Simulation of EPR Spectra with Automatic Fitting of the Spectroscopic Parameters and of the Reorientational Correlation Time

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The simulation of EPR spectra is often necessary for the accurate determination of the principal values of the electronic Zeeman and hyperfine tensors. The automatic adjustment of these principal values and of linewidths enables us rapidly to achieve a satisfactory agreement between the observed and the calculated spectra. The usual criterion of least squares may be applied to the deviations to perform this adjustment. In two or more dimensions, a minimization algorithm derived from that of Levenberg–Marquardt is applied. In one dimension, the algorithm of the Fibonacci series has been used.

This approach lends itself to the determination of parameters, such as the reorientational correlation time, which may not be deduced by a casual inspection of spectra. It is illustrated by the example of a poly(4-vinylpyridine) gel, crosslinked by vanadyl ions. Whereas the gel is rigid at low temperatures, the motion of the paramagnetic probe modifies the spectral shapes for this gel above 260 K.

The first stage involves only the spectral parameters which are fitted from the low-temperature spectrum, using second-order perturbation formulae. The second stage requires a model of reorientation; simulations have clearly shown that a Brownian diffusion model must be preferred to a random-jump model. By keeping the spectral parameters as constants, the reorientational correlation time, as well as linewidths, can be determined at several temperatures by the above minimization.

The determination of the eigenvalues and eigenvectors of the spectroscopic tensor **g**, of the hyperfine coupling tensor **A** and, when appropriate, of the dipolar tensor **D** is done classically by EPR experiments carried out on single crystals, recording the resonance fields as functions of the orientation of the crystal.

Although certainly the most accurate, this method is not always applicable, many paramagnetic species being observable only in microcrystalline powders or in amorphous rigid matrices. In these media, the orientation of the **g** and **A** tensors is not unique; generally, all orientations are equally probable. The EPR spectra recorded in such conditions are weighted sums of spectra corresponding to these orientations. Many articles have been devoted to the analysis of spectra of paramagnetic polyoriented species leading to the above-mentioned spectroscopic parameters and are summarized in the review article of Taylor *et al.*[1] These methods are sometimes complex and yield values which have to be validated by simulation of EPR spectra.

The precision and speed of this approach are greatly enhanced by the automatic fitting of spectroscopic parameters, which is achieved by the minimization of the sum of the squares of the deviations between the experimental and calculated spectra. Several research groups have resorted to the fitting of the spectroscopic parameters from the observed spectra. This fitting becomes a challenge when the observed spectrum entails several well separated lines. In such cases the lines of the calculated spectrum must match those of the observed spectrum before a least-squares minimization may be applied.

This pattern matching problem for EPR spectra has been tackled by Jackson[2] for analysing spectra of free radicals. Having met this problem, Beckwith and Brumby[3] chose the Simplex algorithm in order to analyse hyperfine splittings in organic radicals because this algorithm avoids the calculation of derivatives. Fajer *et al.*[4] also resorted to the Simplex algorithm to determine magnetic tensors and linewidths from powder spectra, bimodal orientation distributions and multiexponential decay times and amplitudes. In order to overcome the pattern-matching problem which results in multiple minima, the Monte Carlo method has been used by Kirste[5] and the simulated annealing method by Heynderickx *et al.*[6]

The calculation of derivatives should not, however, be regarded as a stumbling block, for these derivatives may be approximated in a useful manner by finite differences. And the minimization algorithms which use derivatives are far more efficient than the Simplex algorithm.[7]

In the case of a coordination complex of trivalent uranium[8] in powder form studied in our laboratory, the broad asymmetric line of the spectrum did not raise the pattern matching difficulty mentioned above. Our previous experience with non-linear least-squares optimization for a variety of problems in physical chemistry[9] has shown that the Levenberg–Marquardt[10] algorithm is well suited for such problems. This algorithm uses derivatives at each iteration to select both a search direction and a step size. We have therefore used the latter algorithm to determine the principal values of the **g** tensor and the linewidths from the observed powder spectrum.

The present article deals with the more general case where the spin Hamiltonian entails a hyperfine interaction term as well as the Zeeman electronic term, for a paramagnetic ion or a free radical having an effective electronic spin $S = \frac{1}{2}$. The simulation program is embedded into a computer program, based on the Levenberg–Marquardt algorithm,[10] which fits the principal values of the **g** and **A** tensors according to the least-squares criterion.

To illustrate this approach, we have chosen the example of the vanadyl ion in a gel of poly(4-vinylpyridine) (P4VP) in ethanol, which we have recently studied[11] by EPR spectroscopy.

This gel may be considered as a rigid medium below 260 K, since the resonance lines do not shift as the temperature is lowered. When a reorientational motion takes place and is fast enough, the effective anisotropy of tensors **g** and **A** is gradually

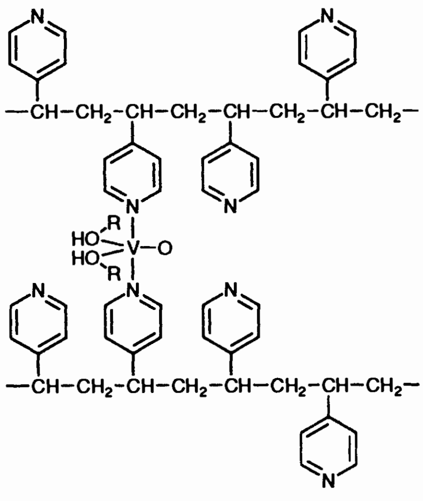

Fig. 1 Bridging of two chains of P4VP by the VO^{2+} ion. ROH denotes an ethanol molecule

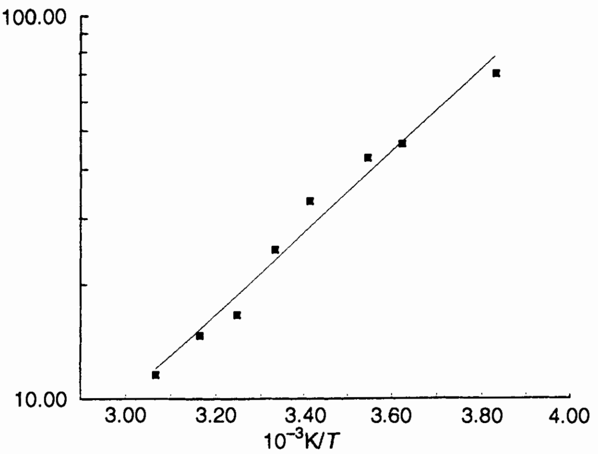

Fig. 2 Arrhenius plot of the reorientation correlation times for V–O bonds deduced from spectral simulations. The slope of the straight line obtained by least-squares fitting to the values of τ_R, obtained by the method described in the text, corresponds to an activation energy of 20.4 kJ mol^{-1}.

reduced along with the decrease of the correlation time τ_R. As a consequence, the resonance lines are shifted and broadened. Two reorientation models have been applied in order to simulate the behaviour of spectra: a reorientation by random jumps of finite amplitude and a reorientation by infinitesimal rotations (Brownian diffusion). As the former model is clearly incompatible with the observed spectral patterns, only the Brownian reorientation will be considered. Knowing the principal values of magnetic tensors, the simulations are made by means of the Bloch equations, modified by a diffusion term.[12] When the only parameter to be adjusted was the reorientation correlation time, we used the algorithm of the Fibonacci series.[13] In the case of two or more adjustable parameters, we use the algorithm and software of Gay.[14]

Experimental

Upon addition of VO^{2+} ions to a solution of P4VP in ethanol with a concentration lower than one ion for twenty monomer units, a gel is obtained, the physical properties of which depend on the degree of crosslinking and on the solvent content.[11] Interchain bonds are maintained by the VO^{2+} ions, each of which is bonded to two pyridyl groups belonging to different chains (Fig. 1). The increase in the flexibility of the three-dimensional network with temperature may be estimated from the reorientational correlation time τ_R of the V–O bond, the direction of which is the cylindrical symmetry axis of the **g** and **A** tensors (Fig. 2). This correlation was determined from spectra recorded in the X-band on a Varian E-109 spectrometer connected to an acquisition system E-935.

Discussion

The Reorientational Model.—The mobility of the V–O bond induces a reduction of the effective anisotropy of the **g** and **A** tensors which, in the X-band, becomes perceptible only for reorientational correlation times shorter than 100 ns (rigid limit). The anisotropy is practically cancelled if τ_R is lower than 0.5 ns. Between these two values, the spectral shape evolves in a complex manner and the dètermination of τ_R requires the simulation of experimental spectra.

The simulation of an EPR spectrum in the slow reorientation regime may be considered as a multisite exchange problem, each site corresponding to a particular orientation of the applied field with respect to the principal axes of the magnetic tensors. In the frame of this model, McCalley *et al.*[12] have proposed an algorithm based on the Bloch equations modified by the addition of a term rotational diffusion. For each point of the spectrum, there is a corresponding system of equations [eqn. (1)], where *m* and *j* stand for the nuclear quantum number and

$$\widehat{M_j^m}[\mathrm{i}\gamma_e(B_j - B_0) + T_{2j}^{-1} + k_j^- \tau_R^{-1}] - \tau_R^{-1}(k_{j-1}^+ \widehat{M_{j-1}^m} + k_{j+1}^+ \widehat{M_{j+1}^m}) = \mathrm{i}\gamma_e B_1 M_0^m P_j \quad (1)$$

the site respectively; $P_j = \sin\theta_j$ is the probability density of an angle θ_j between the applied field B_0 and the symmetry axis of tensors **g** and **A**. B_1 is the microwave field and B_j^m the resonance field. M_0^m is the static electronic magnetization, proportional to the concentration of the paramagnetic species, and $M_j^m = u_j^m + \mathrm{i}v_j^m$ denotes the transverse magnetization for site *j*. The expressions for constants k^-_j and $k_{j\pm1}^+$, to which exchange rates of magnetization between site *j* and adjacent sites are proportional, may be found in ref. 12.

The first step in the analysis consists in the determination of the **g** and **A** tensors of VO^{2+} by a least-squares fit of the simulated spectrum to the observed spectrum run in a rigid matrix. In this case, the Lorentzian and Gaussian lineshapes give about the same agreement with the observed spectrum (Fig. 3).

The simulated spectra in the presence of motion then depends on the following parameters: the reorientation correlation time τ_R of the V–O bond and the half-widths at half height $\Delta L_\parallel$ and $\Delta L_\perp$. We assume that the 'intrinsic' linewidth varies with the orientation of the symmetry axis of tensors **g** and **A** with respect to the applied magnetic field according to eqn. (2), where γ_e

$$(\Delta L_{\frac{1}{2}})_j = (\Delta L_\parallel{}^2 \cos^2\theta_j + \Delta L_\perp^2 \sin^2\theta_j)^{\frac{1}{2}} = (\gamma_e \pi T_{2j})^{-1} \quad (2)$$

is the electron magnetogyric ratio and T_2 the transverse electronic relaxation time, which depends on the dynamics of reorientation.

The parameters τ_R, $\Delta L_\parallel$ and $\Delta L_\perp$ are explicitly or implicitly involved in the equation system (1) and play a role in the shape and position of resonance lines. The observed linewidths are sometimes greater than the intrinsic values used. Further line broadening may thus take place, which does not depend on motion: it may be Gaussian if it stems from unresolved hyperfine interactions of Lorentzian in the case of a dipolar interaction between neighbouring paramagnetic species. This broadening is taken into account by a convolution of the calculated spectrum with a form function; our simulations suggest that the Lorentzian shape results in a much better fit than the Gaussian shape, which is not represented here.

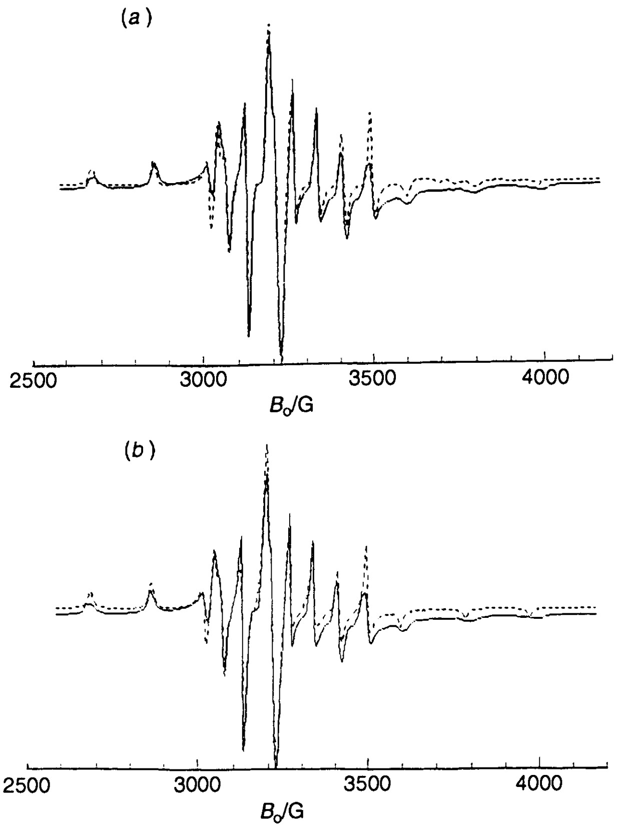

Fig. 3 VO^{2+} ion in a gel of P4VP at 153 K (rigid matrix): -----, experimental spectrum; - - - - -, spectra calculated with $A_{\parallel} = 184.2$ G, $A_{\perp} = 67.3$ G, $g_{\parallel} = 1.93786$, $g_{\perp} = 1.97396$. Halfwidths at half height are $\Delta L_{\parallel} = \Delta L_{\perp} = 6.7$ G. for a Gaussian shape [spectrum (*a*)] or $\Delta_{\parallel} = 8.8$ G and $\Delta_{\perp} = 8.6$ G for a Lorentzian shape [spectrum (*b*)]

Adjusting the Parameters.—A general scheme applies to all fitting problems, the solution of which is approached by successive iterations. Initial values of the adjustable parameters $x_1, x_2, \ldots x_n$ are known. With these values, simulation provides a spectrum in the form of a series of intensities $y_1, y_2, \ldots, y_p$ corresponding to the sampled values $B_1, B_2, \ldots B_p$ of the applied magnetic field.

The intensities observed are $z_1, z_2, \ldots, z_p$; the parameters $x_1, x_2, \ldots, x_n$ will be modified in such a way that the deviations $z_1 - y_1, z_2 - y_2, \ldots, z_p - y_p$ are minimal. The least-squares criterion leads to the most probable parameters if errors affecting measures have a Gaussian distribution and if the mathematical model is perfectly suited.

The sum of the squares of deviations is a twice-derivable function of the adjustable parameters and the minimization algorithm of Newton could, in principle, be applied. It consists of determining the minimum of the quadratic function having the same value of the function, the same gradient and the same second-derivatives or Hessian matrix. In practice, only an approximation of the gradient is determined, by finite differences. The Levenberg–Marquardt algorithm[10] uses the fact that, in the case of a sum of squares, the matrix of the partial derivatives dy_j/dx_i, or Jacobian, provides an approximation of the Hessian matrix. However, in this algorithm, the adjustable parameters may take any value. It is known, *a priori*, that the i-th parameter must be included within some interval (a_i; b_i). The subroutine BSOLVE by Ball[15] implements an algorithm stemming from the previous one, which takes into account the boundary constraints. The approximation of the Hessian matrix used in the two algorithms mentioned above neglects the second derivatives d^2y_j/dx_idx_k. As long as the deviations $z_j - y_j$ are important, a significant error results in the calculated Hessian matrix. We have therefore used the software N2FB of Gay[14] which is also specialized for the minimization of a sum of squares, which implements an algorithm in which a far better approximation of the Hessian matrix is calculated.

When only one parameter is to be adjusted, the algorithm of the Fibonacci series[13] in which derivatives do not play a role, was used.

A complete computer program for parameter fitting entails three parts.

(1) The *executant* monitors the whole calculation. It performs all preliminary calculations, then calls the optimizer and then does the final calculations and calls the subroutine responsible for production of a graphic representation of both the observed and calculated spectra.

(2) The *optimizer* determines approximations of the gradient and Hessian matrix of the sum of the squares of the deviations and modifies the adjustable parameters by successive iterations in such a way that this sum decreases. It calls the simulator at each iteration.

(3) The *simulator* calculates the deviations $z_j - y_j$ for the current values of the adjustable parameters.

Our software is written in FORTRAN 77[16] and executed on a CRAY XMP-28 computer. Execution times range between a few seconds for the rigid matrix and a hundred seconds in the case of the Brownian rotation for 90 values of the θ angle.

Automatic differentiation of algorithms,[17] which we have not yet applied for these simulations, would enable us to obtain a variant of the simulator which calculates not only the deviations, but also the Jacobian matrix dy_j/dx_i. Another type of software, N2GB also by Gay,[14] takes advantage of this Jacobian in order to determine a better approximation of the Hessian matrix and to reach more rapidly the optimal parameters.

Application to the Rigid Matrix.—Knowing that the **g** and **A** tensors have the same principal axes, one can determine, for a given orientation of the paramagnetic species: (*a*) the resonance fields corresponding to the various values of the nuclear quantum number m_I, thanks to an analytical formula derived from a second-order perturbation calculation[1]; (*b*) the corresponding transition probabilities.

The expression enabling the calculation of a spectrum for a given orientation of the applied magnetic field with respect to the principal axes of the magnetic tensors is integrated numerically over the spherical coordinates θ and φ if at least one of the two tensors is non-axial, and over θ only if both tensors are axial.

For a non-axial system, there are nine adjustable parameters: three principal values for each magnetic tensor and three linewidths. Their number is reduced to six for an axial system, or even five in the case of the vanadyl ion. In the latter case indeed, the principal value $A_{\parallel}$ is deduced from the separation between the extreme parallel bumps of the spectrum with good precision.

The fits (see Fig. 3) have shown that in a rigid matrix, the lineshape is intermediate between the Gauss–Laplace (unresolved hyperfine structures) and the Lorentz–Cauchy (electronic relaxation) shapes. A typical fit entails fifty iterations.

Application to Reorientational Motions.—The above described computer program, designed to fit spectra in the slow reorientation regime, is practically applicable for correlation times of between 5 and 100 ns in the case of vanadyl. Above the upper limit, the spectrum is practically independent of τ_R. For a P4VP gel swollen by ethanol, this range of correlation times corresponds to temperatures in the range 260–320 K.

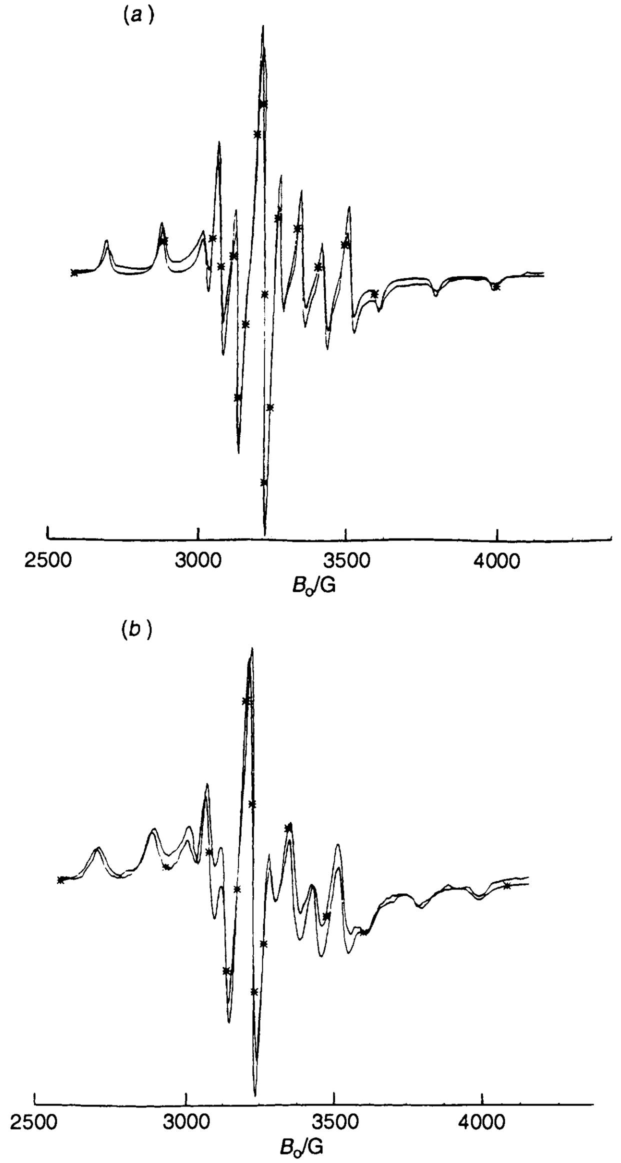

Fig. 4 Experimental (----) and calculated (✱—✱—✱—) spectra of the vanadyl ion in a P4VP gel swollen in ethanol; $T = 261$ K, $\tau_R = 7.6 \times 10^{-8}$ S (*a*), and $T = 308$ K, $\tau_R = 1.66 \times 10^{-8}$ S (*b*)

Since the tensors **g** and **A** are, in principle, independent of the temperature, the adjustment of τ_R by use of the algorithm of the Fibonacci series[13] gives a good agreement between the observed and calculated spectra. This agreement is significantly improved when the intrinsic linewidths $\Delta L_{\parallel}$ and $\Delta L_{\perp}$ and a further Lorentzian broadening, expressing the interactions between electronic spins, are introduced as adjustable parameters and the algorithm of Gay[14] used. Fig. 4 displays examples of the good agreement obtained with the latter method. A typical fit entails twenty iterations.

Acknowledgements

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