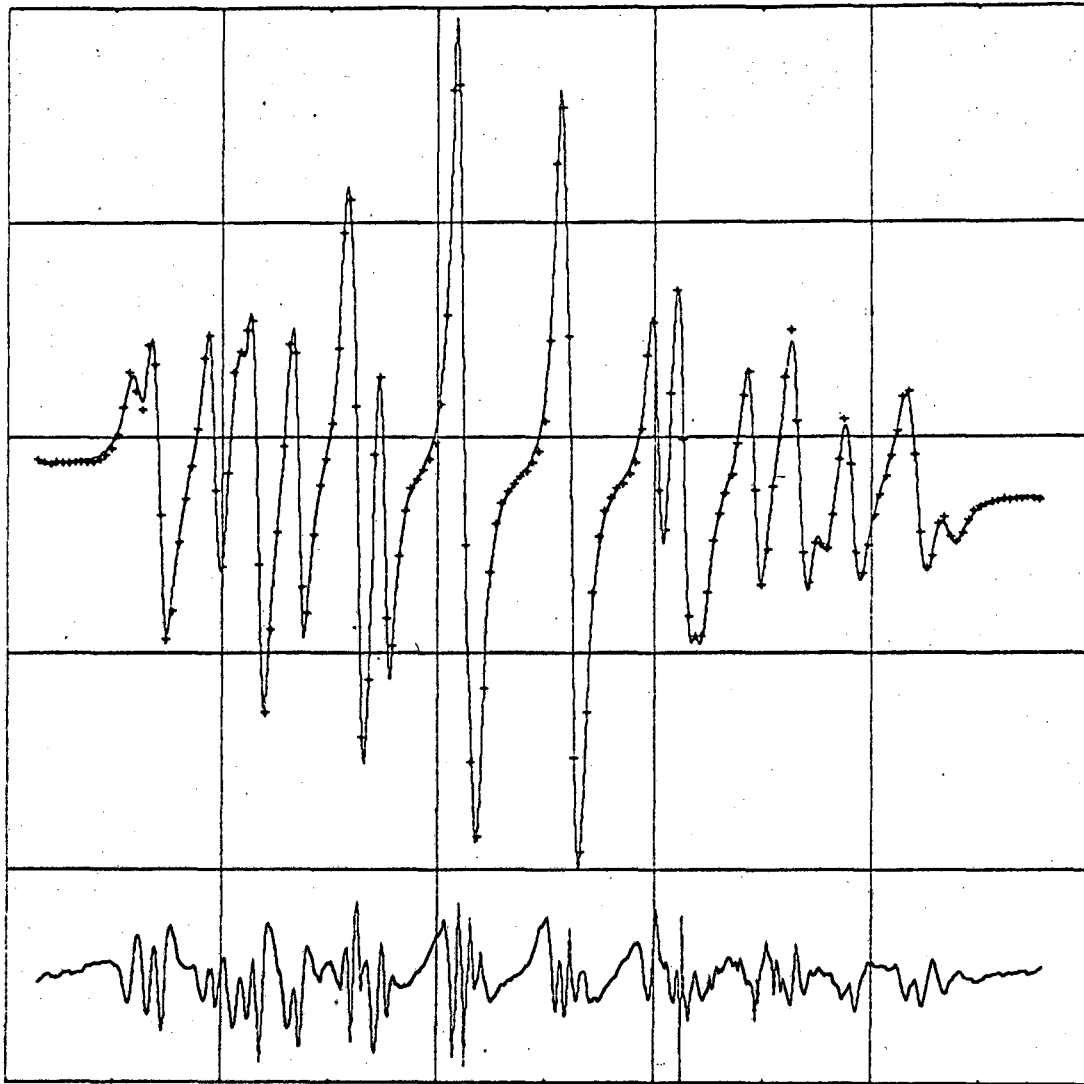
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4. A Savitzky and M. J. E. Golay, Anal. Chemistry, 36, 1627(1964).
5. A Fortran Program written for the CDC 6600 computer at the Lawrence Radiation Laboratory, Berkeley, California.

Figure Captions

Figure 1. Least squares fit to three vanadyl complexes. In the fit there are 24 line width parameters, 3 coupling constants, 3 line centers, 3 integrated intensities and 2 base line parameters. The lower error trace has the scale magnification indicated on the figure.

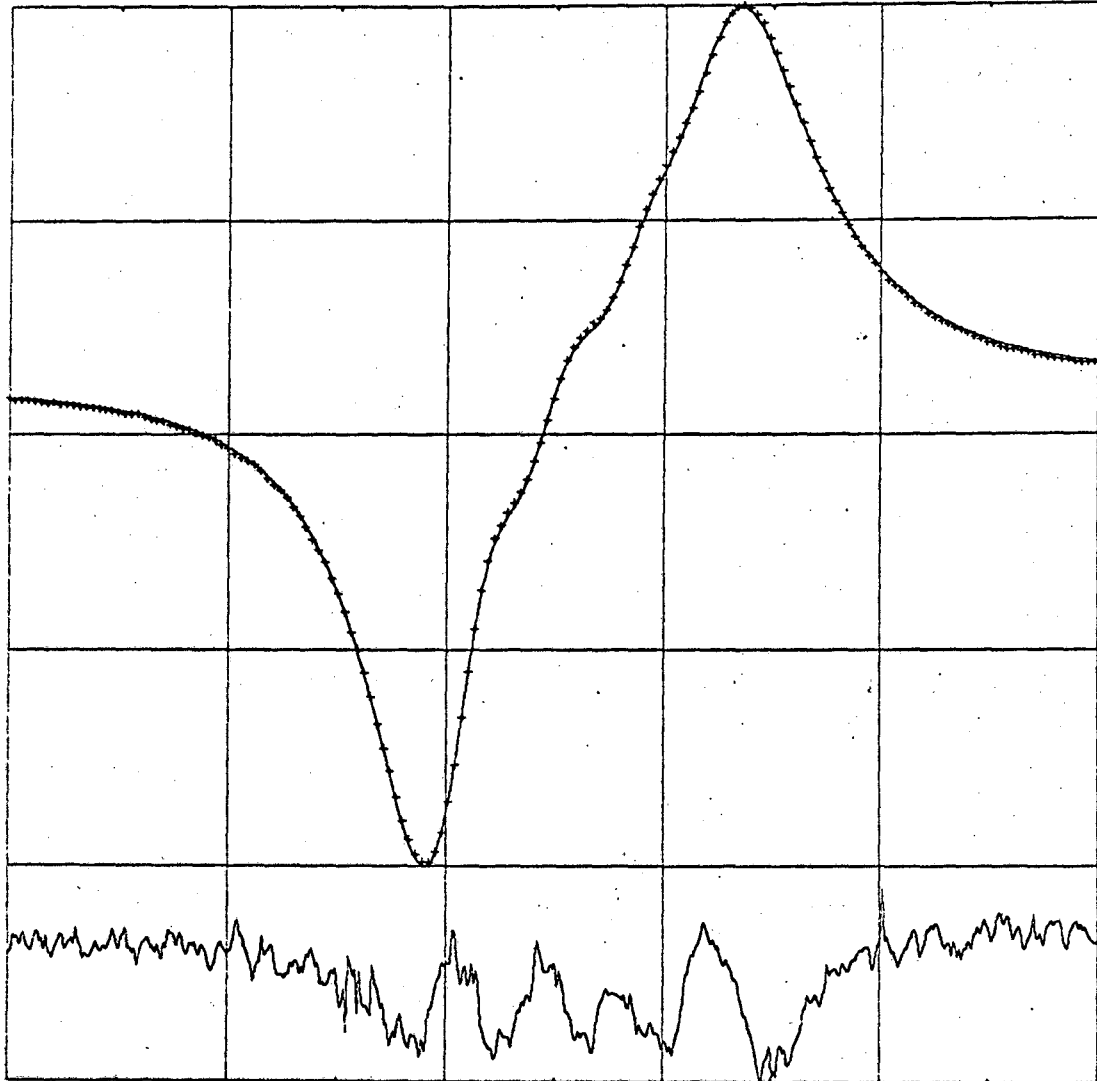
Figure 2. Least squares fit to $\text{Cu}(\text{H}_2\text{O})_6^{+2}$ at 0°C . In the fit there are 4 line width parameters, 1 coupling constant, 1 line center, 1 integrated intensity and 2 base line parameters. The lower error trace has the scale magnification indicated on the figure.



ERRORS * 2.682

XBL679-3820

Fig. 1



ERRORS *15.113

XBL679-3821

Fig. 2

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