2.1. Introduction

Electron paramagnetic resonance is a powerful technique for examining the environment of unpaired electrons in organic free radicals or transition metal complexes, present in biological systems or materials. To perform these measurements meaningfully and quantitatively requires knowledge of the nature of the analytical instrument. Consequently, this chapter focuses on the instrumental and experimental aspects of EPR. Throughout the chapter, maximal use will be made of references to other readily available sources for theoretical background, calculations of spectral parameters, structure of EPR instruments, crystal growth and so on. Also incorporated, the description of the crystal structures of the host lattices namely Diaquamalonatozinc(II) (DAMZ), Diaquamalanato(1, 10 phenanthroline)zinc(II)(DAMPZ), Zinc sodium sulphate hexahydrate (ZSSH), cis-Diaquabis(1,10-phenanthroline-N,N')zinc(II) (1,10-Phenanthroline-N,N')bis(thiosulfato-S)zincate(II) Monohydrate (DPZSZM), Dipotassium diaquabis(malonato-κ²O,O')zinc(II)dihydrate (PMZD), Bis(ammonium) tris(hexaaquamagnesium) tetrakis(hydrogen phosphite) (BAMP).

EPR is a technique for measuring the absorption of electromagnetic radiation by a sample with unpaired electron spins. A variety of paramagnetic centers can be studied by EPR, including organic free radicals, radiation-induced radicals, paramagnetic transition metal complexes, triplet species, defect centers in solids and conduction electrons metals. Irradiation with a second frequency during an EPR experiment can provide much more detailed information about the spin system than can the usual single-frequency
measurement. Generally, EPR studies of the paramagnetic samples can be carried out either by creating paramagnetic centers in diamagnetic host lattices or by doping a paramagnetic ion in a diamagnetic host lattice [1-2]. The reason for doping is twofold: First, the pure paramagnetic complex may not be stable in that configuration; hence study of that environment for the transition metal ion is not possible. Secondly, the pure complex, if it exists gives broad resonances due to dipolar-dipolar interaction between the paramagnetic ions, since the ions are too close to each other. The most common method to produce paramagnetic centers in a diamagnetic lattice can be attained by radiation damage using UV, X-ray or $\gamma$-rays. These techniques may be employed in pure host lattices or doped host lattices. However, in this thesis, paramagnetic centers produced by this irradiation technique are not considered. So no further details about the irradiation techniques are discussed.

In addition, single crystal EPR studies provide valuable information about the structural defects and orientation of various spin Hamiltonian matrices with respect to bond directions in the complex, which is not accessible by powder or solution spectra. However, doping of a paramagnetic impurity in a paramagnetic host lattice yields spin lattice relaxation times by measuring the line width of the resonances as a function of sample temperature. In this case, it is assumed that the paramagnetic lattice is EPR silent at room temperature.

2.2. Instruments

2.2.1. UV-Vis Spectrometer

The optical spectrum has been recorded for powder samples at room temperature using Varian Cary 5000 UV-VIS NIR spectrophotometer.
Electrons exist in energy levels within an atom. These levels have well defined energies and electrons moving between them must absorb or emit energy equal to the difference between them. In optical spectroscopy, the energy absorbed to move an electron to a more energetic level and/or the energy emitted as the electron moves to a less energetic energy level is in the form of a photon (a particle of light). Because this energy is well-defined, an atom's identity can be found by the energy of this transition. The wavelength of light can be related to its energy. It is usually easier to measure the wavelength of light than to directly measure its energy. In atomic absorption spectroscopy, light is passed through a collection of atoms. If the wavelength of the light has energy corresponding to the energy difference between two energy levels in the atoms, a portion of the light will be absorbed. The relationship between the concentrations of atoms, the distance the light travels through the collection of atoms, and the portion of the light absorbed is given by the Beer-Lambert law.

### 2.2.2. Fourier Transform Infrared spectrometer (FTIR)

The FTIR spectra are recorded using Shimadzu FTIR-8300/8700 spectrometer, in the frequency range 4000-400 cm\(^{-1}\). The measurements are made using almost transparent KBr pellets containing fine powdered samples at room temperature. Fourier transform infrared spectroscopy is employed to identify the nature of the bonding between the various groups and the metal ions present in the complex. Depending on the environment around the functional group, a shift in the stretching and bending vibrations is generally observed. Fourier Transform-Infrared Spectroscopy (FT-IR) is a molecular characterization technique that provides information about the chemical make up of materials. The FT-IR technique gives a rapid means of identifying substances,
characterizing contaminants and comparing materials. The technique is applicable to a broad range of samples including polymer systems.

2.2.3. EPR spectrometer

In the beginning, magnetic resonance spectroscopy, both NMR and EPR, started off as continuous wave (CW) techniques and the early instruments used a field or frequency sweep modality to satisfy the resonance condition. In CW EPR, one uses a fixed frequency of very low power (a few tens of mW) and employs a MW or RF bridge circuit which allows the MW/RF flux, after controlled attenuation, to pass through a magic-T or circulator before being coupled to a resonator, usually of the reflection type. Balancing of the bridge assures that there will be no power in the detector arm containing the crystal detector when there is no resonance absorption in the cavity. The EPR spectrometers are classified into S, X, K, Q and E bands depending upon the irradiating microwave frequency and their classifications given Table 2.1.

The most commonly used EPR spectrometer is in the range of 9-10 GHz (X-band). However, advances in electronics have facilitated the development of spectrometers working at frequencies ranging from several hundred MHz to several hundred GHz. EPR spectrometers are working at 1-2 GHz (L-band) and 2-4 GHz (S-band), 8-10 GHz (X-Band), 35 GHz (Q-band) and 95 GHz (W-band) [3-7].

Multifrequency EPR (1 GHz to 100 GHz) provides an experimental route to study the magnetic interactions in paramagnetic materials. The elucidation of parameters like g, A, D, E, and Q, which characterize these interactions, can lead to an understanding of atomic and molecular structure at magnetic sites. High sensitivity and the ability to
investigate small-scale order in powders, polymers, and frozen solutions are key
advantages of EPR over a wide frequency range. EPR spectroscopy, combined with
techniques such as spin trapping, can be used to detect and follow free radical reactions in
biological systems. High-frequency (95 GHz) EPR instrumentation provides the ability
to study very small samples and often provides extraordinary resolution and
discrimination between similar species. Low-frequency EPR spectrometers and special
microwave detectors and circuitry provide the capability to obtain spectra from living
animals and perfuse organs, including the concentration of oxygen in tissues, redox
metabolism, distribution of spin-labeled molecules and biophysical measurement.
Special materials are developed for sensitive EPR probes of both oxygen and nitric oxide
(NO) in tissues.

A typical EPR spectrometer (Fig. 2.1) consists of an electro magnet to generate a
variable magnetic field and a generator of microwaves. Further details about the
functions of various components can be found in the literature [6].

2.2.3. (a) Microwave system

A klystron is normally used to generate microwaves with a frequency adjustable in
the interval 9-10 GHz. The power is about 200 mW maximally and can be attenuated by
0-50 dB.

In order to make the irradiation sufficiently strong and the detection sufficiently
sensitive, the sample is placed in a resonance circuit (cavity). The cavity consists
essentially of a microwave waveguide closed in both ends and tuned so that stationary
waves can arise in it. The cavity is connected through a waveguide to the microwave
generator (klystron) and an adjustable screw is used to adjust the impedance. The cavity has a hole where the sample is placed. The resonance frequency of the cavity is affected by the sample and by the glass tube. The Q-value of the cavity is in the range 2000-8000. A detector crystal rectifies the reflected wave from the cavity that arises when the resonance absorption of the sample occurs. An automatic frequency control locks the frequency of the klystron to the resonance frequency of the cavity.

2.2.3. (b) Magnet

The magnetic flux density of the magnet is regulated with a Hall controller. The field is connected to the X axis on the recorder. The center of the field and the field scale (mT per cm) is set at the console.

2.2.3. (c) Magnetic field modulation

In order to increase the sensitivity and resolution, one uses magnetic field modulation. A coil at each side of the cavity is fed with a current of 100 kHz that can give a modulation with a maximum amplitude of about 2-4 mT. Consequently the detector gives a signal with the frequency 100 kHz whose amplitude is proportional to the derivative of the absorption with respect to the field. The modulation must be optimized with regard to signal/noise and resolution.

2.2.3. (d) Amplifier system

The signal with the frequency 100 kHz is detected in a phase sensitive amplifier and is directed to the Y axis of the recorder. The receiver gain, the time constant of the filter and the offset can be adjusted at the console.
2.2.3. (e) Samples

The sample is held in a quartz tube with an inner diameter of 3 mm. Quartz glass is necessary to avoid unwanted signals from impurity. In the cavity, there is not only an oscillating magnetic field that induces the transitions sought for but also an electric alternating field. In a water solution, one gets a dielectric absorption in the water (compare with a microwave oven) that reduces the Q-value of the cavity and accordingly the strength of the signal. For water solutions, one can use a tube with an internal diameter of about 1mm. Frozen solutions on the other hand absorb much less, and one can use a normal 3mm tube. Crystal rotations are done with the help of a goniometer, with an accuracy of ± 1 degree. To record spectra at 77 K, one place a Dewar vessel filled with nitrogen liquid in the cavity, in which sample was inserted.

2.3. Crystal structure of the host lattices

A brief introduction of the various host lattices employed in this thesis is presented here. The detail crystal structures are discussed in their respective chapters. All the crystals are prepared with five different concentrations (0.05, 0.10, 0.15, 0.20 and 5.0%) of the dopant and are grown at room temperature (300 K) by slow evaporation method.

Crystals of Diaquamalonatozinc(II) (abbreviated as DAMZ) was synthesized according to procedure given in the literature [8]. DAMZ crystal is monoclinic and belongs to the C\textsubscript{4h} point group. The space group is C\textsubscript{2/m} with four molecules per unit cell. The lattice parameters are: \( a = 1.258 \text{ nm}, b = 0.741 \text{ nm}, c = 0.723 \text{ nm}, \beta = 119.0^\circ \). A water molecule is coordinated to each metal ion and the central C of the malonate ion lies on
the mirror plane. Cu(II) doped DAMZ single crystals are grown by doping copper sulphate.

The Diaquamalonato(1,10-phenanthroline)zinc(II) crystals are reported to be monoclinic [9], of space group C2/c, with unit cell parameters a = 1.034, b = 0.967Å, and c = 1.548nm, β = 105.72°, and Z = 4. Each malonate ligand forms a six-membered chelate ring with one Zn(II) ion in a boat-type configuration; the malonate ligand acts only as a chelating ligand and does not act as a bridge between metal atoms. Cu(II) doped DAMPZ single crystals are grown by doping copper sulphate.

Zinc sodium sulphate hexahydrate belongs to the group of Tutton’s salts. These salts have monoclinic crystal structure with space group P2$_1$/n. There are two molecules per unit cell and the unit cell parameters are a = 0.613, b = 1.223, c = 0.909 nm, β = 104.78° [10]. Six water molecules in the form of a compressed octahedron surrounded the Zn ion in ZSSH. In all Tutton’s salts, the shortest Zn-O bond is unique, whereas the longest bond depends on the nature of M’ and M”. VO(II) doped ZSSH single crystals are grown by doping vanadyl sulphate.

\[\text{[Zn}(\text{C}_{12}\text{H}_8\text{N}_2)(\text{H}_2\text{O})_2]\text{[Zn}(\text{S}_2\text{O}_3)_2(\text{C}_{12}\text{H}_8\text{N}_2)]\text{H}_2\text{O}} \text{ (DPZSZM) belongs to the triclinic crystal class, having space group P}^{-1}\text{ with unit cell parameters } a = 1.0545, b = 1.2924, c = 1.4856 \text{ nm, } \alpha = 90.60^\circ, \beta = 100.06^\circ, \gamma = 99.47^\circ \text{ and contains two molecules per unit cell [11]. The structure consists of cationic } [\text{Zn}(\text{C}_{12}\text{H}_8\text{N}_2)(\text{H}_2\text{O})_2]^{2+} \text{ and anionic } [\text{Zn}(\text{S}_2\text{O}_3)_2(\text{C}_{12}\text{H}_8\text{N}_2)]^{2-} \text{ moieties. VO(II) doped DPZSZM single crystals are grown by doping vanadyl sulphate.}

The Dipotassium diaquabis(malonato-κ²O,O’)zincate dihydrate (hereafter abbreviated as PMZD) crystals obtained belong to monoclinic with space group C2/m.
PMZD possesses $C_{2h}$ symmetry. The unit cell dimension values are $a = 0.9397$, $b = 1.088$, $c = 0.7628$ nm, $\beta = 115.03^\circ$ and $Z = 2$ [12]. The central metal ion is coordinated by two water molecules and two malonate ligands, with an elongated octahedral environment is synthesized according to procedure given in the literature. Fe(III) doped PMZD single crystals are grown by doping ferrous sulphate.

Bis(ammonium) tris(hexaaquamagnesium) tetrakis(hydrogenphosphite) crystal have monoclinic crystal structure with space group C2/m. There are two molecules per unit cell and the unit cell values are $a = 3.436$, $b = 0.704$, $c = 0.617$ nm, $\beta = 91.349^\circ$ [13]. The coordination around the two independent Mg(1) and Mg(2) atoms is quite similar. Each Mg atom is strongly coordinated by six water molecules, forming a slightly distorted octahedron. One of the Mg atoms is located on a site with 2/m symmetry, whereas the other Mg atom and the P and N atoms occupy sites with m symmetry.

2.4. Crystal growth

Crystal growth is the major stage of a crystallization process, after the nucleation stage. It occurs from the addition of new atoms, ions, or polymer strings into the characteristic arrangement, or lattice, of a crystal. In the nucleation stage, a small nucleus containing the newly forming crystal is created. Nucleation occurs relatively slowly as the initial crystal components must "bump" into each other in the correct orientation and placement for them to adhere and form the crystal. After crystal nucleation, the second stage, growth, rapidly ensues. Crystal growth spreads outwards from the nucleating site. In this faster process, the elements which form the motif add to the growing crystal in a prearranged system, the crystal lattice, started in crystal
nucleation. As first pointed out by Charles Frank in 1951, perfect crystals would only grow exceedingly slowly; real crystals grow comparatively rapidly because they contain dislocations, which provide the necessary growth points. Some important features during growth are the arrangement, the origin of growth, the interface form (important for the driving force), and the final size. When origin of growth is only in one direction for all the crystals, it can result in the material becoming very anisotropic (different properties in different directions). The interface form determines the additional free energy for each volume of crystal growth.

In order to get full information from EPR measurements, one prefers single crystals rather than powders and solutions. Hence, a brief discussion about crystal growth is mentioned. The main technique involved in crystal growth is slow evaporation method. This is the simplest way to grow crystals and works best for compounds which are not sensitive to ambient conditions in the laboratory. Prepare a solution of the compound in a suitable solvent. The solution should be saturated or nearly saturated. Transfer the solution to a clean crystal growing dish and cover. The covering for the container should not be air tight. Aluminum foil with some holes poked in it works well, or a flat piece of glass with microscope slides used as a spacer also will do the trick. Place the container in a quiet out of the way place and let it evaporate. This method works best where there is enough material to saturate at least a few milliliters of solvent. Growing crystals by allowing a saturated solution of a material to lose solvent by evaporation is one of the simplest methods [14, 15].

The choice of solvent is an important factor that determines the growth of a crystal from solution. Growth of a large crystal is virtually impossible unless a solvent is
found in which the solute is appreciably soluble. In the present work, water is used as the solvent for all crystal growth. No additives are added to the solution except the dopant. The rate of growth depends on the temperature at which the solution is maintained. At higher temperatures, the growth rate will be high. All the crystals are grown at room temperature.

2.4.1. Powders and glasses

In powder and glasses, the paramagnetic ions are randomly oriented. Hence the powder spectrum is a combination of statistically weighed average of all molecules having different orientations. The powder line shapes have been described in detail in the literature [16-18]. The line shapes of EPR spectra with different g and A values is given in Fig. 2.2. In general, the principal values of g and A can be evaluated from powder data. However, complications will arise in powder line shapes, when more than one type of species is present and/or when hyperfine lines overlap, and especially so when the tensors do not coincide. The first two complications can be circumvented to some extent by measuring the spectra at two different frequencies, say X and Q and sorting out the field-dependent and field-independent terms in the Hamiltonian. Some times power saturation techniques [19, 20] and temperature variation may also help in this respect. However, principle direction cosines of the magnetic tensors could not be obtained from powder data. In those cases, measurements have to be done on single crystals. Nevertheless, powder data can be obtained easily with a single measurements and often act as a useful check in the interpretation of single crystal data in EPR and X-ray crystallography.
2.4.2. Solutions

A molecule in a solution can tumble, if the rotation is fast enough, the anisotropy of the g-value-and hyperfine coupling will be averaged as well as the related tensor (g, A). In the absence of hyperfine values, a single is observed. However, in a frozen solution, the shape of the EPR spectrum will be similar to that of a powder sample, if the solution is in the region between the two limit cases (free rotation, frozen solution).

2.4.3. Single crystal

Single crystal, also called mono crystal, is a crystalline solid in which the crystal lattice of the entire sample is continuous and unbroken to the edges of the sample, with no grain boundaries. The opposite of a single crystal sample is an amorphous structure where the atomic position is limited to short range order only. In between the two extremes, polycrystalline and paracrystalline phases exist, which are made up of a number of smaller crystals known as crystallites. Because of a variety of entropic effects on the microstructure of solids, including the distorting effects of impurities and the mobility of crystallographic defects and dislocations, single crystals of meaningful size are exceedingly rare in nature, and can also be difficult to produce in the laboratory under controlled conditions. The factors during crystal growth which affect the size of the crystals are solubility of compound in the solvent chosen for recrystallization, the number of nucleation sites, mechanical agitation to the system, and time.

The detailed procedure for the evaluation of the principal values of magnetic tensors from single crystal measurements have been reported [21-26]. The method consists of measuring the variation of $g(\theta)^{2}$ for rotations about three mutually
perpendicular axes in the crystal, which may coincide with the crystallographic axes or are related to the crystallographic axes by a simple transformation.

The Hamiltonian for a paramagnetic system, including only the electron Zeeman and hyperfine terms can be expressed as

$$\mathcal{H}_S = \beta (g_{11}B_1S_1 + g_{22}B_2S_2 + g_{33}B_3S_3) + (A_{11}I_1 + A_{22}I_2 + A_{33}I_3)$$  \hspace{1cm} (1)

Let \((n_1, n_2, n_3)\) be the direction cosines of the magnetic field \(B\) with reference to the axes of the g tensor and hyperfine tensor. Here, it is assumed that g and hyperfine tensors are coincident. If \(M\) and \(m\) are the electron and nuclear spin quantum numbers, then the energy levels are given by:

$$E_{M,m} = g\beta B + \beta K \frac{m}{M} \quad (2)$$

Here \(g\) and \(K\) are given by the equations

$$g = (g_{11}n_1^2 + g_{22}n_2^2 + g_{33}n_3^2)^{1/2}$$  \hspace{1cm} (3)

and

$$K = \frac{1}{g} \left[ g_{11}^2 A_{11}^2 n_1^2 + g_{22}^2 A_{22}^2 n_2^2 + g_{33}^2 A_{33}^2 n_3^2 \right]^{1/2}$$  \hspace{1cm} (4)

The magnetic field \(B_m\) where the transition \(|M,m> \leftrightarrow |M+1,m>\) occurs is given by

$$h\nu = g\beta B_m + \beta K m \quad (5)$$

i.e.,

$$B_m = \frac{h\nu}{g\beta} - (K/g)m \quad (6)$$

If \(A\) is hyperfine splitting and the lines are centered on \(h\nu/g\beta\), then

$$A = K/g \quad (7)$$

In order to evaluate the matrix elements of the hyperfine tensor, one has to consider the angular variation of \((gK)^2\), since \((gK)\) has a linear angular dependence on \(g\). Therefore,

$$(gK)^2 = g^4 A^2 \quad (8)$$
From this equation, the matrix elements of the hyperfine tensor matrix are evaluated using the same procedure used to get \( g \) tensor matrix.

Schonland has indicated the probable errors in the method described above to get the principal values of \( g \) and hyperfine tensors. But, the errors are very small compared with the experimental errors involved, such as mounting the crystal along the specified axis.

2.5. Interpretation of EPR Spectra

The first step in understanding the nature of a paramagnetic center is to obtain its magnetic parameters such as the principle values of \( g \), A, and D tensors and the direction cosines of these in the molecular framework.

2.6. Calculation of Direction cosines

2.6.1. Direction cosines of the Substitutional sites

The single crystal x-ray analysis data provides the positional parameters \( p, q, r \) and the unit cell dimensions \( a, b, c \) and \( \alpha, \beta, \gamma \). For crystal system with non-orthogonal crystal axes, the positional parameters \( p, q, r \) of the various atoms can be changed over to an orthogonal framework and the Cartesian co-ordinates \( x, y, z \) could be calculated using the relation

\[
\begin{pmatrix}
  x \\
  y \\
  z
\end{pmatrix} =
\begin{pmatrix}
  a & b \cos \gamma & c \cos \beta \\
  0 & b \sin \gamma & (c/\sin \gamma) (\cos \alpha - \cos \beta \cos \gamma) \\
  0 & 0 & d
\end{pmatrix}
\begin{pmatrix}
  p \\
  q \\
  r
\end{pmatrix}
\]

\[9\]
where, \( d = \left[ c^2 - c^2 \cos^2 \beta - \left( c^2 / \sin^2 \gamma \right) \left( \cos \alpha - \cos \beta \cos \gamma \right)^2 \right]^{1/2} \)

By setting the metal atom as the origin, the coordinates of the various atoms in the crystal surrounding the metal are calculated. The normalized Cartesian co-ordinates of these atoms give the direction cosines of the metal-ligand bond of the co-ordination polyhedron. The direction cosines of these metal-ligand bonds can be compared with the direction cosines of the g and A- tensors, obtained by the procedure described in the previous section. Sometimes, it is found that the magnetic tensor directions coincide with some of the bond directions, which may not be so in low symmetry cases.

2.6.2. Direction cosines of the interstitial sites

As in the case of substitutional sites, the direction cosines of magnetic tensors are compared with x-ray data to obtain the location of the dopant. However, a different procedure is adopted to calculate the position of the interstitial ion. From the fractional coordinates and unit cell dimension values of the x-ray data, the Cartesian coordinates are calculated for host lattice metal atoms and surrounding oxygen atoms in a unit cell. The midpoint of opposite oxygen atoms is taken as the location of dopant ion. One of the interstitial positions is suggested for the dopant ion which their direction cosines matched with one of the g and A direction cosines.

2.7. SimFonia powder simulation

The simulation of the powder spectrum is generally carried out to verify the agreement between the experimentally calculated spin Hamiltonian parameters with those predicted from theoretical analysis. The simulation of the powder spectrum is done using the computer program SimFonia developed and supplied by Brucker Company. The
algorithm used in the SimFonia program for powder simulation is based on perturbation theory, which is an approximation. The assumption made is that there is a dominant interaction, which is much larger than the other interactions. As the dominant interaction becomes larger when compared to the other interactions, the approximation becomes better. The five interactions that are considered in the SimFonia simulation program for the powder sample are electron Zeeman interaction, zero-field splitting, nuclear hyperfine interaction, nuclear quadrupole interaction and nuclear Zeeman interaction.

The assumption made in the simulations is that the electron Zeeman interaction is the largest, followed by the zero-field splitting, hyperfine interaction, nuclear quadrupole interaction and the nuclear Zeeman term is the smallest. Perturbation theory works best when the ratio between the successive interactions is at least ten. And if the EPR spectrum is to be simulated with larger hyperfine interactions, then second order perturbation theory is selected to increase the accuracy of the simulation. The zero-field splitting is always treated to second order because they do not produce a non-zero first order term.

The SimFonia powder simulation program simulates EPR spectra for spin 1/2 to spin 7/2 electronic systems. There are essentially no restrictions on the spin of the nuclei. All the naturally occurring spins have been programmed. The principal axes of the electron Zeeman interaction and the zero-field splitting are assumed to be coincident.

SimFonia can simulate both types of line shapes i.e., Lorentzian and Gaussian, as well as combination of the two. This technique is most efficient for many line-complicated spectra. Detailed theory of the powder spectra simulation can be obtained from the references [19, 20].
2.8. **Computer Program EPR-NMR** [27]

The program sets up spin-Hamiltonian (SH) matrices and determines their eigenvalues (energies) using “exact” diagonalization. It is a versatile program, having many operating models customized to a variety of applications. These modes can be grouped into four categories, in increasing order of complexity as follows:

1. Energy-level calculation
2. Spectrum simulation
3. Comparison with observed data
4. Parameter optimization

For each category, most of the operations of the lower categories remain available, so that a good way to learn how to use the program effectively is to start at the lowest category and work one’s way up.

**Category 1:** In this category, the user provides the program with SH parameters, and direction and magnitudes of applied magnetic fields.

**Category 2:** In category 2, the user also specifies an experiment, chosen from field-swept or frequency-swept electron paramagnetic resonance (EPR) or nuclear magnetic resonance (NMR), electron nucleus double resonance (ENDOR), or electron spin echo envelope modulation (ESEEM). In addition, the user must identify the transitions of interest. The “spectra” simulated consists of sets of transition frequencies or magnetic field values, and possibly relative transition probabilities. The program can also convolute these data with a line-shape function (Lorentzian and Gaussian) to produce a plot.
**Category 3:** For this category, the user also supplies appropriate observed single crystal data, with transition labels assigned, and the program determines the degree of consistency with data calculated from the given SH parameters. This can include an error analysis on a user-selected subsets of SH parameters and/or magnetic-field directions.

**Category 4:** In the category 4, the user-selected subsets of parameters may be optimized, so as to give better agreement between observed and calculated transition frequencies. These users a non-linear least squares routine, which systematically varies the parameters so as to minimize weighted difference between observed and calculated transition frequencies (or fields). In this category, user-supplied SH parameters need only be estimates or outright guesses. This program has been used in the calculation of SH parameters for all the systems studied in this thesis.
References


