DOE Technical Report No. DOE/PC/88921-3

Third Quarterly Report on Research Grant No. DE-FG22-88PC88921

Title: SPIN-MAPPING OF COAL STRUCTURES WITH ESE AND ENDOR

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Date: June 1, 1989

US/DOE Patent Clearance is not required prior to publication of this document.

ABSTRACT

A procedure has been developed to automate the fitting of spectral parameters in electron paramagnetic resonance (EPR) and related types of spectra. An automated system for simulating such spectra will allow us to obtain better spectral parameters with less time and effort allowing for the efficient simulation of spectra that previously were considered too complicated for routine simulation. The procedure is based on the simplex method of optimization and has been shown to greatly improve our ability to simulate complicated spectra.

GENERAL SUMMARY

The electron paramagnetic resonance (EPR) and electron nuclear double resonance (ENDOR) spectroscopies that have been used to study coal and coal model systems in our laboratory require spectral simulations in order to extract the available information from the spectra. Simulating an experimental spectrum involves varying the values of several spectral parameters until the resultant simulation best reproduces the experimental spectrum. We have developed a computer program which automates this process by mathematically comparing a trial simulation to the experimental spectrum and choosing new spectral parameters for the next trial simulation. Such a procedure has become necessary to permit routine simulation of the complicated spectral systems and spectroscopies now studied. In addition, it should allow for faster and more accurate simulation of all spectra.

OBJECTIVES AND BACKGROUND

Spectral parameters of EPR and related types of spectra are typically obtained by simulating the experimental spectrum. Trial and error fitting of the spectral parameters can be time consuming and difficult especially if there are many adjustable spectral parameters and overlapping features. Often, as a result, the number of spectra that are feasible to simulate is severely limited, and it is difficult to arrive at a satisfactory fit. This is especially true of the ENDOR spectra of coal model systems. This has led us to develop a method to assist in the fitting of simulation parameters.

We have designed a procedure to automate the fitting of spectral parameters in simulations. Each trial simulation is mathematically compared to the experimental spectrum and a new set of trial spectral parameters is chosen based on the results of all the previous simulations in the optimization. This process continues until a satisfactory simulation is obtained. The spectral parameters are chosen according to the simplex method of optimization. This method was chosen for use because its flexibility makes the program applicable to a variety of spectra. Thus, the fitting procedure can be used with any of our simulation programs to optimize the spectral parameters of EPR, ENDOR, and ESEEM spectra.

Our goal is to use the optimization procedure routinely in the course of our data analysis both as a time saving device and as a way to insure that the most accurate spectral parameters result from our simulations.

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EXPERIMENTAL PROCEDURES

The automation procedure which we have developed makes use of the simplex method of optimization. Simplex optimization can be used to vary any number of parameters to find the set of values which gives the optimum response. The response is a function of the parameters which quantifies the results at each set of parameter values. The optimum is the maximum or minimum of the response function, depending on how it is defined. In this case the parameters are the variables in the simulations, the response is some measure of the match between the experimental spectrum and the simulation created with the set of parameter values that correspond to the vertex whose response is being measured, and the optimum would represent the values of the parameters leading to a simulation as nearly identical as possible to the experimental spectrum.

Figure 1: Movement of the simplex method on a two variable response surface. ABC is the initial simplex. The vertex with the worst response, A, is replaced by its reflection, D. The simplex proceeds towards the optimum by replacing B with E, C with F, and D with G.

The simplex method employs an n -dimensional polyhedron, where n is the number of variables being optimized. This polyhedron, called a simplex, has $n + 1$ vertices, each having n coordinates which represent values of the variable parameters. For example, the simplex for an optimization of two variables (x, y) is a triangle in which each of the three vertices has two coordinates which represent values of the two variables - i.e., (x_1, y_1) , (x_2, y_2) , (x_3, y_3) ; the simplex for a three-variable optimization is a tetrahedron, and so on. After the initial simplex is determined, the response at each vertex is measured. The vertex with the worst response is replaced by its reflection through the hyperface of the remaining vertices. The response at the new vertex is measured and again the worst vertex is replaced. Repetition of this process causes the simplex to move over the response surface in the direction of the optimum as illustrated in Figure 1 for an optimization of two variables.

The modified simplex method was used in this project. It allows the worst vertex to be replaced not only by a reflected vertex but also by vertices that represent an expansion or contraction of the simplex. This allows the simplex to adjust its size in order to move more rapidly towards the optimum.

The response function used in the procedure can include any number of terms which quantify the goodness of fit between the experimental spectrum and the simulation. A least squares response provides a measure of the overall fit of the simulation. It is the sum over the data points of the squares

of the differences between the experimental and simulated intensities. We have used this term as a response function both on its own and in combination with other terms which quantify how well the simulation reproduces the extrema of the experimental spectrum.

RESULTS AND DISCUSSION

We have used the optimization procedure with a number of our simulation programs. Included are the simulations of EPR powder spectra, ENDOR spectra with isotropic and anisotropic g -values, and ESEEM spectra. It has been shown to provide us with accurate spectral parameters in a fraction of time previously needed for simulation. We are now able to more routinely simulate complicated spectra such as the ENDOR spectra that we obtain on polycyclic and polynuclear aromatic cations, our model systems for coal.

Figure 2: The ENDOR spectrum of coronene cations on silica-alumina and its simplex-generated simulation.

One of the systems we have studied using the optimization procedure is the ENDOR spectra of polycyclic aromatic cations adsorbed on the surface of activated silica-alumina. In the case of coronene cations the hyperfine splittings could be easily estimated from the experimental spectrum. Reasonable bounds in a 2 MHz range were assigned to each of the anisotropic components and the optimization was begun. Hyperfine values obtained from the optimization are 1.212, 2.598, and 6.354 MHz. Figure 2 shows that the optimized simulation matches the experimental one well in overall appearance with only small discrepancies in the intensities. We feel that the intensities are as well matched as possible given the level of theory in the present simulation program. Although this spectrum would not have been a particularly difficult spectrum to simulate, the optimization procedure worked well and saved time over a by-hand fit of the spectral parameters. It was also a very useful developmental tool for testing the procedure on an elementary case.

ENDOR spectra of the perylene cation include the effects of three sets of equivalent protons, each of which is anisotropic. The largest and smallest splittings are, like those of the coronene radical ion, easily approximated; however, overlap of the other features makes good estimation of the remaining hyperfine splittings nearly impossible. The hyperfine components are given bounds in a 2 MHz range if they can be estimated and 4 MHz if they cannot. The simulation obtained from an optimization of

these values, shown in Figure 3, resembles the experimental spectrum quite well; the notable spectral features are reproduced with the only minor discrepancies in their relative intensities. Here a direct comparison with the time and effort necessary for a manual fit is possible because we had spent a considerable

Figure 3: A comparison of the ENDOR spectrum of perylene adsorbed on silica-alumina and the simulation from the optimization procedure.

amount of time attempting to simulate this spectrum before the optimization procedure had been developed. The simplex procedure produces a slightly better simulation in a small fraction of the time and effort. This example is more representative of the types of difficult spectra which we hope to be able to simulate routinely with the automated procedure.

CONCLUSIONS AND RECOMMENDATIONS

The optimization procedure has proven to be much more efficient with respect to both human time and effort and computational time than manual fitting of spectral parameters. This permits the routine simulation of more complicated spectra and for more accurate simulation of all spectra.

We need to continue to gain experience in using the fitting procedure on a variety of spectra. Possible improvements to the procedure exist in the form of developing novel response functions which make the response a better indicator of the fit between the experimental and simulated spectra. We have explored the use of responses which include a measure of how well the particular features of the spectra such as the minima and maxima are reproduced in the simulation. These have been found to be useful in some spectral systems but, again, we need to gain more experience with them.

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