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Abstract

Two types of automatic fitting procedures for EPR spectra of disordered systems have been developed, one based on matrix diagonalisation of a general spin Hamiltonian, the other on 2nd order perturbation theory. The first program is based on a previous Fortran code complemented with a newly written interface in Java to provide user-friendly in- and output. The second is intended for the special case of free radicals with several relatively weakly interacting nuclei, in which case the general method becomes slow. A least squares' fitting procedure utilizing analytical or numerical derivatives of the theoretically calculated spectrum with respect to the g-and hyperfine structure (hfs) tensors was used to refine those parameters in both cases. 'Rigid limit' ESR spectra from radicals in organic matrices and in polymers, previously studied experimentally at low temperature, were analysed by both methods. Fluoro-carbon anion radicals could be *simulated*, quite accurately with the exact method, whereas automatic fitting on e.g. the c-$C_4F_8^-$ anion radical is only feasible with the 2nd order approximative treatment. Initial values for the ^{19}F hfs tensors estimated by DFT calculations were quite close to the final. For neutral radicals of the type XCF_2CF_2• the refinement of the hfs tensors by the exact method worked better than the approximate. The reasons are discussed. The ability of the fitting procedures to recover the correct magnetic parameters of disordered systems was investigated by fittings to synthetic spectra with known hfs tensors. The exact and the approximate methods are concluded to be complementary, one being general, but limited to relatively small systems, the other being a special treatment, suited for S=½ systems with several moderately large hfs.

Keywords: automatic fitting, EPR spectra, fluorocarbon radicals

1. Introduction

Single crystal measurements are among the most straightforward but not always applicable methods to determine the values of magnetic couplings in solids. It is for instance difficult to obtain single crystals of biochemical materials. In other cases the paramagnetic species are intentionally trapped in a disordered matrix or in a frozen solution. The ESR lines are then usually broadened by the anisotropy of the magnetic couplings. Some data, e.g. the position of the paramagnetic species in the lattice that a single crystal analysis can provide, are difficult to extract from a powder. However, a considerable amount of information can often be extracted from a spectral analysis even from disordered systems as shown in many preceding works e.g. concerned with:

- Free radicals or other S=½ species with anisotropic g and hyperfine couplings
- S>½ species with zero-field splittings

In some cases a visual analysis is sufficient, in other refinement by computer simulation is required. A large number of simulation methods have been developed during the last 40 years, the earlier ones, e.g. in [1-3] being based on perturbation theory. Methods based on exact diagonalization of the spin Hamiltonian have been described more recently, see for example [4-6]. The mathematical form (1) used in this work is also adopted in many of those programs for the calculated spectrum.

$$S(B, A) = C\int_0^{\pi} \sin\Theta d\Theta \int_0^{2\pi} d\varphi \sum_{p->q} I_{pq} f(\frac{B - B_{pq}}{w}) \tag{1}$$

The summation is over the transitions between the magnetic states p and q. I_{pq} is the transition probability and B_{pq} is the resonance field. The microwave frequency ν is constant and the spectrum $S(B,\boldsymbol{A})$ is calculated as a function of the applied magnetic field B. The shape of the spectrum is determined by a set of parameters $\boldsymbol{A}$ representing e.g. the components of g- and hyperfine coupling tensors, line width w, and total intensity C. The line shape $f(x)$ is usually approximated by 1st derivatives of Gaussian, Lorentzian or Voigt functions.

Automatic fitting procedures to EPR spectra of disordered solids have only recently appeared following the initial work by Misra [7] using the non-linear least-squares method. In this method the function (2) is minimised [8].

$$\chi^2 = \sum_{i=1}^{M} \left[\frac{S_i - S(B, \mathbf{A})}{\sigma_i} \right]^2 \tag{2}$$

S_i is the experimental ESR spectrum measured in M points. The Hellmann-Feynman theorem (3) was applied to obtain analytical expressions for the derivatives entering the equations of the non-linear least squares method. The parameter A_k is a component of the coupling tensors in eq.(1).

$$\frac{\partial E_p}{\partial A_k} = < \Psi_p \,|\, \frac{\partial H}{\partial A_k} \,|\, \Psi_p > \tag{3}$$

This approach is applicable when the energies E_p and wavefunctons ψ_p are obtained by diagonalization of the spin_Hamiltonian matrix. It provides a possibility of obtaining analytical derivatives of the energy differences E_p - E_q used to calculate the resonance field, and consequently of the coupling tensors. An alternative method to obtain analytical derivatives when the resonance fields B_{pq} were obtained by perturbation theory was recently published [9].

In this study we employ automatic fitting procedures for disordered systems using both matrix diagonalization and perturbation methods in two least-squares programmes. The first method is intended for general spin systems. A graphical interface for input generation and output display has been added after the programme was first described. [10]. The programme was slow when applied to the analysis of fluorocarbon radical ESR spectra with anisotropic hyperfine couplings from several ^{19}F nuclei in this work, however. A perturbation method was therefore developed to treat this special case. Fitting of fluoro-carbon anion radicals containing up to 8 F atoms was feasible with this 2nd order, approximate, treatment.

The magnitudes and relative orientations of ^{19}F hyperfine and g-tensors can in favorable cases be obtained entirely by an analysis of experimental data [11]. Several studies have shown, however, that the tensor axes from ^{19}F in fluorocarbon radicals need not have any relation to the geometric structure, contrary to the case of H in hydrocarbon radicals [12,13]. DFT calculations have recently proved useful to obtain the principal values and directions of ^{19}F hyperfine coupling tensors of perfluorocarbon radicals [14]. The principal values *and* directions from theory were therefore employed as initial parameters for the analysis of the experimental spectra of this work.

2. Theoretical methods

Two methods were employed to calculate the intensities and positions (I_{pq},B_{pq}) in eq. (1), one exact, based on diagonalization of the full spin Hamiltonian matrix, the other approximative using 2nd order perturbation theory. The refinement of the parameters, i.e. the elements of e.g. the g- and hyperfine coupling tensors, by the non-linear least squares method proceeded by similar methods in the two cases. The non-linear least squares fit procedures of the exact and approximate methods followed those described by Press et al. [8]. In this method derivatives, $\frac{\partial S}{\partial A_k}$, of the spectrum (1) with respect to parameters A_k must be provided.

2.1 Matrix diagonalization method

The *exact* method based on matrix diagonalization of the full spin Hamiltonian has been described previously. In brief it includes terms of the type $\mu_B\mathbf{BgS}$, $\mu_N g_N\mathbf{BI}$, **SDS**, **SAI**, **IQI**, and $\mathbf{S_1JS_2}$ allowing fits of the **g**-, **D**-, **A**-, **Q**-, and **J**-tensors, the latter including both isotropic and anisotropic interactions between two electronic spins. The energies were calculated by diagonalization of the Hamiltonian matrix expressed in the basis $|L\rangle = |m_1 m_2 ... m_N\rangle$, where similar symbols are used for totally N electron and nuclear spins. The matrix was set up automatically by obtaining the quantum numbers m_1 to m_N needed to compute the elements $\langle L|H|L'\rangle$ by a division algorithm sweeping through the L and L′ indices. The derivatives, $\frac{\partial S}{\partial A_k}$, of the spectrum (1) with respect to parameters A_k were calculated analytically with the help of the Hellmann/Feynman theorem (3) to reduce computation times as described in [10,16]. The Hamiltonian matrix elements are linear functions of the parameters A. The derivatives $\partial H/\partial A_k$ were therefore computed by putting A_k=1, A_j=0, j≠k in the Hamiltonian matrix. The intensity of the transition I_{pq} is a generalized expression of that by Kottis and Lefebvre [15] for a disordered system, taking into account all (N) magnetic particles, electrons as well as nuclei and with the microwave magnetic field perpendicular to the static field [16].

2.2 2nd order perturbation method

The *approximate* method is a development of a procedure described previously [17] to simulate EPR spectra of disordered anisotropic S=1/2 systems with hyperfine and nuclear interactions due to several (n) nuclei:

$$H = H_e + \sum_{i=1}^{n} H_{ai} + H_{Ni} + H_{qi} \tag{4}$$

In contrast to the classical treatment by Lefebvre and Maruani [2] a nuclear quadrupole term H_{qi} is taken into account for each nucleus with I>½ in addition to the hyperfine coupling, H_{ai}, and nuclear Zeeman, H_{Ni}, terms. The quadrupole term is unnecessary for this application, but was retained to avoid changing a functioning programme. The electron Zeeman energy $E_e = \mu_B B g M_S$ dominates over the energies obtained from (H_{ai}+H_{Ni}+H_{qi}), but no assumption is made about the relative magnitudes of the individual terms. These energies are calculated by diagonalizing a perturbation operator for each nucleus of the following form

$$H_i = \mathbf{I}_i \mathbf{A}_i \mathbf{u} S_u + \mathbf{I}_i \mathbf{Q}_i \mathbf{I}_i - B\mu_N g_i \ell \mathbf{I} \tag{5}$$

Here $\ell = \mathbf{B}/B$ and $\mathbf{u} = \mathbf{g}\ell / g$ are unit vectors along the applied and effective static field; the latter is the quantization axis for the electron spin with the component S_u. The g-factor is obtained from $g^2 = (\mathbf{g}\ell)^2$. The tensors **g**, $\mathbf{A}_i$ and $\mathbf{Q}_i$ need not have parallel axes. The procedure to obtain the transition fields B_{pq} and intensities I_{pq} in eq.(1) due to all nuclei to 2nd order is described in [17c]; here *p* and *q* refer to the nuclear states within the M_S = ½ and -½ manifolds, respectively. The intensities were corrected by the factor $|G|^2/g$ in Appendix A taking g-anisotropy into account for possible future applications. An automatic procedure to treat equivalent nuclei (nuclei of the same kind and with equal principal values *and* axes of the **A**-tensors) has been implemented in the present work.

The procedure when applied to an arbitrary number of equivalent I=½ results in a set of coupled spin angular moments with their multiplicities. The procedure was introduced to correctly calculate the 2nd order contributions to the energy and to reduce the computation times e.g. for the c-$C_4F_8^-$ radical anion in this work. The procedure is applicable also for I>½ nuclei provided that the nuclear quadrupole interaction is neglected, but this feature has not been employed in the present work.

Derivatives $\frac{\partial S}{\partial A_k}$ of the spectrum (1) with respect to parameters A_k were calculated as follows. Equation (6) was used to obtain the derivatives with respect to the g-tensor components g_{ij} analytically.

$$\frac{\partial S}{\partial g_{ij}} = \frac{CB_g}{2gw}(l_i u_j + l_j u_i)\int_0^{\pi} \sin\theta d\theta \int_0^{2\pi} d\varphi \sum_{p->q}^{M} I_{pq} \frac{\partial f}{\partial x} \tag{6}$$

Here $B_g = \frac{h\nu}{g\mu_B}$, w is the line-width and $\frac{\partial f}{\partial x}$ the derivative of the line-shape function. The latter is obtained analytically for the Gauss and Lorentz functions, numerically for the additionally employed Voigt line-shape function.

Analytic expressions for the derivatives with respect to the line-width have been given previously for a Gauss or Lorentz function [7]. The derivative with respect to the line-width for a Voigt function was obtained with the help of (7) . This enters as a factor in the expression for $\frac{\partial S}{\partial w}$ in the least-squares fit of the line-width w to experiment [10].

$$\frac{\partial f}{\partial w} = -\left(2f(x) + x\frac{\partial f}{\partial x}\right)\Big/ w \tag{7}$$

Derivatives $\frac{\partial S}{\partial A_k}$ with respect to the components of the hyperfine coupling tensors were calculated numerically in the approximate theory because of difficulties to implement analytical formulae in the computer code. The potential option of optimizing nuclear quadrupole couplings was not made use of because of lacking experimental data to test the theory.

2.3 Line shapes

The line-shapes were approximated by first derivatives of Gaussian or Lorentzian functions, in the approximate theory also by the derivative of the Voigt profile. The last function was calculated as a convolution of the two first. The shape is determined by the Lorentzian to Gaussian line-width ratio.

4. Programming

Two separate programmes were prepared, one based on the matrix diagonalization method, the other on 2nd order perturbation theory. The code for the least- squares fit using the Levenberg-Marquardt method was taken from the literature [8]. A free-ware code was employed to diagonalize the spin Hamiltonian matrix. Except for a graphical interface these and other parts of the programmes are in Fortran 77 with a few recent additions in Fortran 90.

4.1 The XFit programme

. A graphical user interface has been implemented in the Xfit program described in previous reports [10,16]. The interface was written in Java using its graphic library. The input data, referred to below as the simulation file, are given in fields labelled to be understandable for users familiar with ESR terminology. The fields are contained in three main windows that are opened separately. The first window provides the number of orientations for the numeric integration of eq.(1), the microwave frequency and an initial estimate of the linewidth. Another window is used to give initial resonance parameters for the species under study. The **g**- tensor is specified with the principal values and direction cosines for the principal axes. The same format is employed for the **A-**, **D-** ($S>½$), and Q- ($I>½$) tensors. Nuclear spin values and g_N factors are automatically inserted by opening an auxiliary window showing the periodic table and pressing the corresponding atom symbol. Different isotopes can be selected. More than one species can be specified, allowing coupled systems to be analyzed. . A coupled system is specified by introducing another set of **g- A-**,**D** and **Q**-tensors plus a **J**-tensor for the interaction between the two species. The principal values of the **A**-,**D** and **Q**- and **J**-tensors are in MHz units. By opening a summary window, the simulation file can be viewed in the style used in the previous version of Xfit [10,16]. Buttons for saving and reloading the file are available on the three main windows. A simulation file can be edited after loading or by using a text editor on the saved file. A directory containing the spectrum to be fitted is opened by a button that can be activated from the main windows. A button to start the Xfit program becomes active after the simulation file has been completed and the experimental file has been loaded. It is also possible to start the process by loading ready-made simulation files from a directory. Output and diagram files can be viewed after Xfit stops. An output file contains the initial and final parameters. The experimental and and computed spectra are displayed in the same diagram.

4.2 The 2ndorderFit programme

The programme is a development of a simulation program for free radicals described previously [17 a-c]. That program was written with the purpose of analyzing esr spectra for the case when the quadrupole and hyperfine couplings of a nucleus are of comparable magnitude but much smaller than the electronic Zeeman term of an unpaired electron with S=1/2. The matrix of the perturbation spin Hamiltonian (5) containing the hyperfine, nuclear quadrupole and Zeeman terms is diagonalized for each nucleus separately, thus the matrices to be diagonalized will be small. To give accurate results, the perturbation due to (5) has to be small compared with the electronic Zeeman term. Second order corrections, taking into account equivalent nuclei, were therefore included in the version employed in this work [17c]. A routine that computes effective spin values and multiplicities for an arbitrary number of equivalent nuclei with nuclear spin ≥ ½ was implemented for the purpose.

The line positions and intensities due to all nuclei were computed in a loop with only temporary storage of the contributions from each nucleus. This made it difficult to implement analytical formulae $\frac{\partial S}{\partial A_k}$ with respect to the components of the hyperfine coupling tensors in the computer code. Derivatives were therefore calculated numerically. The Voigt line-shape function, employed in addition to the Gauss and Lorentz functions was calculated by the Gautschi algorithm, using a Fortran translation of a published code. [18]. Numerical differentiation was employed in this case to give the quantity $\frac{\partial f}{\partial x}$ used in (6) and to compute $\frac{\partial f}{\partial w}$ according to eq (7). The experimental spectrum file to which the fit is made consists of two columns giving the field and the intensity. A third column giving the uncertainty σ_i at each point in eq.(2) can be added. Spectrum parts arising from overlapping species are eliminated from the fit by assigning artificially large σ_i values to those regions. This method was applied to the centre of the spectrum in figure 4 for example. The field is in Gauss units.

5. Fitting of ESR Spectra

Fittings of ESR spectra by the method employed in Xfit, is limited to systems with relatively small dimensions of the spin Hamiltonian matrix. The chain-end radical fluorocarbon radical, $XCF_2CF_2\bullet$ detected in the Nafion polymer, with hfs due to two F_α and two F_β ^{19}F nuclei with matrix size of 32x32 is the most complex system that so far could be examined with this method. It is therefore of interest to compare this method with approximative ones based on perturbutation theory for the analysis of free radical spectra that often contain hfs from several nuclei. The fittings of fluorocarbon radical ESR spectra reported here are based on recent experimental and theoretical studies of chain-end [19,20] and cyclic fluorocarbon radicals [14]. The analysis of hydrocarbon radical spectra in disordered systems is much more studied, in part by our own work [17c] and is therefore not considered here.

5.1 $XCF_2CF_2\bullet$

The full line spectrum in Fig. 1, obtained after chemical/UV-light treatment of a perfluorinated polymer, Nafion, has been assigned to a chain end radical, $XCF_2CF_2\bullet$ [19].

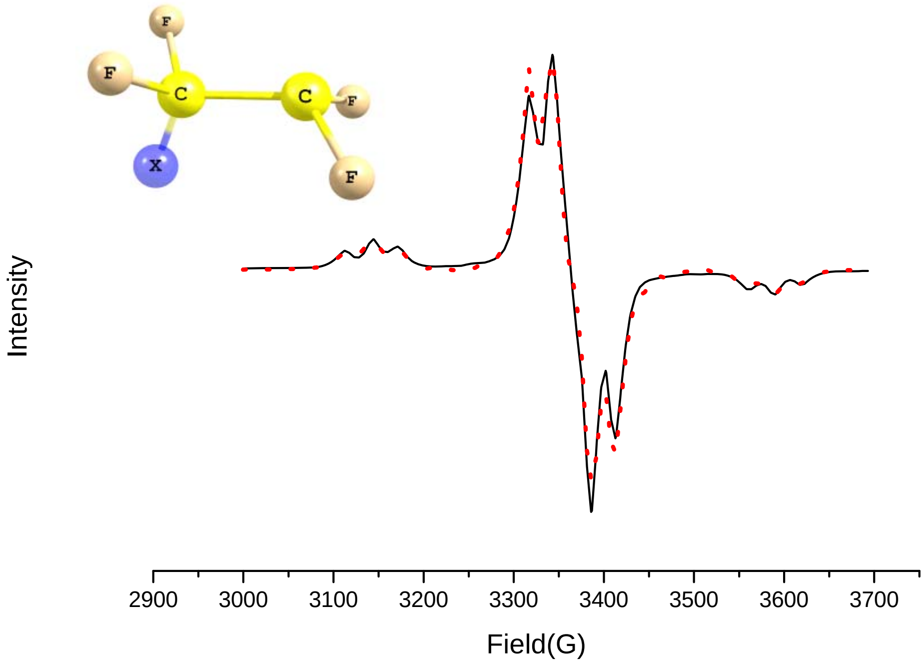

Figure 1. Experimental (line) and fitted(dot) X-band spectra of $XCF_2CF_2\bullet$ *detected in the Nafion polymer with parameters* $A_{\alpha1} = A_{\alpha2} = (622, 50, 50)$ *MHz,* $A_{\beta1}= (95.9, 71.5, 42.0)$ *MHz,* $A_{\beta2}= (82.1, 65.6, 83.6)$ *MHz, line-width = (34.5, 26.8, 23.9) MHz (Lorentz). The axes of the 622 MHz components of the* $F_{\alpha1}$ *and* $F_{\alpha2}$ *are inclined* 12.6^0 *according to the fit, in agreement with DFT calculations. The axes of the* A_α*- and* A_β*- tensors were taken from DFT results.*

The dotted line is a fit to the experimental using Xfit. The central features could be explained only by assuming non-parallel axes for the two αF indicating a non-planar geometry about —$CF_2^\bullet$. The hyperfine coupling tensors were obtained by combining the predictions of DFT calculations with the ESR results [20]. The principal values of the ^{19}F hyperfine coupling tensors were adjusted, while the principal axes obtained from DFT were used as initial parameters to start the fitting procedure.

Fittings with the Xfit program for this system were computationally demanding; each spectrum required several hours of computation time. It was therefore difficult to test if the final parameters were unique or depended e.g. on the guessed initial values used to start the automatic fitting procedure. Automatic fitting procedures based on perturbation theory [9] are better suited for such tests, particularly in free radical systems with several interacting nuclei. In the present work ESR spectra of the —$CF_2^{\bullet}$ radical fragment were synthesized by using matrix diagonalization and 2nd order perturbation methods. An attempted least squares analysis of the synthesized spectra with the 2ndorderFit program shown in Figure 2 succeeded relatively well with collinear hyperfine coupling tensor axes of the two F atoms.

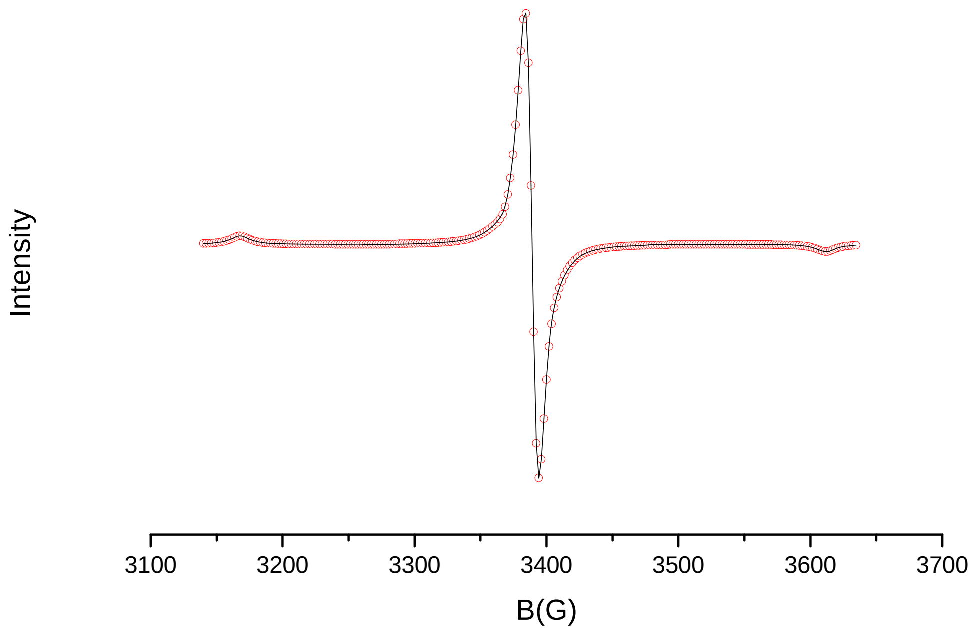

Figure 2. synthetic (black line) and fitted (dot) X-band spectra of —$CF_2^{\bullet}$ *radical fragment with parameters* $A_{\alpha 1} = A_{\alpha 2}$ *(18, 18, 222) G. The axes of the 222 G components of the* $F_{\alpha 1}$ *and* $F_{\alpha 2}$ *hyperfine coupling tensors are parallel.*

This case occurs for the four pairs of F atoms in the ESR spectrum of c-$C_4F_8^-$ discussed below. The axes of the A_z = 222 G tensor components of the $F_{\alpha 1}$ and $F_{\alpha 2}$ atoms in XCF_2CF_2• were, however, estimated to be inclined 12.6^0 [19]. The assumed axial symmetry with A_x=A_y =18 G was not recovered in the fit to the —$CF_2^•$ model spectrum but the values deviated by ca ±10 G. The failure to give right values can in part be attributed to a smearing of the central portion of the spectrum when the tensor axes are not parallel so that features characteristic of the 18 G coupling becomes unresolved. Another, more fundamental reason is that a coupling term involving the hyperfine couplings occurs between the two F_α nuclei in 2nd order perturbation theory [21]. This is not taken into account in the simulation code employed here, except for completely equivalent nuclei occurring for example in the case considered in Figure 2. The perturbation method as applied here is therefore not suited to analyze the X-band spectra with anisotropic hyperfine couplings of inequivalent nuclei of the relatively large size found for the XCF_2CF_2• radical. This is in agreement with the finding that the ESR spectrum of $^•CF_3$ radicals in a disordered solid matrix cannot be completely accounted for by the classical simulation technique developed by Maruani [2,11]. Simulation or fitting using matrix diagonalization are the most straightforward although computer demanding methods to handle such systems, characterized by sizeable anisotropic hyperfine couplings due to two or more inequivalent nuclei. . For the $C_4F_8^-$ anion radical showing hfs from 8 ^{19}F nuclei in the next section the perturbation method is the only alternative, however, although the hfs is of the same size as for the XCF_2CF_2• radical.

5.2 c-$C_4F_8^-$

The experimental ESR spectrum in Figure 3, obtained after γ-irradiation of 1 mol % *c*-C_4F_8 in a matrix of 2-methyltetrahydrofuran (MTHF) at 77 K contains several components. The features present in both wings have been attributed to the rigid-state spectrum of *c*-$C_4F_8^-$ [14(b)]. The central part of the *c*-$C_4F_8^-$ spectrum is obscured by a strong quintet pattern from the matrix radical. The two sharp lines, on each side of the centre are due to hydrogen atoms. The simulated spectrum was obtained by the matrix diagonalization method using hyperfine coupling tensors from DFT theory [14(b)]. The simulation was time consuming, ca 60 hours, making parameter fitting impractical with this method.

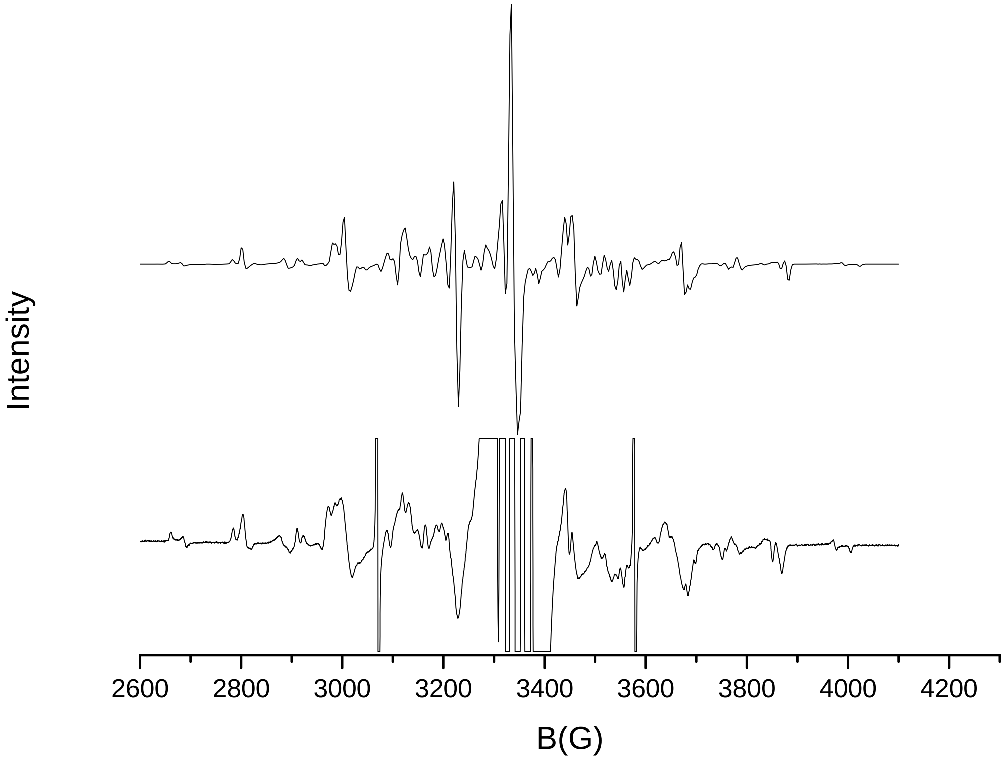

Figure 3. Experimental (below) and simulated (above) X-band ESR spectra of c-$C_4F_8^-$. The central part of the c-$C_4F_8^-$ spectrum is obscured by a strong quintet pattern from the matrix radical. The two sharp lines, on each side of the center are due to hydrogen atoms. The simulated spectrum was obtained by the matrix diagonalization method using the hyperfine coupling tensors from DFT theory [14(b)]. Only the line-width and the amplitude were adjusted to the experimental spectrum.

The method based on 2nd order perturbation theory was therefore applied, in least-squares fittings to the experimental spectrum of $C_4F_8^-$, with one example shown in Figure 4.

The theoretically predicted D_{4h} symmetry leads to complete equivalence of the (F1,F6), (F2,F5), (F3,F8), and (F4,F7) pairs of ^{19}F nuclei. The 2nd order corrections to the hyperfine couplings could therefore be correctly calculated for each pair as described earlier. The different pairs have different principal axes, but the principal values of the hyperfine couplings should be the same. This was not achieved in the fittings, since point group symmetry was not taken into account in the computer code. When only the principal values of the (F1,F6) pair were fitted as in Figure 4, **A1**=**A**6 =(107.0, 135.8, 208.9) G was obtained to be compared with the values (113.1 113.7 218.8) G of the pairs that were not fitted. The symmetry was broken to approximately the same extent when the principal values of two or all four pairs were varied. The quality of the fit did not improve, compared to that in Figure 4, however.

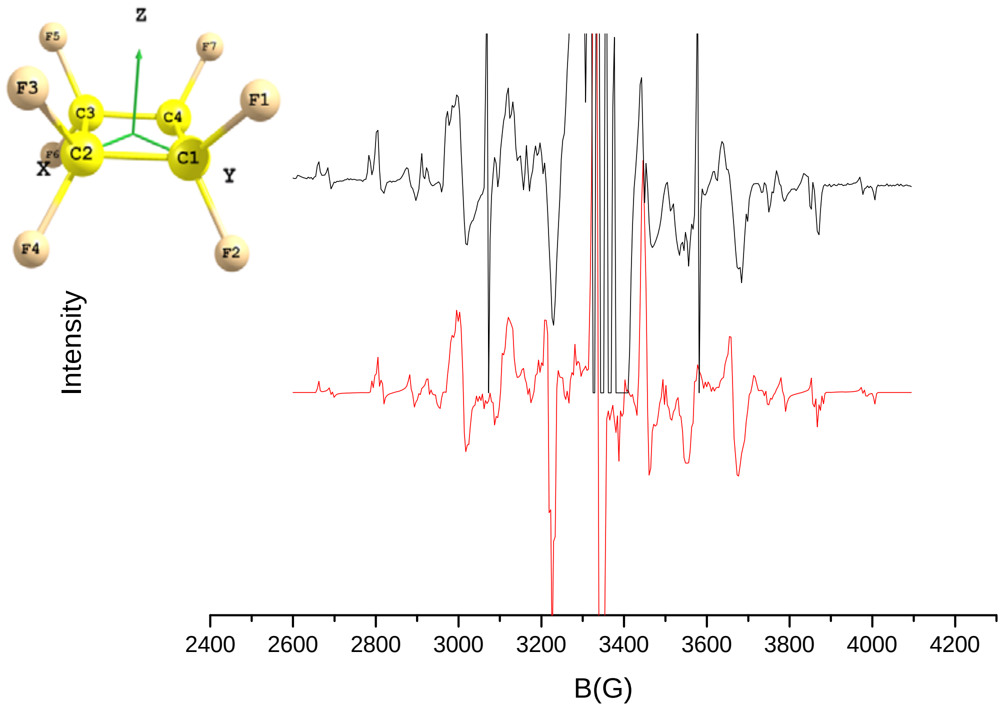

Figure 4. Experimental (below) and simulated (above) X-band ESR spectra of c-$C_4F_8^-$. The central part of the c-$C_4F_8^-$ spectrum is obscured by a strong quintet pattern from the matrix radical. The two sharp lines, on each side of the center are due to hydrogen atoms. The simulated spectrum was obtained by the 2nd order perturbation method. The principal values of the (F1,F6) pair were fitted to give ***A1*****=*****A****6 =(107.0, 135.8, 208.9) G while the values (113.1, 113.7, 218.8) G of the pairs that were not fitted were from DFT theory [14b].*

6. Discussion

The methods of matrix diagonalization of a general spin Hamiltonian matrix and 2nd order perturbation theory are complementary techniques in the least-squares procedures used here and by other authors. The first method, first developed by Misra [7] in seminal work is general but limited to relatively small systems; it was used e.g to analyse the zero-field splitting of a Mn^{2+} complex from its 249 GHz powder spectrum by the least squares method. A recently published treatment [9] employing perturbation theory, is better suited for systems with hyperfine couplings due to several nuclei or with a moderately large zero-field splitting in case S>½. In both methods analytical expressions for the derivatives of the fitted spectrum with respect to the spin Hamiltonian parameters were employed. Misra [7] may have been the first to employ analytical derivatives using the Hellmann-Feynman theorem (3) to obtain these derivatives in the context of ESR spectral analysis of disordered systems. This method is employed also here in the Xfit programme. Analytic derivatives were generated automatically in the programme by Soulié and Berclaz [9] based on perturbation theory. In both cases the extra computational load to obtain the derivatives together with the spectrum (1) appears to the relatively low, compared to that for numeric differentiation. It seems reasonable that the speed of analysis could be shortened considerably by employing these analytic procedures in place of the numeric treatment that until recently have been the only option. Surprisingly, in this work the implementation of analytical procedures was easier with the matrix diagonalization method, than with the perturbation method. Accordingly, the fitting of hyperfine coupling tensors had to be done using numerical derivatives in the latter case; the fitting of the g-tensor and the line-width using analytical formulae (6) and (7) proceeded significantly faster.

Fittings to synthesized spectra initiated with parameter values far from the true ones might produce wrong solutions for these values. With the accurate method for computing the spectrum and its derivatives with respect to the parameters used in the matrix diagonalization method, the wrong values probably reflect the presence of several or imprecisely determined minima of the function (2). Thus, the lack of clear features for the

50 MHz (18 G) principal component in the $RCF_2C^{\cdot}F_2$• radical [20] makes it difficult to obtain precise coupling values when the line-width is of comparable magnitude. A rather trivial condition to obtain accurate parameters by fitting is therefore that a change of the parameters should affect the shape of the spectrum. Another, more fundamental problem became obvious in this work during the analysis of the —$CF_2^{\bullet}$ model compound using perturbation theory. The neglect of a 2nd order cross term involving products of the anisotropic couplings of the two F atoms [21] in the applied method is considered to be an additional reason for not regaining the 18 G coupling used for the model 'experimental' spectrum. An experimental remedy by measurements at higher fields, where 2nd order terms are suppressed may not always be available. In the present implementation 2nd order shifts of the line positions due to the anisotropic hyperfine couplings of equivalent nuclei were taken into account in fittings to the model spectrum in figure 2, and the experimental spectrum in Figure 4 due to the *c*-$C_4F_8^-$ anion radical. An analysis with the same approximate method of the $RCF_2C^{\cdot}F_2$• radical with non-parallel axes does not seem recommendable.

7. Conclusions

Two types of automatic fitting procedures have been applied to extract anisotropic ^{19}F hyperfine coupling data from fluorocarbon radical X-band EPR spectra in disordered matrices. One is based on matrix diagonalization of a general spin Hamiltonian, the other on 2nd order perturbation theory. The exact and the approximate methods are complementary, the first being general, but limited to relatively small systems, the second a special treatment, suited for $S=½$ systems with several moderately large hfs. The hyperfine couplings due to ^{19}F in this work were quite large, resulting in poor fits with the approximate method that became pronounced when the principal axes did not coincide. The approximate method might, however be well suited to analyze X-band ESR spectra of hydrocarbon radicals with their usually small proton hyperfine couplings. A set of simulation programs that rely on the second order treatment of the spin Hamiltonian written in APL language [24] provides an alternative in this case.

Although initial values of the principal values of e.g. the hyperfine coupling tensors can be deduced reasonably from the powder spectra, the corresponding directions of axes can hardly be obtained experimentally. In this case molecular orbital calculations are helpful, as these directions can often be predicted quite well, and were used for the analysis of the *c*-$C_4F_8^-$ radical anion studied here and also the $XCF_2C^{\cdot}F_2$• radical.

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Appendix A: EPR intensity for S=½ species due to g-anisotropy in disordered systems

The intensity of an ESR transition in a single crystal has been given as [22]

$$|G|^2 = 0.25\mu_B^2 B_1^2 \left(\mathbf{rg^2r} - (\ell\mathbf{g^2r})^2 / g^2\right) \tag{A1}$$

The factor takes into account the anisotropy of the g-tensor on the intensity for a single crystal with the static and microwave magnetic fields along the unit vectors $\ell = \mathbf{B}/B$ and $\mathbf{r} = \mathbf{B}_1/B_1$, respectively. For a polycrystalline sample the intensity is obtained by performing the averages in equations (A2) and (A3).

$$\overline{\mathbf{rg^2r}} = \sum_{i=1}^{3}\sum_{j,k=1}^{3} g_{ij} g_{ik} \overline{r_j r_k} = \frac{1}{2}\left(Tr(\mathbf{g}^2) - g^2\right) \tag{A2}$$

$$\overline{(\ell\mathbf{g}^2\mathbf{r})^2} / g^2 = \sum_{m,n=1}^{3} u_m u_n \sum_{j,k=1}^{3} g_{mj} g_{nk} \overline{r_j r_k} = \frac{1}{2}\left(\mathbf{ug^2u} - g^2\right) \tag{A3}$$

Here $\mathbf{u} = \mathbf{g}\ell/g$ has been introduced.

(A2) and (A3) follow from the expression (A4), obtained from equations given in [15] under the normal experimental condition with B perpendicular to B_1.

$$\overline{r_j r_k} = ½(\delta_{jk} - l_j l_k) \tag{A4}$$

According to this treatment the $|G|^2$ factor of a disordered solid is given by equation (A5)

$$|G|^2 = 0.125\mu_B^2 B_1^2 \left(Tr(\mathbf{g^2}) - \mathbf{ug^2u}\right) \tag{A5}$$

This does not take into account the 1/g factor suggested by Aasa and Vänngård [23]. Thus, the intensities I_{pq} in equation (1) should be multiplied by the factor $|G|^2/g$. The factor is nearly constant in the applications considered in the present work, but has been implemented in the 2nd orderfit code for possible future applications.