

**Department of Physics and Astronomy
Heidelberg University**

Master thesis
in Physics
submitted by

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born in Heidelberg, Germany

2024

Electron paramagnetic resonance and magnetisation studies on metal-organic complexes, polymers and bioinspired systems

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Static and dynamic magnetic measurements have been used to investigate selected organic and metal-organic materials. Static magnetisation measurements on monoindeno-diazatetracene-dimer-diradicals reveal an antiferromagnetic (AFM) interaction with $J_{e-e} \simeq 120$ K between the radical electron spins. Furthermore, the data unravel a significant portion of monoradical molecules, the formation of which can be steered by the chemical sample processing method. Similarly, AFM coupling is found in dinuclear Fe_2^{3+} -complexes of the family $[\text{X}(\text{L}^{\text{N}^{\text{7H}}})\text{Fe}^{\text{III}} - \text{O} - \text{Fe}^{\text{III}}(\text{L}^{\text{N}^{\text{7H}}})\text{X}]$ ($\text{X} = \text{Br}, \text{Cl}$), where $J_{\text{Fe-Fe}}^{\text{Br}} = 288(3)$ K for $\text{X} = \text{Br}$ and $J_{\text{Fe-Fe}}^{\text{Cl}} = 312(24)$ K for $\text{X} = \text{Cl}$. The field-induced slow relaxation of the magnetisation in a mononuclear muffin-shaped Er^{3+} phenanthroline-pyridine-triazole complex is explained by an energetically well-isolated ground state Kramers doublet ($\Delta_{\text{KD1} \rightarrow \text{KD2}} > 550$ GHz) as evidenced by high-field/high-frequency electron paramagnetic resonance (HF-EPR). Analysis of the spectra using a pseudo-spin- $1/2$ -model suggest an easy-plane-type magnetic anisotropy of the energetically-lowest Kramers doublet with $m_J = \pm 7/2$. Combined magnetic and HF-EPR studies on $\text{Ln}^{3+}/\text{Ca}^{2+}$ -methanol-dehydrogenase-enzymes and corresponding biomimetics ($\text{Ln} = \text{Nd}, \text{La}, \text{Gd}, \text{Dy}, \text{Lu}$) reveal hyperfine interactions between the radical electron in the pyrrolo-quinoline quinone (PQQ) molecule and a nitrogen nuclear spin and, therefore, allow for a localisation of the radical. Moreover, numerical simulations quantify the magnetic $4f$ - e -coupling and local anisotropies of the Ln^{3+} -ions.

Elektronenspinresonanz- und Magnetisierungsmessungen an metallorganischen Komplexen, Polymeren und bioinspirierten Systemen

Mit Hilfe von statischen und dynamischen Magnetisierungsmessungen wurden verschiedene ausgewählte organische und metallorganische Materialien untersucht. Durch Messungen der statischen Magnetisierung an Monoindeno-Diazatetracen-Dimer-Diradikalen wurde die antiferromagnetische (AFM) Wechselwirkung zwischen den Elektronenspins der Radikale bestätigt, wobei diese $J_{e-e} \simeq 120$ K beträgt. Zusätzlich wurde ein signifikanter Anteil von monoradikalischen Molekülen nachgewiesen, welcher durch die chemische Probenaufarbeitung kontrolliert werden kann. Auf ähnliche Weise, wurde eine AFM-Kopplung in dinuklearen Fe_2^{3+} -Komplexen der Familie $[\text{X}(\text{L}^{\text{N}^7\text{H}})\text{Fe}^{\text{III}} - \text{O} - \text{Fe}^{\text{III}}(\text{L}^{\text{N}^7\text{H}})\text{X}]$ ($\text{X} = \text{Br}, \text{Cl}$), mit $J_{\text{Fe-Fe}}^{\text{Br}} = 288(3)$ K für $\text{X} = \text{Br}$ und $J_{\text{Fe-Fe}}^{\text{Cl}} = 312(24)$ K für $\text{X} = \text{Cl}$, bestimmt. Die feldinduzierte langsame Relaxation der Magnetisierung eines mononuklearen Muffin-förmigen Er^{3+} Phenanthrolin-Pyridin-Triazol-Komplexes konnte durch ein energetisch gut isoliertes Grundzustands-Kramers-Doublet ($\Delta_{\text{KD1} \rightarrow \text{KD2}} > 550$ GHz), was anhand von Hochfeld-/Hochfrequenz-Elektronenspinresonanz (HF-ESR) gezeigt wurde, erklärt werden. Die Analyse der Spektren unter Verwendung eines Pseudo-Spin- $1/2$ -Modells deutet auf eine planare magnetische Anisotropie des energetisch niedrigsten Kramers-Doublets, mit $m_J = \pm 7/2$, hin. Kombinierte magnetische und HF-ESR Messungen an $\text{Ln}^{3+}/\text{Ca}^{2+}$ -Methanol-Dehydrogenase-Enzymen und entsprechenden Biomimetika ($\text{Ln} = \text{Nd}, \text{La}, \text{Gd}, \text{Dy}, \text{Lu}$) zeigen Hyperfein-Wechselwirkungen zwischen dem Radikalelektron des Pyrrolochinolinchinon (PQQ)-Moleküls und einem Stickstoff-Kernspin und ermöglichen somit eine Lokalisierung des Radikals. Darüber hinaus quantifizieren numerische Simulationen die magnetische $4f$ -e-Kopplung und lokale Anisotropien der Ln^{3+} -Ionen.

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Chapter 1

Introduction

Honey bees use magnetic receptors that assist them in orientation and in building their hives [1]. Even the smallest magnetic fields in the microtesla range can be detected by these receptors [2]. They are built from ferromagnetic magnetite [3–7].

Furthermore, even smaller living organisms contain magnetic material, which is essential for their survival: Research has demonstrated that the thermoacidophilic bacterium *Methylophilum ferrireducens* SolV, which was extracted from a volcanic mudpot in the Solfatara crater in 2007, requires the presence of lanthanide salts for its growth [8–10]. The necessity of lanthanide salts is related to its metabolic process [10]: The bacterium contains genes for the lanthanide methanol dehydrogenase (Ln-MDH) enzyme [8, 10]. The MDH enzyme is crucial for the metabolism of the methylotrophic bacteria [10]. The active site of the MDH enzyme is composed of a metal cation, which in the case of SolV is cerium [8, 10], coordinated to a pyrrolo-quinoline quinone molecule [10]. This type of metal-containing molecules belongs to the class of metal-organic complexes, which are also important in technology. For example, metal-containing complexes can potentially be used as refrigerants for magnetocaloric applications [11–14]. A fundamental property, which metal-organic complexes can feature, that makes them especially interesting for both applications and fundamental research, is magnetic anisotropy. Anisotropy refers to the alignment of magnetic moments along a preferred direction. In molecules, the local anisotropy of the metal centres is generated by the electric fields of the surrounding ligand atoms. Such anisotropy can lead to slow magnetic relaxation of the magnetisation of the molecule. Molecules exhibiting slow magnetic relaxation are called single-molecular magnets (SMMs). SMMs have potential applications in medicine as contrast agents in MRI [15, 16]. Furthermore, they are also promising candidates for information storage and processing, for example as qubits in quantum computers [11, 17, 18] or for spintronic applications [19].

To understand the fundamental physics of the aforementioned molecular-scale magnetic systems it is especially important to investigate the mechanisms that influence interactions of magnetic moments and local anisotropies in these systems. For this, electron paramagnetic resonance (EPR) is highly suited, as EPR can, for exam-

ple, unravel hyperfine interactions, magnetic anisotropies and interactions between magnetic moments. Combining this technique with magnetisation measurements, which allow for the quantitative determination of magnetisation and the investigation of relaxation behaviour in SMMs, provides deep insights into the underlying mechanisms of diverse systems on the molecular scale [20–22].

This thesis is structured into eight sections: Chapter 2 presents the theoretical background required for the analysis and understanding of EPR and magnetisation measurements. This is followed by a description of the measurement methods, used in this work, in chapter 3. Chapters 4 and 5 show the results of magnetisation measurements on monoindeno-diazatetracene-dimer-diradicals and dinuclear Fe_2^{3+} -complexes of the family $[\text{X}(\text{L}^{\text{N7H}})\text{Fe}^{\text{III}} - \text{O} - \text{Fe}^{\text{III}}(\text{L}^{\text{N7H}})\text{X}]$ ($\text{X} = \text{Br}, \text{Cl}$). Chapter 6 discusses the results of combined HF-EPR and magnetisation measurements on a mononuclear muffin-shaped Er^{3+} phenanthroline-pyridine-triazole complex. Combined HF-EPR and magnetisation measurements on $\text{Ln}^{3+}/\text{Ca}^{2+}$ -methanol-dehydrogenase-enzymes and corresponding biomimetics ($\text{Ln} = \text{Nd}, \text{La}, \text{Gd}, \text{Dy}, \text{Lu}$) are discussed in chapter 7 and 8. Finally, the findings are summarized in chapter 9.

Chapter 2

Theoretical background

The following chapter is based on the books *Electron Paramagnetic Resonance Spectroscopy* by Patrick Bertrand [23], *Lanthanide Single Molecule Magnets* by Jinkui Tang and Peng Zhang [24], *Quantum Theory of Magnetism* by Wolfgang Nolting and Anupuru Ramakanth [25] and *Molecular Nanomagnets* by Dante Gatteschi, Roberta Sessoli and Jacques Villain [26] and *Electron Paramagnetic Resonance of Transition Ions* by Anatole Abragam and Brebis Bleaney [27]. Unless stated otherwise, the following information has been taken from there.

Throughout this thesis, magnetisation and EPR measurements play a crucial role, as they are the measurement methods used. With EPR the magnetic excitations of paramagnetic ions are probed. In an EPR measurement the energy of an electromagnetic wave (in the microwave range) with a certain frequency f is partly absorbed by a sample. The transmitted amplitude of the microwave is measured. Meanwhile the temperature is kept constant and the magnetic field is swept. The transmitted amplitude is, therefore, measured as a function of magnetic field - the so called EPR spectrum.

When the energy difference ΔE between the final and initial magnetic state is equal to the energy hf of a photon, a photon can be absorbed and a minimum in the EPR spectrum occurs, with the resonance condition being

$$hf = \Delta E, \tag{2.1}$$

where h is the Planck constant.

The energy ΔE needed for the transition depends on the magnetic system under investigation. Furthermore, also the magnetisation is dependent on the magnetic system. Therefore, in the following different Hamiltonians describing diverse magnetic systems are introduced.

2.1 Spin-Orbit Coupling

The magnetic moment of a paramagnetic ion is given by the magnetic moments of its electrons. Only the electrons in non-closed shells contribute to the total magnetic moment of the ion. The magnetic state of each electron can be described by two quantum numbers: s , the spin quantum number and l the orbital angular momentum quantum number, which is determined by the atomic orbital the electron occupies. l and s are coupled via the relativistic spin-orbit coupling, which is, for an individual electron, described by the Hamiltonian

$$\hat{H}_{\text{SO}} = \xi \mathbf{l}^T \mathbf{s}, \quad (2.2)$$

where ξ is the spin-orbit coupling constant [28].

In the case of LS -coupling, the total magnetic moment $\mathbf{J}$ of the ion is given by

$$\mathbf{J} = \mathbf{L} + \mathbf{S}, \quad (2.3)$$

where $\mathbf{L} = \sum_{i=1}^{\eta} \mathbf{l}_i$ is the sum of the orbital angular momentum quantum numbers of the η electrons in non-closed shells and $\mathbf{S} = \sum_{i=1}^{\eta} \mathbf{s}_i$ is the sum of the spin quantum numbers of these electrons.

The total magnetic moment of the ion $\mu_{\mathbf{J}}$ is consequently given by

$$\mu_{\mathbf{J}} = \mu_{\mathbf{L}} + \mu_{\mathbf{S}}, \quad (2.4)$$

where $\mu_{\mathbf{L}/\mathbf{S}}$ is the orbital and spin magnetic moment, respectively. The projection of $\mu_{\mathbf{J}}$ onto $\mathbf{J}$ is given by

$$\mu_{\mathbf{J}} = -g_{\mathbf{J}} \mu_{\text{B}} J, \quad (2.5)$$

which is the saturated magnetic moment of the ion. $g_{\mathbf{J}}$ is the Landé g-factor given by

$$g_{\mathbf{J}} = \frac{1}{2} + \frac{3}{2} \frac{S(S+1) - L(L+1)}{J(J+1)}. \quad (2.6)$$

2.2 Effective Spin Hamiltonian

The Spin Hamiltonian approach

For the interpretation of experimental results, especially spectroscopic results, the spin Hamiltonian approach is quite handy. The reason is, that in the spin Hamiltonian approach fundamental theories do not have to be used, which would complicate the analysis of the experimental results. In this approach, all orbital coordinates are eliminated and replaced by spin coordinates. For EPR often only transitions within the ground state multiplet (energetically lowest lying J multiplet) occur, as the ground state multiplet is well separated from the excited ones. In this case, the spin Hamiltonian approach is usually sufficient to describe the experimental data.

The Hamiltonian resulting from this approach is called the effective spin Hamiltonian. Throughout this thesis different contributions to this Hamiltonian are used, which are introduced in the following.

2.2.1 Zeeman Hamiltonian

The Hamiltonian for a magnetic moment in an external magnetic field $\mathbf{B}$ is given by the Zeeman Hamiltonian

$$\hat{H}_Z = \mu_B \mathbf{B}^T \mathbf{g} \hat{\mathbf{S}}, \quad (2.7)$$

where $\mathbf{g}$ is the g -tensor.

Brillouin function

The magnetisation M of an ensemble of identical and independent paramagnetic moments is defined as:

$$\mathbf{M} = n \langle \mathbf{m} \rangle = n \frac{\sum_{\mathbf{j}} \mathbf{m}_{\mathbf{j}} e^{-\frac{\langle E_{\mathbf{j}} \rangle}{k_B T}}}{Z} \quad (2.8)$$

where n is the density of magnetic moments and $\langle \mathbf{m} \rangle$ is the expectation value of a single magnetic moment. $\langle \mathbf{m} \rangle$ is given by the sum of all possible states $\mathbf{m}_{\mathbf{j}}$ weighted by the respective thermal occupation probability. Z is the partition function given by

$$Z = \sum_{\mathbf{j}} e^{-\frac{\langle E_{\mathbf{j}} \rangle}{k_B T}}, \quad (2.9)$$

where $\langle E_{\mathbf{j}} \rangle$ is the expectation value of the energy of the state $\mathbf{m}_{\mathbf{j}}$. In case the Hamiltonian for each magnetic moment is given by eq.(2.7), the magnetisation in the direction of the applied magnetic field is

$$M = n g \mu_B S B_S(x), \quad (2.10)$$

as derived from eq.(2.8) and (2.9). $B_J(x)$ is the Brillouin function with

$$x = \frac{g \mu_B S B}{k_B T}. \quad (2.11)$$

μ_B is the Bohr magneton, g is the Landé g -factor, k_B is the Boltzmann constant and T is the temperature. The Brillouin function describes the alignment of the magnetic moments of the ensemble in the direction of the applied magnetic field. It reads

$$B_S(x) = \frac{2S+1}{2S} \coth \frac{(2S+1)x}{2S} - \frac{1}{2S} \coth \frac{x}{2S}. \quad (2.12)$$

Curie law

In an experimental environment the magnetic susceptibility χ is defined as

$$\chi = \frac{M}{H}, \quad (2.13)$$

where H is the magnetic field strength with $B = \mu_0(H + M)$ and μ_0 is the vacuum permeability. In the limit of $\mu_B B \gg k_B T$ ($x \ll 1$ in eq. (2.11)), the Brillouin-function can be Taylor-expanded around $x = 0$, which results, when including only the first order term, in a magnetic susceptibility of

$$\chi \simeq \frac{C}{T}, \quad (2.14)$$

where

$$C = \frac{n\mu_0 g^2 S(S+1)\mu_B^2}{3k_B} \quad (2.15)$$

is the Curie constant. When multiplying the magnetic susceptibility with temperature, the resulting χT value is equal to the Curie constant. Consequently, in the limit of $x \ll 1$, χT is constant, which is shown in Fig. 2.1: At high temperatures the exact formula (red line), given by eq.(2.13) with eq.(2.10), for χT asymptotically reaches the Curie-limit (dashed blue line), meaning that $\chi T \rightarrow C$ for $T \rightarrow \infty$.

Note that eq.(2.8) and (2.13) also hold for Hamiltonians other than the Zeeman Hamiltonian.

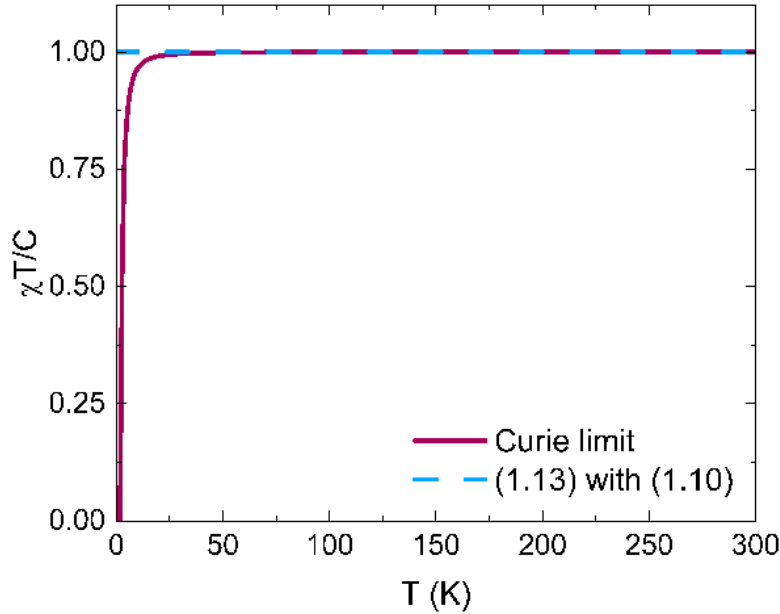


Fig. 2.1: χT product as a function of temperature, given by eq.(2.13) and (2.10), for $S = 1/2$ and $B = 1$ T in units of C . The dashed line represents the Curie limit, described by eq.(2.14).

Electron Paramagnetic Resonance Spectrum for $S = 1/2$

In case of $S = 1/2$, the Zeeman Hamiltonian in eq.(2.7) leads to a splitting of the $m_S = \pm 1/2$ states, as shown in Fig. 2.2(a), where m_S , classically, is the component of the spin in the direction of the external magnetic field. At the resonance magnetic

field B_{res} , at which the resonance condition

$$hf_{\text{res}} = \frac{\mu_B g}{h} \Delta m B_{\text{res}} \quad (2.16)$$

is fulfilled, a transition between the two m_S states is possible. Symmetry-allowed transitions correspond to $\Delta m = \pm 1$. In Fig. 2.2(b) the EPR spectrum for the transition indicated in Fig. 2.2(a) is shown. The microwave transmission exhibits a minimum at the resonance magnetic field. The width of the resonance feature is ΔB and the amplitude of the resonance is A . Consequently, the intensity of the resonance feature can be approximated by $I \approx A\Delta B$. It can be shown that the EPR signal, in the limit of $hf \ll 2k_B T$, is inversely proportional to the temperature. Therefore, for the used approximations, it holds that the intensity is inversely proportional to the temperature:

$$I \sim \frac{1}{T}. \quad (2.17)$$

This is, despite different prefactors, the Curie-law (see eq.(2.14)).

When repeating the EPR experiment at different frequencies, the pairs of $(f_{\text{res}}, B_{\text{res}})$ can be plotted in a resonance-frequency-versus-resonance-magnetic-field-diagram (fB -diagram), as shown in Fig. 2.3. The obtained resonance positions, of named spin-1/2 system, result in a single gapless resonance branch with a slope proportional to the effective g -factor

$$g_{\text{eff}} = \frac{h}{\mu_B} \frac{\partial f}{\partial B}. \quad (2.18)$$

In the case presented in Fig. 2.3(b), the effective g -factor is given by $g_{\text{eff}} = g\Delta m$, with $\Delta m = 1$.

2.2.2 Hyperfine Interaction Hamiltonian

The electronic spin of a paramagnetic centre S can interact with the nuclear spin I of an atom. The position of the atom has to be such that the spin density of the paramagnetic centre is finite at the atom position. The Hamiltonian for this "hyperfine" coupling, in the case that the coupling is isotropic, reads

$$\hat{H}_{HF} = \hat{\mathbf{S}}^T \mathbf{A}_{\text{iso}} \hat{\mathbf{I}}, \quad (2.19)$$

where $\mathbf{A}_{\text{iso}}$ is the isotropic hyperfine coupling tensor. Due to the hyperfine coupling the quantum numbers S and I are not good quantum numbers. However, the quantum number F with

$$\mathbf{F} = \mathbf{S} + \mathbf{I} \quad (2.20)$$

is a good quantum number and can be used to describe the magnetic state of the system.

In the case of a spin-1/2 system which interacts via hyperfine coupling with a nuclear spin of $I = 1$, F can take the values $F = 1/2$ and $F = 3/2$. The energy level diagram for the Hamiltonian

$$\hat{H} = \hat{H}_Z + \hat{H}_{HF} \quad (2.21)$$

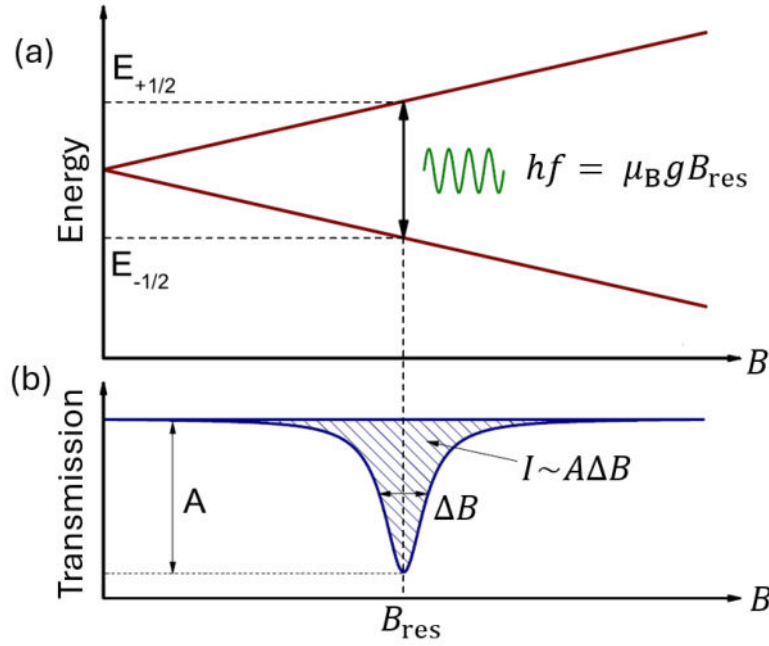


Fig. 2.2: (a) Energy level diagram for a spin- $1/2$ system in a magnetic field. The black arrow marks the photon induced transition. (b) Microwave transmission for the transition indicated in (a). A : Amplitude of the resonance feature; ΔB : width of the resonance feature; I : Intensity of the resonance feature. The figure is adapted from [29].

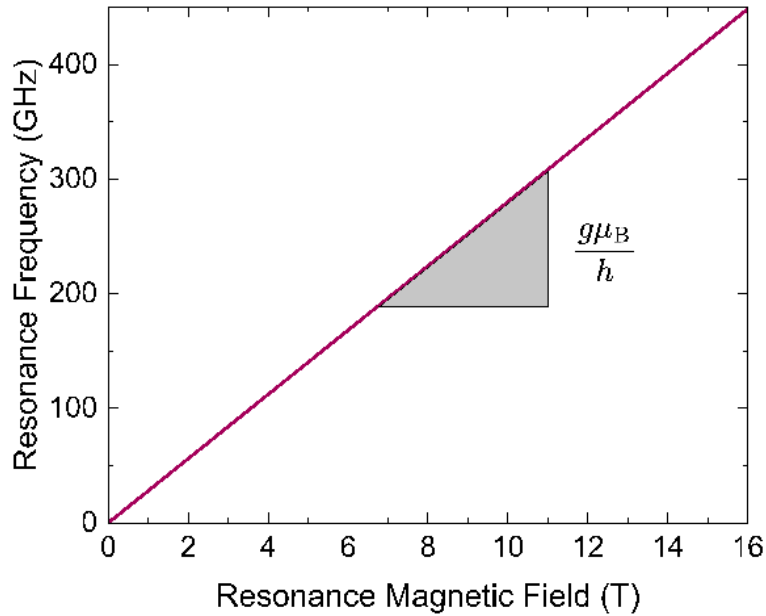


Fig. 2.3: Resonance magnetic field positions for various frequencies for a spin- $1/2$ system. The grey triangle depicts the slope of the resonance branch.

is shown in Fig. 2.4(a). Due to the Zeeman term in the Hamiltonian, the energy levels

with different m_S split for large magnetic fields, as shown in the figure. Furthermore, the energy levels corresponding to each m_S -state split into three distinct levels with $M_I = -1, 0, 1$ for large magnetic fields. M_I is the component of the nuclear spin in the direction of the external magnetic field. The symmetry-allowed transitions ($\Delta m_S = \pm 1$ and $\Delta M_I = 0$) are indicated by red arrows resulting in three resonances in a field-swept absorption spectrum shown in Fig. 2.4(b). The resonance at B_0 corresponds to a transition between the two states with $M_I = 0$ in (a), whereas the other two resonances correspond to transitions between two states with finite M_I -values. The distance in resonance magnetic field between two resonance features is proportional to the hyperfine coupling constant A_{iso} , as indicated in Fig. 2.4(b).

In a fB -diagram for a spin- $1/2$ system interacting via hyperfine coupling with a nuclear spin of $I = 1$, three parallel resonance branches are observed with

$$f_{\text{res}} = \frac{g_{\text{eff}}\mu_B}{h}B_{\text{res}} + A_{\text{iso}}M_I, \quad M_I = -1, 0, +1 \quad (2.22)$$

in the magnetic field region, where the energy levels are parallel in Fig. 2.4(a). This is the region, where the energy contribution of the Zeeman term is large compared to the contribution of the hyperfine-coupling term.

2.2.3 Crystal Field Hamiltonian

The atoms surrounding a paramagnetic centre in a system (e.g. in a complex) have an electrostatic influence on the magnetic moment of the paramagnetic centre. The electrostatic influence of the surrounding atoms on the paramagnetic centre is described by the crystal-field Hamiltonian. In the Stevens notation, the crystal-field Hamiltonian reads

$$\hat{H}_{\text{CF}} = \sum_{N=2}^{2S} \sum_{k=-N}^N B_N^k \hat{\mathcal{O}}_N^k. \quad (2.23)$$

B_N^k are the crystal-field parameters and $\hat{\mathcal{O}}_N^k$ are the Stevens operators [27]. Only even order terms (even N) have to be included [27].

The simplest possible crystal-field Hamiltonian is given by only including terms up to second order. The crystal-field Hamiltonian in this case is written as

$$\hat{H}_{\text{CF}} = \hat{\mathbf{S}}^T \mathbf{D} \hat{\mathbf{S}}, \quad (2.24)$$

where $\mathbf{D}$ is the anisotropy tensor, which is a real symmetric tensor. In the eigenframe of $\mathbf{D}$, eq.(2.24) reads

$$\hat{H}_{\text{CF}} = D_{\text{xx}} \hat{\mathbf{S}}_{\text{x}}^2 + D_{\text{yy}} \hat{\mathbf{S}}_{\text{y}}^2 + D_{\text{zz}} \hat{\mathbf{S}}_{\text{z}}^2. \quad (2.25)$$

The Hamiltonian of eq.(2.25) can be further simplified by defining the axial and transversal anisotropy parameters E and D - also called second-order zero field splitting parameters, as they are given by $D = 3B_0^2$ and $E = B_2^2$ - as

$$D = \frac{3}{2}D_{\text{zz}}, E = \frac{D_{\text{xx}} - D_{\text{yy}}}{2}. \quad (2.26)$$

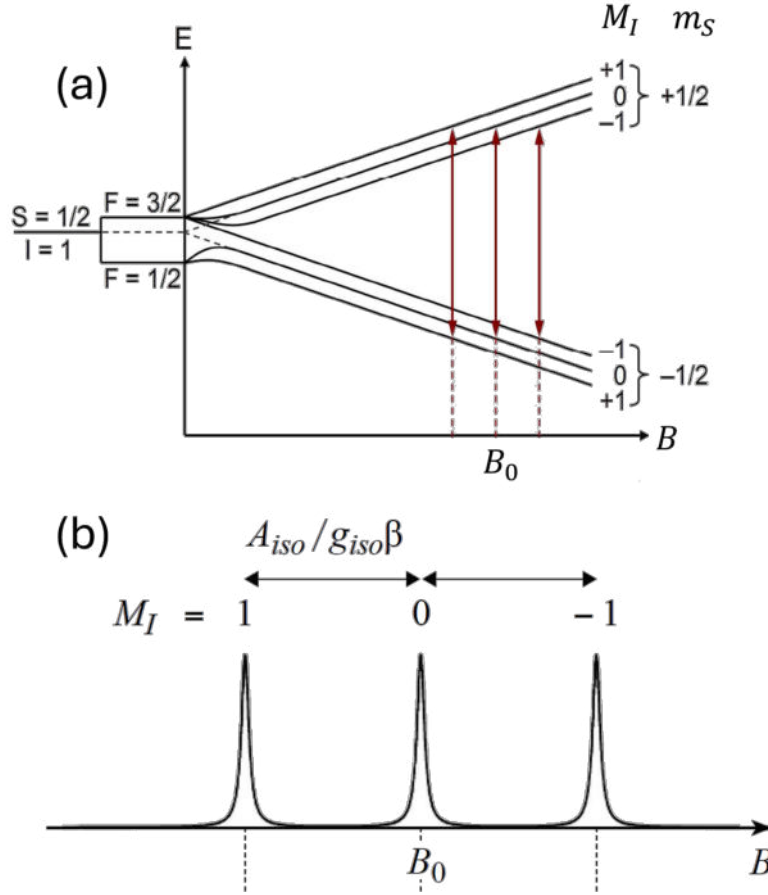


Fig. 2.4: (a) Energy level diagram for a spin-1/2 system interacting via hyperfine coupling with a nuclear spin of $I = 1$. A_{iso} is chosen positive. Symmetry-allowed transitions are indicated by red arrows. The figure is adapted from [29]. (b) EPR absorption spectrum for the transitions indicated in (a). $\beta = \mu_B$. The figure is taken from [23].

The crystal field Hamiltonian of eq.(2.25) can then be rewritten to

$$\hat{H}_{CF} = D \left(\hat{S}_z^2 - \frac{S(S+1)}{3} \right) + E \left(\frac{\hat{S}_+^2 + \hat{S}_-^2}{2} \right), \quad (2.27)$$

where $\hat{S}_z$ is the total spin operator in the direction of the largest principal value of $\mathbf{D}$, and $\hat{S}_{+/-}$ are the creation and annihilation operators. As $\mathbf{D}$ is traceless, for D and E the condition $0 \leq |E/D| \leq 1/3$ holds. E/D is a measure of the axiality of the crystal field: if $E/D = 0$ ($D_{xx} = D_{yy}$) the crystal field is completely axial and if $|E/D| = 1/3$ ($D_{xx} = D_{yy} = D_{zz}$) the crystal field has an orthorhombic symmetry.

In Fig. 2.5(a) the splitting of the energy levels for an axial spin-1 system ($D < 0$, $E = 0$) are shown. Due to the crystal field, the states $|-1\rangle, |0\rangle$ and $|1\rangle$ are not degenerate at zero magnetic field. The Hamiltonian of eq.(2.27) is therefore also called zero-field-splitting Hamiltonian. Two transitions are symmetry-allowed ($\Delta m_S = \pm 1$), which are depicted by pink and blue arrows. The EPR spectrum for the allowed

transitions is shown at the bottom of the figure. Following the resonance positions of the allowed transitions for multiple frequencies leads to two resonance branches in the fB -diagram, shown in Fig. 2.5(b), with

$$f_{\text{res}}^{\text{blue}} = \left| -\frac{g_{\text{eff}}\mu_B}{h}B_{\text{res}} + \Delta \right|, \quad f_{\text{res}}^{\text{pink}} = +\frac{g_{\text{eff}}\mu_B}{h}B_{\text{res}} + \Delta, \quad (2.28)$$

where $\Delta = |D|(S^2 - (S - 1)^2)$ is the zero-field-splitting energy. In the case of $D < 0$, the population of the $|-1\rangle$ state at low temperatures and finite magnetic field is higher as the population of the $|0\rangle$ and $|1\rangle$ states according to the Boltzmann distribution, as the energy of $|-1\rangle$ is lower as the energy of $|0\rangle$ and $|1\rangle$. Consequently, for $g\mu_B B$, $\Delta \gg k_B T$, the intensity of the resonance feature in an EPR spectrum corresponding to the pink transition is higher than the intensity of the resonance feature corresponding to the blue transition.

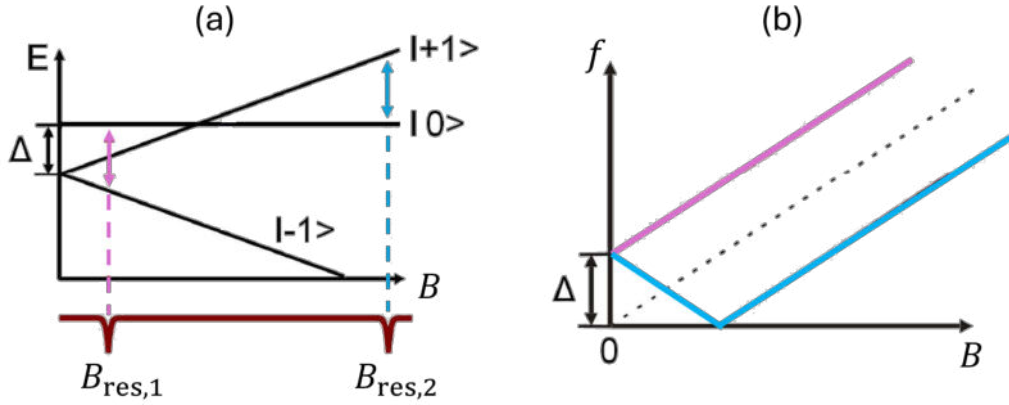


Fig. 2.5: (a) Energy level diagram for a spin-1 system in an axial crystal field ($E = 0$) with $D < 0$. Symmetry-allowed transitions are indicated by pink and blue arrows. At the bottom the EPR transmission spectrum for the transitions indicated at the top is visualised. (b) Resonance magnetic field positions for various frequencies for a spin-1 system in an axial crystal field with $D < 0$. The figures are adapted from [29].

2.2.4 Spin-Spin Exchange Coupling

Multiple mechanisms lead to a magnetic interaction between the magnetic moments of two paramagnetic centres (e.g. dipole-dipole interaction, superexchange,...). The Hamiltonian that describes the interaction between two paramagnetic centres (S_1 and S_2) is in its simplest form given by

$$\hat{H}_J = \hat{\mathbf{S}}_1^T \mathbf{J}_{12} \hat{\mathbf{S}}_2, \quad (2.29)$$

where $\mathbf{J}_{12}$ is the interaction tensor.

Bleaney-Bowers equation

In the case that two spin- $1/2$ particles magnetically interact with each other with an isotropic interaction, the Hamiltonian in eq.(2.29), can, in the eigenframe of $\mathbf{J}_{12}$, be

written as

$$\hat{H}_J = \hat{\mathbf{S}}_1^T J_{12} \hat{\mathbf{S}}_2. \quad (2.30)$$

In the case $J_{12} > 0$ the interaction is antiferromagnetic (AFM), resulting in a ground state, where the spins are aligned antiparallel. In the case $J_{12} < 0$ the interaction is ferromagnetic (FM), resulting in a ground state, where the spins are aligned parallel. It can be shown that in such a model the susceptibility in the limit of $x \ll 1$ (see eq.(2.11)) and small energy of the applied magnetic field (magnetic energy) compared to the interaction energy is given by

$$\chi = 0.375 \left(\frac{g^2}{T} \right) \frac{2}{3 + e^{-\frac{J_{12}}{k_B T}}}, \quad (2.31)$$

which is the Bleaney-Bowers equation [30].

Simulations

Throughout this work, the aforementioned Hamiltonians are employed to simulate magnetisation data (by using eq.(2.8) and (2.13)) and EPR data. For these simulations, the software package EasySpin [31] was used.

2.3 Dynamic Magnetisation

The following paragraph is based on the review paper *A.C. susceptibility as a probe of low-frequency magnetic dynamics* by Craig Topping and Stephen Blundell [32]. Unless stated otherwise, the following information has been taken from there.

In the previous sections it was assumed, that the external applied magnetic field is time (t) independent. In the following, the case where the magnetic field has a time-dependent oscillating component is discussed. The external applied field in this case reads

$$B = B_{dc} + B_{ac} \cos(\omega t), \quad (2.32)$$

where B_{dc} is the amplitude of the time-independent part of the magnetic field, B_{ac} is the amplitude of the time-dependent part of the magnetic field and ω is the frequency of the oscillating magnetic field. In an experiment, the response of a magnetic system to the time-dependent magnetic field, is measured by measuring the amplitude of the time-dependent part of the magnetisation M_{ac} . The AC susceptibility is defined by

$$\chi_{ac} = \mu_0 \frac{M_{ac}}{B_{ac}}. \quad (2.33)$$

The magnetic moments of the system do not necessarily follow the change in applied magnetic field instantaneously. The system takes the time τ , called relaxation time, until equilibrium is reached after the external magnetic field changes. Three distinct regimes can be identified for the ratio of ω and $1/\tau$:

- $\omega \ll 1/\tau$: The external magnetic field changes slowly compared to the relaxation time of the system, meaning that the system responds nearly instantaneously to any changes of the magnetic field. Therefore, $\chi_{ac} = \chi_T$, where χ_T is the isothermal susceptibility - the susceptibility in the limit that solely a static magnetic field is applied.
- $\omega \gg 1/\tau$: The external magnetic field changes fast compared to the relaxation time of the system. The magnetic moments of the system cannot respond to the changes in magnetic field fast enough to obtain an equilibrium state, resulting in $\chi_{ac} = \chi_S$, where χ_S is called adiabatic susceptibility [26].
- $\omega \approx 1/\tau$: The time the system takes to reach equilibrium after an external magnetic field change is comparable to the time scale in which the external magnetic field changes. Consequently, the response of the system is time-delayed against the change in applied magnetic field.

Especially in the latter case it is useful to separate χ_{ac} into its real χ_{ac}' and imaginary part χ_{ac}'' . In this intermediate regime it is possible to write χ_{ac} as

$$\chi_{ac}(\omega) = \chi_{ac}' + i\chi_{ac}'' = \left(\frac{\chi_T - \chi_S}{1 + \omega^2\tau^2} + \chi_S \right) + i\omega\tau \left(\frac{\chi_T - \chi_S}{1 + \omega^2\tau^2} \right) = \chi_S + \frac{\chi_T - \chi_S}{1 + i\omega\tau}, \quad (2.34)$$

which is also called the "Debye model" (as it is analogue to the formula for the dielectric relaxation, described in the Debye model) [32, 33].

In real systems there is not only a certain relaxation process contributing to the relaxation time, but there are multiple processes. Therefore, there is a distribution of relaxation times in the system. This can be accounted for by introducing a phenomenological parameter α , which is a measure for the width of the distribution (spread) of relaxation times in a system. The Debye model is then modified to

$$\chi_{ac}(\omega) = \chi_S + \frac{\chi_T - \chi_S}{1 + (i\omega\tau)^{1-\alpha}} \quad (2.35)$$

where $0 \leq \alpha \leq 1$ [26, 32, 34]. This model is called the "generalised Debye model". In this model χ_{ac}' and χ_{ac}'' read

$$\chi_{ac}' = \chi_S + (\chi_T - \chi_S) \frac{1 + (\omega\tau)^{1-\alpha} \sin \frac{\pi\alpha}{2}}{1 + 2(\omega\tau)^{1-\alpha} \sin \frac{\pi\alpha}{2} + (\omega\tau)^{2-2\alpha}} \quad (2.36)$$

and

$$\chi_{ac}'' = (\chi_T - \chi_S) \frac{(\omega\tau)^{1-\alpha} \cos \frac{\pi\alpha}{2}}{1 + 2(\omega\tau)^{1-\alpha} \sin \frac{\pi\alpha}{2} + (\omega\tau)^{2-2\alpha}}. \quad (2.37)$$

In case, that there are two independent relaxation mechanisms, each with a certain spread in relaxation time, χ_{ac} is given by the sum of two generalised Debye functions (each given by eq.(2.35)) - a so called "generalised double Debye function".

It may be beneficial to use a Cole-Cole plot [26, 32, 34] for data analysis. Such a plot shows χ_{ac}'' as a function of χ_{ac}' and allows for the direct determination of α .

In Fig. 2.6 an exemplary Cole-Cole plot is shown. For $\alpha = 0$ the Debye function results in semicircle in a Cole-Cole plot. For $\alpha \neq 0$ the semicircle is shifted below the χ''_{ac} -axis and the angle of the crossing of the semicircle with the χ'_{ac} -axis is given by $(1 - \alpha)\pi$.

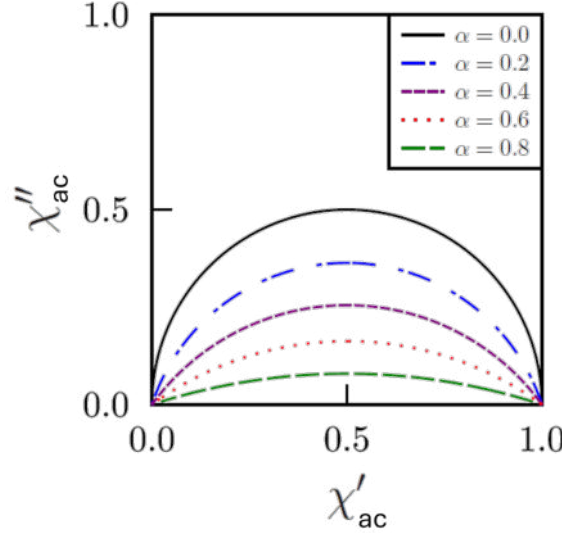


Fig. 2.6: Cole-Cole plot obtained by the generalised Debye model (eq.(2.35)) for $\chi_S = 0$ and $\chi_T = 1$ and various values of α . Figure adapted from [32].

Relaxation Processes in Molecular Systems

The relaxation time τ of a magnetic system is determined by the underlying relaxation mechanisms. For molecular magnets there are four main contributions, which are introduced in the following. The mechanisms all have in common that there is some kind of energy barrier that has to be overcome/or is tunnelled through to make the magnetic transition possible that leads to the equilibrium alignment of the magnetic moments of the system relative to the external applied magnetic field. The probability to overcome the barrier depends on the underlying mechanism, resulting in different contributions to τ for each process. The processes which are the most relevant are:

- Direct process $\tilde{\tau}_D$: A phonon is absorbed (in the case that the energy of the final magnetic state is larger than that of the initial state) or emitted (energy of the final state is smaller than that of the initial state), where the energy of the phonon is equal to the energy difference between the final and initial magnetic state.
- Orbach process $\tilde{\tau}_O$: Two phonons are included in this process: The first one is absorbed by the spin system to make a transition into an excited state. The final state is reached via emitting a second phonon. The effective barrier height for this process is U_{eff} .

- Raman process $\tilde{\tau}_R$: The process is, as well as the Orbach process, a two-phonon process. However, the main difference is that the intermediate state is a virtual state. For molecular magnets, the effective barrier height for the Raman process is W , which corresponds to the barrier to the next optical phonon [35].
- Quantum tunnelling $\tilde{\tau}_{QTM}$: In the case that the overlap integral of the initial and final state states is finite, quantum tunnelling is possible.

To obtain the relaxation time τ resulting from all processes in total, the relaxation times for all processes need to be summed reciprocal:

$$\begin{aligned} \tau^{-1}(T) &= \tilde{\tau}_D^{-1} + \tilde{\tau}_{QTM}^{-1} + \tilde{\tau}_R^{-1} + \tilde{\tau}_O^{-1} \\ &= AT + \tau_{QTM}^{-1} + \tau_R^{-1} \left(\frac{e^{-\frac{W}{k_B T}}}{\left(e^{\frac{-W}{k_B T}} - 1\right)^2} \right) + \tau_O^{-1} e^{\frac{-U_{\text{eff}}}{k_B T}}, \quad (2.38) \end{aligned}$$

where A is a time-independent constant and $\tau_{QTM/O/R}$ are the attempt frequencies for quantum tunneling, Orbach and Raman processes, respectively [32, 35]. The formula for $\tilde{\tau}_R$ is taken from [35], which is only valid under the assumption that in molecular magnets only optical phonons are relevant [35].

Chapter 3

Experimental Methods

The following chapter is based on the PhD thesis *Experimentelle Untersuchungen der Magnetisierung und der Elektronenspinresonanz an Übergangsmetallverbindungen mit konkurrierenden Wechselwirkungen* by Johannes Werner [36] and *High-field Electron Spin Resonance study on Correlated Transition Metal Compounds and Metal-Organic Compounds* by Jaena Park [37], the *Magnetic Property Measurement System MPMS3 User's Manual* and *Vibrating Sample Magnetometer (VSM) Option User's Manual* by Quantum Design [38, 39] and private correspondence with Jan Arneth [40], Luca Bischof [41] and Changyun Koo [42]. Unless otherwise stated, the following information has been taken from there.

3.1 High-frequency/High-field Electron Paramagnetic Resonance

The HF-EPR setup can generate and detect microwaves with frequencies between 30 – 1000 GHz. A magnetic field can be swepted continuously between 0 – 16 T and temperatures between 1.8 – 300 K can be reached. In Fig. 3.1, a schematic diagram of the HF-EPR setup is shown.

An absolute reference frequency is provided by an external EIP 575B Source Locking Microwave Counter (counter) from *Phase Matrix Inc., National Instruments*. It provides a reference electromagnetic wave with a frequency of $f_{\text{ref}} = 10.488 \text{ kHz}$.

The microwaves, which are used for the actual measurement, are generated by two "Gunn"-diodes inside of a microwave vector network analyser (MVNA) from *AB millimetre, Paris*, which uses the microwave frequency from the counter as a reference. The MVNA can generate microwaves with frequencies in the range of 8 – 18 GHz. The generated microwave with frequency f_1 is coupled into a harmonic generator (HG) via coaxial cables. The HG includes Shottky diodes from *AB millimetre, Paris*. Multiple different HGs are used, which convert the microwave with frequency f_1 to a microwave with a frequency of a higher harmonic: $f_S = Nf_1$, where N depends on the HG used, with $N = 4, 6, 12, 18, 24, 36$, and 54. The microwave is then trans-

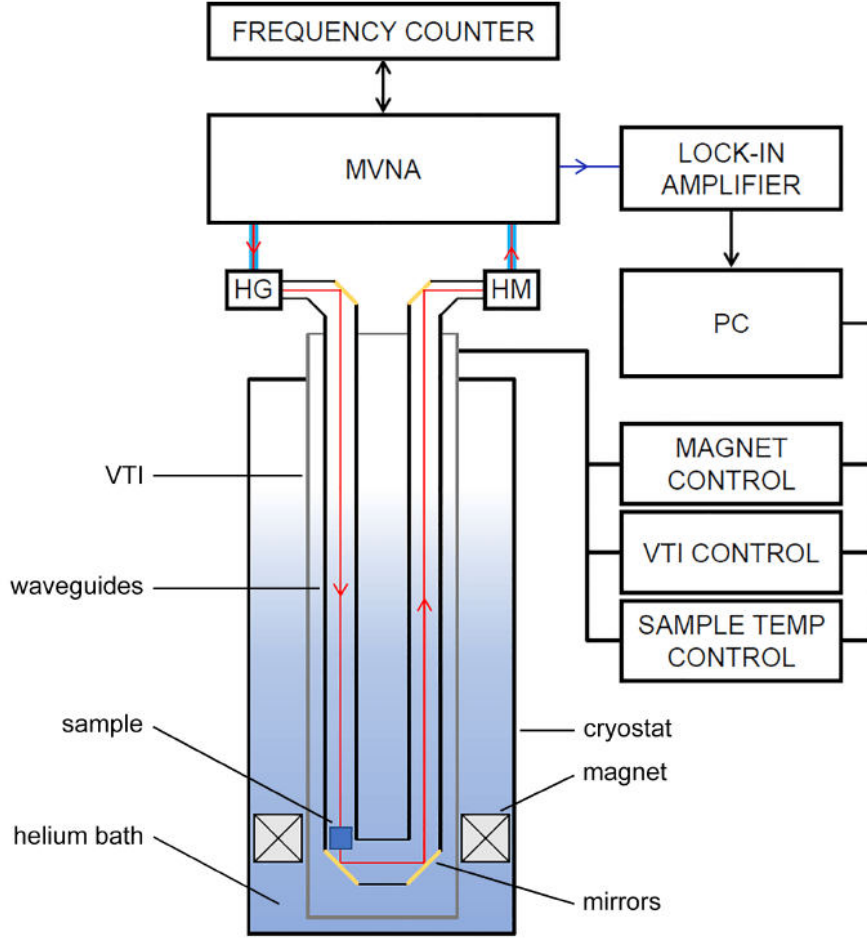


Fig. 3.1: Schematic diagram of the HF-EPR setup. The figure is taken from [36, 43, 44].

mitted through the sample by cylindrical waveguides and two gold-coated mirrors and is finally coupled into a harmonic mixer (HM) from *AB millimetre, Paris*. In the HM, the microwave with frequency Nf_S is converted back to a microwave with frequency $f_2 = \frac{f_S}{N}$. Multiple different HMs are used. The HM is chosen such, that N matches the one used in the HG to convert f_1 to f_S . Subsequently, the microwave is coupled into the MVNA using coaxial cables. In the MVNA the microwaves with the frequencies f_1 and f_2 are subtracted from each other and the resulting signal is converted to the counter frequency f_{ref} . The resulting signal can also be amplified by the MVNA and is transmitted via coaxial cables to a lock-in amplifier SR 830 DSP from *Stanford Research Systems*. The lock-in compares the signal, which is transmitted from the MVNA with the reference signal transmitted from the counter and extracts the amplitude and phase of the measured signal. The amplitude and phase information is then transferred to a computer.

The cylindrical waveguides and mirrors together with the sample space are part of the sample rod, which is placed inside a jacket. This jacket is made of stainless steel

at the top (which is outside the cryostat, as is explained in the following) in order to ensure isolation against the environment. The bottom (which is inside the cryostat, as explained in the following) is made of copper to ensure thermal contact.

The HF-EPR setup includes a liquid helium magnetocryostat from *Oxford Instruments*. The Nb₃Sn superconducting solenoid magnet from *Oxford Instruments* provides the magnetic field. The magnet is cooled by a liquid helium bath, which means that the magnet is at a temperature of 4.2 K. To control the magnet a superconducting intelligent magnet power supply (Mercury iPS) from *Oxford Instruments* is used.

Prior to insertion of the jacket into the cryostat, the jacket with the sample rod is pumped and flushed with helium three times. After pumping and flushing, helium is flushed into the jacket up to a pressure of about 250 mbar to ensure thermal contact. The jacket is then inserted into the sample chamber, such that only the top part, made of stainless steel, is in contact with the environment. The sample chamber is separated from the helium bath by the variable temperature inset (VTI). It thermally disconnects the sample chamber from the helium bath as the inside of the VTI (sample chamber) is pumped continuously. The sample chamber and helium bath are connected via a needle valve in the wall of the VTI. By opening the needle valve, helium from the bath evaporates through the needle valve into the sample chamber, thereby cooling the sample in the jacket. The control of the temperature is ensured via adjusting the needle valve and using resistive heaters at the needle valve and near the sample. Furthermore, cernox temperature sensors are used to measure the temperature near the needle valve and near the sample. The heaters and temperature sensors near the needle valve and the needle valve itself are controlled by a cryogenic programmable intelligent temperature controller (Mercury iTC) from *Oxford Instruments*. The heaters and temperature sensors near the sample are controlled by the LS340 Temperature Controller from *Lake Shore*.

3.1.1 Sample preparation

Loose and fixed powder samples were prepared in brass rings, which are sealed at the top and bottom with double sided Kapton tape (such that the sample does not stick to the Kapton tape), as shown in Fig. 3.2. The ring is then inserted into the sample space in the sample rod.

For loose powder measurements, the powder was loosely inserted into the brass ring and sealed with double sided Kapton tape. Therefore, when sweeping the magnetic field for the first time, the crystallites align with their magnetic easy anisotropy axis parallel to the external magnetic field, which was observable by jumps in the transmission spectrum. Due to possible disordering of the crystallites in zero external magnetic field, the magnetic field was only swept down to 0.1 T such that the crystallites do not disorder before the next up sweep. Consequently, only one crystal orientation of the crystallites is measured, resulting in pseudo-single-crystal spectra.

For fixed powder measurements the powder was inserted into the brass ring together with eicosan. The brass ring was sealed by double sided Kapton tape and was heated to approximately 50°C to melt the eicosan. Upon cooling down to room temperature, eicosan solidifies and, thereby, fixes the crystallites in their initial random orientations. Consequently, a powder-average spectrum is measured and no jumps are visible in the transmission when sweeping the external magnetic field for the first time.

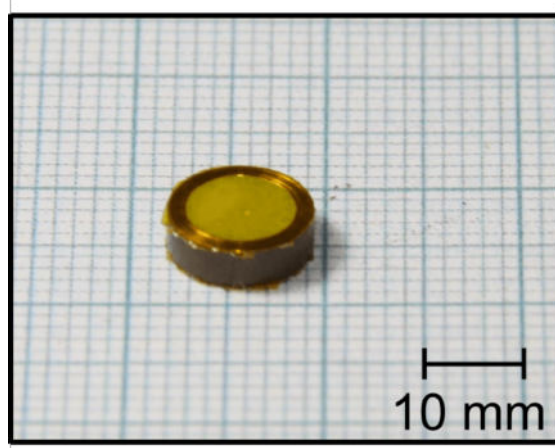


Fig. 3.2: Sample preparation of a fixed powder sample in a brass ring sealed with double sided Kapton tape. The figure is taken from [43].

Liquid solutions (biomimetics of $\text{Ln}^{3+}/\text{Ca}^{2+}$ -MDH enzymes) were measured using home built teflon sample holders, which are sealed with parafilm before inserting them into the sample space in the sample rod. When cooling down to the measurement temperature, which was below the melting point of these samples, the solution freezes. As no magnetic field is applied during cooling down, the molecules are fixed in random crystal orientations. Therefore, a "powder"-average spectrum is measured.

For the samples containing Nd-MDH enzymes, the sample was delivered in a frozen state (melting point of approximately 297 K) and was not supposed to melt, as another freezing routine could possibly harm the enzymes. Therefore, the teflon sample holders with the frozen solution were cooled using dry ice during the sample mounting procedure. Prior to insertion of the sample, the sample rod was cooled in liquid nitrogen. During the process of insertion of the sample into the sample rod, both the sample and the sample rod are placed in dry ice to ensure that the sample does not melt. After the sample was inserted into the sample rod, the sample rod was inserted into the jacket. The jacket was already prepared and inserted into the sample chamber, which was held at a constant temperature of 200 K, before insertion of the sample rod. The jacket was prepared by pumping once and flushing it with helium up to a pressure of 1020 mbar. Subsequently, the jacket was inserted into the sample chamber and pumped and flushed once, followed by flushing with helium up to a pressure of 1020 mbar. After insertion of the sample rod into the jacket, the

jacket with sample rod was then pumped and flushed two times, followed by flushing with helium up to a pressure of approximately 150 mbar to ensure thermal contact.

3.1.2 Background and Phase Mixing Correction

The measurement background of the transmission spectra was approximated by a polynomial function, which was fitted to the data of each spectrum (excluding resonance features) and subsequently subtracted from the corresponding spectrum.

Due to the microwave interacting with the sample, phase mixing may occur [45, 46]. Phase mixing refers to the mixing of the phase (dispersion) of the measured signal into the amplitude of the measured signal (absorption) [45, 46]. An example of phase mixing is presented in Fig. 3.3. In the top figure the absorption and dispersion is shown. The absorption features a maximum at the resonance position, whereas the dispersion features a zero crossing at the resonance position. Both the dispersion and the absorption are symmetric around the resonance position and feature a flat baseline. At the bottom figure an example, for the case that a fraction $\epsilon = 1/2$ of the dispersion is mixed into the absorption, is presented. The resulting signal, given by $y = (1 + \epsilon^2)^{-1/2}[A(x) + \epsilon D(x)]$ [45, 46], is not symmetric around the resonance position and the maximum of the signal is not located at the resonance position. Furthermore, the baseline is not flat.

To correct for phase mixing, the measured phase is multiplied by variable values of ϵ and is subsequently added to the measured transmission. The value of ϵ is varied until the resulting signal y features a flat baseline and exhibits an approximately lorentzian-like line shape (in the case of a sharp resonance feature without any shoulder features).

3.2 X-Band Electron Paramagnetic Resonance

The X-Band EPR setup of the working group of Peter Comba at Heidelberg University allows for EPR measurements at a frequency of $f = 9.6$ GHz. The magnetic field can be varied between 0 – 1.2 T and temperatures between 5 – 300 K can be reached.

The aforementioned spectrometer is the commercial Bruker Elexsys E500 EPR spectrometer from *Bruker*. The EPR setup includes an ER 041 XK VW Microwave Bridge, an ER41116DM CW dual mode resonator with irradiation grid and an ER 4112HV-CF58nc In-Cavity Cryogen Free (VT) System. To generate the magnetic field a water-cooled B-E25 electromagnet is used. To reach low temperatures, a cryostat, from *Cryo Edge*, with a compressor system is used. A Mercury iTC, from *Oxford Instruments*, is used for temperature control.

Additionally to the external applied static magnetic field, a small oscillating magnetic field is superimposed and the change in the transmission is measured. Consequently, the measured signal is the first derivative of the transmission with respect

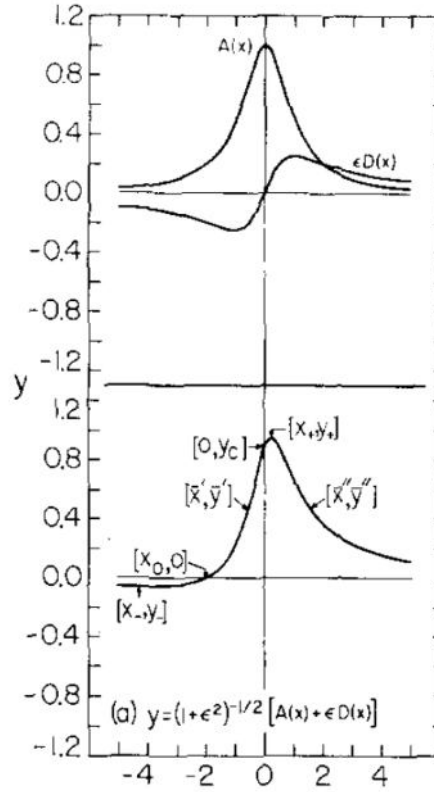


Fig. 3.3: Top: Absorption ($A(x)$) and dispersion multiplied with $\epsilon = 1/2$ ($\epsilon D(x)$) of a Lorentzian resonance signal. Bottom: Resulting measured signal $y = (1 + \epsilon^2)^{-1/2} [A(x) + \epsilon D(x)]$. The resonance position is marked with a vertical line. The figure is taken from [45].

to the magnetic field (dP/dB).

An advantage of the X-band setup compared to the aforementioned HF-EPR setup is, that a resonator cavity is used. Due to the resonance, the microwave field strength is increased in the resonator. As a result, the stronger microwave field strength in the resonator leads to a better signal-to-noise ratio.

The aforementioned modifications of the X-band EPR setup compared to the HF-EPR setup result in a high resolution of the measured spectra at a fixed frequency.

3.2.1 Sample preparation

Wilmad quartz (CFQ) EPR tubes were used for the X-band EPR measurements. They were filled with the liquid solutions up to approximately 2 cm, measured from the bottom of the sample tube. Subsequently, argon gas is flushed into the sample tubes for a few minutes, followed by closing the sample tube with the lid and sealing the lid with parafilm. Prior to insertion into the pre-cooled X-band EPR, the prepared sample tubes were cooled in liquid nitrogen.

3.3 Magnetisation measurements

3.3.1 Measurement Devices

For measuring static and dynamic properties of the samples, the magnetic property measurement system (MPMS3) from *Quantum Design* was used. It provides magnetic fields of 0 – 7 T and the temperature can be varied within 1.8 – 400 K. AC magnetic susceptibility measurements are possible within a frequency range of 1 – 1000 Hz and a modulation amplitude in the range of 0 – 0.01 T. Furthermore, it is possible to apply a static magnetic field during ac susceptibility measurements.

For measuring isothermal magnetisation for magnetic fields exceeding 7 T the vibrating sample magnetometer (VSM) option of the physical property measurement system (PPMS) from *Quantum Design* was used. The used PPMS provides magnetic fields of 0 – 14 T and the temperature can be varied within 1.8 – 300 K. The sample is vibrated within the pick up coils and the induced voltage in the coils, which is proportional to the magnetisation of the sample, is read out by the VSM detection module.

For the isothermal magnetisation and static magnetic susceptibility measurements performed in the MPMS3 the dc measurement option was used. When using the dc measurement option, the sample is gradually moved inside of the pick-up coils. The resulting magnetic flux induced in the pick-up coils is measured with a superconducting quantum interference device (SQUID). An example of the obtained voltage-versus-position-curve (vvpc) is illustrated by the red curve in Fig. 3.5. The vvpc is fitted by a dipole response function (shown as a dashed pink line in the figure) to obtain the magnetisation of the sample. Note, that the red curve in the figure was background corrected manually prior to fitting.

3.3.2 Sample preparation

Samples in polycrystalline powder form were measured using the VSM Powder Sample Holders (QDC-4096-388) from *Quantum Design*. The sample holder is made of two equal parts. The powder was filled into one of the open ends of one part. Subsequently, the stamp of the other capsule part is pushed into the open end of the first capsule part, containing the powder, to fix the powder in place. The capsule is then clipped into a brass holder. After clipping the capsule in the brass holder, the brass holder is mounted to a sample rod and inserted into either the MPMS3 or the PPMS.

Throughout this work different other sample preparation methods for liquids and frozen solutions were tested, which are described in section A.1 and section B.1.

3.3.3 Background correction

Both the brass holder and the measuring capsules contribute to the measured signal. For samples measured in the PPMS the background contribution to the total mea-

sured signal was less than 1 %. Consequently, the uncertainty intervals were chosen accordingly and no background correction was performed. For some of the samples measured in the MPMS the background contribution to the total measured signal exceeded 1 %. In this case a background correction was performed as described in the following.

The order of magnitude and the qualitative behaviour of the background signal was obtained by measuring the isothermal magnetisation and magnetisation as a function of temperature at a constant applied magnetic field for three different VSM capsules.

The isothermal magnetisation for all capsules was quasi-linear with magnetic field. At zero magnetic field the isothermal magnetisation was approximately zero for all capsules. The order of magnitude of the isothermal magnetisation of the background at 7 T and the order of magnitude of the slope of the isothermal magnetisation of the background are presented in Tab. 3.1. Note, that the values in the table are the largest values obtained from the measurement of three different VSM capsules. The sign, the absolute value and the slope of the isothermal magnetisation depends on the position of the capsule in the brass sample holder and how far the stamp of one of the capsule parts is pushed inside the open end of the other capsule part. The order of magnitude of the largest observed differences in the isothermal magnetisation at 7 T and the slope of the isothermal magnetisation of two capsules is also included in Tab. 3.1.

The magnetisation at a constant magnetic field as a function of temperature features the qualitative behaviour shown in Fig. 3.4. The magnetisation data measured at 1 T for three capsules, which were clicked into the sample holder with the same orientation ¹, are shown. The qualitative behaviour of the backgrounds is similar for all capsules. However, the measured curves of the magnetisation as a function of temperature of the different capsules are approximately shifted along y against each other by a constant value. In Tab. 3.1 the largest measured magnetisation of the three capsules and the largest difference in magnetisation between two capsules at the same temperature are presented.

Throughout this thesis, two different background correction methods were used:

- For measurements, where the largest value of the background was smaller than 2 % of the measured signal, the influence of the temperature- and field-dependent behaviour of the background can be neglected. The measured data was fitted by including a temperature- and field-independent parameter χ_0 to all fit functions to account for the background and the diamagnetic contribution of the sample. The resulting value of χ_0 was subsequently compared to the order of magnitude of the background and the diamagnetic contribution of the sample. This routine was applied for the Fe_2^{3+} -complexes in chapter 5.
- For measurements, where the largest value of the background exceeds 2 % of the measured signal, the influence of the temperature- and field-dependent

¹The signals can be mirrored at the temperature axis when changing the orientation of the capsule. Therefore, throughout this thesis, always the same orientation of the capsule was used.

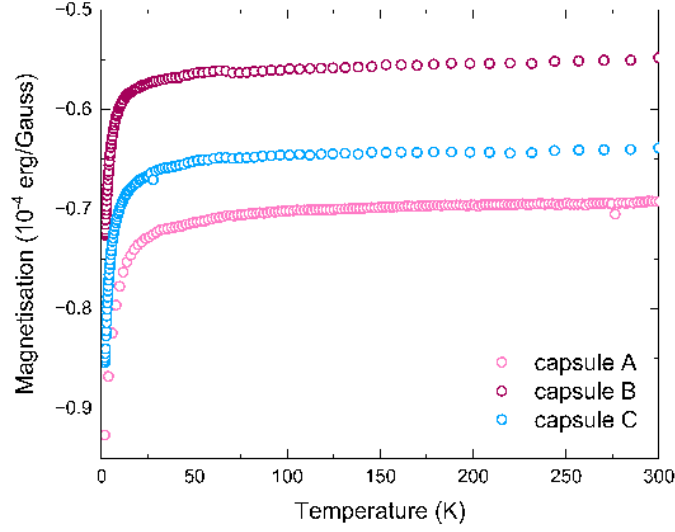


Fig. 3.4: Magnetisation of the brass holder and VSM capsule as a function of temperature measured at 1 T for three different capsules.

Values obtained for $M(B)$ at $T = 1.8$ K	
$ M(B = 7 \text{ T}) $ [erg G ⁻¹]	$1 \cdot 10^{-4}$
$ \Delta M(B = 7 \text{ T}) $ [erg G ⁻¹]	$2 \cdot 10^{-5}$
$ \frac{\partial M}{\partial B} $ [erg G ⁻²]	$4 \cdot 10^{-9}$
$ \Delta \frac{\partial M}{\partial B} $ [erg G ⁻²]	$2 \cdot 10^{-10}$
Values obtained for $M(T)$ at $B = 1$ T	
$ M(T = 1.8 \text{ K}) $ [erg/G]	$9 \cdot 10^{-5}$
$ \Delta M(T = 1.8 \text{ K}) $ [erg/G]	$2 \cdot 10^{-5}$

Tab. 3.1: Largest observed background values of three VSM capsules. $|M(B = 7 \text{ T})|$ is the largest observed absolute value of the isothermal magnetisation measured at 7 T. $|\Delta M(B = 7 \text{ T})|$ is the largest observed difference in the isothermal magnetisation measured at 7 T of two capsule backgrounds. $|\frac{\partial M}{\partial B}|$ is the largest observed absolute value of the slope of the isothermal magnetisation. $|\Delta \frac{\partial M}{\partial B}|$ is the largest observed difference in the absolute value of the slope of the isothermal magnetisation of two capsule backgrounds. $|M(T = 1.8 \text{ K})|$ is the largest measured value of the magnetisation at 1 T and 1.8 K. $|\Delta M(T = 1.8 \text{ K})|$ is the largest observed difference in the magnetisation measured at 1 T of two different capsules.

behaviour of the background was corrected by subtracting the vvpv of the background from the measured vvpv, as shown in Fig. 3.5. The dark blue line is the non-background corrected measured vvpv and the light blue line is the vvpv of the background. The red line is the vvpv after the background vvpv is subtracted from the measured vvpv. A dipole response fit, indicated by a dashed pink line, is performed to the background corrected vvpv in order to determine the magnetisation of the sample. This procedure accounts for the

qualitative behaviour of the background. As the absolute values of the background differ for different measurements capsules, the remaining contribution of the background due to this difference was approximated by including χ_0 to all fit functions. The resulting value of χ_0 was subsequently compared to the order of magnitude of the difference in backgrounds and the diamagnetic contribution of the sample. This routine was applied for the diradicals in chapter 4. Furthermore, it was applied for the frozen solutions in chapter 8. For this, a polycarbonate capsule (QDC-AGC3) in a straw sample holder (both from *Quantum Design*), including the solution in which the sample is dissolved, was used to measure the background, see section B.1.

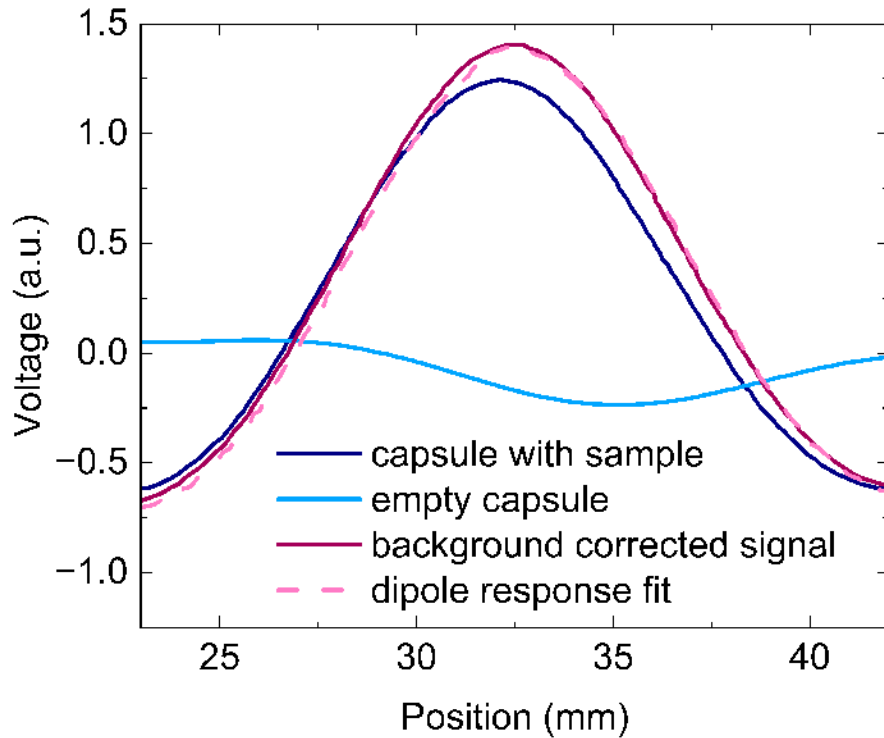


Fig. 3.5: Voltage-versus-position-curves measured at 1 T and 2.9 K. The capsule is a VSM Powder Sample Holder (QDC-4096-388) from *Quantum Design*.

Chapter 4

Monoindeno-Diazatetracene-Dimer-Diradicals

Throughout this thesis the term "radical" is used as an equivalent to the corresponding unpaired electron of the molecule hosting the radical. The unpaired electron is a particle with spin $1/2$ and $g \approx 2.002$ [47]. The probability density of finding this unpaired electron at a specific position in the molecule is given by the spin density. In this work, the unpaired electron, of the molecule hosting the radical, is assumed to be a localised particle located at the point of highest spin density.

This section focuses on the investigation of monoindeno-diazatetracene-dimer-diradicals. As the name implies, these molecules comprise two radicals whose spins are capable of interacting with each other. In the literature, SQUID measurements on a reference substance (Haley's diindenoanthracene) revealed an antiferromagnetic coupling of the spins of the two radicals with a magnetic interaction strength (J_{12} in eq.(2.29)) of approximately 4200 K [48]. Nuclear magnetic resonance (NMR) measurements on the monoindeno-diazatetracene-dimer-diradicals indicated a higher population of the triplet state $S = 1$ compared to Haley's diindenoanthracene [49]. This suggests a smaller energy gap between the triplet and the singlet state, which in turn implies a weaker magnetic interaction for the molecules investigated here.

4.1 Molecular Structure

In Fig. 4.1(a) the structural formula of the monoindeno-diazatetracene-dimer-diradical is shown. The molecule is composed of two identical components (monoindeno-diazatetracenes), which are linked by a covalent carbon bond. Each of the two parts of the molecule forms a radical. The radical positions are depicted in the figure with black dots. In Figure 4.1(b) the molecular structure of the monoindeno-diazatetracene-dimer-diradical is presented. The triisopropylsilane (R) and 1,3,5-trichlorobenzene (Ar) residues are depicted with thin lines in the figure, whereas the main part of the molecule is depicted with thicker lines. The monoindeno-diazatetracene parts of the molecule are rotated against each other with

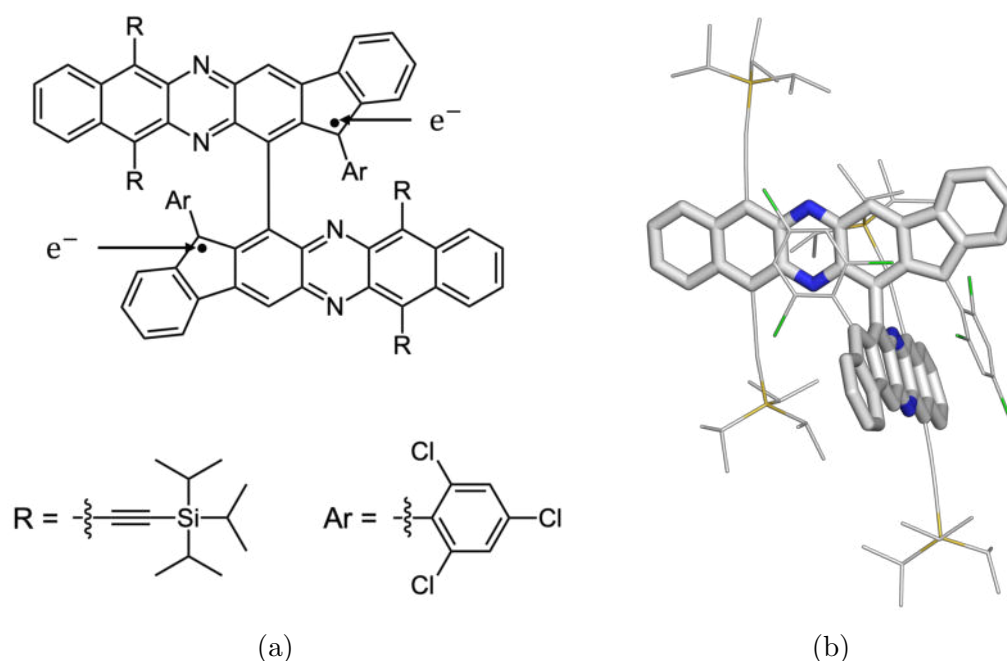


Fig. 4.1: Structural formula (a) of the monoindeno-diazatetracene-dimer-diradical. R and Ar residues are depicted at the bottom of the figure. The locations of the radicals are depicted with black dots. (b) Molecular structure of the monoindeno-diazatetracene-dimer-diradical. Grey: C; blue: N; yellow: Si; green: Cl. The terminal methyl groups and hydrogen atoms are excluded in (a) and (b) to increase visibility. The figures were provided by Pascal Merten [50].

the rotational axis being parallel to the central carbon bond.

Two samples (hereafter referred to as **i** and **ii**) containing these molecules were synthesised by Pascal Merten (group of Uwe Bunz at Heidelberg University) and were studied as polycrystalline powder. The distinction between the two samples lies in the manner of their refurbishment (processing) subsequent to sample synthesis. **i** was processed on silica gel using column chromatography, while **ii** was processed on alox alkaline using column chromatography [49].

4.2 Magnetisation Studies

The data presented in this chapter has been background-corrected in accordance with the methodology outlined in subsection 3.3.3. The obtained values for χ_0 can be explained by the background¹ and the diamagnetic contribution of the samples. The diamagnetic contribution was approximated by using $\chi_{\text{diam}} \approx -MW/2 \cdot 10^{-6} \text{erg G}^{-2} \text{mol}^{-1}$ [51], where MW is the molecular weight of the sample.

In Fig. 4.2(a) the isothermal magnetisation of a fixed powder sample of **i** (sample mass 1.69(10) mg) as a function of the applied magnetic field at 1.8 K is visualised. Coming from low magnetic fields, the isothermal magnetisation increases with in-

¹Typical values are given in subsection 3.3.3.

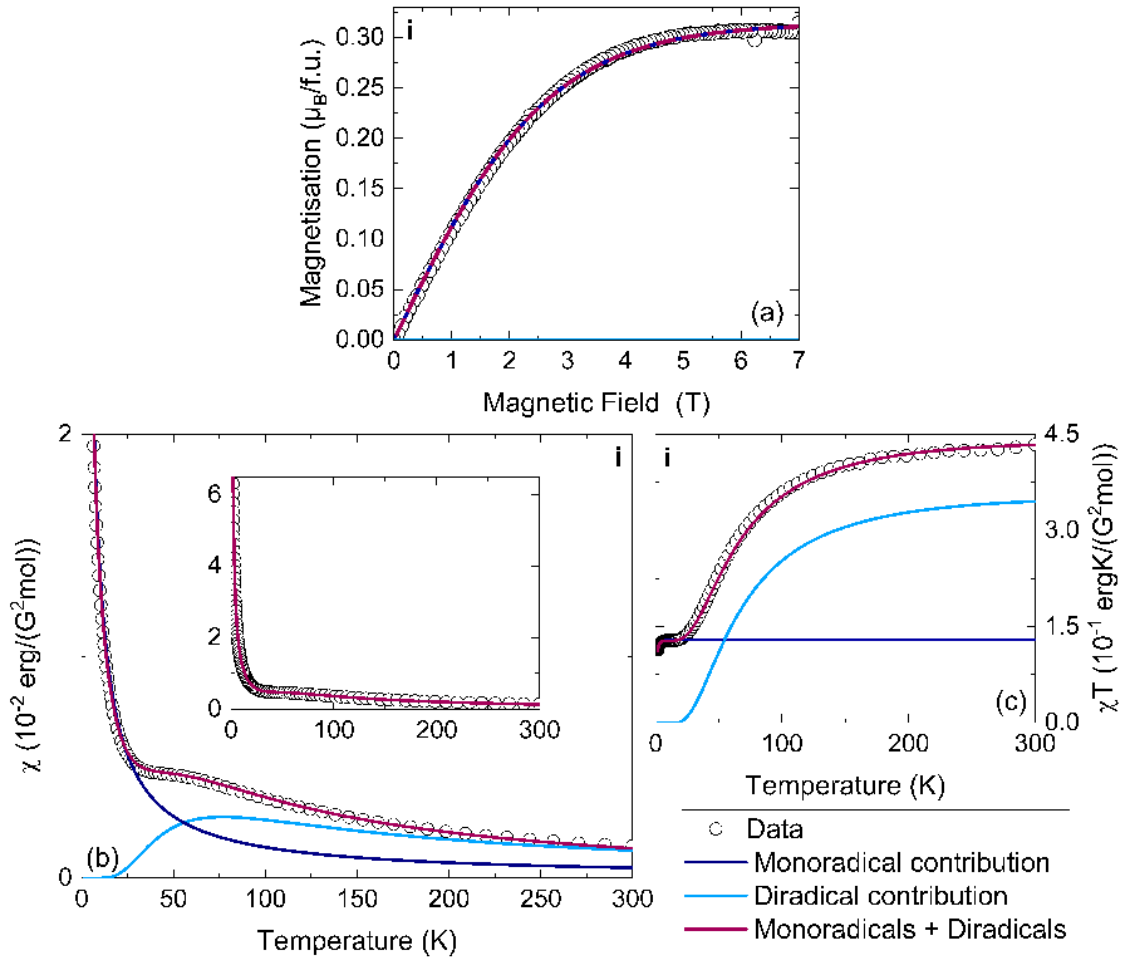


Fig. 4.2: (a) Magnetisation as a function of external magnetic field measured at 1.8 K for sample **i**. (b) Static magnetic susceptibility $\chi = M/B$ as a function of temperature measured at 1 T for sample **i**. The inset shows all measured data. (c) Static magnetic susceptibility $\chi = M/B$ multiplied by the temperature as a function of temperature measured at 1 T for sample **i**. Solid lines in all figures represent fits to the data as described in the text.

creasing magnetic field. The slope of the isothermal magnetisation decreases with rising temperature.

In Fig. 4.2(b) the temperature dependence of the static magnetic susceptibility of **i**, measured at 1 T, is presented. The inset shows all measured data, whereas Fig. 4.2(b) provides a closer examination of the lower magnetic susceptibility values. At low temperatures, χ decreases with increasing temperature until a plateau is reached at approximately 32 K. For temperatures exceeding 60 K, χ decreases again with increasing temperature.

In Fig. 4.2(c) the temperature dependence of the static magnetic susceptibility of **i** multiplied by the temperature at 1 T is shown. At low temperatures, the product of the temperature and the magnetic susceptibility χT , increases with increasing temperature until an intermediate plateau is reached at approximately 8 K. For

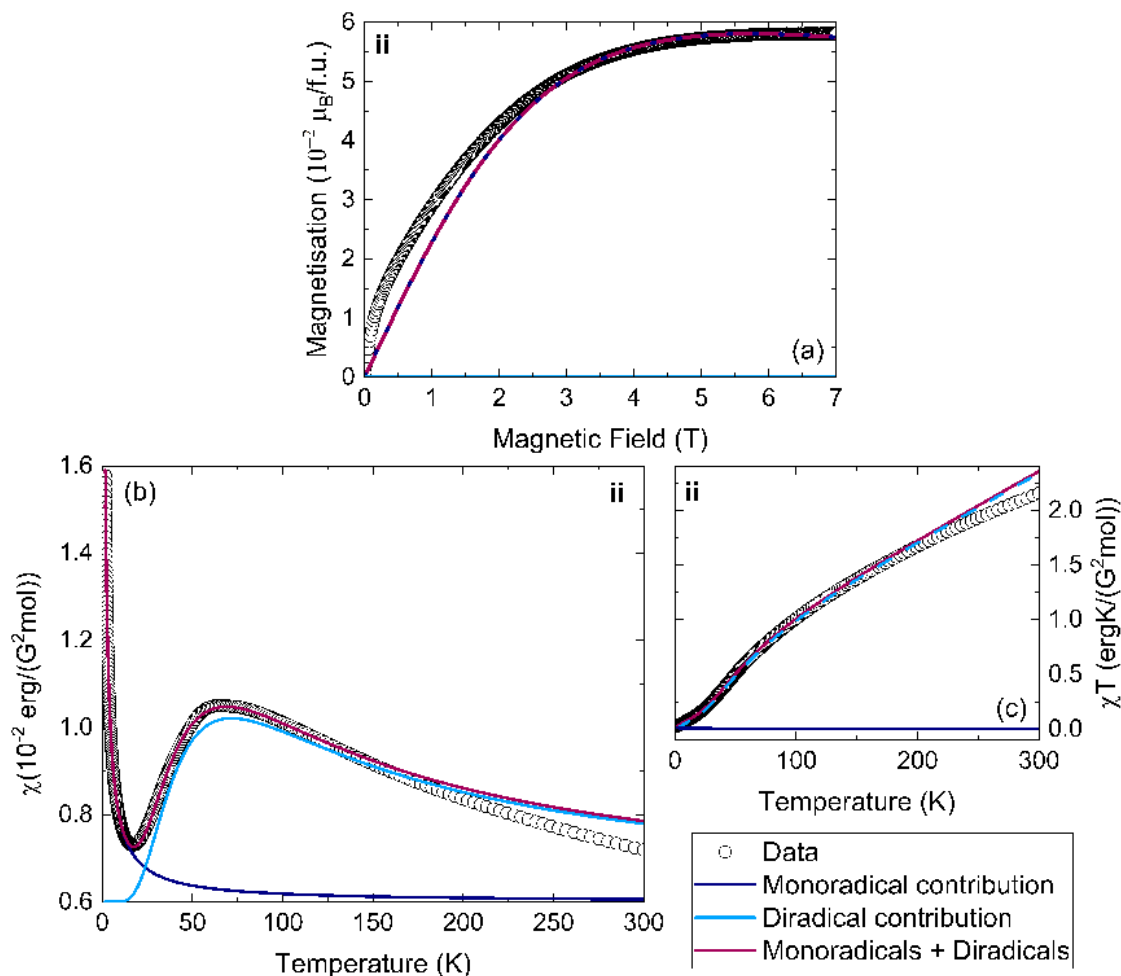


Fig. 4.3: (a) Magnetisation as a function of external magnetic field measured at 1.8 K for sample **ii**. (b) Static magnetic susceptibility $\chi = M/B$ as a function of temperature measured at 1 T for sample **ii**. (c) Static magnetic susceptibility $\chi = M/B$ multiplied by the temperature as a function of temperature measured at 1 T for sample **ii**. Solid lines in all figures represent fits to the data as described in the text.

temperatures above approximately 15 K, the χT product rises with increasing temperature, while the slope decreases with rising temperature.

In Fig. 4.3(a) the isothermal magnetisation of a fixed powder sample of **ii** (sample mass 9.13(10) mg) as a function of the applied magnetic field at 1.8 K is shown. At low magnetic fields, the isothermal magnetisation increases with increasing magnetic field. The increase is stronger than expected for a free spin- $\frac{1}{2}$ system, as evidenced by the comparison with a Brillouin function, depicted by the red line in the figure. This may be due to some kind of magnetic impurities. For magnetic fields exceeding approximately 5 T, the isothermal magnetisation saturates at a value of approximately $5.8 \cdot 10^{-2} \mu_B \text{ f.u.}^{-1}$.

In Fig. 4.3(b), the temperature dependence of the static magnetic susceptibility of **ii**, measured at 1 T, is presented. At low temperatures, χ decreases with increasing

temperature until a minimum is reached at approximately 17 K. For temperatures exceeding 17 K, χ increases with increasing temperature until a maximum is reached at approximately 65 K. As the temperature is increased further, the value of χ decreases finally with increasing temperature.

In Fig. 4.3(c) the temperature dependence of the static magnetic susceptibility multiplied by the temperature at 1 T is shown. At low temperatures, χT increases quasi-linear with increasing temperature. At approximately 26 K, the slope undergoes an increase, followed by a decrease at temperatures above approximately 100 K.

The data shown in Figs. 4.2 and 4.3 indicate the presence of two types of molecular species in the samples: molecules hosting diradicals and molecules hosting monoradicals². The intermediate plateau for **i** and the quasi-linear increase for **ii** at low temperatures in χT (Figs. 4.2(c) and 4.3(c)) in combination with the isothermal magnetisation data (Figs. 4.2(a) and 4.3(a)) suggest the presence of paramagnetic monoradicals in the sample. χT of paramagnetic monoradicals typically features a strong increase at low temperatures and a plateau at high temperatures, see Fig. 2.1 in subsection 2.2.1. The observed increase in χT with increasing temperature for temperatures above the intermediate plateau for **i** or the quasi-linear increase for **ii**, indicates the presence of antiferromagnetic (AFM) coupled radicals in the sample. At low temperatures, due to the AFM interaction, the diradicals populate the singlet state with $S = 0$. Upon increasing the temperature, the triplet state with $S = 1$ gets populated. The resulting behaviour of χ is described by the Bleaney-Bowers equation (see eq. (2.31)).

The static magnetic susceptibility data of **i** and **ii** was fitted using a sum of the exact formula for χ for non-interacting paramagnetic moments (see eq.(2.13) with eq.(2.10)) weighted by the fraction of monoradicals M_M and the Bleaney-Bowers equation (see eq.(2.31)), for the diradicals, scaled by the fraction of diradicals M_D . A fit including the entire temperature range for **ii** did not yield a satisfactory qualitative description of χT . This is due to the fact that at temperatures exceeding approximately 134 K, the curvature of χT cannot be explained by a diradical system: It can be observed that the curvature is larger for a diradical system than the observed curvature of the data in Fig. 4.3(b). This discrepancy in curvature may be attributed to the presence of some kind of magnetic impurities in the sample that leads to a quasi-linear decrease of χ at high temperatures³. The fit was, therefore, only performed for the data obtained at temperatures below 134 K. The best fit for **i** and **ii** is illustrated by the red lines in Figs. 4.2(b) and 4.3(b). The corresponding monoradical and diradical contributions (including χ_0 for **ii** to enhance comparability with the data) are depicted with dark blue and light blue lines in the figure. The parameters obtained from the fit are presented in Tab. 4.1.

²The data would also be described by a system of $(2n + 1)$ -AFM-coupled radicals with a large interaction strength. Nevertheless, the existence of such $(2n + 1)$ -radical systems is rather unlikely [50].

³These impurities can be of a different type as the ones leading to the discrepancy of the isothermal magnetisation from the Brillouin function.

		Fit to $M(B)$		Fit to $\chi(T)$			
	χ_D [erg G ⁻²]	M_M [%]	χ_0 [erg G ⁻²]	M_D [%]	J [K]	M_M [%]	χ_0 [erg G ⁻²]
i	$5 \cdot 10^{-10}$	31(3)	$2 \cdot 10^{-9}$	56(8)	123(7)	37(4)	$2 \cdot 10^{-10}$
ii	$4.5 \cdot 10^{-9}$	≤ 7	$3.8 \cdot 10^{-9}$	80(5)	115(11)	5(2)	$3.2 \cdot 10^{-8}$

Tab. 4.1: Overview of the fit parameters obtained from fits to the data as described in the text for **i** and **ii**. The values for χ_D and χ_0 are approximate values. χ_D was approximated as described in the text ⁴.

The isothermal magnetisation data of **i** and **ii** was fitted using a Brillouin function (see eq.(2.10), which is scaled by the fraction of monoradicals in the sample M_M together with a simulated diradical contribution, obtained using the microscopic parameters for the diradicals from the Bleaney-Bowers-fit to χT . The best fits to the isothermal magnetisation are depicted in Figs. 4.2(a) and 4.3(a). For **i** the fitted curve fits well to the data. For **ii** the saturation of the isothermal magnetisation yields $M_M = 7\%$, which includes monoradicals and impurities, as previously explained. The contribution of the diradicals to the isothermal magnetisation was found to be zero, thereby demonstrating that the measured isothermal magnetisation is dominated by the monoradical fraction. The fit parameters obtained from fitting the isothermal magnetisation data are presented in Tab. 4.1. The concentration of monoradicals obtained from the fit to the isothermal magnetisation data and susceptibility data are found to be in agreement with each other within the uncertainty ranges.

A comparison of the results obtained for **i** and **ii** reveals that the interaction strength of the diradicals in **i** and **ii** are consistent with each other within the uncertainty range, indicating that the difference in processing does not influence the interaction of the diradicals. The interaction strength observed for **i** and **ii** is approximately 35 times smaller than that observed for Haley’s diindenoanthracene [48]. This corroborates the hypothesis derived from NMR that the interaction strength of the molecules under investigation in this work is smaller than that of Haley’s diindenoanthracene. Haley’s diindenoanthracene has a monomer structure (molecule consists of a single part), whereas the here investigated monoindeno-diazatetracene-dimer-diradicals feature a dimer structure (molecule consists of two parts). The smaller interaction strength can be attributed to this difference: The dimer structure of the here investigated molecule leads to an exchange path for the radical interaction which is longer than for Haley’s diindenofluoren, resulting in a weaker interaction strength for the compounds investigated here.

The concentration of diradicals is higher for **ii** as compared to **i**. This can be attributed to the disparate processing methodologies employed subsequent to the syn-

⁴To compare the values of χ_0 with the sample holder signal and the diamagnetic contribution of the sample, the values of χ_0 and χ_D were converted into an absolute susceptibility in units of erg G⁻². This absolute value for the susceptibility is obtained from multiplying the value of the susceptibility in units of erg G⁻² mol⁻¹ with the number of moles in the measured sample.

thesis of **i** and **ii**. In Fig. 4.4 the synthesis of the diradical hosting molecule is shown. The synthesis is started with the left molecule, where there are two H-atoms bound to the N-atoms, resulting in the absence of unpaired electrons [50]. When adding 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) to the reactant, the H-atoms are removed in a proton coupled oxidation process, resulting in the presence of diradicals [50]. When processing via silica gel (as done for **i**) or alox alkaline (as done for **ii**) using column chromatography, this step can be partially reversed meaning that some H-atoms bond to the N-atoms again [50]. Consequently, it is possible that only one H-atom bonds to a N-atom in one molecule. This results in the presence of monoradicals. Alox alkaline is less protic (meaning that it is less likely that it donates protons) compared to silica gel which suggests a smaller concentration of molecules including only a monoradical for the processing with alox alkaline [50].

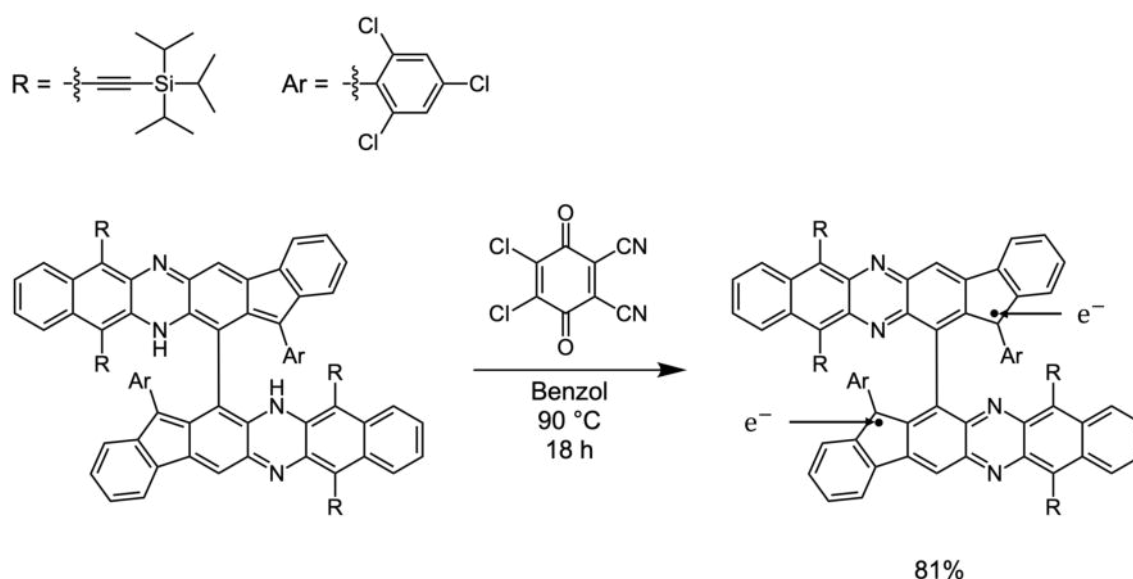


Fig. 4.4: Synthesis scheme of the monoindeno-diazatetracene-dimer-diradical. R and Ar residues are depicted at the top of the figure. The locations of the radicals are depicted with black dots in the product. The terminal methyl groups and hydrogen atoms, except those bond to nitrogen atoms, are excluded to increase visibility. The yield of this synthesis is 81 %. The figure was provided by Pascal Merten [50].

Chapter 5

Dinuclear Fe^{3+} Complexes

The type of complexes investigated in this chapter are possible candidates for so-called "resting-states" of a proposed mechanism for a halogenation process [52, 53]. In this work, diiron-complexes containing halogenates, specifically Br and Cl, are studied.

In order to validate this proposed process, a magnetic characterisation of this type of complexes is necessary [54]. Further magnetic characterisation of them requires the determination of the coupling constant of the interaction between the spins of the Fe^{3+} -centres. Furthermore, magnetic simulations permit the determination of the concentration of the dinuclear complexes and mononuclear residues in the samples in combination with measurements of the static magnetic susceptibility and isothermal magnetisation.

5.1 Molecular Structure

In Fig. 5.1 the structural formula of the $[\text{Br}(\text{L}^{\text{N7H}})\text{Fe}^{\text{III}} - \text{O} - \text{Fe}^{\text{III}}(\text{L}^{\text{N7H}})\text{Br}]$ (hereafter referred to as **A**) and $[\text{Cl}(\text{L}^{\text{N7H}})\text{Fe}^{\text{III}} - \text{O} - \text{Fe}^{\text{III}}(\text{L}^{\text{N7H}})\text{Cl}]$ (hereafter referred to as **B**) complex and the molecular structure thereof are depicted. The complexes were synthesised by Rejith Radhamani (group of Peter Comba at Heidelberg University) and were studied as polycrystalline powder. **A** and **B** have the same molecular structure, except that the Br-atoms in **A** are exchanged for Cl-atoms in **B**. The two paramagnetic Fe^{3+} -ions are connected to each other via an oxygen atom. The ligand atoms are arranged centro-symmetrically with respect to this oxygen atom connecting the two Fe^{3+} -ions [52]. Each of the two Br/Cl-atoms is bonded to one of the Fe^{3+} -ions. In total, each Fe^{3+} -ion is six-fold coordinated by four nitrogen, one bromine/chlorine and one oxygen atom. The iron ions in this type of coordination occupy the three-times ionised Fe^{3+} ground state [55]. The Fe^{3+} -ions can occupy either the high spin $S = 5/2$ or the low spin $S = 1/2$ state.

The potential residues of mononuclear species in the sample include Fe^{2+} -ions as magnetic centres since the synthesis of the Fe_2^{3+} complexes was started from

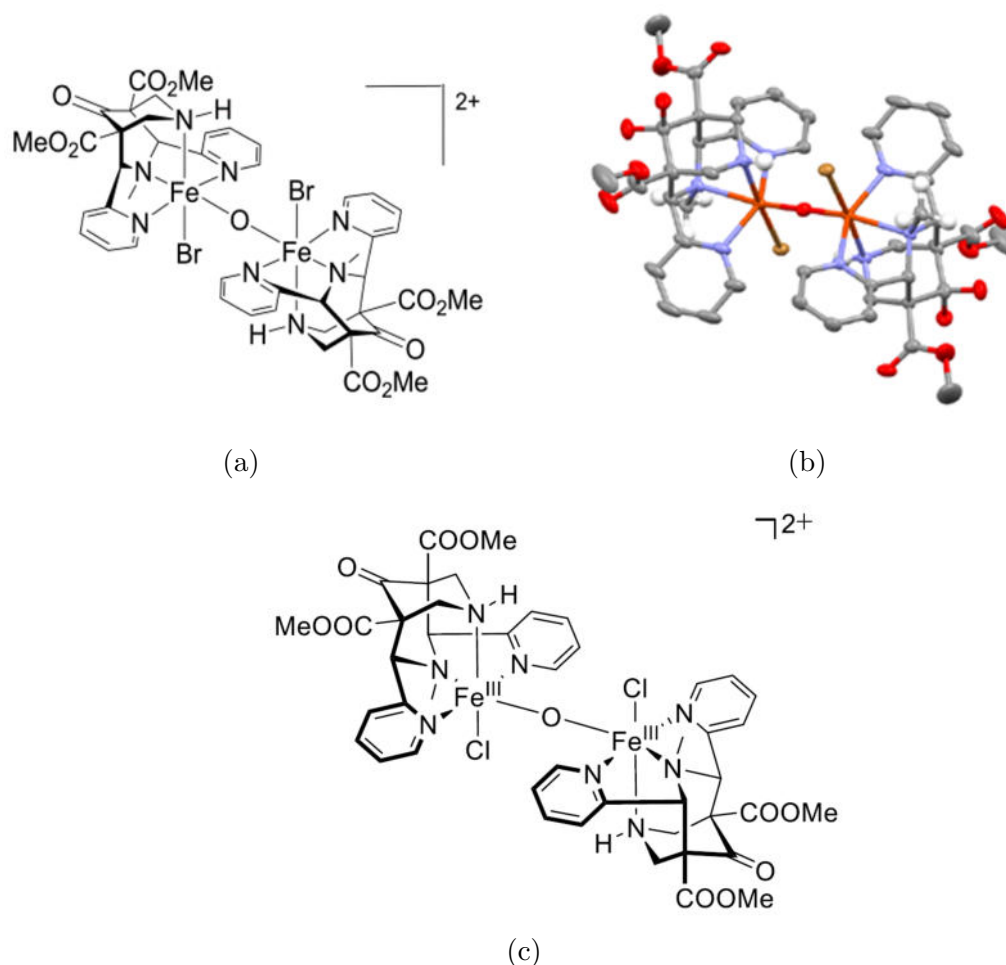


Fig. 5.1: (a) Structural formula of **A**. (b) Molecular structure of **A**. Orange: Fe³⁺; grey: C; blue: N; red: O; brown: Br; white: H. The figures are taken from [56]. (c) Structural formula of **B**. The figure is taken from [54]. Hydrogen atoms, except for N^{7H} and N³-CH₃, are excluded to increase visibility.

Fe²⁺ [55]. Fe²⁺ can occupy either the low spin $S = 0$ or the high spin $S = 2$ state.

5.2 Magnetisation Studies

The following data have been background-corrected in accordance with the methodology outlined in subsection 3.3.3. The obtained values for χ_0 can be explained by the background ¹ and the diamagnetic contribution of the samples. The χT data were corrected for the obtained χ_0 value to increase visibility. For the isothermal magnetisation, the simulation includes the obtained χ_0 value.

In Figs. 5.2(a) and (c) the magnetisation of the fixed powder sample of **A** and **B** (sample mass 14.30(10) mg for **A** and 13.82(10) mg for **B**) as a function of the

¹Typical values are given in subsection 3.3.3.

applied magnetic field for various constant temperatures is shown. At low magnetic fields, the magnetisation at 1.8 K increases strongly with increasing magnetic field compared to the magnetisation of a free magnetic moment. This is an indication for the magnetic anisotropy of the magnetic moment of the iron-ions, dominating the isothermal magnetisation value at low temperatures. Upon increasing magnetic field the slope of the magnetisation decreases but does not reach a constant value. A comparison of the magnetisation measured at 1.8 K with measurements at 3 K and 5 K reveals that the slope of the increase in magnetisation at low magnetic fields decreases with increasing temperature.

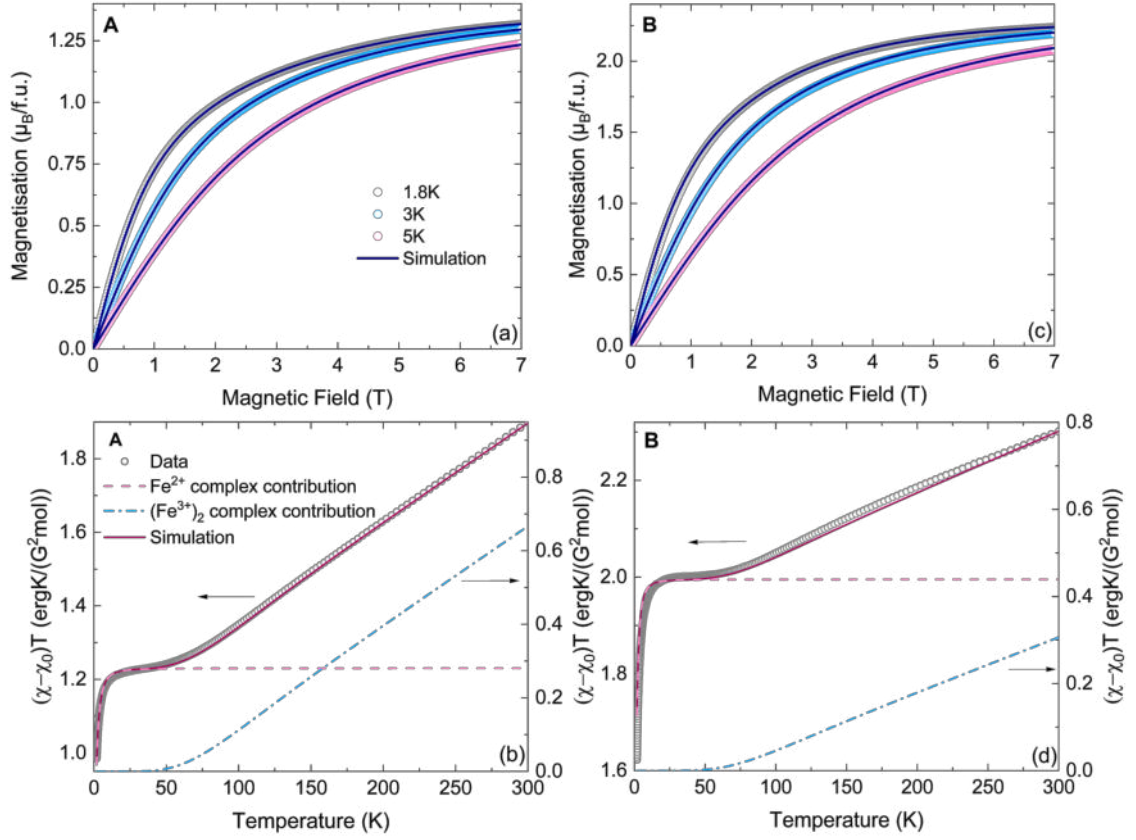


Fig. 5.2: (a) and (c): Magnetisation as a function of external magnetic field measured at three different temperatures for sample **A** and **B**, respectively. (b) and (d): Static magnetic susceptibility $\chi = M/B$ multiplied by the temperature as a function of temperature measured at 0.1 T for sample **A** and **B**, respectively. Solid, dashed and pointed lines represent simulations using the Hamiltonian in eq. (5.1).

In Figs. 5.2(b) and (d) the temperature dependence of the static magnetic susceptibility multiplied by temperature, measured at 0.1 T is shown. At low temperatures, the product of the temperature and the magnetic susceptibility χT increases rapidly with temperature. At $T \approx 30$ K an intermediate plateau at approximately $1.23 \text{ erg K G}^{-2} \text{ mol}^{-1}$ for **A** and $2.00 \text{ erg K G}^{-2} \text{ mol}^{-1}$ for **B** is reached. For temperatures above approximately 45 K χT increases quasi-linearly up to the highest measured temperature of 300 K.

The data shown in Fig. 5.2 indicate the presence of two types of complexes in the samples: dinuclear Fe_2^{3+} complexes and mononuclear Fe^{2+} complexes. The intermediate plateau in Figs. 5.2(b) and (d) and the magnetisation data in Figs. 5.2(a) and (b) suggest the presence of paramagnetic Fe^{2+} complexes: χT of paramagnetic moments typically features a strong increase at low temperatures and a plateau at high temperatures. The temperature at which the plateau is reached and the slope of the increase at low temperatures is determined by the anisotropy and the magnetic moment. The isothermal magnetisation of paramagnetic moments increases with increasing magnetic field and saturates at high magnetic fields. The slope of the increase at low magnetic fields is dominated by the anisotropy. Upon increasing temperature thermal fluctuations increase, which causes the magnetisation to approach that of a free magnetic moment in the limit of high temperatures, resulting in a decrease of the slope of the magnetisation. The observed increase in χT with temperatures above 45 K indicates the additional presence of complexes where the Fe^{3+} -ions are coupled antiferromagnetically (AFM): At low temperatures, due to the AFM interaction, the magnetic moments of the two Fe^{3+} -ions in the Fe_2^{3+} complexes are oriented antiparallel to each other, resulting in a zero net magnetisation (and therefore, zero net susceptibility). As the temperature is increased, thermal fluctuations result in a reduction in the degree of alignment of the magnetic moments. Consequently, χT approaches that of free Fe^{3+} -ions at high temperatures, resulting in a second plateau. The temperature at which the second plateau is reached is dependent on the interaction strength. In the case of **A** and **B** the plateau is not reached within the measured temperature region.

The isothermal magnetisation and static magnetic susceptibility was simulated using a model including a contribution of the Fe^{2+} complexes and Fe_2^{3+} complexes. The following Hamiltonian was employed for the simulations:

$$\hat{H} = \hat{H}_{\text{Fe}^{2+}} + \hat{H}_{\text{Fe}_2^{3+}} \quad (5.1)$$

with $\hat{H}_{\text{Fe}^{2+}}$ being the Hamiltonian describing the contribution of the Fe^{2+} complexes and $\hat{H}_{\text{Fe}_2^{3+}}$ being the Hamiltonian describing the contribution of the Fe_2^{3+} complexes. Both include the Zeeman Hamiltonian (eq.(2.7)) assuming an isotropic g -tensor. In addition to this $\hat{H}_{\text{Fe}^{2+}}$ includes the CF-Hamiltonian describing the influence of the ligands on the Fe^{2+} -ions magnetic moments, given by the second-order zero-field splitting parameters D and E , see eq.(2.27). $\hat{H}_{\text{Fe}^{2+}}$ thereof reads:

$$\hat{H}_{\text{Fe}^{2+}} = \hat{H}_Z^{\text{Fe}^{2+}} + \hat{H}_{\text{CF}}^{\text{Fe}^{2+}} \quad (5.2)$$

$\hat{H}_{\text{Fe}_2^{3+}}$ only includes the Hamiltonian describing the interacting system of the two magnetic moments of the Fe^{3+} -ions, assuming an isotropic interaction $\mathbf{J}$, in addition to the Zeeman Hamiltonian:

$$\hat{H}_{\text{Fe}_2^{3+}} = \sum_{i=1}^2 \hat{H}_Z^{\text{Fe}_2^{3+},i} + \hat{H}_J^{\text{Fe}_2^{3+}} \quad (5.3)$$

with

$$\hat{H}_J^{\text{Fe}_2^{3+}} = \hat{\mathbf{S}}_{\text{Fe}_2^{3+},1}^T \mathbf{J} \hat{\mathbf{S}}_{\text{Fe}_2^{3+},2} \quad (5.4)$$

A crystal field term was not included for the Fe_2^{3+} complexes, as the orbital momentum of Fe^{3+} -ions is approximately zero, resulting in $E, D \approx 0$.

The isothermal magnetisation curves resulting from this model (weighted by the Fe^{2+} complex fraction M_M and the Fe_2^{3+} complex fraction M_D in the sample) at temperatures of 1.8 K, 3 K, and 5 K were fitted simultaneously to the measured magnetisation at all three temperatures. Analogously the χT curve resulting from this model, also weighted by the two different contributions, was fitted to the measured χT curve. The parameters obtained for the best fit are listed in Table 5.1. For the simulations the following assumptions were used: Fe^{2+} -ions adopt the high spin state. This is due to the fact that in the low-spin state, the Fe^{2+} -ions do not exhibit unpaired electrons, rendering them diamagnetic. The magnetisation data indicates paramagnetic behaviour, suggesting that the high-spin state is occupied. For the Fe^{3+} -ions of the Fe_2^{3+} complexes, it was assumed that the high-spin state is occupied. Assuming that the Fe^{3+} -ions of the Fe_2^{3+} complexes are in the low-spin state did not explain the data: The increase of the simulated χT , assuming the low spin state, with increasing temperature above approximately 45 K did not show the quasi-linear behaviour observed in the data, but rather a left-bended curve.

The isothermal magnetisation data was fitted without a contribution of Fe_2^{3+} -ions. For the simulation of the χT data, the parameters obtained from the simulation of the isothermal magnetisation for the Fe^{2+} complexes were fixed. Nevertheless, M_M was not fixed to account for slight changes in the plateau height due to the measurement uncertainty. Using the Fe_2^{3+} complex fraction obtained from the fit to χT to model the isothermal magnetisation data yields no contribution of the Fe_2^{3+} complexes to the isothermal magnetisation.

The isothermal magnetisation and static magnetic susceptibility shown in Fig. 5.2 are well described by the aforementioned model and assumptions, as can be seen by comparing the red and dark blue lines with the data in the figures. The pink dashed lines in Fig. 5.2(b) and (d) represent the contributions of the Fe^{2+} complexes to the data. This contribution describes the pronounced increase in χT at low temperatures and the subsequent plateau. The contribution of the Fe_2^{3+} complexes is displayed as a blue dashed and pointed line and describes the increase of χT at temperatures above approximately 45 K. The Fe^{2+} complex fraction for each sample determined from the fit to the isothermal magnetisation is in agreement with the one obtained from the χT curves within their uncertainty ranges for both samples respectively, see Table 5.1.

As the simulated χT product of the contribution of Fe_2^{3+} complexes is multiplied by the Fe_2^{3+} complex fraction it is not possible to determine the fraction of Fe_2^{3+} complexes M_D and the square of the g -value independently from each other. This is due to both parameters being prefactors in the simulation function in the limit of small magnetic energy compared to the interaction energy and high thermal energy compared to the magnetic energy. The product that best describes the data of **A** is $M_D \cdot g_{\text{Fe}^{3+}}^2 = 3.06(14)$. Assuming $g_{\text{Fe}^{3+}} = 2$ (where $g = 2$ is assumed as the g -factor of magnetically interacting Fe^{3+} -ions was previously found to be approximately 2 [57])

		Fit to $M(B)$			
Sample	χ_D [erg G ⁻²]	M_M [%]	$ D $ [GHz]	$ E $ [GHz]	χ_0 [erg G ⁻²]
A	$-7 \cdot 10^{-9}$	30(2)	55(5)	17(3)	$6 \cdot 10^{-9}$
B	$-7 \cdot 10^{-9}$	51(2)	37(3)	5.4(46)	$6 \cdot 10^{-9}$
		Fit to $\chi T(T)$			
Sample	χ_D [erg G ⁻²]	M_D [%]	J [K]	M_M [%]	χ_0 [erg G ⁻²]
A	$-7 \cdot 10^{-9}$	77(4)	288(3)	31(2)	$1 \cdot 10^{-11}$
B	$-7 \cdot 10^{-9}$	39(7)	312(24)	53(2)	$1 \cdot 10^{-10}$

Tab. 5.1: Overview of the parameters obtained from simulations to the magnetisation versus magnetic field curves and magnetic susceptibility multiplied by temperature versus temperature curves for **A** and **B**. The values for χ_0 and χ_D are approximate values. The value of χ_D for **A** in units of erg G⁻² was approximated by using the formula $\chi_{\text{diam}} \approx -MW/2 \cdot 10^{-6} \text{erg G}^{-2} \text{mol}^{-1}$ [51], where MW is the molecular weight of the sample. The value of χ_D for **B** is obtained by approximating the diamagnetic contribution in units of erg G⁻² of the sample using $\chi_{\text{diam}} = -6.6717 \cdot 10^{-4} \text{erg G}^{-2} \text{mol}^{-1}$ [54]².

yields a fraction of 77(4) % of Fe_2^{3+} complexes in the sample. Analogously, for **B** the Fe_2^{3+} complex fraction is 39(7) % assuming $g_{\text{Fe}^{3+}} = 2$, as the value of $M_D \cdot g_{\text{Fe}^{3+}}^2$ was found to be equal to 1.55(28).

A comparison of the two samples reveals that sample **A** exhibits a higher Fe_2^{3+} complex fraction. The interaction strength between the magnetic moments of the Fe^{3+} -ions of the Fe_2^{3+} complexes of **A** and **B** coincide within their uncertainty ranges. In conclusion, the exchange of bromine atoms by chloride atoms did not result in an altered interaction strength for the AFM interaction between the magnetic moments of the Fe^{3+} -ions of the Fe_2^{3+} complexes within the measurement sensitivity. Nevertheless, the isothermal magnetisation of the Fe^{2+} complexes as a function of the magnetic field can be described by different CF-parameters for both samples. A comparison of the CF parameter D for the two samples reveals that the value of D is smaller for sample **B** than for **A**. This shows that the anisotropy is larger for sample **A**. Furthermore, the ratio of E/D is larger for **A** as for **B**. As E/D is a measure of the axiality of the crystal field, this implies that the crystal field is more axial for **B**. These results match the naive expectation that the coordination to differing halogenates changes the crystal field approximately only in the geometric direction of the halogenates. Consequently, the crystal field is altered and the interaction between the magnetic moments of the Fe^{3+} -ions via the oxygen atom stays approximately unchanged.

²To compare the values of χ_0 with the sample holder signal and the diamagnetic contribution of the sample, the values of χ_0 and χ_D were converted into an absolute susceptibility in units of erg G⁻². This absolute value for the susceptibility is obtained from multiplying the value of the susceptibility in units of erg G⁻² mol⁻¹ with the number of moles in the measured sample.

Chapter 6

Mononuclear Er^{3+} Complex

In the preceding chapter, dinuclear Fe^{3+} complexes - a subset of transition metal complexes - were investigated. However, with the discovery of the first single molecular magnet (SMM) containing only a single lanthanide (Ln) ion [58, 59], a new research field on rare earth metal-based complexes arose. It is typically the case that electronic $4f$ -orbitals are more shielded from the ligand field than $3d$ -orbitals. This is due to the fact that the probability of finding the $4f$ -electron in the vicinity of the core is always greater than that of the $5s/5p$ -electrons [60–62]. As a consequence (of the effective shielding of the $4f$ -electrons by the $5s$ - and $5p$ -electrons), they exhibit a strong spin orbit coupling, in contrast to most $3d$ -ions [24]. The latter ones are typically less shielded, resulting in a partial or complete quenching of their orbital momentum, which in turn leads to a weaker spin-orbit coupling [24]. As a result, $4f$ -electrons (excluding Gd, La and Lu) are appropriately described by the total angular momentum J (as S and L are not good quantum numbers in case of strong spin-orbit coupling). The electronic $3d$ - and $4f$ -orbitals display pronounced angular-dependent charge distributions [24]. Therefore, spin-orbit coupling results in an anisotropy of the total spin. The enhanced spin-orbit coupling of $4f$ -electrons in $4f$ single ion systems results typically in a greater anisotropy compared to that of most $3d$ single ion systems. Therefore Ln-based single molecular magnets are promising candidates for SMMs, as they can exhibit higher effective barriers. It should be noted, however, that they often show unfavourable fast relaxation, as for example quantum tunnelling can be more enhanced ¹.

Previous studies have demonstrated the suitability of Er-containing complexes for HF-EPR measurements [40, 63–66]. In these studies, the investigation of not only the ground state but also multiple energetically higher-lying Kramers doublets was possible [40, 63, 64]. The objective of such measurements is to gain deeper insights into the influence of complex geometry on its magnetic behaviour. Pentagonal-bipyramidally-coordinated Er^{3+} complexes have already been subject of investigations, which revealed that the exchange of two of the coordinating molecules yields

¹This is due to the strong anisotropy, which leads to the mixing of different $|m_J|$ states. Therefore the overlap integral between two eigenstates is finite.

markedly distinct characteristics [63, 67]. The present study on a muffin-shaped Er^{3+} complex seeks to determine whether even more substantial structural modifications result in similar disparate magnetic properties.

6.1 Molecular and Crystal Structure

In Fig. 6.1a the molecular structure of the phenanthroline-pyridine-triazole (PPT) complex $[\text{Er}(\text{PPTMP})_2(\text{MeOH})][\text{OTf}]_3 \cdot 3\text{MeOH}$, which is investigated in this work, is depicted. The complex was synthesised and characterized (including the structural analysis) by Gerlinde Greif (group of Peter Roesky at KIT) and was studied as polycrystalline powder. The benzene rings, which are bound to the coordination atoms of the central Er^{3+} -ion, form two planes which are nearly perpendicular to each other. The planes are slightly tilted in themselves, creating a cone-like shape. The Er^{3+} -ion is nine-fold coordinated by 8 nitrogen atoms and one methanol molecule, which results in a muffin-shaped arrangement, as shown in Fig. 6.1b. In Fig. 6.1c it is illustrated that a single structural unit cell contains two distinct Er^{3+} -sites whose surrounding ligand fields are point-symmetric to each other with the Er^{3+} -ion serving as the inversion centre. From the overall structure it can be deduced that the erbium-ion is in the three-times ionised Er^{3+} ground state [68] resulting in a total angular momentum of $J = 15/2$ of the Er^{3+} -ion.

6.2 Magnetisation Studies

6.2.1 Static Magnetisation and Magnetic Susceptibility

In Fig. 6.2(a) the isothermal magnetisation of the fixed powder sample as a function of the applied magnetic field for various constant temperatures is shown. The sample mass for this measurement was 5.27(10) mg. At low magnetic fields, the magnetisation at 1.8 K increases strongly with increasing magnetic field compared to the magnetisation of a free magnetic moment. This indicates a strong magnetic anisotropy of the Er^{3+} -ions total magnetic moment. At high fields, a quasi-linear field-dependence of the magnetisation is visible. Up to a magnetic field of 14 T the magnetisation is not saturated. At 3 K and 5 K, the magnetisation increases with increasing magnetic field. When comparing the slope of the increase in magnetisation at low magnetic fields for the three different temperatures, it can be observed that the slope decreases with increasing temperature. The decrease of the slope of the magnetisation at low magnetic fields with increasing temperature is due to the increase in thermal fluctuations. Therefore the magnetisation of a free magnetic moment is approached in the limit of high temperatures. At high magnetic fields, the magnetisation measured at 3 K and 5 K reaches the one measured at 1.8 K.

By interpolating the gradient of the quasi-linear part of the magnetisation at 1.8 K to zero field, a magnetisation of about $4.6 \mu_B$ is obtained. Dividing this by the Er^{3+} Landé g -factor of $g_J = 6/5$ [24] suggests that the $|m_J| \approx 7/2$ Kramers doublet is

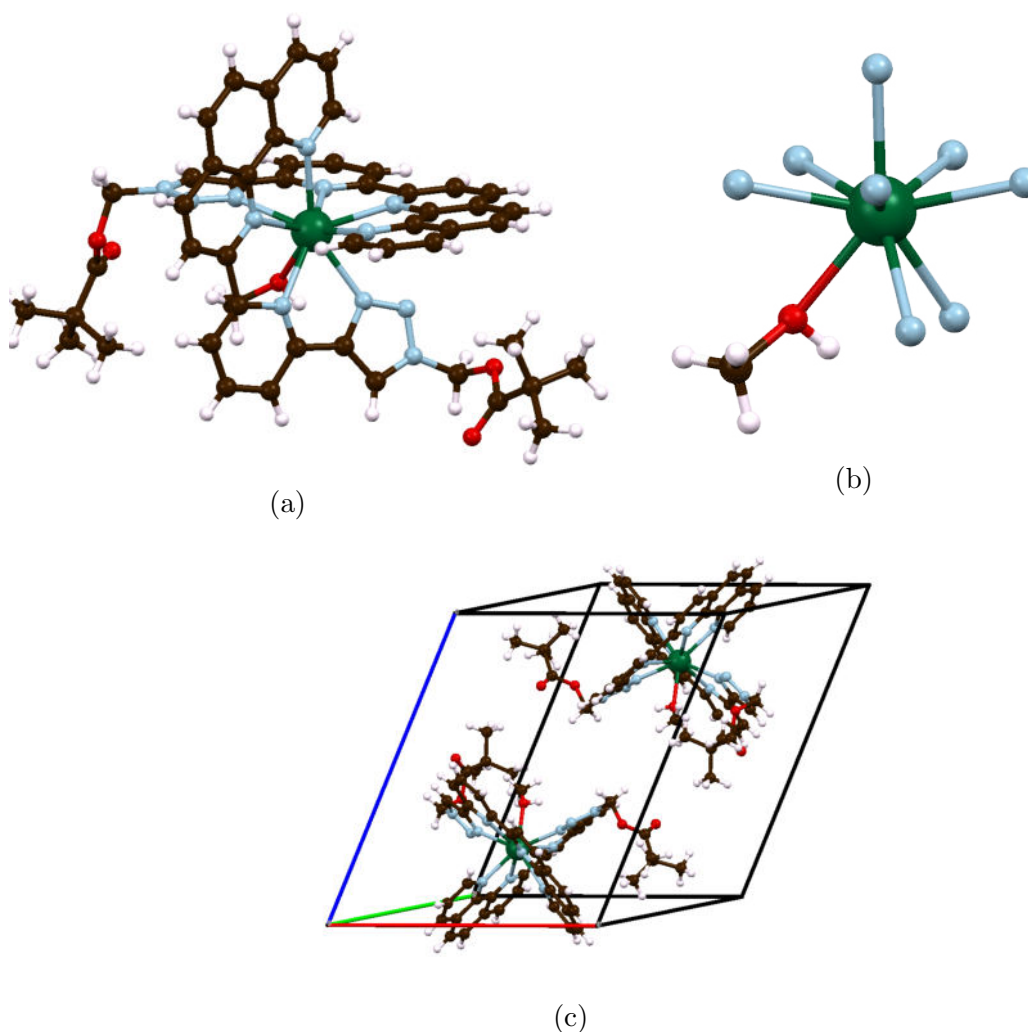


Fig. 6.1: Molecular structure (a), first coordination sphere of the Er^{3+} -ion (b) and crystal packing (c) of the phenanthroline-pyridine-triazole (PPT) complex $[\text{Er}(\text{PPTMP})_2(\text{MeOH})][\text{OTf}]_3 \cdot 3\text{MeOH}$. Green: Er^{3+} -ion; light blue: N, red: O; brown: C; white: H. Uncoordinated solvent molecules, including 6 methyl alcohol and 6 trifluoromethanesulfonic acid molecules, were excluded to increase visibility. Images were generated with Mercury [69].

the energetically lowest-lying Kramers doublet up to 14 T. The inset of Fig. 6.2(a) shows a zoom into the hysteresis loop around zero magnetic field of the isothermal magnetisation at 1.8 K. The data exhibits a small hysteresis centered around 0 T with a coercivity of ≈ 14 G. This coercivity is in the order of the remanence field of the superconducting magnet [38]. It can therefore be concluded that the studied complex is not subject to considerable magnetic hysteresis.

In Fig. 6.2(b) the temperature dependence of the static magnetic susceptibility multiplied by temperature, measured at various external magnetic fields is shown. The measurements were performed for a sample with a mass of 17.79(10) mg of the same batch as the one used for the isothermal magnetisation measurements. At low temperatures, the product of temperature and magnetic susceptibility χT , increases

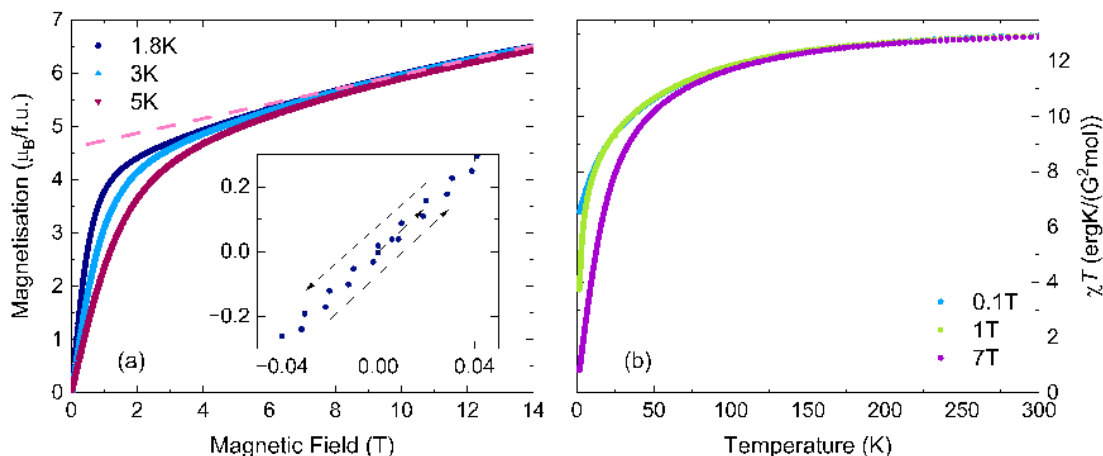


Fig. 6.2: (a) Isothermal magnetisation as a function of external magnetic field measured at three different temperatures. The dashed line is an interpolation of the quasi-linear part of the isothermal magnetisation at 1.8 K. The inset shows a zoom into a measurement of the full hysteresis loop of the isothermal magnetisation at 1.8 K. The arrows indicate the order in which the data points were measured, starting with the small arrow. (b) Static magnetic susceptibility $\chi = M/B$ multiplied by the temperature as a function of temperature measured at three different external magnetic fields.

rapidly with increasing temperature. In contrast, for temperatures above approximately 50 K, the increase with magnetic field is smaller. This observed behaviour supports the strong magnetic anisotropy of the studied complex. The highest measured value of χT is $12.89 \text{ erg K G}^{-2} \text{ mol}^{-1}$, which is about 12% larger than the value expected for free Er^{3+} -ions of $11.48 \text{ erg K G}^{-2} \text{ mol}^{-1}$ [24]. This deviation cannot be explained by the measurement uncertainty determined by errors in the background correction, the measurement resolution of the device and the uncertainty of the sample mass. Furthermore, the isothermal magnetisation up to 7 T and static magnetic susceptibility were measured for two samples, with differing sample mass, from the same batch. The data obtained for both samples are in good agreement with each other. Therefore, the discrepancy is most likely due to normalisation. For the purpose of normalisation, a molar mass of $1523.47 \text{ g mol}^{-1}$ (obtained by assuming that uncoordinated methyl alcohol is evaporated) was utilised. However, the molar mass is contingent upon the consideration of the differing contributions of coordinated solvent molecules (methyl alcohol) and the non coordinated solvent molecules (methyl alcohol and trifluoromethanesulfonic acid). Therefore, the molar mass varies between $1491.43 \text{ g mol}^{-1}$ (excluding coordinated and non coordinated methyl alcohol, including only the trifluoromethanesulfonic acid) and $1651.65 \text{ g mol}^{-1}$ (including all solvent molecules). Nevertheless, for all of the aforementioned molar masses, the discrepancy between the highest observed χT value and the expected value for free Er^{3+} -ions is greater than the measurement uncertainty. It should be noted that the uncertainty of the normalisation does neither affect the qualitative behaviour of the magnetisation discussed here and below nor the from the linear part of the isothermal magnetisation versus magnetic field curves obtained value for $|m_J|$. The

reason for the latter is that a change in the saturation value of 12% does not rule out that $|m_J| = 7/2$ could be the ground state Kramers doublet.

6.2.2 Dynamic Magnetic Susceptibility

The response of the samples magnetic moment to an oscillating external magnetic field in a constant applied external magnetic field was investigated for magnetic fields between 0 T and 0.5 T. The resulting imaginary part of the AC susceptibility at $f = 750$ Hz is shown in Fig. 6.3. At $B_{DC} = 0$ T there is no slow magnetic relaxation. This implies that a fast relaxation process occurs, resulting in a response time of the samples' magnetic moment to changes in the external magnetic field that cannot be accessed in this measurement. When a non-zero DC field is applied, this fast relaxation process is suppressed and a slow magnetic relaxation occurs, which is indicated by χ'' being finite. This observation shows that the sample exhibits field-induced slow magnetic relaxation behaviour.

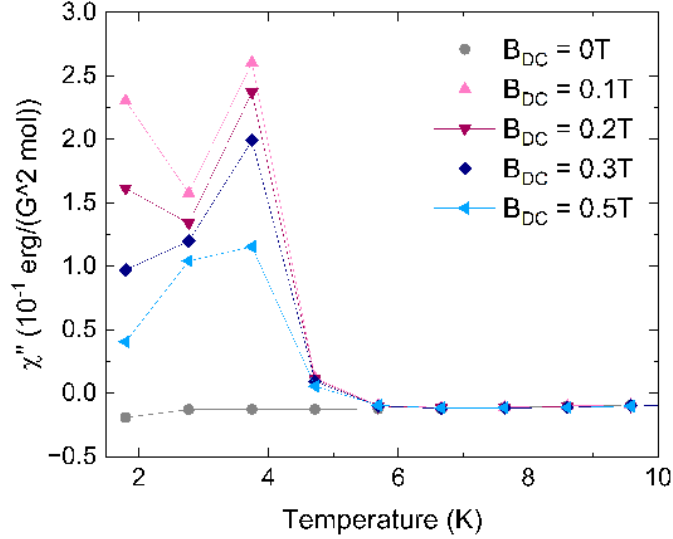


Fig. 6.3: Imaginary part of the AC susceptibility, obtained for an AC magnetic field amplitude of 3 Oe and a frequency of 750 Hz, at various DC magnetic fields.

At $B_{DC} = 0.1$ T the largest signal is observed. Therefore, to investigate the underlying processes further, AC susceptibility was measured for $B_{DC} = 0.1$ T for frequencies up to 1 kHz, see Fig. 6.4. For χ'' in Fig. 6.4(a) two distinct maxima are observed for low temperatures: a slower process (process 1) and a faster process (process 2) can be distinguished. The slower process corresponds to the maximum of χ'' which is observable at low temperatures at low frequencies and then shifts to higher frequencies with increasing temperature. The faster process corresponds to the maximum of χ'' at low temperatures at high frequencies. It is therefore outside the observable field range for higher temperatures as it shifts to higher frequencies with higher temperature. As it is not possible to extract the exact position of the maxima of χ'' corresponding to process 2 (due to it lying outside the measured frequency range), the following study concentrates only on process 1.

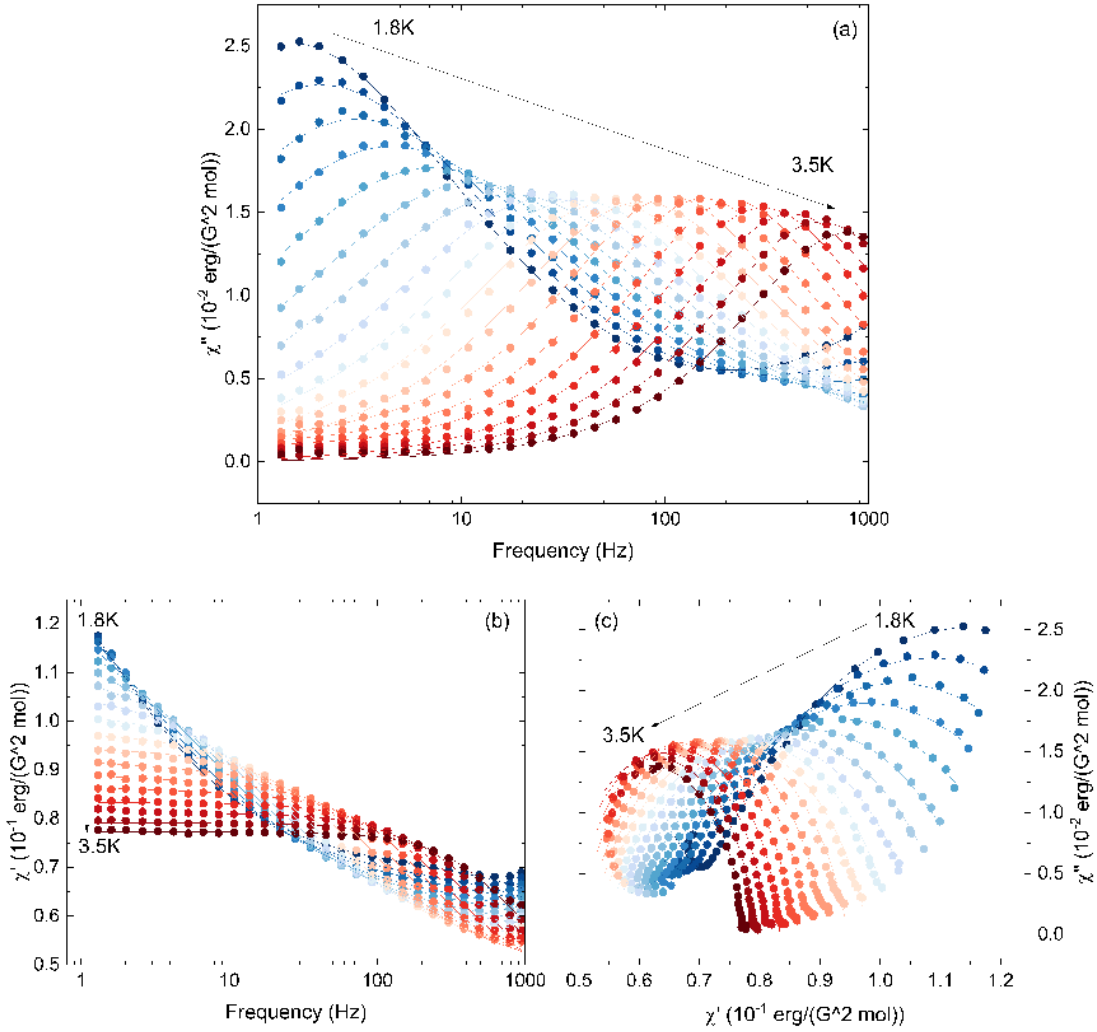


Fig. 6.4: Imaginary (a) and real part (b) of the AC susceptibility as a function of frequency and Cole-Cole plot (c) obtained by applying an AC magnetic field amplitude of 3 Oe at a DC magnetic field of 0.1 T. The data was collected at various temperatures ranging from 1.8 K to 3.5 K in steps of 0.1 K. Solid lines depict fits to the data as described in the text.

χ'' was fitted using a generalised Debye function (see eq.(2.37)) for temperatures in the range of $2.3 \text{ K} < T < 2.9 \text{ K}$ and $3.1 \text{ K} < T$. For any other temperature a generalised double-Debye-fit is performed by adding up two generalised Debye functions (each given by eq.(2.37)), each for one of the two visible processes. The corresponding fit parameter obtained for χ'' yield an eccentricity for process 1 starting from 0.38 at 1.8 K and decreasing with rising temperature to 0.07 (see Fig. 6.5(b)), indicating that multiple underlying relaxation paths exist for process 1 [32].

In Fig. 6.5(a) the temperature dependence of the time constant τ of process 1 is shown. To determine the contribution of the different underlying relaxation paths to process 1, eq.(2.38)) was used as a fitting function. The temperature-dependent behaviour of τ can be well described by a combination of the direct, Orbach and Ra-

man process. The Orbach process describes the high temperature behaviour, while the Raman and the direct processes describe the low and intermediate temperature regime, respectively. The resulting fit parameters are $A = 0.54(12) \text{ s}^{-1} \text{ K}^{-1}$, $\tau_0^{-1} = 2.6(80) \text{ s}^{-1}$, $U_{\text{eff}} = 54.9(14) \text{ K}$, $\tau_R = 5.0(9) \text{ s}^{-1}$ and $W = 24.9(3) \text{ K}$. The determined Raman barrier W , corresponding to the barrier to the next optical phonon [35], is about half of the thermal Orbach barrier U_{eff} . Quantum tunnelling could not be observed as there is no saturation at low temperatures, where quantum tunnelling would have the largest contribution. Measurements down to lower temperatures would be required to observe quantum tunnelling.

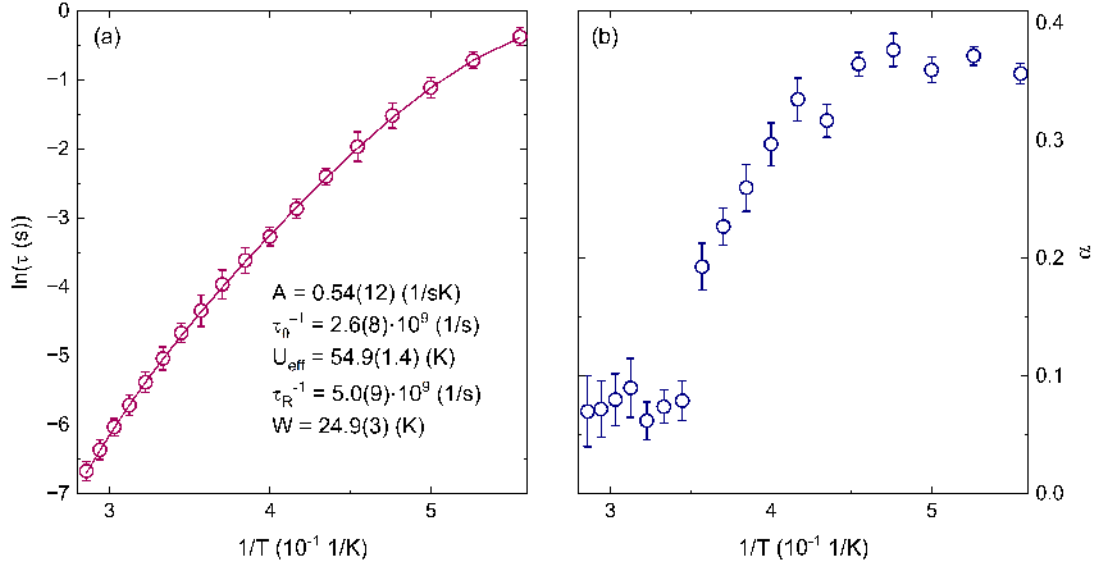


Fig. 6.5: (a) Arrhenius-plot of the time constant values obtained from a fit to the imaginary part of the magnetic susceptibility measured at a DC magnetic field of 0.1 T, as described in the text. The solid line corresponds to a fit to the time constant values as explained in the text. The resulting parameters are written inside the graph. (b) Eccentricity parameter α as a function of inverse temperature. The values of α were obtained from the same fit as the time constant values in (a).

6.3 High-Field/High-Frequency Electron Spin Resonance

6.3.1 Studies on an Oriented Loose Powder

Pseudo-single-crystal HF-EPR spectra were measured by preparing an oriented loose powder as described in subsection 3.1.1. The obtained microwave transmission spectra are shown in Figs. 6.6 and 6.7. Resonance features which are observed in both the up- and down-field-sweeps are marked with symbols in the figures. All measured spectra display a single resonance feature across the entire magnetic field range. Additionally, no other resonance features are visible up to $f = 550 \text{ GHz}$, which was the highest frequency at which measurements could be properly performed for this

sample. At higher frequencies, the sensitivity was insufficient for detecting the small signals of the magnetic transitions in this complex.

In Fig. 6.8(a) the resonance frequency versus resonance magnetic field diagram of the resonances, marked by black squares in Figs. 6.6 and 6.7, is shown. The resonance positions in Fig. 6.8(a) result in a gapless resonance branch with a linear slope. The slope corresponds to $g_{\text{eff}} = 8.5(4)$, as obtained from a linear fit through the origin.

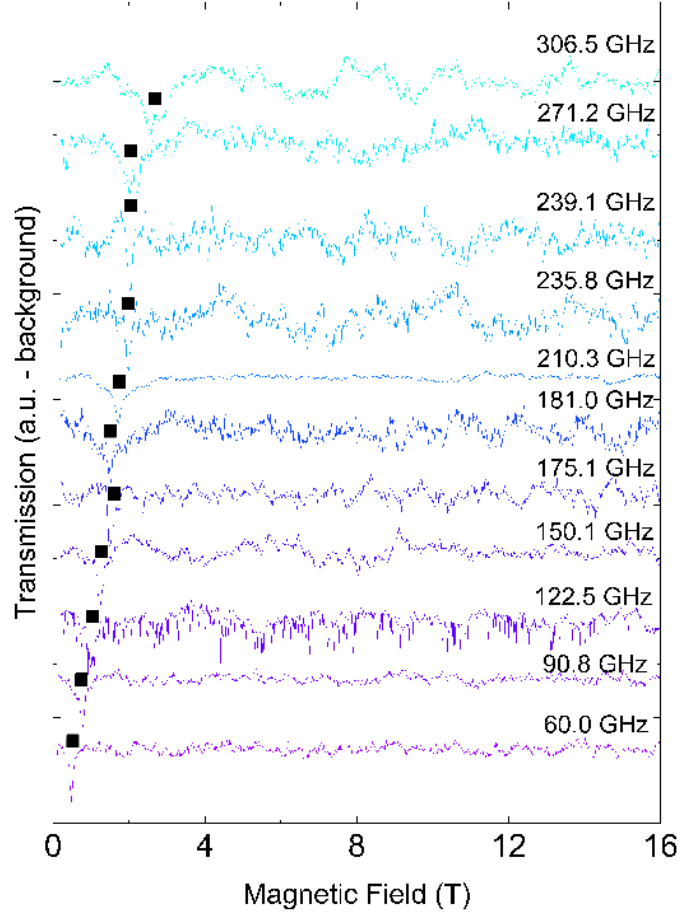


Fig. 6.6: HF-EPR transmission spectra measured at $T = 2\text{ K}$ and frequencies ranging from 60.0 GHz to 306.5 GHz on an oriented loose powder. All spectra were background and phase mixing corrected, normalised to the absolute of the lowest value and shifted along y . The black squares correspond to the resonance positions of the observed features, as explained in the text.

In Fig. 6.8(b) the evolution of the observed resonance feature with increasing temperature at a fixed frequency of $f = 235.8\text{ GHz}$ is shown. The intensity of the resonance feature decreases with increasing temperature, and no other transitions occur up to 30 K. Therefore the observed transition at 2 K can be assigned to a ground state transition within a Kramers doublet. The slope of the corresponding resonance branch of $g_{\text{eff}} = 8.5(4)$ implies a transition where the change in m_J is $|m_J| = 7$. Therefore, the transition observed at 2 K is a transition within the

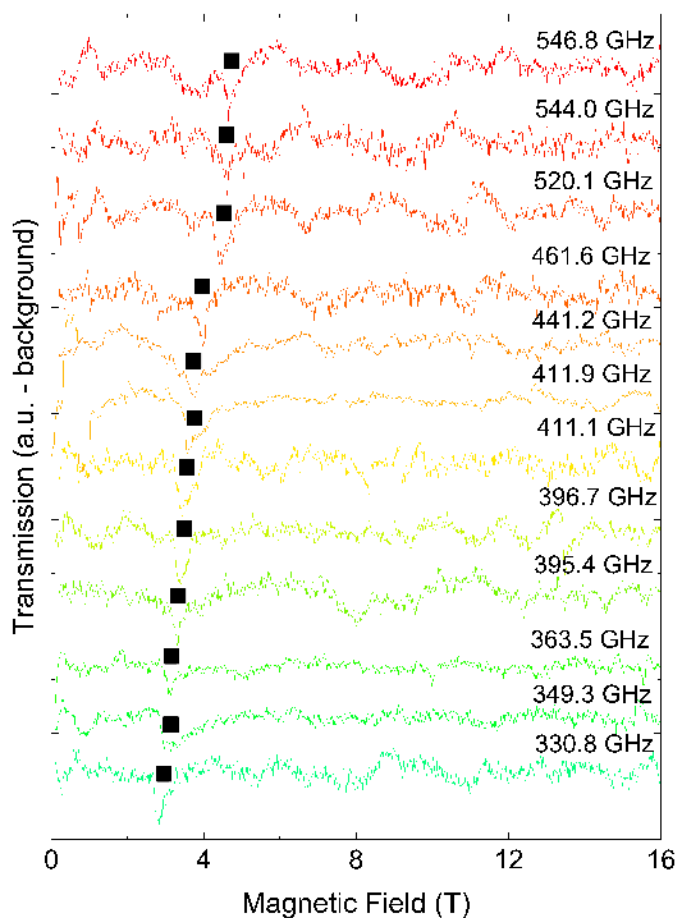


Fig. 6.7: HF-EPR transmission spectra measured at $T = 2$ K and frequencies ranging from 330.8 GHz to 546.8 GHz on an oriented loose powder. All spectra were background and phase mixing corrected, normalised to the absolute of the lowest value and shifted along y . The black squares correspond to the resonance positions of the observed features, as explained in the text.

$|m_J| = 7/2$ Kramers doublet. This demonstrates that $|m_J| = 7/2$ is the ground state Kramers doublet, being consistent with the magnetisation data presented in the previous section. Additionally, the absence of any other resonance features in Figs. 6.6 and 6.7 leads to the conclusion that the energy gap to the next excited Kramers doublet is greater than 550 GHz.

6.3.2 Studies on a Non-Oriented Fixed Powder

Owing to the alignment of the crystallites' easy-orientation with the external magnetic field during a loose powder measurement, the resulting resonance spectra reflect solely one molecular orientation. Consequently, only the g -tensor component corresponding to this orientation can be measured with this technique. To also investigate the other components, and thus the g -anisotropy, a fixed powder sample was prepared as described in subsection 3.1.1.

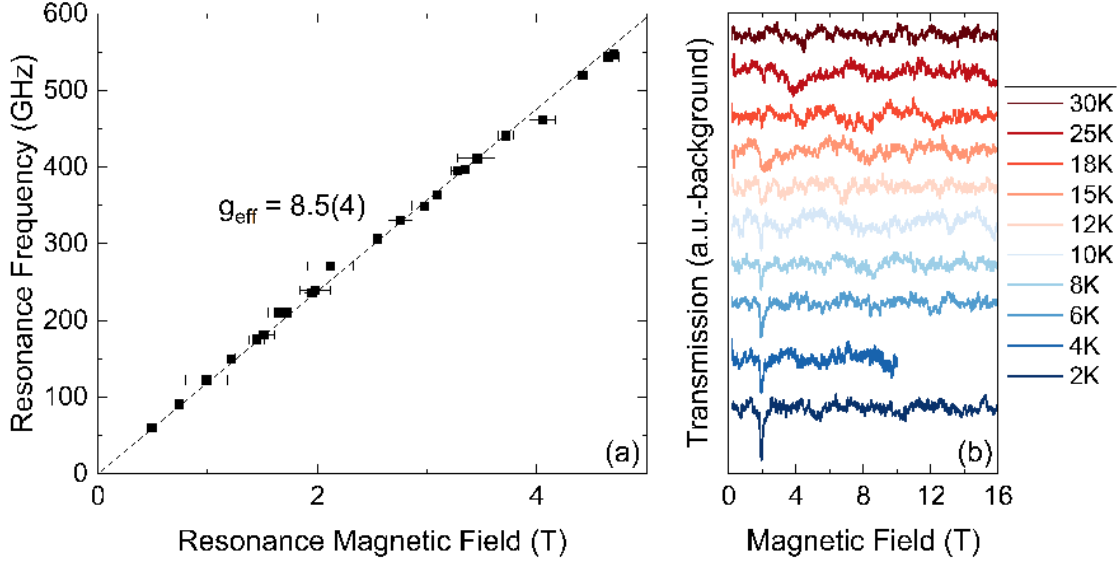


Fig. 6.8: (a) Resonance magnetic field positions obtained from the transmission spectra measured at $T = 2$ K for various frequencies on an oriented loose powder (Figs. 6.6 and 6.7). The solid black line represents a gapless linear fit to the resonance positions. (b) HF-EPR spectra measured at $f = 235.8$ GHz for different temperatures ranging from 2 K to 30 K. The spectrum at 4 K was truncated at 10 T due to changes in the diode temperature, resulting in a drastic change in the transmission in this region.

The measured transmission spectra are shown in Figs. 6.9, 6.10 and 6.11, where the resonance features which are observed in both the up- and down-field-sweeps are marked with symbols. A main feature, marked with a black square, is observed together with a shoulder ranging to higher magnetic fields. The upper limit of the shoulder is marked with a light blue circle. The feature as a whole has a width of approximately 2 – 3 T, indicating that the g -tensor is non-isotropic. By tracking the positions of the main (black square) and shoulder (light blue circle) features, the resonance positions shown as black squares and light blue circles in Fig. 6.12(a) are obtained, resulting in two gapless linear resonance branches.

In order to ascertain the principle values of the g -tensor describing the observed resonance, a spectral simulation was performed for the four measured spectra which include both features, shown in Fig. 6.13. The four spectra were selected such that their resonance positions are part of the linear resonance frequency versus resonance magnetic field regime. The energy gap between the energetically lowest-lying Kramers doublet and the next excited one (determined by the measurements of the oriented loose powder) is greater than 550 GHz. Therefore, the energetically lowest-lying Kramers doublet is energetically well isolated, with the vast majority of the molecules occupying this energy level. To describe this Kramers doublet, a pseudo-spin-1/2 Heisenberg model with an effective g -tensor was used. The corresponding Zeeman-Hamiltonian in this model is given by:

$$\hat{H}_Z = \mu_B \mathbf{B}^T \mathbf{g} \hat{\mathbf{S}} = \mu_B \mathbf{B}^T \mathbf{g}_{\text{eff}} \hat{\mathbf{S}}^* \quad (6.1)$$

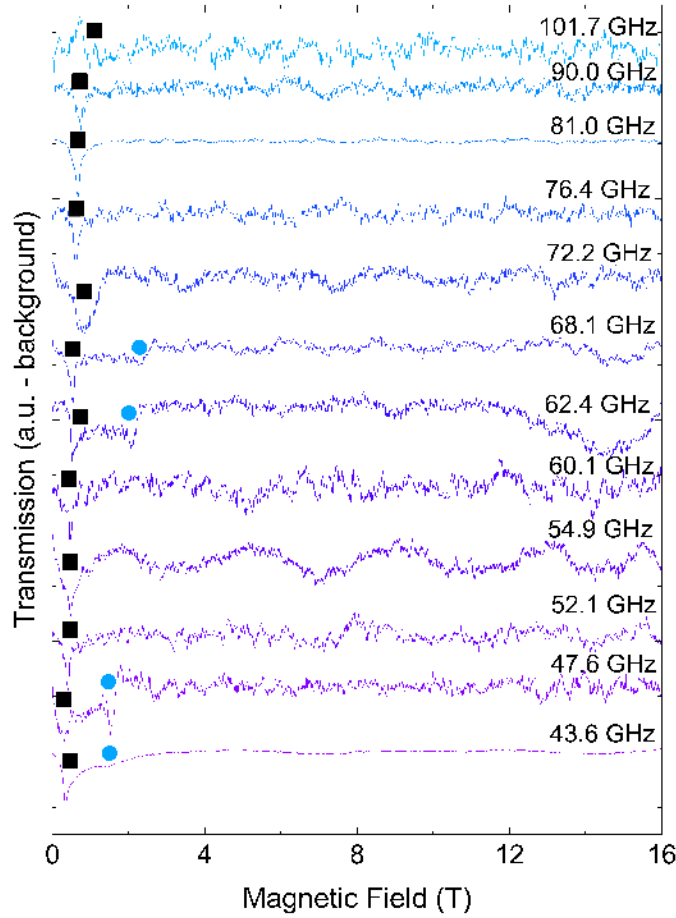


Fig. 6.9: HF-EPR transmission spectra measured at $T = 2\text{ K}$ and frequencies ranging from 43.6 GHz to 101.7 GHz on a non-oriented fixed powder. All spectra were background and phase mixing corrected, normalised to the absolute of the lowest value and shifted along y . The black squares and light blue circles correspond to the resonance positions of the observed features, as explained in the text.

where $\mathbf{g}_{\text{eff}}$ is the effective g -tensor composed out of the g -tensor $\mathbf{g}$ and $\Delta m_J = 2 \cdot 7/2$, the change in m_J for a transition within the energetically lowest-lying Kramers doublet. $\hat{\mathbf{S}}^*$ is the spin corresponding to the pseudo-spin- $1/2$, meaning that the total value of S^* is $1/2$ instead of $7/2$ for S .

The simulated spectra are displayed as solid red lines in Fig. 6.13. The spectral simulations yield the following principal effective g -tensor entries, resulting in an easy-plane anisotropy: $g_x = 8.9(14)$, $g_y = 8.9(14)$, $g_z = 2.0(4)$. These values were determined as follows: The g_x component was chosen within the uncertainty range of the effective g -value resulting from the loose powder measurements (Fig. 6.8(a)). The remaining components of the g -factor, g_y and g_z , were then varied to achieve the best fit to the measured fixed powder spectra. The uncertainties were determined by varying each of the principle g -tensor entries until the simulation just barely

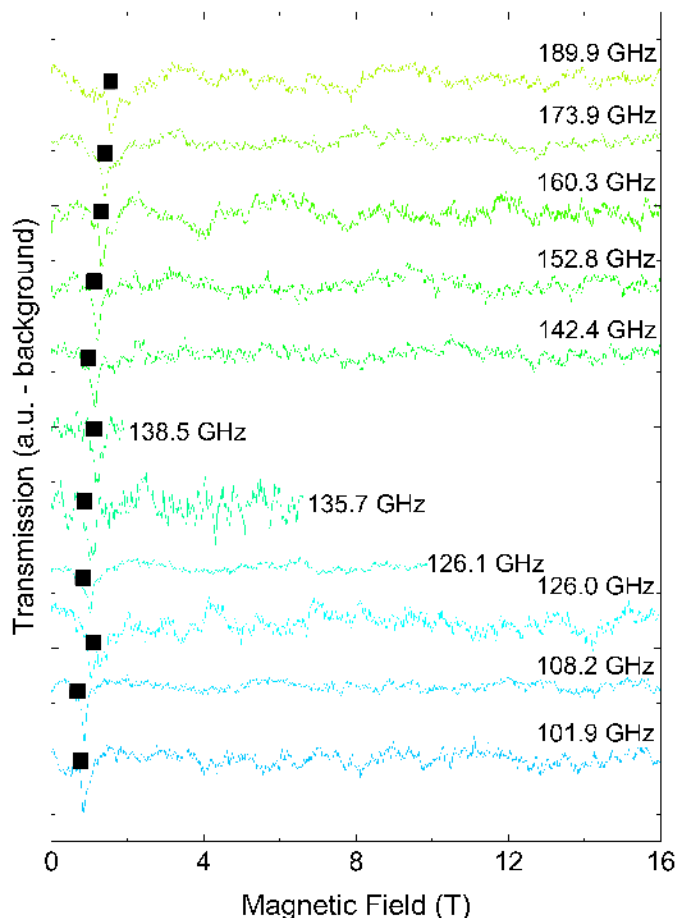


Fig. 6.10: HF-EPR transmission spectra measured at $T = 2\text{ K}$ and frequencies ranging from 101.9 GHz to 189.9 GHz on a non-oriented fixed powder. All spectra were background and phase mixing corrected, normalised to the absolute of the lowest value and shifted along y . The black squares correspond to the resonance positions of the observed features, as explained in the text. The spectra measured at 126.1 GHz, 135.7 GHz, and 138.5 GHz were measured for a smaller magnetic field range compared to the other spectra.

matches the measured spectrum ². The spectral simulations describe the qualitative behaviour of the measured spectra in Fig. 6.13 and the obtained principle values of the g -tensor agree well with the slopes of the linear fits to the resonance positions shown in Fig. 6.12(a).

However, there are slight differences in the ratio of spectral weights of the shoulder and main feature between the simulated and measured spectra in Fig. 6.13. Those differences could arise for technical reasons, such as a special shape of the crystallites that makes a certain orientation of the crystallites more probable than other orientations. As a result not all crystal orientations would occur equally frequently in the

²Changes in the spectral shape of the spectra obtained from up- and down-field-sweeps, as well as differences in the resonance positions resulting from remanence of the superconducting magnet, were also taken into account during the fitting process.

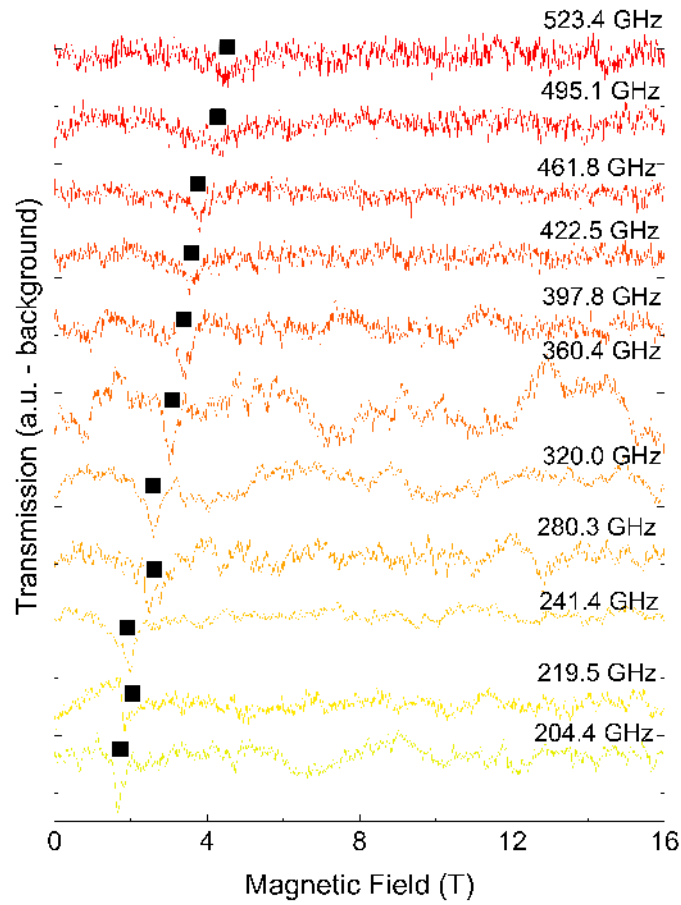


Fig. 6.11: HF-EPR transmission spectra measured at $T = 2\text{ K}$ and frequencies ranging from 204.4 GHz to 523.4 GHz on a non-oriented fixed powder. All spectra were background and phase mixing corrected, normalised to the absolute of the lowest value and shifted along y . The black squares correspond to the resonance positions of the observed features, as explained in the text.

sample, so that the resulting spectra would have more contributions from certain crystal orientations. Additionally, the used pseudo-spin- $1/2$ Heisenberg model is a highly simplified model, as only the energetically-lowest lying state is accounted for and the information about the m_J -state is shifted to the effective g -tensor.

To demonstrate that the observed shoulder in the transmission spectra is also part of the ground state transition, the evolution of the microwave transmission with rising temperature was measured at $f = 43.6\text{ GHz}$, as shown in Fig. 6.12(b). The spectral simulations are represented in red and match the measured data well. They include the parameters obtained from fitting the 2 K data (Fig. 6.13) and the expected decrease of the intensity of the overall feature with increasing temperature according to Curie's law (see eq.(2.17)). The intensity of the shoulder decreases with rising temperature. This decrease can be described by the Curie law, as the decrease of the simulation matches that of the measurements. Consequently, the shoulder feature is part of the ground state transition, implying that the aforementioned determination

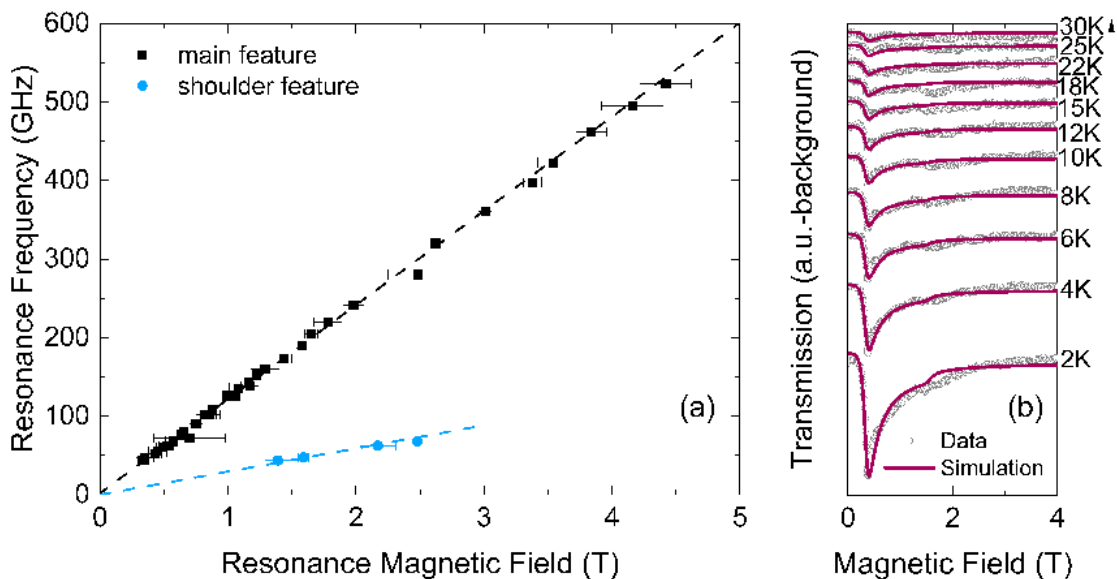


Fig. 6.12: (a) Resonance positions of the measured HF-EPR spectra at $T = 2$ K for various frequencies on a non-oriented fixed powder. The black and light blue data points correspond to the main and shoulder feature of the broad resonance feature (marked with black squares and light blue circles in Figs. 6.9, 6.10 and 6.11). The dotted lines correspond to gapless linear fits with slopes of $g_{\text{eff}} = 8.7$ and $g_{\text{eff}} = 2.1$ to the resonance positions. (b) HF-EPR spectra measured at $f = 43.6$ GHz for different temperatures ranging from 2 K to 30 K. The measured spectra are represented by open grey points, while the red lines represent spectral simulations conducted in accordance with the assumptions described in the text.

of the g -tensor entries via fitting spectral simulations (including only the ground state Kramers doublet) to the overall feature including the shoulder feature is valid.

6.4 Comparison to Previously Investigated Er^{3+} Complexes

This section compares the here investigated 9-fold coordinated Er^{3+} complex with a muffin-shaped first coordination sphere to three other 7-fold coordinated Er^{3+} complexes with a pentagonal-bipyramidal first coordination sphere. The latter were previously measured by Lena Spillecke [63] and Jan Arneth [40].

As shown in the first row of Tab. 6.1, all complexes exhibit a shared geometric feature of the first coordination sphere: there are five atoms in a plane surrounding the central Er^{3+} -ion. For the first three compounds in the first row of Tab. 6.1 (labelled **1**, **2**, **3** according to their appearance in the table), the five atoms of the plane consist of three nitrogen and two oxygen atoms. In addition to the five atoms of the plane, the Er^{3+} -ions of **1**, **2** and **3** are coordinated to two other atoms/molecules that differ between the three compounds: For **1** this is a chlorine atom above the plane and a water molecule below the plane. Whereas for **2** the Er^{3+} -ion is coordinated to

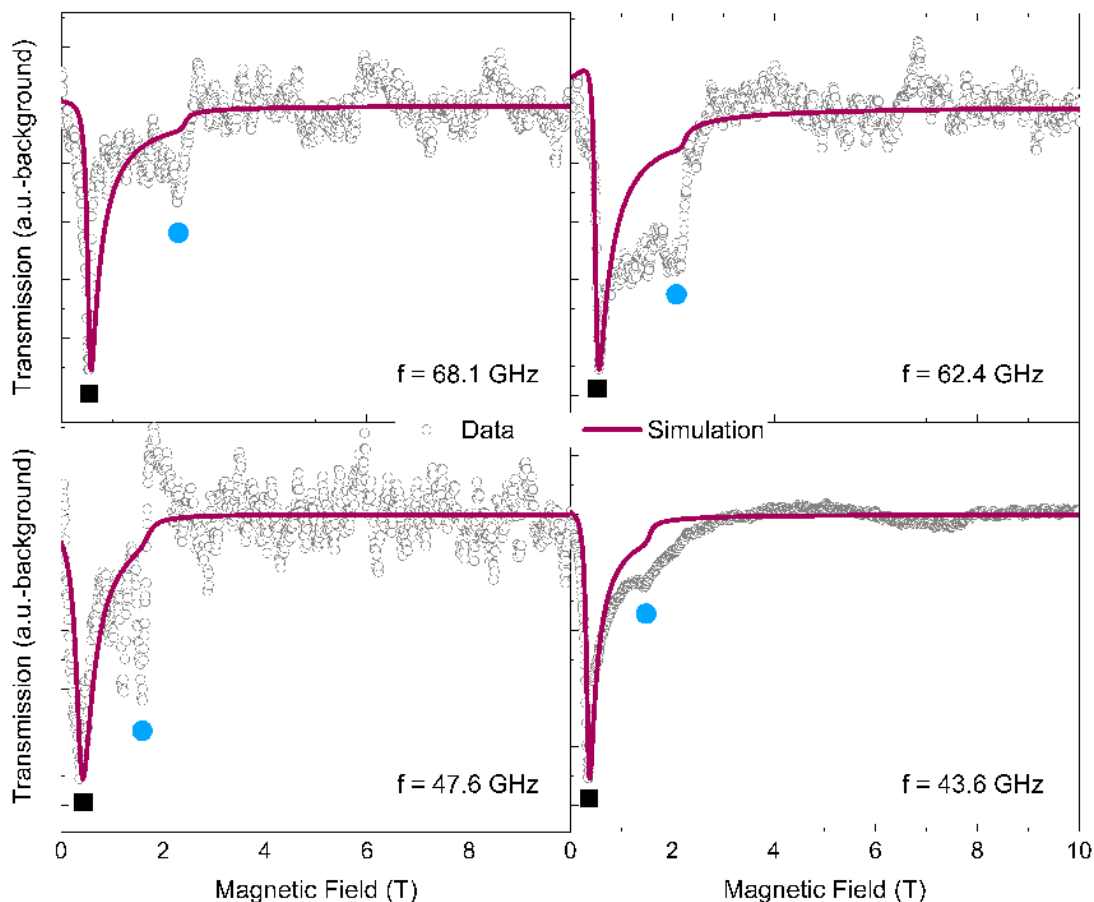


Fig. 6.13: Exemplary HF-EPR transmission spectra measured at $T = 2$ K for 4 different frequencies on a non-oriented fixed powder. The spectra are shown as open grey points, and have been background and phase mixing corrected and are normalised to the absolute of the lowest value. The red lines represent spectral simulations conducted in accordance with the assumptions described in the text. The black square and light blue circle mark the resonance positions of the main and shoulder feature as described in the text.

N_3 above the plane and methyl alcohol below the plane. And the Er^{3+} -ion of **3** is bound to two chloride atoms, one below and the other above the plane. The fourth compound, investigated in this work, in the first line of Tab. 6.1 is labelled **4** in the following. In contrast to **1**, **2** and **3**, the five atoms in the plane are all nitrogen atoms. The Er^{3+} -ion is furthermore coordinated to one nitrogen atom above the plane and two nitrogen atoms and one methyl alcohol molecule below the plane.

The second row of Tab. 6.1 compares the principal values of the effective g -tensor of the energetically lowest-lying Kramers doublet. **1**, **2**, **3** exhibit an uniaxial anisotropy, as their x and y components of the effective g -tensor are relatively small compared to the z component. The axiality of **1** and **2** is slightly higher than that of **3**, as the x and y components of the effective g -tensor are more pronounced for **3**. This is due to non-axial crystal field terms in the Hamiltonian describing **3** [67].

4 figures a planar g -anisotropy as evidenced by the equal values of the x and y components and the smaller value of the z component in comparison to x and y .

The main contribution of the $|m_J|$ state to the ground state (third row of Tab. 6.1) is $|m_J| = 11/2$ [67] for both **1** and **2**. Whereas for **3** and **4**, the main contributions are $|m_J| = 9/2$ and $|m_J| = 7/2$, respectively. The differing main contributions are consequences of the non-axial crystal field terms in the Hamiltonians that describe **3** and **4**. These terms result in the mixing of different $|m_J|$ states (in comparison to **1** and **2**) into the ground state.

The energy gap to the next excited Kramers doublet is comparable in size for both **1** and **2**, as shown in the fourth row of Tab. 6.1. The energy gap to the next excited Kramers doublet of **4** is greater than 550 GHz, which suggests that it may be even larger than that of **1** and **2**. The energy gap of **3** is 290 GHz, which is lower than the energy gaps of **1**, **2** and **4**.

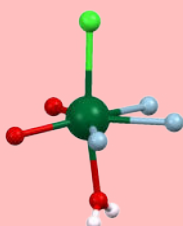
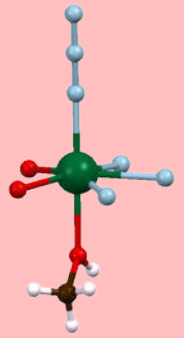
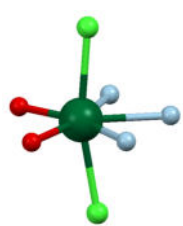
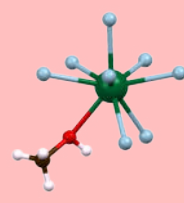
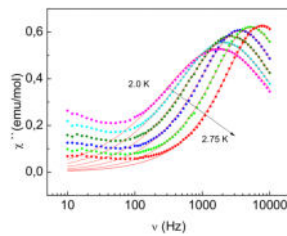
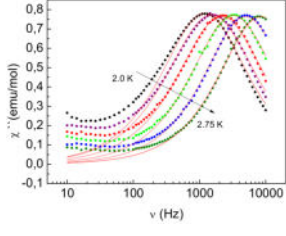
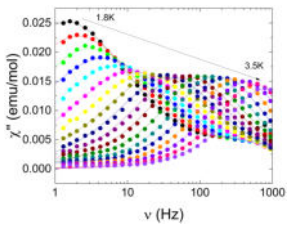
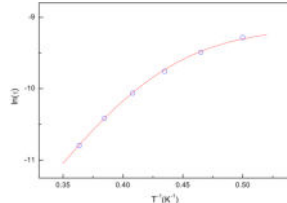
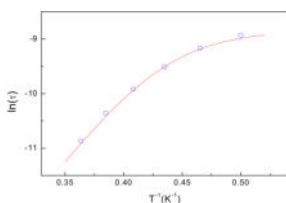
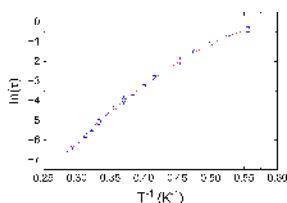
Due to the lower energy gap of **3**, less thermal energy is required to populate the next excited Kramers doublet as is needed for **1**, **2** and **4**. Consequently, thermally assisted quantum tunnelling is enhanced for **3** compared to the other compounds [63, 64, 67]³. Additionally, also the quantum tunnelling for the energetically lowest-lying Kramers doublet of **3** is enhanced compared to **1** and **2**. This is due to the slight reduction in axial g -anisotropy of the ground state Kramers doublet (second row of Tab. 6.1) of **3** compared to that of **1** and **2** [63, 64, 67]. This enhanced probability for direct and thermally assisted quantum tunnelling in **3** compared to the other compounds, results in a fast magnetic relaxation, which cannot be suppressed by applying a magnetic field [67]. Conversely, for **1**, **2** and **4**, quantum tunnelling is suppressed by applying a magnetic field, resulting in a slow magnetic relaxation [63, 67].

The final two rows of Tab. 6.1 compare AC susceptibility measurements of **1**, **2** and **4**. The slow magnetic relaxation is evidenced by a finite imaginary part of the AC susceptibility, shown in the second last row of Tab. 6.1. The field strength required for observing the field-induced magnetic slow relaxation is comparable in size between the different compounds [67]. **1** and **2** figure similar g -anisotropy and energy gaps between the energetically lowest and next excited Kramers doublet. Their slow magnetic relaxation behaviour can be described by quantum tunneling and Orbach process [67], see last row of Tab. 6.1. **4** has a distinct molecular structure and g -anisotropy as **1** and **2**. Its slow magnetic relaxation behaviour cannot be explained by quantum tunnelling, but rather by a combination of Raman and direct processes, along with the Orbach process. A comparison of the Orbach barrier U_{eff} between all three compounds reveals a tendency that for **1** and **2**, which exhibit a similar energy gap between energetically lowest-lying and next excited Kramers doublet, U_{eff} is also comparable in size. For **4**, which may exhibit a higher energy

³Furthermore, quantum tunnelling is enhanced for the first excited Kramers doublet as compared to the ground state Kramers doublet of **3**. This is due to the first excited Kramers doublet exhibiting a reduced g -anisotropy compared to the one of the ground state Kramers doublet [63, 64, 67].

gap than **1** and **2**, a higher value of U_{eff} is observed.

However, this comparison should be treated with caution, as it is also possible to describe the temperature dependence of the time constant of **1** and **2** by the same processes as **4**, shown in Fig. 6.14. For **1** and **2** only six values for the time constant were measured. Therefore, for the fit, the barrier heights W and U_{eff} were fixed to the values obtained from the fit for **4** in order to avoid over-parametrisation. The fits indicate that the time constants obtained for **1** and **2** can be described by assuming the same barrier heights as were obtained for **4**.

Compound	1		2		3		4	
								
	Cl/H ₂ O		N ₃ /CH ₃ OH		Cl/Cl		N/2 · N, MeOH	
$i =$	z	x, y	z	x, y	z	x, y	z	x, y
g_{eff}^i	12.0(1)	< 0.5(5), 2.6(5)	13.1(2)	1.5(1), 1.5(3)	12.5(1)	2.6(3), 3.2(3)	2.0(4)	8.9(14), 8.9(14)
Main ground state $\langle m_J \rangle$ contribution	$\frac{11}{2}$ [67]		$\frac{11}{2}$ [67]		$\frac{9}{2}$		$\frac{7}{2}$	
Energy gap to next excited Kramers doublet	825 GHz		767 GHz		290 GHz		> 550 GHz	
Compound	1		2		4			
AC Susceptibility χ''	 $B = 0.112 \text{ T}$ Taken from [67]		 $B = 0.1 \text{ T}$ Taken from [67]		 $B = 0.1 \text{ T}$			
Time constant τ	 QT & Orbach: $\tau_0^{-1} = 1.7 \cdot 10^8 \text{ s}^{-1}$, $U_{\text{eff}} = 23 \text{ K}$, $\tau_{\text{QT}}^{-1} = 9.1 \cdot 10^3 \text{ s}^{-1}$ Taken from [67]		 QT & Orbach: $\tau_0^{-1} = 1.3 \cdot 10^8 \text{ s}^{-1}$, $U_{\text{eff}} = 28 \text{ K}$, $\tau_{\text{QT}}^{-1} = 7.1 \cdot 10^3 \text{ s}^{-1}$ Taken from [67]		 Direct, Orbach & Raman: $A = 0.54(12) \text{ s}^{-1} \text{ K}^{-1}$, $\tau_0^{-1} = 2.6(8) \cdot 10^9 \text{ s}^{-1}$, $U_{\text{eff}} = 54.9(14) \text{ K}$, $\tau_{\text{R}}^{-1} = 5.0(9) \cdot 10^9 \text{ s}^{-1}$, $W = 24.9(3) \text{ K}$			

Tab. 6.1: Comparison of four different Er³⁺ complexes. Unless otherwise stated, the information was obtained from measurements performed in this work (compound **4**), Lena Spillecke's research [63, 64] (compound **1** and **3**) and Jan Arneth's research [40] (compound **2**). **1-3** were synthesised and characterised by Vycheslav Kopotkov [63], while **4** was synthesised and characterised by Gerlinde Greif [70]. The colour code shows whether the compound exhibits field-induced slow magnetic relaxation (light pink = slow magnetic relaxation, white = no slow magnetic relaxation). Dark green: Er³⁺-ion; blue: N; light green: Cl; red: O; brown: C; white: H.

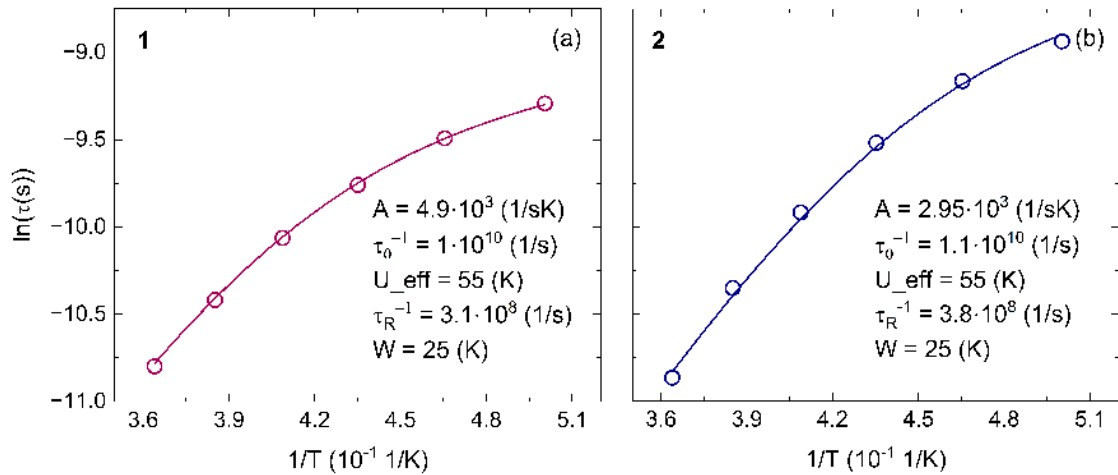


Fig. 6.14: Arrhenius-plot for **1** (a) and **2** (b). The open points correspond to the time constant values taken from [67]. The solid line corresponds to a fit of eq.(2.38) to the data as described in the text. The resulting parameters are written inside the graph.

Chapter 7

Nd Containing MDH Enzyme

Rare earth metal-containing complexes are not confined to laboratory settings. They are also part of active sites of special enzymes - known as lanthanide metalloenzymes - in bacteria [10].¹

The type of enzymes studied here are methanol dehydrogenase (MDH) enzymes, found in the group of methylotrophic bacteria which derive their energy from C1 carbon substrates like methane and methanol. MDH contains a metal cation alongside the redox cofactor pyrroloquinoline quinone (PQQ) in their active site. Where PQQ contains a radical [71]. Certain bacteria, such as *Methylophilum thermophilum* SolV, contain Ce-MDH [8, 10]. Other bacteria, such as *Methylobacterium buryatense* 5GB1C, host for example La-MDH [10, 72]. MDH is required for the bacteria's metabolic process, where methanol is oxidized to formaldehyde. PQQ plays a role in this methanol dehydrogenation, for which two distinct mechanisms were suggested [10, 73–80]. The electronic structure of PQQ could be altered when coordinated with different Ln-ions, potentially affecting these mechanisms, e.g. rendering one of the processes more likely in presence of different Ln-ions [81]. It is therefore of great interest to study the potential interactions between the lanthanide ion and the radical and to gain further insight into the localisation of the radical in PQQ.

The following two chapters therefore focus on the investigation of the Nd-MDH enzyme and the active sites of Ln-MDH (Ln = La, Gd, Dy, Lu) and Ca-MDH enzymes using magnetic probes. The question addressed here is whether the chosen type of magnetic measurements are suitable for better understanding the role of the lanthanides in the active site. Specifically, it examines the feasibility of discerning details considering the localisation of the radical within the active site and investigating potential interactions between the lanthanide ion and the PQQ radical. Moreover, in a broader context, this study aims to ascertain whether magnetic

¹The following paragraph is based on the review paper *Essential and Ubiquitous: The Emergence of Lanthanide Metallobiochemistry* by Lena Daumann [10]. Unless otherwise stated, the following information has been taken from there.

measurements can contribute to elucidating the impact of lanthanide ions on these enzymes and their respective active sites.

7.1 Protein Structure of Nd-MDH

For the following measurements, frozen solutions from the same batch were used. The solution contains the buffer PIPES in water. Samples used for background measurements, containing only this solution, are hereafter referred to as blank. The samples containing Nd-MDH dissolved in this solution are hereafter referred to as Nd-MDH. The concentration of Nd-MDH in the respective samples is 2.25 μM . The samples were provided by Manh Tri Phi (group of Lena Daumann at LMU Munich). In Fig. 7.1 the protein structure of the investigated Nd-MDH enzyme is shown. In the active site the magnetic neodym ion is coordinated to PQQ via an oxygen atom, a carboxylate moiety and a nitrogen atom. It is furthermore coordinated to MDH via a Glu-residue, two Asp-residues and an Asn-residue. The neodym ion is in the three-times ionised Nd^{3+} ground state, resulting in a total spin of $J = 9/2$ of the Nd^{3+} -ion. The radical in PQQ is an electron that is not assigned to a certain atom. Therefore it can be described as a "quasi-free" electron, meaning that its magnetic moment is given by the electron spin of $1/2$. The term "quasi" refers to the possibility of the electron being influenced by nearby atoms via hyperfine coupling [71]. The proposed radical environment [71] is depicted with a green oval in Fig. 7.1.

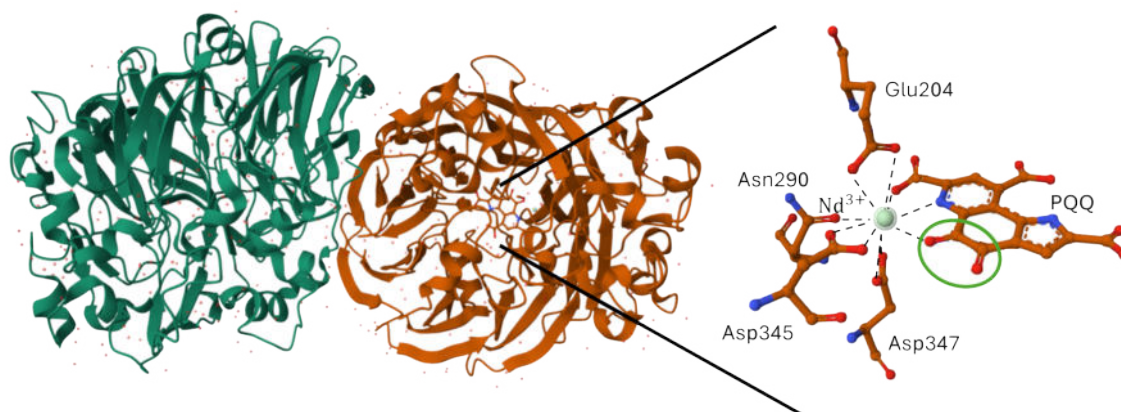


Fig. 7.1: Protein structure of the Nd-MDH enzyme (PDB ID:7O6Z) and zoom in its active site [82]. Asp, Asn and Glu are amino acids of MDH coordinating to the Nd^{3+} -ion. The green oval shows the proposed radical environment [71]. The images were generated with Mol* [83] from the RCSB PDB website (RCSB.org) [84]. Light green: Nd^{3+} -ion; brown: C; red: O; blue: N; creme white: H_2O . Hydrogen atoms are excluded from the zoom in the active site to increase visibility.

7.2 Magnetisation Studies

In order to ascertain the magnetic ground state of the Nd^{3+} -ion, and to investigate potential interactions between the magnetic moments, isothermal magnetisation and static magnetic susceptibility were measured for both the blank and Nd-MDH samples. However, it turned out that the used sample preparation in VSM Powder Sample Holders (QDC-4096-388) from *Quantum Design* is not suited for the sample under investigation. The reason for this is that the signal of Nd-MDH is superimposed by the background signal originating from Teflon tape, which was used to seal the sample holders. Further details are given in section A.1. It may be beneficial to conduct future experiments to ascertain whether different sample preparation such as using homebuilt 3D-printed resin sample holders [85] is more effective. This method allows the measurement of a larger sample quantity.

7.3 High-Field/High-Frequency Electron Spin Resonance

Microwave transmission spectra were measured at a fixed temperature of 2 K for frozen solutions that were frozen without an external magnetic field before inserting them into the HF-EPR sample rod, as described in subsection 3.1.1. The obtained transmission spectra for Nd-MDH are presented in Figs. 7.2 and 7.3. In Fig. 7.4 the spectra for the blank are shown. Resonance features which are observed in both the up- and down-field-sweeps are marked with symbols in the figures.

The spectra obtained for Nd-MDH display two distinct resonance features, for which the resonance positions are indicated as black squares and red points in Figs. 7.2 and 7.3. The sharp resonance feature (RF1), indicated by black squares, is observed for frequencies above 350 GHz. The broader resonance feature (RF2), indicated by the red points, is observed for frequencies below 260 GHz. Furthermore, for $f = 180.9$ GHz and 198.0 GHz, resonance features at approximately 13.0 T and 2.3 T (marked with a blue star) are observed. These resonances are disregarded in the following as they cannot be assigned to specific resonance branches.

In Fig. 7.5(a) the resonance frequency versus resonance magnetic field diagram of the resonances, marked by black squares, blue stars and red circles in Figs. 7.2 and 7.3, is shown. Feature RF1 arranges in a gapless resonance branch with a linear slope corresponding to an effective g -factor of 2.007(21), as obtained from a linear fit through the origin. Whereas feature RF2 belongs to a resonance branch with a non-zero y-intersection Δ . A linear fit yields a zero-field energy gap of $\Delta = 54(5)$ GHz and a slope that correlates with $g_{\text{eff}} = 2.007(21)$.

The spectra obtained for the blank display a single resonance feature (feature RF3), with the resonance positions indicated as black squares in Fig. 7.4. These resonance features result in a gapless resonance branch as shown in Fig. 7.5(b). The slope of this resonance branch correlates to $g_{\text{eff}} = 2.007(17)$, obtained by a linear fit through

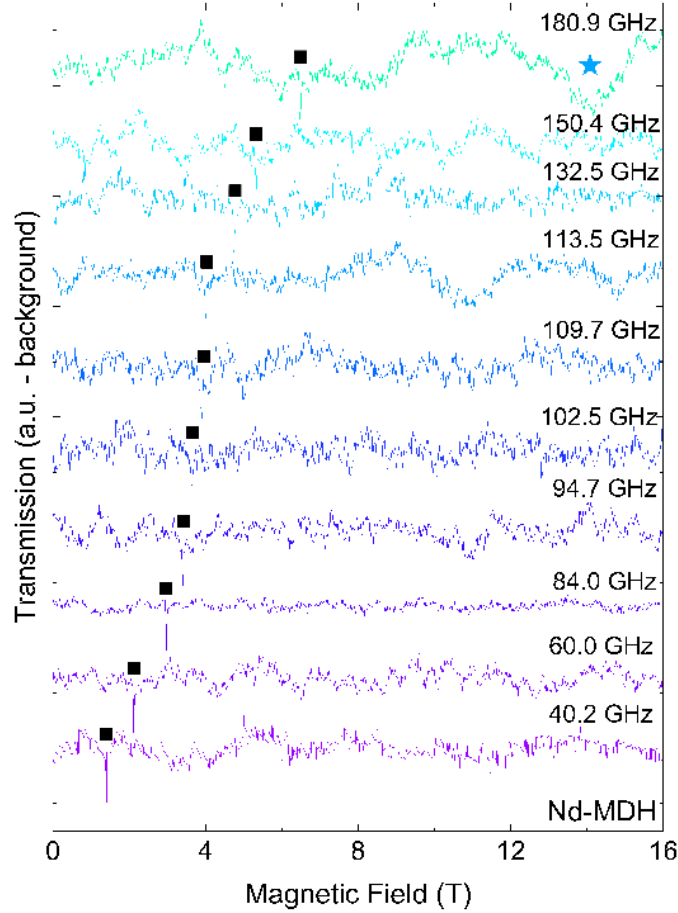


Fig. 7.2: HF-EPR transmission spectra measured at $T = 2$ K and frequencies ranging from 40.2 GHz to 180.9 GHz on a frozen solution of the Nd-MDH sample. All spectra were background and phase mixing corrected, normalised to the absolute of the lowest value and shifted along y . The black squares and blue star correspond to the resonance positions of the observed features, as explained in the text.

the origin.

The common sharp resonance feature (feature RF1 and RF3, visualized as black squares in Fig. 7.5) was studied in further detail by measuring the transmission with higher magnetic field resolution around the resonance field position for both samples. The microwave transmission was measured at two distinct frequencies. The measured up- and down-field-sweeps are shown in Figs. 7.6(a)-(d). The up- and down-field-sweeps were (in addition to background and phase mixing correction) corrected for the remanence of the superconducting magnet of the device. The remanence was estimated by comparing the resonance positions of up- and down-field-sweeps.

As can be seen in the Nd-MDH spectra (7.6(a) and (c)), the resonance feature is actually composed of two distinct resonances. The field-separation between the two resonances is $\Delta B = 5.0(6)$ mT at $f = 109.7$ GHz and $\Delta B = 3.2(5)$ mT at $f = 84.0$ GHz, as indicated by grey double arrows. The resonance positions of

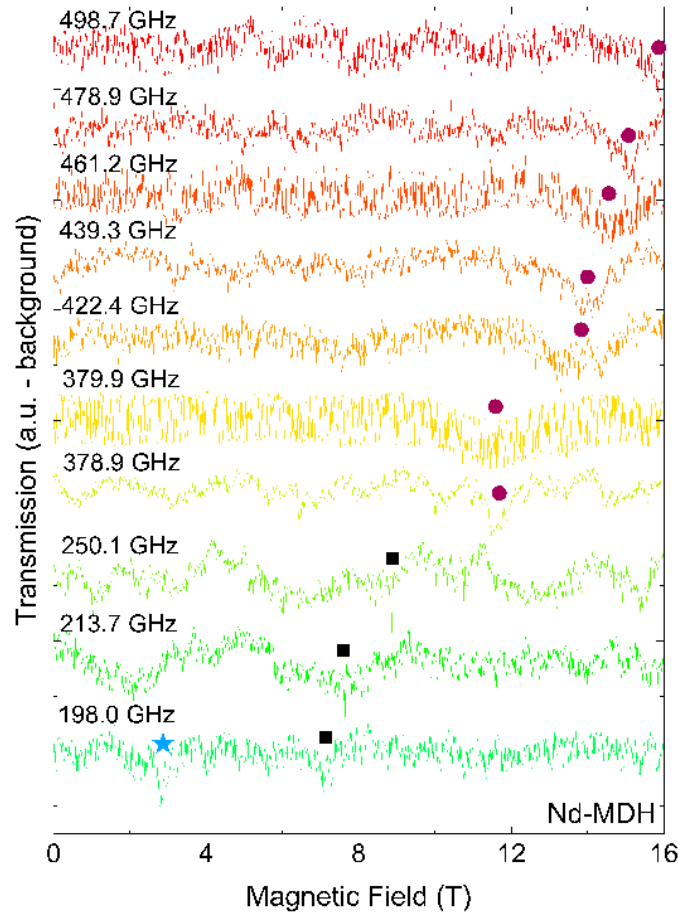


Fig. 7.3: HF-EPR transmission spectra measured at $T = 2$ K and frequencies ranging from 198.0 GHz to 498.7 GHz on a frozen solution of the Nd-MDH sample. All spectra were background and phase mixing corrected, normalised to the absolute of the lowest value and shifted along y . The black squares, red circles and blue star correspond to the resonance positions of the observed features, as explained in the text.

the two observed resonances for Nd-MDH are furthermore highlighted by vertical dashed lines.

The blank spectra (7.6(b) and (d)) measured at $f = 109.7$ GHz also show that the resonance feature is composed of two distinct resonances with a field-separation of $\Delta B = 3.71(12)$ mT, indicated by a grey double arrow. This field-separation is consistent with the observed field-separation for Nd-MDH, considering the error-bars². For the blank spectra measured at $f = 84.0$ GHz, a single broad resonance feature is observed with a width of approximately $\Delta B = 3.1(14)$ mT, as indicated by the grey double arrow. The width of this broad resonance feature is comparable in size to the field-separation between the two resonances observed for Nd-MDH at this frequency. However, it is not possible to distinguish two resonance features.

²The difference between both obtained ΔB values lies inside the 3σ interval.

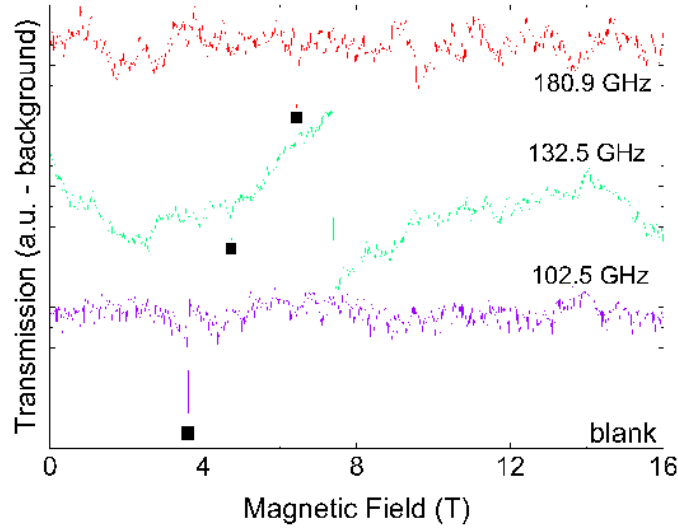


Fig. 7.4: HF-EPR transmission spectra measured at $T = 2$ K and $f = 102.5$ GHz, 132.5 GHz, and 180.9 GHz on a frozen solution of the blank sample. All spectra were background and phase mixing corrected, normalised to the absolute of the lowest value and shifted along y . The black squares correspond to the resonance positions of the observed features, as explained in the text.

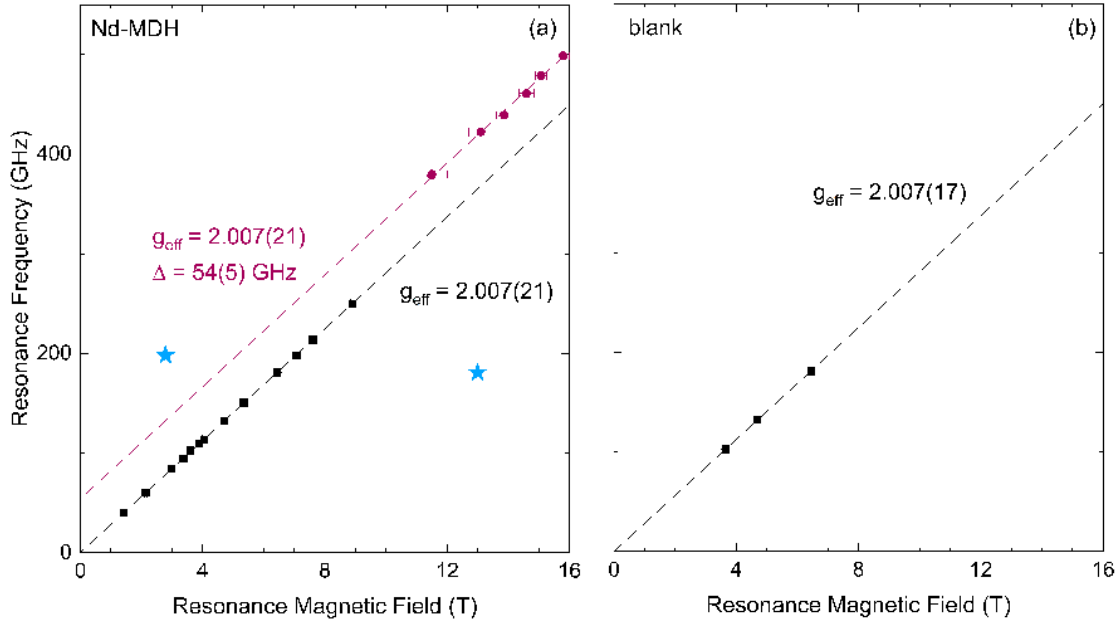


Fig. 7.5: Resonance magnetic field positions obtained from the transmission spectra measured at $T = 2$ K and various frequencies for Nd-MDH (a) (see Figs. 7.2 and 7.3) and blank (b) (see Fig. 7.4). The solid black/red lines represents a linear fit to the black/red resonance positions. In the case of the black lines, the fit was performed with the y -intersection fixed to zero.

A comparison of the resonance field positions of the resonances measured at $f = 109.7$ GHz for Nd-MDH and blank, reveals that the resonances observed for

the blank are shifted towards lower magnetic fields by a value of approximately $0.245 - 1 \text{ mT}$ against the resonances observed for Nd-MDH. The uncertainty in resonance position is dominated by the uncertainty of the measurement frequency ($\Delta f = 1 \cdot 10^{-3} \text{ GHz}$) and correction of the remanence field, which results in uncertainties in the resonance position of 0.2 mT and 2.5 mT , respectively. Consequently, the observed deviations of the resonance positions measured at $f = 109.7 \text{ GHz}$ are within the range of the measurement uncertainty. In a similar manner, the uncertainties of the resonance positions corresponding to the measurements performed at $f = 84.0 \text{ GHz}$ yield an uncertainty of 0.2 mT due to the uncertainty in frequency and 2 mT due to the uncertainty in remanence field correction. The differences in resonance positions between the Nd-MDH and the blank spectra are approximately $1.3 - 2 \text{ mT}$ (the blank resonance here being shifted to higher magnetic fields against the ones obtained for Nd-MDH), which are within the range of the measurement uncertainty.

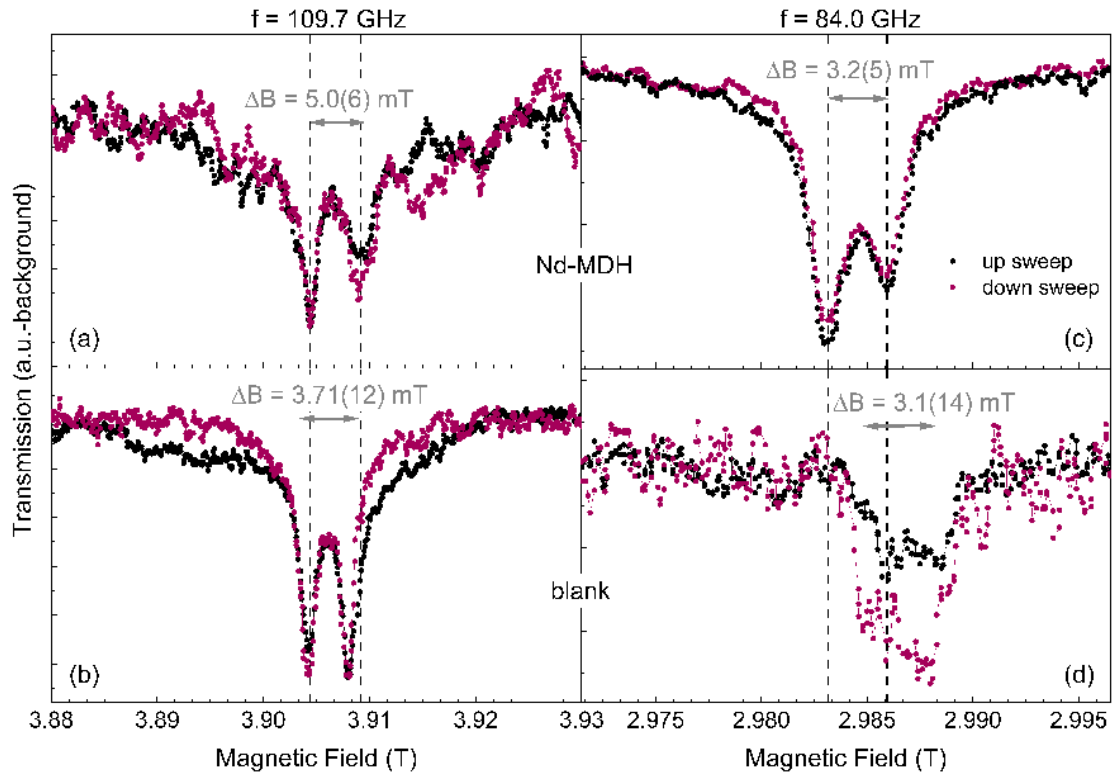


Fig. 7.6: Exemplary HF-EPR transmission spectra measured at $T = 2 \text{ K}$ at $f = 109.7 \text{ GHz}$ ((a) and (b)) and $f = 84.0 \text{ GHz}$ ((c) and (d)) for the Nd-MDH (top row) and blank (bottom row). All spectra are background and phase mixing corrected and furthermore corrected for the remanence of the superconducting magnet of the device, as described in the text. The difference in resonance magnetic field between the two resonance features is indicated by grey arrows. Vertical dashed lines depict the resonance positions observed for the Nd-MDH sample.

In Figs. 7.7(a) and (b) the evolution of the (twofold) resonance feature RF1 (marked with a black square) and the resonance feature RF2 (marked with a red circle)

observed at 2 K for Nd-MDH with increasing temperature at a fixed frequency of $f = 40.2$ GHz and $f = 439.3$ GHz are illustrated, respectively. The intensity of feature RF1 in Fig. 7.7(a) decreases steadily with increasing temperature. For feature RF2 in Fig. 7.7(b), the trend (for all temperatures except 4 K) that the intensity of feature RF2 decreases with increasing temperature is observed. However, the spectrum measured at 4 K does not follow the trend of the other spectra. This may be attributed to the occurrence of phase mixing (see subsection 3.1.2). Phase mixing means that the dispersion is mixed into the absorption [45, 46]. In a purely dispersion spectrum, a zero-crossing is observable at the resonance position, see subsection 3.1.2 [45, 46]. Therefore, the mixing of dispersion into the measured signal may result in a reduction of the signal at the resonance position. The overall trend (of a decrease in the intensity of the resonance feature with an increasing temperature) indicates that the transitions observed at 2 K can be attributed to transitions from the energetically lowest-lying state. Furthermore, no other transitions occur up to 60 K (see Fig. B.3).

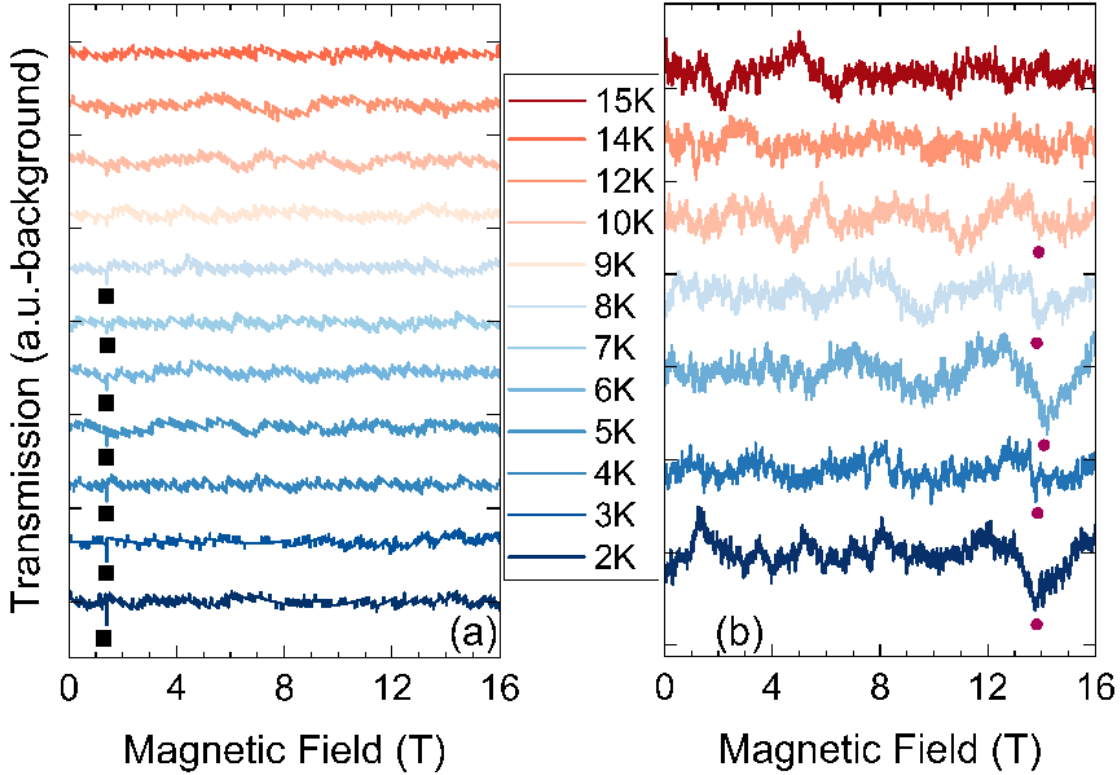


Fig. 7.7: (a) HF-EPR spectra of Nd-MDH measured at $f = 40.2$ GHz for different temperatures ranging from 2 K to 14 K. The black squares mark the resonance position of the resonance feature RF1. (b) HF-EPR spectra of Nd-MDH measured at $f = 439.3$ GHz for different temperatures ranging from 2 K to 15 K. The red circles mark the resonance position of the resonance feature RF2.

The effective g -factor of the resonance feature RF1 matches the electron g -factor of approximately 2.002 [47] within the errorbars. Furthermore, the corresponding resonance branch is gapless. The evolution with temperature of feature RF1

(Fig. 7.7(a)) is comparable to the one observed for "quasi-free" radicals in subsection 8.4.1. Therefore, it is concluded that the observed feature RF1 corresponds to a transition of such a "quasi-free" radical³. As this resonance feature and its splitting into two distinct resonance lines are observed in both the Nd-MDH and the blank sample, it can be assumed that the feature results from the buffer PIPES. PIPES is capable of forming radicals, as observed, for example, in combination with iron [86]. Nevertheless, it cannot be ruled out that minor contributions to the observed signal in the Nd-MDH sample may originate from radicals in enzymes where no Nd³⁺-ion is present in the active site or where the Nd³⁺ moment and radical moment do not interact. The occurrence of enzymes lacking a Nd³⁺-ion in the active site has been previously observed, but it is uncertain if radicals are formed in this case [87].

The resonance positions correspond to an effective g -factor of 2.007(21) and a zero-field energy gap of $\Delta = 54(5)$ GHz. Furthermore, the resonance of feature RF2 in Figs. 7.2, 7.3 and 7.7(b) is broader than the free radical feature RF1 (Figs. 7.2, 7.3 and 7.7(a)). This indicates that this signal is no transition of a "quasi-free" radical. The presence of a gap additionally demonstrates that this branch corresponds to a transition between two states, for which their respective energy levels figure an energy gap between each other in the absence of a magnetic field. This could be the case for a transition between two states that are separated in energy due to anisotropy or via magnetic interaction. For lanthanide ions, anisotropy is common [24]. Therefore, a zero-field energy gap would generally be possible for Nd³⁺-ions. However, the observed energy gap cannot be assigned to transitions between different Kramers doublets of Nd³⁺, as this would not result in the observed effective g -factor: The total angular momentum of the Nd³⁺-ion is $J = 9/2$ and its Landé-factor is $8/11$ [24]. Therefore, it follows that $g_{\text{eff}} = \Delta m_J \cdot g_L \neq 2$. A spin- $1/2$ particle would not lead to a zero-field energy gap, as its two spin states $m_s = \pm 1/2$ are degenerate at zero field. Consequently, the observed feature is attributed to the interacting system of the magnetic moments of the Nd³⁺-ion and the electron with an interaction energy of $\Delta = 54(5)$ GHz.

A simple model to describe this system would be to assume that only the energetically lowest-lying Kramers doublet contributes to the magnetic properties at 2 K, as it is assumed for the Er³⁺ complex in chapter 6. In the following, it is assumed that the energetically lowest lying Kramers doublet takes the largest possible value for $|m_J|$, namely $m_J = \pm 9/2$. Assuming isotropic g -tensors for the radical and the Nd³⁺-ion, the Hamiltonian can be written as⁴:

$$\hat{H} = \hat{H}_Z^e + \hat{H}_Z^{\text{Nd}^{3+}} + \hat{H}_J \quad (7.1)$$

where $\hat{H}_Z^e$ is the Zeeman term for the radical, given by:

$$\hat{H}_Z^e = \mu_B \mathbf{B}^T \mathbf{g}_e \hat{\mathbf{S}}_e \quad (7.2)$$

$\hat{H}_Z^{\text{Nd}^{3+}}$ is the Zeeman term for the Nd³⁺-ion, in general form given by:

$$\hat{H}_Z^{\text{Nd}^{3+}} = \mu_B \mathbf{B}^T \mathbf{g}_{\text{Nd}^{3+}} \hat{\mathbf{S}}_{\text{Nd}^{3+}} \quad (7.3)$$

³The meaning of term "quasi-free" is further discussed in section 7.1.

⁴In the following equations the total angular momentum of the Nd³⁺-ion is labelled as $S_{\text{Nd}^{3+}}$

and $\hat{H}_J$ is the Hamiltonian describing the interacting system of the total spin of the Nd^{3+} -ion and the radical spin, in general form given by:

$$\hat{H}_J = \hat{\mathbf{S}}_{\text{e}}^{\text{T}} \mathbf{J} \hat{\mathbf{S}}_{\text{Nd}^{3+}} \quad (7.4)$$

In order to describe the energetically lowest-lying Kramers doublet of the Nd^{3+} -ion, a pseudo-spin-1/2 model with an effective g -tensor is used, as it was done for the Er^{3+} complex in eq. (6.1). In this model $\mathbf{g}_{\text{Nd}^{3+}} \mapsto \mathbf{g}_{\text{eff}, \text{Nd}^{3+}} = \mathbf{g}_{\text{Nd}^{3+}} \cdot 2|m_J|$ and $\hat{\mathbf{S}}_{\text{Nd}^{3+}} \mapsto \hat{\mathbf{S}}_{\text{Nd}^{3+}}^*$ with $|\mathbf{S}_{\text{Nd}^{3+}}^*| = 1/2$ (being equal to the radical spin) and $\pm m_J \mapsto \pm 1/2$. As a result, the total spin of the Nd^{3+} -ion is of the Ising type in this model. The direction of the total spin of the Nd^{3+} -ion is arbitrarily chosen to be along the molecular z -direction. As the radical spin equals the spin of the Nd^{3+} -ion in the chosen model and the interaction between the Nd^{3+} -ion and radical is assumed to be isotropic, the total spin of the Nd^{3+} -ion can only exert an influence on the electron spin in the direction of its total spin [27]. Consequently, the interaction matrix $\mathbf{J}$ between the magnetic moments of the Nd^{3+} -ion and the radical is finite only in the z -direction, resulting in the following Hamiltonian:

$$\hat{H} = \mu_{\text{B}} \mathbf{B}^{\text{T}} \mathbf{g}_{\text{e-}} \hat{\mathbf{S}}_{\text{e-}} + \mu_{\text{B}} \mathbf{B}^{\text{T}} \mathbf{g}_{\text{eff}, \text{Nd}^{3+}} \hat{\mathbf{S}}_{\text{Nd}^{3+}}^* + J_{\text{zz}} \hat{S}_{\text{e-}}^z \hat{S}_{\text{Nd}^{3+}}^{*z} \cdot 2m_J \quad (7.5)$$

where the factor $2m_J$ accounts for the change in the absolute value of the total spin of the Nd^{3+} -ion due to the application of a pseudo-spin-1/2 model.

The observed interaction energy of $\Delta = 54(5)$ GHz corresponds to an interaction strength of $|J_{\text{zz}}| = 12.0(11)$ GHz for $|m_J| = 9/2$. The resulting energy levels and resonance branches, as derived from the chosen model (see eq. (7.5)), are presented in Figs. 7.8(a)-(d). These figures illustrate the behaviour for an antiferromagnetic ((a) and (c)) and a ferromagnetic ((b) and (d)) interaction, respectively. As illustrated in the top figures, the model under consideration exhibits two pairs of degenerate states at zero-field and a zero-field energy gap of Δ between the two pairs. It arises from the spin-spin interaction in eq. (7.4). In the presence of magnetic fields, the pairs become non-degenerate due to the Zeeman terms in the Hamiltonian (eq. (7.2) - eq. (7.3)). In the bottom figures, the "allowed" resonance branches, corresponding to transitions where only the electron spin changes, are shown. Two distinct resonance branches can be identified: one exhibiting a positive slope, equal to the electron g -factor, throughout the entire measured magnetic field range. The other branch figures a negative slope for magnetic fields below the field at which the energy levels of the $|1/2, -9/2\rangle$ and $|-1/2, -9/2\rangle$ states cross. At this point the slope of the resonance branch changes sign.

The transition indicated by the red arrow includes the energetically lowest-lying state, thus, exhibiting a slightly higher transition probability than the transition indicated by the black arrow at low temperature. In the case that the actual $|m_J|$ -value of the Nd^{3+} -ion is $9/2$, the higher probability of the red resonance branches indicates that the observed interaction between the magnetic moment of the Nd^{3+} -ion and the radical is ferromagnetic, as this branch is observed in the measurements (Fig. 7.5(a)). When increasing the temperature, the $|-1/2, 9/2\rangle/|1/2, 9/2\rangle$ state gets more populated,

resulting in an increase in probability for the black resonance branch. Despite the increase in temperature, this resonance branch was not observed at about 0.5 T or 3.4 T in Fig. 7.7(a).

However, the interpretation that the interaction is of the FM type is altered in the case that the energetically lowest-lying Kramers doublet exhibits a different $|m_J|$ value: As $|m_J|$ in this case does not equal the absolute of the total spin, there exist finite x - and y -components of the total spin of the Nd^{3+} -ion. These finite x and y components lead to off-diagonal elements in the effective J -tensor resulting from the mapping of the total Nd^{3+} spin onto a pseudo-spin- $\frac{1}{2}$ [88, 89]. Therefore, in the case of $|m_J| \neq 9/2$, a prediction, whether the interaction is of the FM or AFM type, is not possible by using simple models.

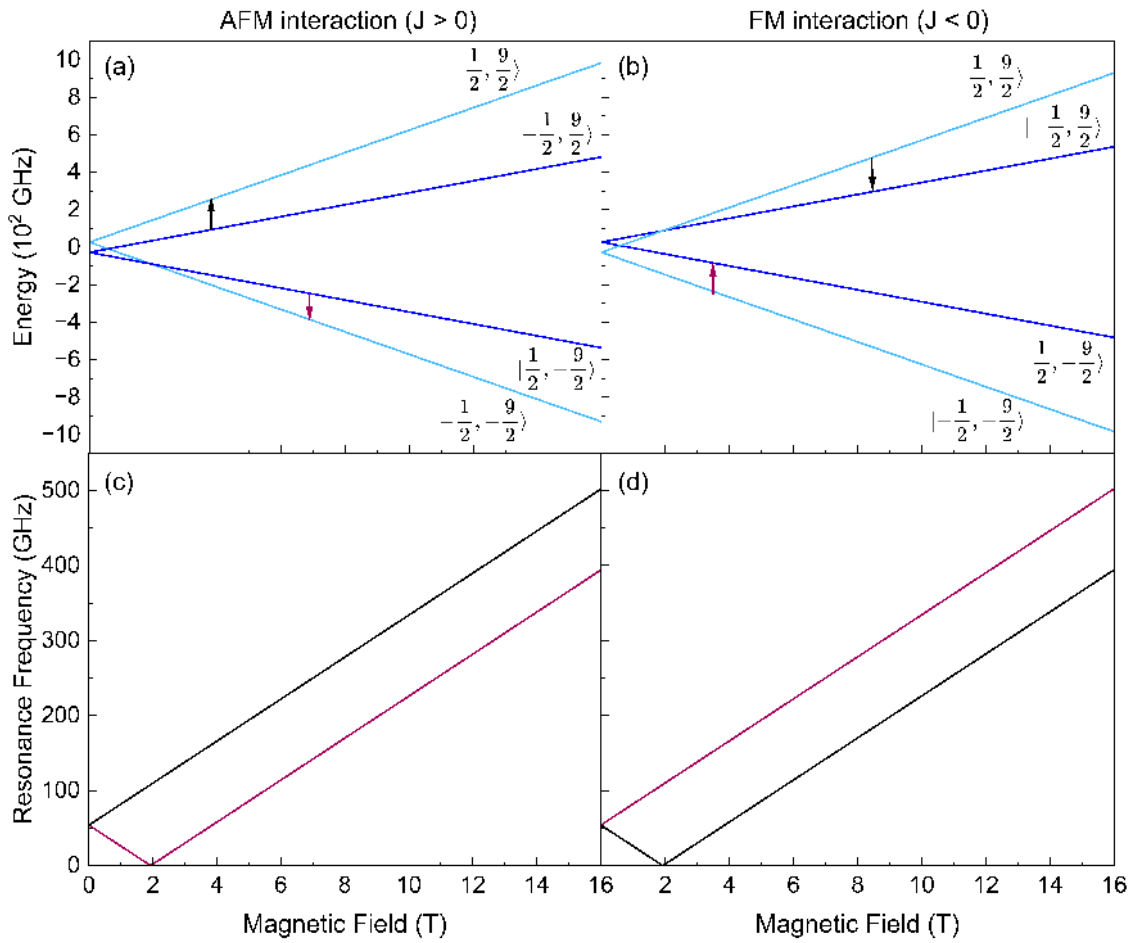


Fig. 7.8: Top ((a) and (b)): Calculated energy level diagram for the Hamiltonian in eq. (7.5) for $|m_J| = 9/2$ of the total spin of the Nd^{3+} -ion. The m_J -values of the electron and Nd total spin corresponding to the respective energy levels are indicated in parenthesis adjacent to them. Bottom ((c) and (d)): Calculated resonance frequency versus magnetic field diagram for the transitions indicated by the black and red arrows at the top plot. For (a) and (c) an antiferromagnetic interaction and for (b) and (d) a ferromagnetic interaction is assumed.

In conclusion, the HF-EPR measurements reveal an interaction between the radical spin and the Nd^{3+} spin, with an interaction energy of 54(5) GHz. Assuming that $m_J = \pm 9/2$ for the Nd^{3+} -ions, the HF-EPR spectra suggest a ferromagnetic interaction between the radical spin and the Nd^{3+} spin. Whereas for the other case it is not possible to determine the type of interaction with simple models.

Assuming a dipolar interaction between the radical and Nd^{3+} -ion magnetic moments, the measured interaction energy would imply a distance between the Nd^{3+} -ion and the radical of approximately 0.35 – 1.9 Å. The actual value depends on the value of $|m_J|$ and the orientation of the Nd^{3+} -ion and radical magnetic moments with respect to their connection vector. However, it should be noted that other research on interactions between terbium and radical (the interaction strength is comparable in size with the one investigated in this work) yields that a pure dipole interaction is rather unlikely for interactions between the terbium and radical magnetic moments [90]. Exchange-like interactions allow for greater distances between the radical and terbium ion for a given interaction strength [90].

Chapter 8

Biomimetic Samples for Metal Containing MDH Enzymes

In the previous chapter Nd-MDH, an MDH enzyme which is required for the bacteria's metabolic process, was studied. The samples studied in this chapter are mimics of the active site of such metal containing MDH enzymes. These samples contain only the active site model composed out of pyrroloquinoline quinone dimethyl ester/trimethyl ester (PQQDME/ PQQTME) together with the metal cation.

Such mimics are so-called biomimetic systems: Biomimetics is a useful tool to study complex biological systems. The overall biological system is understood by first understanding simpler model systems - the biomimetic system. The biological systems studied here are the same as the ones of the previous chapter: methylotrophic bacteria.

8.1 Molecular Structure

For this work various samples containing PQQDME or PQQTME together with lanthanide ions or calcium ions ¹ and the base DBU dissolved in acetonitrile were provided by Ioana Ciubutaro (group of Lena Daumann at LMU Munich):

- samples containing PQQDME:
 - PQQDME (hereafter referred to as **a**)
 - PQQDME with La³⁺ (hereafter referred to as **b**)
 - PQQDME with Gd³⁺ (hereafter referred to as **c**)
 - PQQDME with Dy³⁺ (hereafter referred to as **d**)

¹Calcium is hereafter included in the notation as a part of the Ln-group, although it is not a rare earth metal.

- samples containing PQQTME:
 - PQQTME (hereafter referred to as **e**)
 - PQQTME with La^{3+} (hereafter referred to as **f**)
 - PQQTME with Lu^{3+} (hereafter referred to as **g**)
 - PQQTME with Ca^{2+} (hereafter referred to as **h**)

In Fig. 8.1(a) and (b) the structural formulas of PQQDME and PQQTME are shown, respectively. PQQDME/PQQTME differs from PQQ (which is part of the active site in Ln-MDHs) only by the replacement of H-atoms by two/three terminal methyl groups. The latter are added to block possible coordination sites for the Ln-ion that are not available in the actual enzyme. Like PQQ, PQQDME and PQQTME are capable of hosting radicals, whose possible positions are marked with pink circles in the figure [81, 91]. When Ln-ions are added to the solution, it is possible for them to coordinate to PQQDME/PQQTME as shown by the blue circles in the figures.

The probability ratio of molecules within a sample containing a radical is not yet known and differs when different Ln-ions are added [81, 91]. Furthermore, it is not a priori clear whether every PQQDME/PQQTME molecule is coordinated to a Ln-ion, leaving the possibility of free PQQDME/PQQTME radicals and free Ln-ions [81, 91].

In this section the following effective Hamiltonian, describing three distinct magnetic molecular species of the samples, is used for simulations

$$\hat{H} = \hat{H}_1 + \hat{H}_2 + \hat{H}_3. \quad (8.1)$$

$\hat{H}_1$ describes the radicals in PQQDME/PQQTME, that are not interacting with Ln-ions, as free spin-1/2 particles ($g_{e-} \approx 2.002$ [47]):

$$\hat{H}_1 = \mu_B \mathbf{B}^T \mathbf{g}_{e-} \hat{\mathbf{S}}_{e-,1}. \quad (8.2)$$

$\hat{H}_2$ describes a system including the radical of PQQDME/PQQTME and the Ln-ion coordinated to PQQDME/PQQTME. The magnetic moments of the radical and the Ln-ion interact with each other. The Ln-ion is influenced by the crystal field due to the ligand atoms:

$$\begin{aligned} \hat{H}_2 = & \mu_B \mathbf{B}^T \mathbf{g}_{e-} \hat{\mathbf{S}}_{e-,2} + \mu_B \mathbf{B}^T \mathbf{g}_{\text{Ln}} \hat{\mathbf{S}}_{\text{Ln},2} + \hat{\mathbf{S}}_{e-,2}^T \mathbf{J} \hat{\mathbf{S}}_{\text{Ln},2} \\ & + D \left(\hat{\mathbf{S}}_{\text{z,Ln},2}^2 - \frac{S_{\text{Ln},2} (S_{\text{Ln},2} + 1)}{3} \right) + E \frac{\hat{\mathbf{S}}_{+, \text{Ln},2}^2 + \hat{\mathbf{S}}_{-, \text{Ln},2}^2}{2} \end{aligned} \quad (8.3)$$

$\hat{H}_3$ describes Ln-ions, that do not interact with radicals, as free spins with $S_{\text{Ln},3}$ being the total magnetic moment of the Ln-ion:

$$\hat{H}_3 = \mu_B \mathbf{B}^T \mathbf{g}_{\text{Ln}} \hat{\mathbf{S}}_{\text{Ln},3} \quad (8.4)$$

The Ln-ions which are not interacting with radicals are Ln-ions at arbitrary positions in the frozen solution. Consequently, their surrounding atoms/molecules

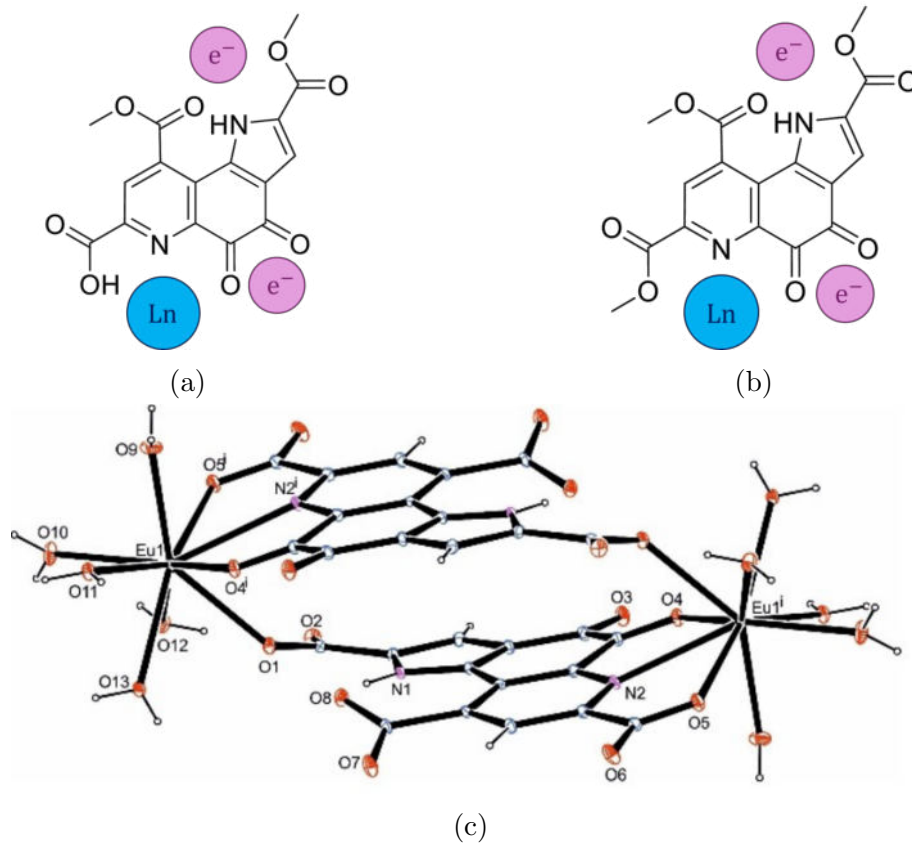


Fig. 8.1: Structural formula of PQQDME (a) and PQQTME (b) with the corresponding possible positions of the Ln-ion and of the radical marked with blue and pink circles, respectively. The terminal methyl groups are excluded. (c) Possible stacking of Eu-containing compounds. The layering of Eu-containing molecules is repeated above and below the shown molecules in the same manner. The figures are adapted from figures provided by Ioana Ciubutaro [91, 92].

can be any of the atoms/molecules which are present in the frozen solution. The surrounding atoms/molecules can in general interact with the Ln-ion and thereby influence the resonance feature observed for transitions of this Ln-ion. As a sample average is measured, it can be assumed in first approximation that the influence of other atoms/molecules on the non-interacting Ln-ions averages out resulting in the effective Hamiltonian of eq. (8.4). For example a resonance feature in an EPR measurement would exhibit the same resonance position calculated from eq. (8.4), but the width of the feature is larger due to the influence of the other atoms/molecules on the Ln-ions. The g -tensor of the Ln-ions, that do and do not interact with the radicals of PQQDME/PQQTME, described by $\hat{H}_2$ and $\hat{H}_3$, is assumed to be identical.

It has been observed in previous research that similar molecules, to those investigated in this work, containing Eu can in principle stack on top of each other, as shown in Fig. 8.1(c) [91]. In such a system the magnetic moment of coordinated Ln-ions with a non-zero magnetic moment of one molecular plane may interact with the magnetic

moment of the Ln-ion of the next-nearest planes [81]. Therefore, the magnetic moments of the Ln-ions coordinated to neighbouring PQQDME/PQQTME could in principle also interact with each other in the samples studied in this work.

8.2 Magnetisation Studies

8.2.1 Magnetisation Studies on Samples e-h

To investigate the influence of the Ln-ions on the concentration of radical-hosting PQQTME molecules, the isothermal magnetisation and the static magnetic susceptibility was measured for **e-h**. The objective was to quantify the concentration of radicals in these samples and to ascertain whether the concentration of radicals in the sample varies in the presence of different Ln-ions. However, the sample preparation method in polycarbonate capsules (QDC-AGC3), from *Quantum Design*, used in this work is not suited for the samples. This is due to the low signal to background ratio. Further details are provided in section B.1. It may be beneficial to conduct future experiments to ascertain whether different sample preparation techniques, such as the use of homebuilt 3D-printed resin sample holders [85] are more effective, as mentioned in section 7.2. These sample holders can be designed in such a way that the signal originating from the sample holder itself is more homogeneous around the sample position than that of the polycarbonate capsules [85].

8.2.2 Magnetisation Studies on Sample d

Static magnetic susceptibility and isothermal magnetisation was measured for **d** in order to investigate potential interactions between the radical and the Dy^{3+} magnetic moments, as shown in Fig. 8.2 ². For the measurement 100(3) μL of **d** were used, which include 6 mM $\text{Dy}(\text{OTf})_3$ and 3 mM PQQDME. The data was background corrected as explained in subsection 3.3.3. The respective background signal was obtained by repeating the measurements conducted on **d** with a capsule filled with 100(3) μL acetonitrile. The background corrected magnetisation data were normalised to the amount of Dy^{3+} -ions in the sample.

The χT -product of **e** increases with rising temperature and reaches a saturation value of 11.9(27) $\text{erg K G}^{-2} \text{mol}^{-1}$ above 50 K, as shown in Fig. 8.2 ³. The χT -value for a free Dy^{3+} -ion is 14.17 $\text{erg K G}^{-2} \text{mol}^{-1}$ [24], which is within the range of the uncertainty of the measured saturation value. Assuming that all PQQDME molecules host a radical, the χT -value of those radicals is 0.38 $\text{erg K G}^{-2} \text{mol}^{-1}$. When adding this to the χT -value of free Dy^{3+} -ions this results in a total χT -value

²It was possible to measure this sample with the sample preparation procedure described in section B.1, due to the large magnetic moment of Dy^{3+} -ions compared to the magnetic background signal of the polycarbonate capsules and the larger amount of Dy^{3+} -ions compared to the amount of radicals in the samples **e-h**.

³The jump-like changes in the χT product are artefacts of the fitting procedure. They arise due to differences in the maxima of the measured voltage versus position curves and the dipole response fit.

of $14.55 \text{ erg K G}^{-2} \text{ mol}^{-1}$, which is within the range of the uncertainty of the measured saturation value. As only one plateau is observed in χT , there is no clear indication of an interaction between the radical and Dy^{3+} -ion magnetic moment.

The inset of Fig. 8.2 shows the isothermal magnetisation as a function of magnetic field. At low magnetic fields, the magnetisation increases strongly with increasing magnetic field as compared to the magnetisation of a free magnetic moment. This indicates a strong magnetic anisotropy of the total magnetic moment of the Dy^{3+} -ions, a contribution of the radicals or the admixture of higher lying crystal-field levels of the Dy^{3+} -ion. At high magnetic fields, a quasi-linear field-dependence of the magnetisation is observed. The magnetisation remains unsaturated up to a magnetic field of 7 T. By interpolating the gradient of the quasi-linear part of the magnetisation to zero field, a saturation magnetisation of $4.7(4) \mu_B$ is obtained. Since the fraction of radical-hosting PQQDME molecules, and hence the exact number of radical moments, is unknown a determination of the magnetic ground state of the Dy^{3+} -ions from the saturation magnetisation is not straightforwardly possible.

χT was only measured up to 200 K, as the melting point of acetonitrile is approximately 228 K [93]. This means that the data do not rule out strong magnetic interactions of the magnetic moments of the Dy^{3+} -ion and the radical of the species described by $\hat{H}_2$ in eq.(8.3), affecting the χT values at temperatures exceeding 200 K.

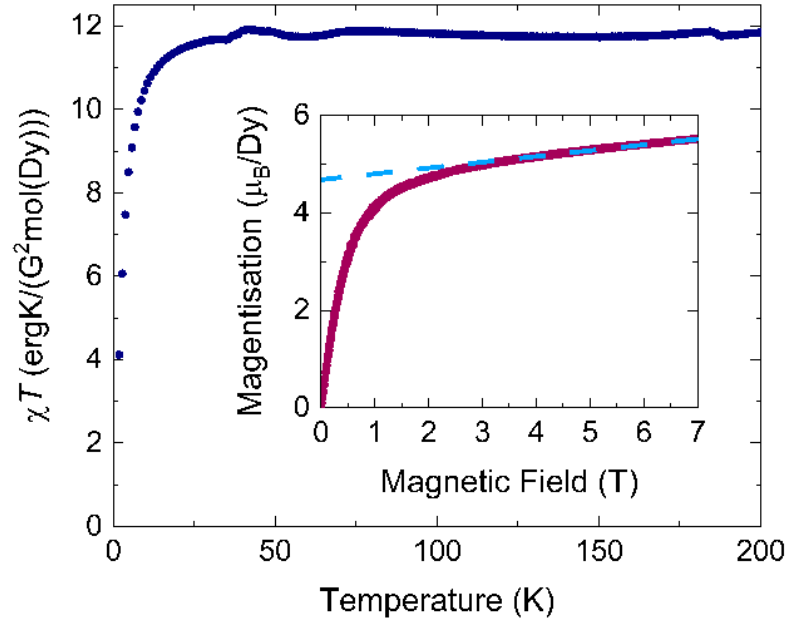


Fig. 8.2: Static magnetic susceptibility $\chi = M/B$ multiplied by the temperature as a function of temperature measured at an external magnetic field of 1 T. The inset shows the isothermal magnetisation as a function of external magnetic field, measured at 1.8 K. The dashed line is an interpolation of the quasi-linear part of the magnetisation. The data are normalised to the amount of Dy^{3+} -ions present in the sample.

8.3 X-Band Electron Spin Resonance

In order to determine the hyperfine coupling between the radical spin and the nuclear spin of a nearby atom (which would mean including a hyperfine-coupling term into eq.(8.2) and eq.(8.3) for the spin- $1/2$ species), X-Band EPR measurements were performed for samples **a-d** and **f** at approximately 5 K and at a frequency of about 9.6 GHz. The EPR-spectra (grey lines) and their smoothened version (red lines) together with a background of the empty Wilmad quartz (CFQ) EPR tube (light blue lines) measured at 300 K are shown in Fig. 8.3. For **a**, the measured spectrum coincides with the background spectrum, as is visible in Fig. 8.3(a). The background spectrum exhibits two resonance features corresponding to effective g -factors of approximately $g_{\text{eff}} = 2.09$ (feature at approximately $B = 0.33$ T) and $g_{\text{eff}} = 0.77$ (feature at approximately $B = 0.895$ T), respectively. Unfortunately, the expected signal of a radical with $g_{\text{eff}} = g_{\text{electron}} \approx 2.002$ [47] could not be observed, as the background also exhibits a feature in the vicinity of g_{electron} .

Similarly, for **c**, the measured spectrum exhibits the same features as the background spectrum, as illustrated in Fig. 8.3(c). A slight increase in the amplitude of the feature at approximately $g_{\text{eff}} = 2.09$ is observed in the spectrum of **c** in comparison to that of the background. However, the spectra were obtained under differing conditions, including temperatures, microwave frequencies, sample tubes (identical product number, but different tube) and resonator settings. Consequently, it is not possible to ascertain whether the observed change in the signal amplitude is due to the addition of Gd-ions ($g_L = 2$ [24]) to the sample or to the altered measurement environment.

In Fig. 8.3(b) and (d) the spectra measured for **b** and **f** are shown, respectively. For both samples, additionally to the two resonance features that are also observed in the background, a sharp resonance feature is observed at approximately 0.345 T, corresponding to an effective g -factor of 1.995(4) for **b** and 1.997(2) for **f**. Similar sharp features at similar resonance positions were previously observed for radicals of PQQ [71]. Therefore, and due to the g -factor values being close to that of free electrons [47] (the deviation is within the 3σ interval), it can be concluded that the signals originate from the radicals formed by PQQDME and PQQTME. The resonance is only single-fold and, thus, no hyperfine-coupling can be identified in these spectra. However, it should be noted, that the background feature at around $g_{\text{eff}} = 2.09$ could, in principle, superimpose other features corresponding to hyperfine-coupling.

The spectrum obtained for **d** is presented in Fig. 8.3(e). It exhibits, analogous to those obtained for **c**, a feature at approximately $g_{\text{eff}} = 2.09$ with an amplitude that is larger than the one obtained for the background. However, as previously stated for **c**, this change cannot be straightforwardly attributed to the sample itself. Furthermore, a second, broader feature (in comparison to those observed for **b** and **f**) is observed at approximately 0.056 T, corresponding to an effective g -factor of 12.35.

In the literature a molecule containing a single Dy^{3+} -ion [94] was studied. The

literature spectrum is shown as dark blue line in Fig. 8.3(e). The spectrum shows a single resonance feature at a resonance position corresponding to approximately $g_{\text{eff}} = 13.9$ [94]. The feature was described as a transition within the ground state Kramers doublet by a pseudo-spin-1/2 model with an effective isotropic g -factor of $g_{\text{eff}} = 13.9$ [94].

The resonance feature observed for **e** is broader and has a different resonance position than the resonance of the single Dy^{3+} -ion in the literature [94]. There are multiple reasons why the feature observed for **e** is broader. First of all, the feature could originate solely from a transition within the ground state Kramers doublet of the non-interacting Dy^{3+} -ions, as is the case in [94]. In this case the broader width would be due to Dy^{3+} species in the sample that have slightly changed g or D -values, which could also explain the altered resonance position. The Dy^{3+} ions are randomly distributed over the whole sample. This results in an ensemble of Dy^{3+} -ions in the sample that differ by the local field acting on them. In the case that the feature originates solely from a transition within the ground state Kramers doublet of single Dy^{3+} -ions, the effective g -tensor would indicate a transition within the $|m_J| = 9/2$ Kramers doublet, as the Landé factor for a free Dy^{3+} -ion is $g_L = 4/3$ [71].

Another option would be that the feature originates from a system where the Dy^{3+} -ion and the radical magnetic moments interact. Such a feature would exhibit a larger width due to the varying interaction strength, for example as a result of changes in the distance between the radical and the Dy^{3+} -ion. In the case, that the transition corresponds to a transition from $|-m_s^e, -m_s^{\text{Gd}^{3+}}\rangle \rightarrow |m_s^e, -m_s^{\text{Gd}^{3+}}\rangle$, the resonance branch of such a transition in the resonance-frequency-versus-resonance-magnetic-field-diagram would have a slope corresponding to $g = 2$ and a non-zero y -intersection. This is similar to the the discussion of the resonance in Nd-MDH, see section 7.3. For the resonance observed for **e**, this would imply an interaction energy of $\Delta_1 = 8$ GHz or $\Delta_2 = 11.2$ GHz depending on whether the interaction strength is AFM or FM.

In conclusion, alternative sample tubes, that do not show an impurity feature in the vicinity of the expected radical feature, should be used in future experiments. Moreover, additional measurements at different frequencies are required to determine whether the observed feature for **d** corresponds to an interaction between the radical and Dy^{3+} -ion magnetic moments. The slope of the corresponding branch in a resonance-frequency-versus-resonance-magnetic-field-diagram may differ depending on the origin of the transition (transition within an interacting system or an intra-/inter-Kramers-doublet transition).

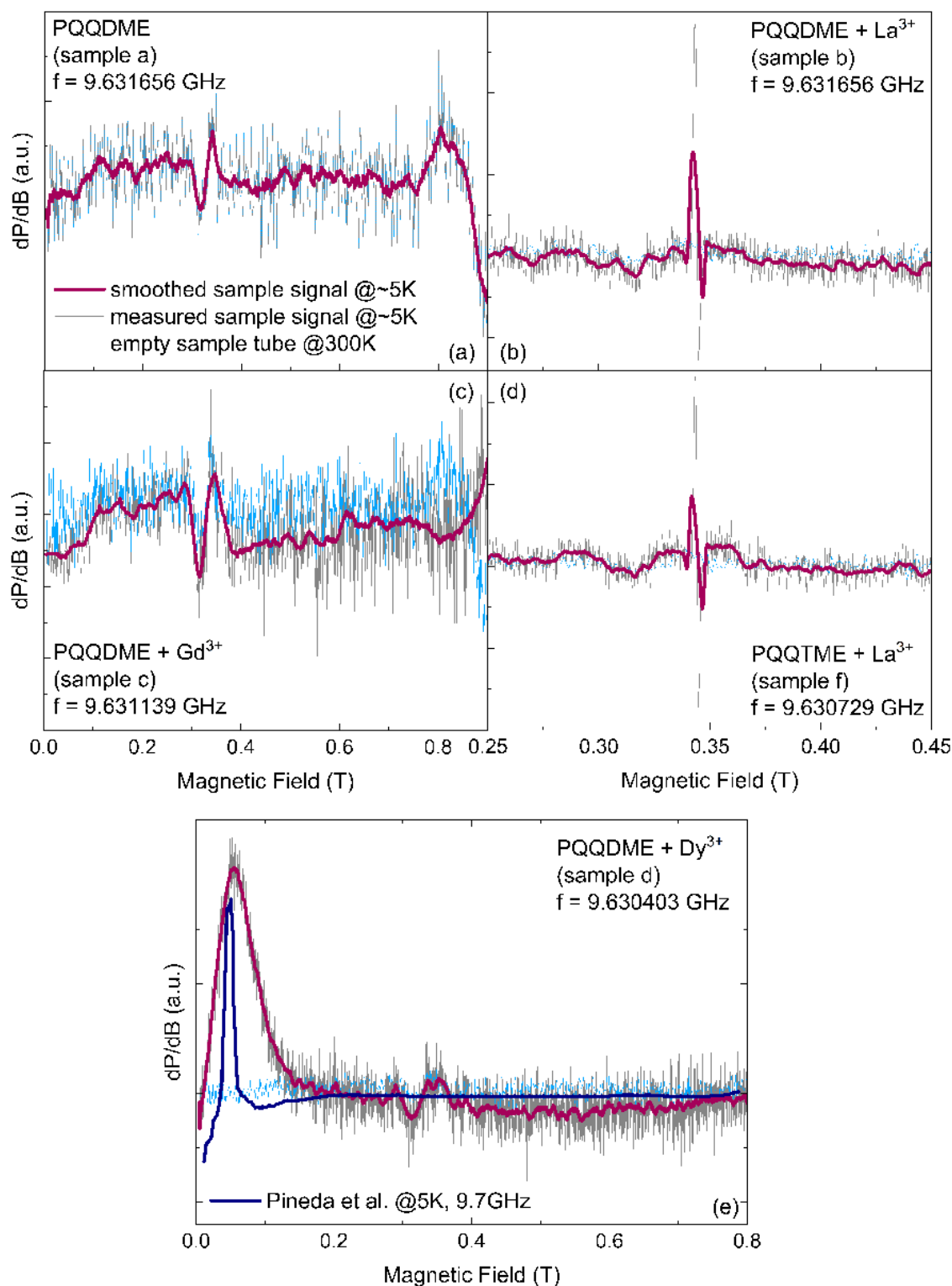


Fig. 8.3: X-Band EPR signal (dP/dB) for samples **a-f** measured at approximately 5 K, illustrated as grey lines. The smoothed curves are shown as red lines. Light blue lines correspond to a background signal of the empty sample tube measured at 300 K [41]. The reference spectrum (dark blue line) for **c** was taken from literature [94].

8.4 High-Field/High-Frequency Electron Spin Resonance

Microwave transmission spectra were measured at a fixed temperature of 2 K for frozen samples, as described in subsection 3.1.1.

8.4.1 HF-EPR Studies on samples **a**, **b** and **d**

The obtained transmission spectra for **a** are presented in Fig. 8.4. Resonance features which are observed in both the up- and down-field-sweeps are marked by black squares. All spectra exhibit a single resonance feature across the entire magnetic field range. The corresponding resonance positions, depicted in the resonance-frequency-versus-resonance-magnetic-field-diagram (fB -diagram) in Fig. 8.5(a), result in a gapless resonance branch with a linear slope. The slope corresponds to $g_{\text{eff}} = 2.005(15)$, as determined by a linear fit through the origin.

In Fig. 8.5(b) the evolution of the observed resonance feature with increasing temperature at a fixed frequency of $f = 123.1$ GHz is shown. The intensity of the resonance feature decreases with increasing temperature, and no other transitions occur up to 60 K.

As **a** only includes PQQDME the Hamiltonian in eq.(8.1) is reduced to $\hat{H}_1$. Consequently, the resonance features correspond to transitions of the electron of the PQQDME radical where m_s changes from $\mp 1/2$ to $\pm 1/2$ ⁴. This yields the observed effective g -factor of $g_{\text{eff}} = g_{\text{electron}} \approx 2.002$ [47]⁵. This is furthermore supported by the observed decrease of the intensity of the resonance feature with rising temperature: For the free spin- $1/2$ system, described by eq.(8.2), the intensity of the resonance decreases with rising temperature, as the $1/2$ state becomes thermally populated with rising temperature. Consequently, the stimulated emission rate approaches the absorption rate.

In Figs. 8.6 and 8.7 the microwave transmission spectra obtained for **b** and **d** are shown, respectively. Resonance features which are observed in both the up- and down-field-sweeps are marked with black squares. The spectra exhibit a single resonance feature of comparable width to that observed for **a** in Fig. 8.4. The corresponding resonance positions are depicted in the fB -diagrams in Fig. 8.8. The figure also includes a resonance feature at 312.2 GHz for **d**, which was observed for measurements with higher resolution, see Fig. 8.9(a). The resonance positions of Fig. 8.8 form a gapless resonance branch for both samples. A linear fit through the origin to the resonance positions yields the slopes of the resonance branches corresponding to effective g -values of 2.005(6) for **b** and 2.007(9) for **d**. These values agree with the one obtained for **a** within their errorbars. The similar lineshape of the resonance feature and the matching g -values compared to that of **a**, show that

⁴ $-1/2$ to $1/2$ in the case of absorption and $1/2$ to $-1/2$ in the case of stimulated emission.

⁵The discrepancy between the literature and the measured effective g -factor is within the 3σ interval.

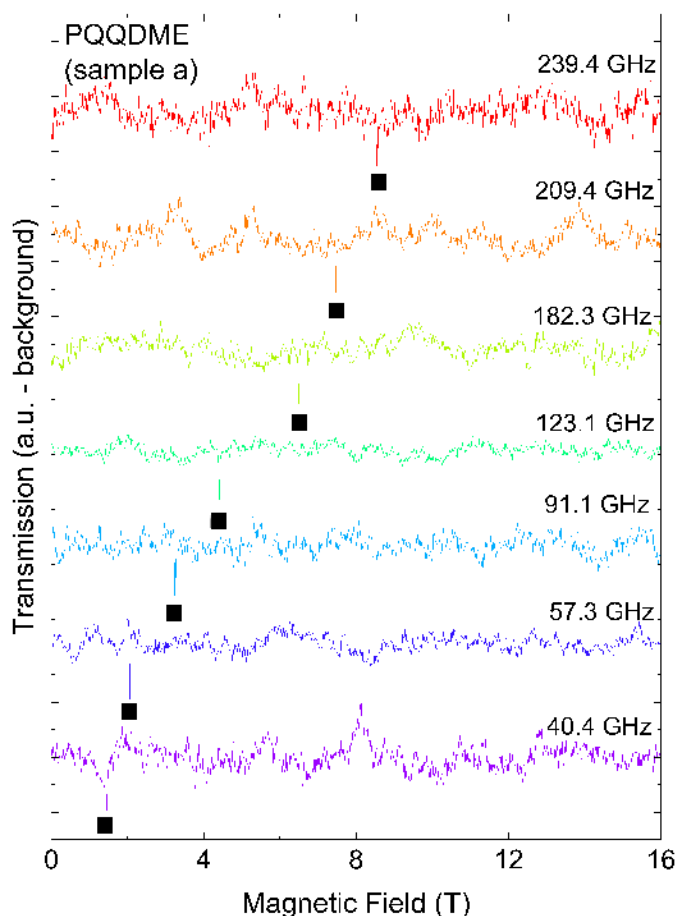


Fig. 8.4: HF-EPR transmission spectra measured at $T = 2\text{ K}$ and frequencies ranging from 40.4 GHz to 239.4 GHz on a frozen solution of **a**. All spectra were background and phase mixing corrected, normalised to the absolute of the lowest value and shifted along y . The black squares correspond to the resonance positions of the observed features, as explained in the text.

the resonance features observed for **b** and **d** correspond to transitions of the radical, as it is the case for **a**.

The resonance feature obtained for **b** and **d** was further investigated by means of microwave transmission measurements conducted at higher magnetic field resolution around the resonance field position for both samples, as shown in Fig. 8.9(a) and (b). In addition to background and phase mixing correction, the up- and down-field-sweeps were corrected for the remanence of the superconducting magnet of the device. The remanence was estimated by comparing the resonance positions of the up- and down-field-sweeps.

As can be observed in both samples, the resonance feature is comprised of three distinct features, each marked with a vertical dashed line: one main resonance feature situated between two shoulder-like features. The distance between the main resonance position and the shoulders, labelled ΔB , was determined by calculating the distance between the main feature and each shoulder and then averaging the

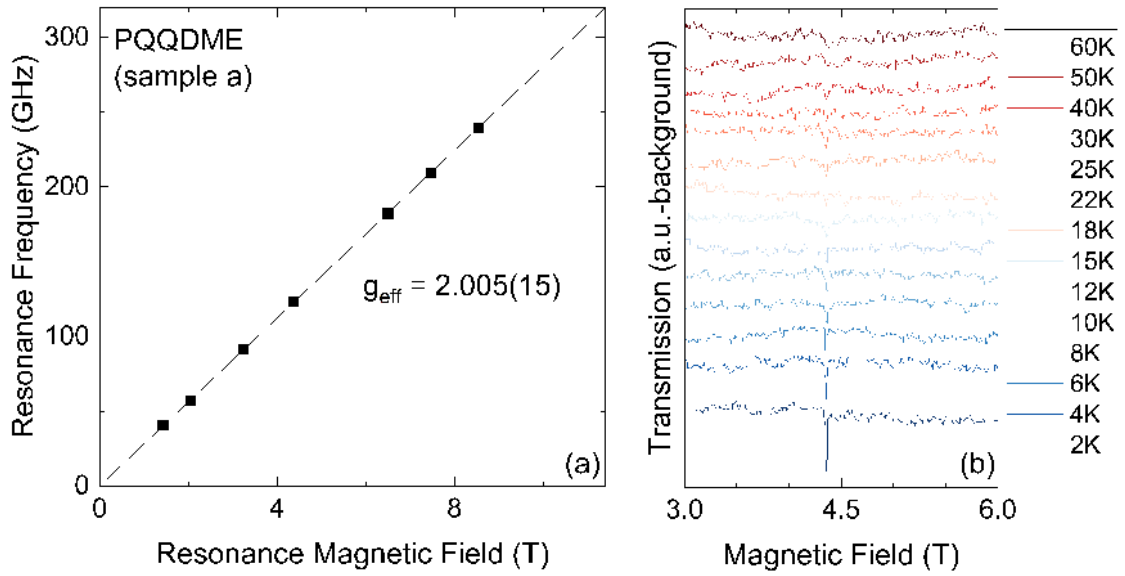


Fig. 8.5: (a) Resonance positions obtained from the transmission spectra measured at $T = 2$ K for various frequencies on a frozen solution of **a** (Fig. 8.4). The solid black line represents a linear fit to the data as described in the text. (b) HF-EPR spectra measured at $f = 123.1$ GHz for different temperatures ranging from 2 K to 60 K.

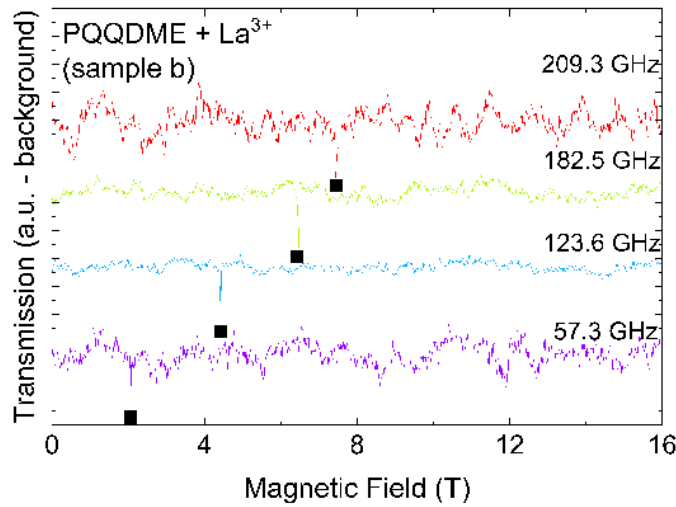


Fig. 8.6: HF-EPR transmission spectra measured at $T = 2$ K and frequencies ranging from 57.3 GHz to 312.2 GHz on a frozen solution of **b**. All spectra were background and phase mixing corrected, normalised to the absolute of the lowest value and shifted along y . The black squares correspond to the resonance positions of the observed features, as explained in the text.

two values for each sample. For **b** $\Delta B = 3.9(9)$ mT whereas for **d** $\Delta B = 5.1(7)$ mT. The discrepancy between the two values is within the 2σ -interval.

In order to ascertain whether the observed splitting of the resonance line is due to hyperfine coupling, similar measurements were performed for five different fre-

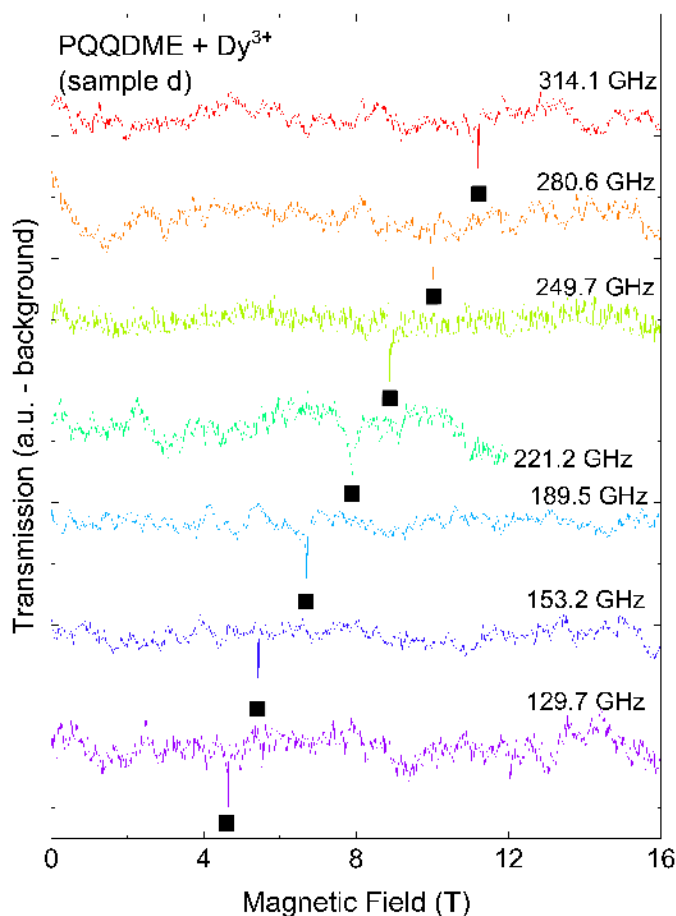


Fig. 8.7: HF-EPR transmission spectra measured at $T = 2\text{ K}$ and frequencies ranging from 129.7 GHz to 314.1 GHz on a frozen solution of **d**. All spectra were background and phase mixing corrected, normalised to the absolute of the lowest value and shifted along y . The black squares correspond to the resonance positions of the observed features, as explained in the text. The spectrum at 221.2 GHz was truncated at 12 T due to changes in the diode temperature, resulting in drastic changes in the transmission in this region.

quencies (ranging from 57.3 GHz to 312.2 GHz) for **a**. Two exemplary spectra are presented in Figs. 8.9(c) and (d), the other spectra are shown in Figure B.4. All measured spectra (except the one measured at $f = 234.9\text{ GHz}$, see Figure B.4) exhibit a three-fold resonance feature, as illustrated in Fig. 8.9 for $f = 312.2\text{ GHz}$ and $f = 91.9\text{ GHz}$. The distance between the two shoulders and the middle feature varies from $\Delta B = 9(4)\text{ mT}$ to $\Delta B = 3.1(7)\text{ mT}$, with a mean value of $\overline{\Delta B} = 5.8(9)\text{ mT}$. Given that no discernible trend indicating an increase or decrease in ΔB with rising magnetic field exists, it can be concluded that the three features correspond to three resonance branches with the same effective g -factors. There is no Ln-ion present in **a**, whose magnetic moment could interact with that of the radical spin in PQQDME. Therefore, the shoulder features can only originate from hyperfine coupling between the radical spin and the nuclear spin of a surrounding atom.

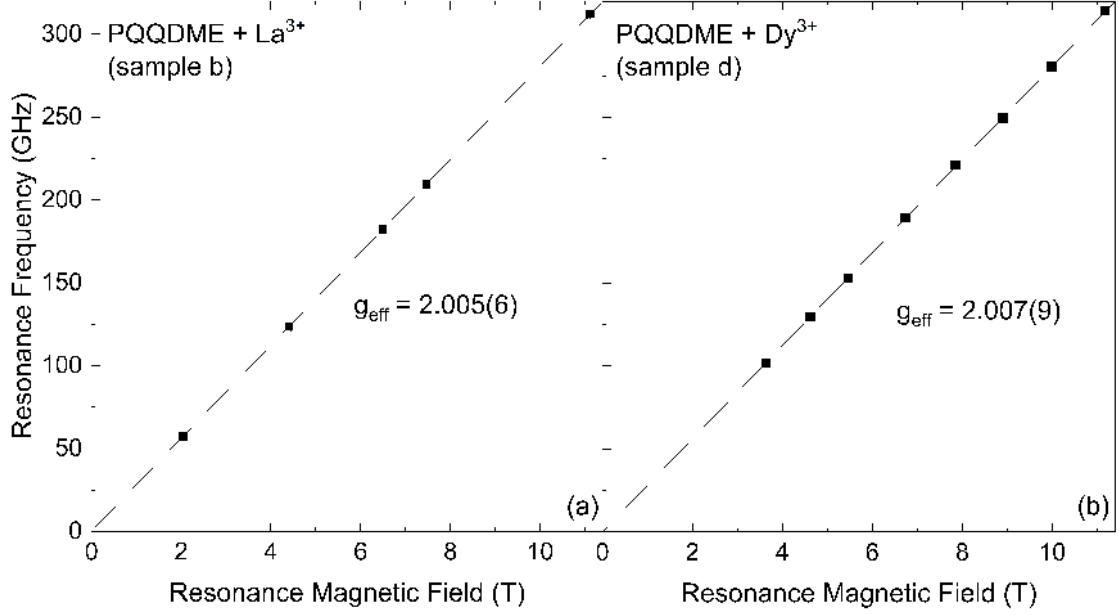


Fig. 8.8: Resonance positions obtained from the transmission spectra measured at $T = 2\text{ K}$ for various frequencies on a frozen solution of **b** (a) (Fig. 8.6) and **d** (b) (Fig. 8.7). The solid black lines represent linear fits as described in the text.

The presence of different molecular species in the sample with differing g -factors, as it was observed for PQQ [95], would not explain the presence of three resonance features: A change in the value of the g -factor by 0.0003, as observed for PQQ [95], would result in a splitting between the lines of $\Delta B = 22\text{ mT}$ at $f = 312.2\text{ GHz}$, which is about 7-times larger than the splitting measured in the here presented data. Moreover, in [95] only a larger g -value for a minority species in the sample was observed. However, to explain a three-fold feature, as observed in this work, the additional presence of a species with a smaller g -value would be necessary.

Consequently, the observed parallel resonance branches are attributed to hyperfine coupling of the electron spin (radical) with the nuclear spin of a surrounding atom. Given that the splitting of the resonance line is threefold, it can be assigned to a hyperfine coupling between the radical spin and a nuclear spin of $I = 1$. PQQDME is composed of four elements: hydrogen, oxygen, carbon and nitrogen. Assuming that only the most abundant isotopes of each atom are present in the sample, nitrogen is the only one with a nuclear spin of $I = 1$. Consequently, there is a hyperfine coupling between the electron spin (radical) and the nuclear spin of nitrogen. Assuming that the hyperfine interaction is isotropic, the Hamiltonian in eq.(8.2) is extended to

$$\hat{H}_1 = \mu_B \mathbf{B}^T \mathbf{g}_{e-} \hat{\mathbf{S}}_{e-,1} + \hat{\mathbf{S}}_{e-,1}^T \mathbf{A}_{\text{iso}} \hat{\mathbf{I}} \quad (8.5)$$

where $\hat{\mathbf{I}}$ is the nuclear spin operator of the nitrogen [23]. In this case, the interaction observed for **a** results in $A_{\text{iso}} = 5.8(9)\text{ mT}$ (A_{iso} is the principle value of $\mathbf{A}_{\text{iso}}$). This value for A_{iso} is approximately five times larger than the maximum value measured for different nitrogene-containing molecules, where the spin-density of the radical is maximal at the nitrogen atom, in [96]. The data presented in Figs. 8.9(c) and (d)

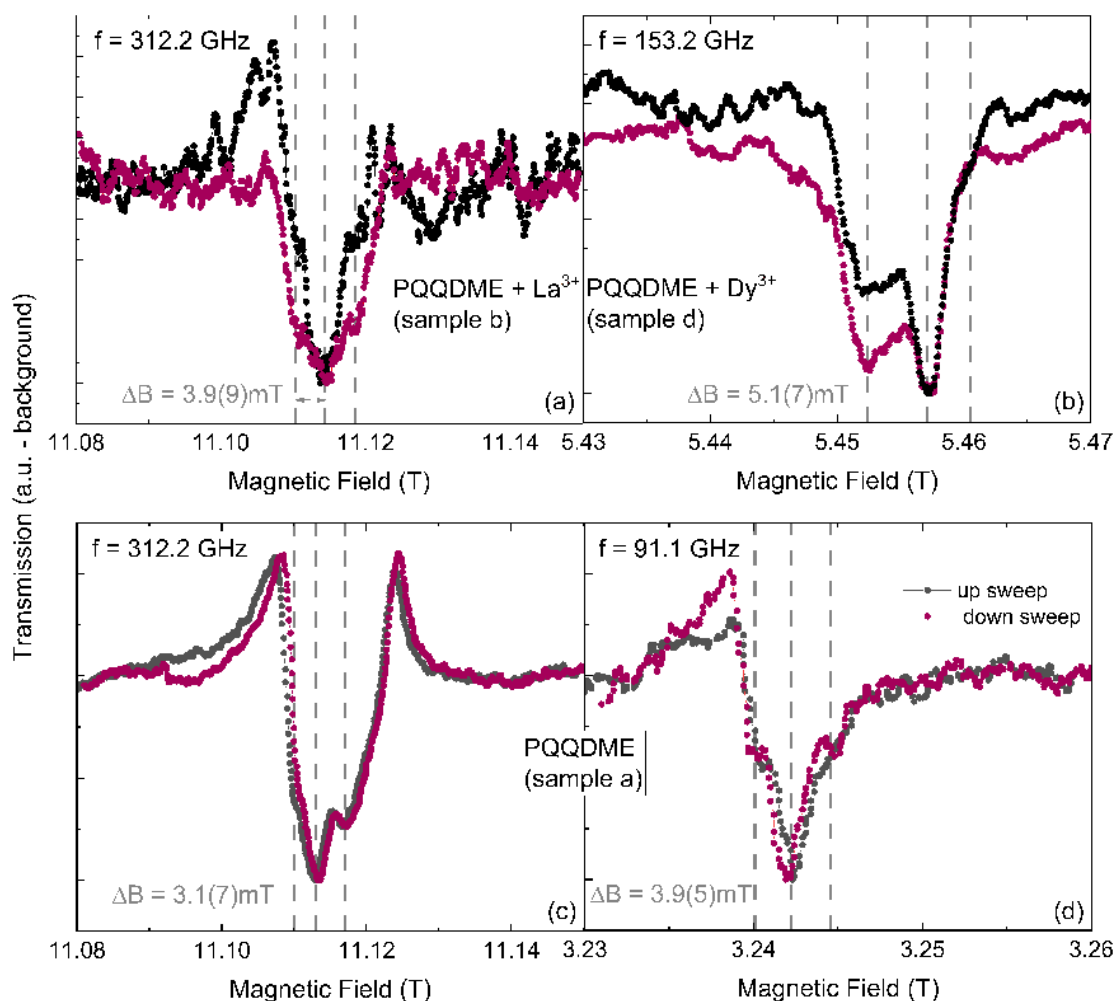


Fig. 8.9: Exemplary HF-EPR transmission spectra measured at $T = 2\text{ K}$ at various frequencies for **b** (a), **d** (b) and **a** (c) and (d). All spectra are background and phase mixing corrected and furthermore corrected for the remanence of the superconducting magnet of the device, as described in the text. The difference in resonance magnetic field between the shoulders and the middle feature, calculated as described in the text, is included as ΔB . Vertical dashed lines depict the resonance positions of the two shoulder and middle features.

and Fig. B.4, show that the radical is localised at a nitrogen or a neighbouring atom of the nitrogen, as there are two mechanisms that can lead to hyperfine coupling. In the case of contact/ core polarisation mechanism, the electron spin population is centred at the atom with which nuclear spin the interaction takes place [23]. In the case of spin polarisation mechanism, the electron spin population is centred at an atom which forms a covalent bond with the atom whose nuclear spin interacts with the radical spin [23].

When comparing Figs. 8.9(a) and (b) with Figs. 8.9(c) and (d) and Fig. B.4, it is reasonable to assume that the splitting of the resonance feature for **b** and **d** has the same origin as the splitting observed in **a**. The distance between the shoulders and

the main feature is comparable in size to the one obtained for **a**. Nevertheless, it cannot be excluded that the splitting of the resonance feature for **b** and **d** arises from another interaction. For example, the shoulder at high fields is only recognisable in the down sweep for **b**. The resonance feature may, therefore, eventually be only two-fold.

8.4.2 HF-EPR Studies on sample **c**

In Figs. 8.10, 8.11 and 8.12 the measured microwave transmission spectra of **c**, where resonance features, which are observed in both the up- and down-field-sweeps, are marked by different symbols, are shown. Each spectrum exhibits a feature with a total width of 1 – 3 T. It is composed out of a main feature, ■, which is located in the centre of the overall feature. Furthermore, in the vicinity of ■, there is a sharper feature, ●, which exhibits a stronger mixing of dispersion into the transmission for certain frequencies (e.g. $f = 50.5$ GHz, 231.6 GHz, and 312.2 GHz) than the rest of the overall feature. In addition, two shoulder features can be observed, one at lower magnetic fields, ▲, and one at higher magnetic fields, ★.

The resonance positions of the four features, as illustrated in Figs. 8.10, 8.11 and 8.11 result in four resonance branches that feature linear slopes across the entire magnetic field range, visualized in Fig. 8.13. Feature ● arranges in a gapless resonance branch whereas ■, ▲ and ★ result in resonance branches with a non-zero y -intersection, Δ . The effective g -factors and Δ -values for the four resonance branches were obtained by linear fits, the results of whom are listed in Table 8.1. For ● a gapless linear fit was performed.

Resonance branch	g_{eff}	Δ [GHz]
■	1.98(4)	2(4)
●	2.005(22)	-
▲	2.00(5)	11(6)
★	1.97(3)	-3(5)

Tab. 8.1: g_{eff} and Δ obtained from linear fits to the resonance positions in Fig. 8.13.

The spectra presented in Fig. 8.14 display the evolution of the measured resonance features at 2 K with increasing temperature. The intensity of the overall feature decreases with rising temperature except for the temperature range of 15 – 150 K. The evolution of the measured resonance features in the temperature range of 15 – 150 K is however most presumingly not intrinsic as, in this temperature region, the overall feature exhibits finite phase mixing, leading to an altered intensity. Consequently, it cannot be directly determined from the spectra whether the intensity of the dispersion decreases with temperature in this temperature region. Furthermore, the width of the overall feature decreases with increasing temperatures, resulting in a single sharp resonance feature at temperatures around 180 K.

■, marked with a light blue dashed line in Fig. 8.14, is observable up to a temper-

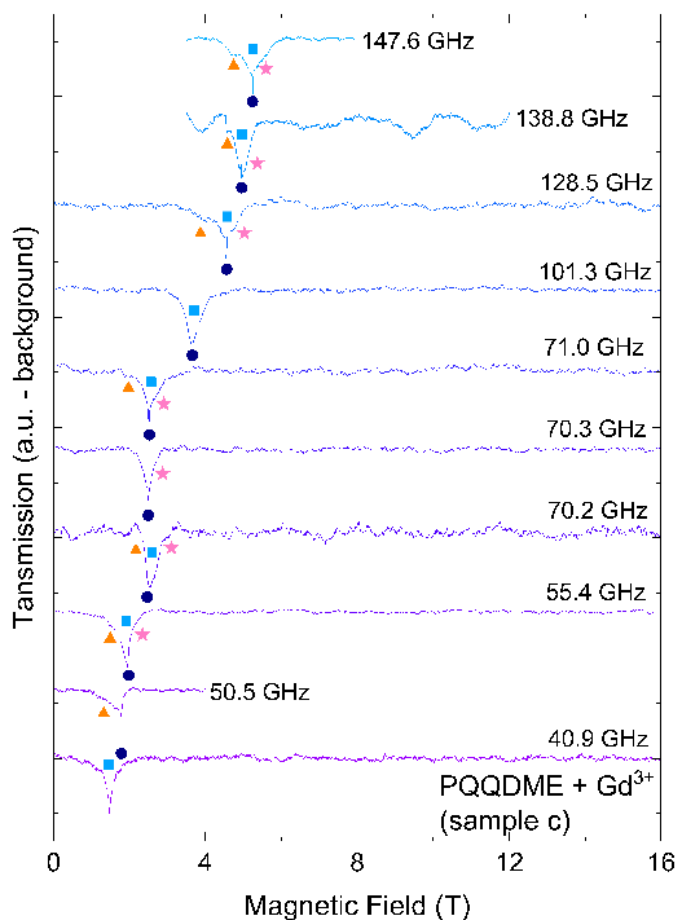


Fig. 8.10: HF-EPR transmission spectra measured at $T = 2\text{ K}$ and frequencies ranging from 40.9 GHz to 147.6 GHz on a frozen solution of **c**. All spectra were background and phase mixing corrected, normalised to the absolute of the lowest value and shifted along y . ■, ●, ▲ and ★ mark the resonance features. Some of the spectra were measured with a higher resolution and therefore in a limited magnetic field range.

ature of 190 K. This is the highest temperature measured as the melting point of acetonitrile is approximately 228 K [93]. ●, marked with a dark blue dashed line in the figure, is observable in the spectra up to 15 K. ▲, marked with an orange dashed line, becomes undetectable at temperatures above 10 K. In contrast, ★, marked with a pink dashed line, is observable up to a temperature of 130 K. The width of the shoulder feature ★ reduces with increasing temperature.

When comparing the evolution of ▲ and ★ with increasing temperature in Fig. 8.14 it is visible that the spectral weight of ▲ decreases faster with increasing temperature as the one of ★. The reason for this may be the change in the amount of phase mixing with increasing temperature.

● exhibits an effective g -factor that is in agreement with the free electron g -factor of approximately 2.002 [47] within the errorbars. Moreover, the corresponding resonance branch exhibits no zero-field splitting and the width of ● is notably smaller

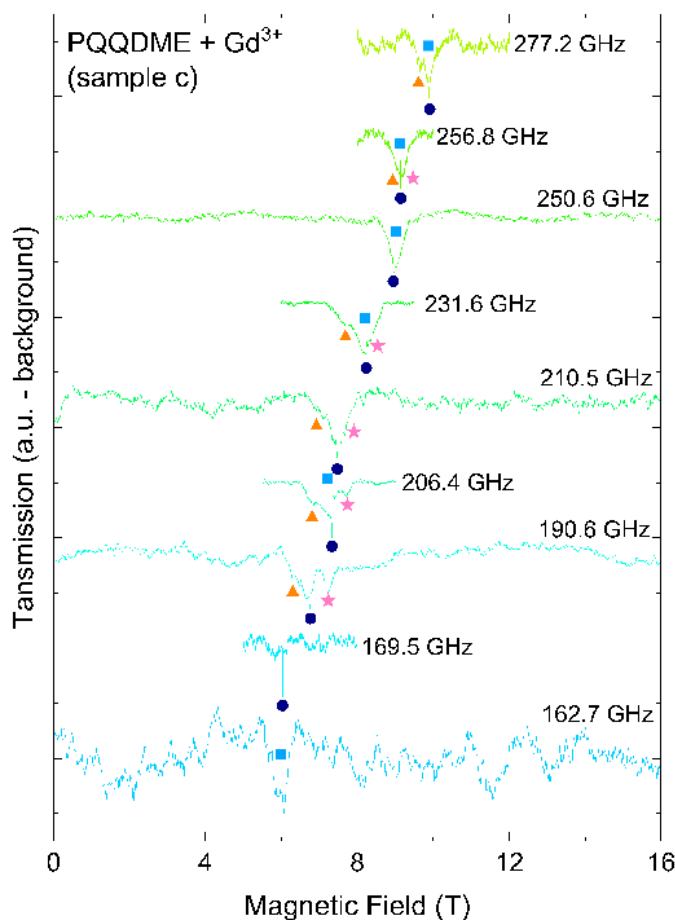


Fig. 8.11: HF-EPR transmission spectra measured at $T = 2\text{ K}$ and frequencies ranging from 162.7 GHz to 277.2 GHz on a frozen solution of **c**. All spectra were background and phase mixing corrected, normalised to the absolute of the lowest value and shifted along y . ■, ●, ▲ and ★ mark the resonance features. Some of the spectra were measured with a higher resolution and therefore in a limited magnetic field range.

than that of the other observed features. The line shape and evolution with temperature of ● is comparable to that observed for the radical spin-flip-transition of **a** in subsection 8.4.1. It can therefore be concluded, that ● corresponds to a radical spin-flip-transition. ● exhibits a different grade of phase mixing as the other resonance features observed for **c**. As the amount of dispersion mixed into the transmission is also dependent on the material for equal measurement conditions [45, 46], this indicates, that ● is a resonance originating from another molecular species in the sample than the other resonance features. ● cannot be attributed to transitions of the magnetic moment of Gd^{3+} -ions described by the Hamiltonian in eq.(8.3), as the crystal-field effects would lead to a broader resonance feature. However, the broader feature (including ■, ▲ and ★) exhibits an altered amount of phase mixing compared to that of ●. Consequently, ● is attributed to the radical of a PQQDME molecule described by the Hamiltonian in eq.(8.2).

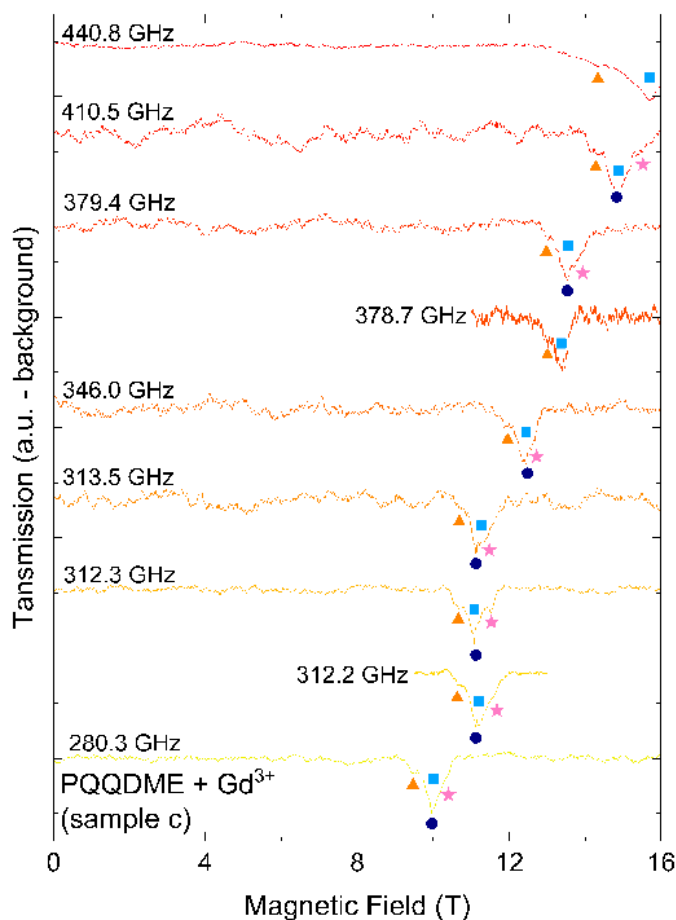


Fig. 8.12: HF-EPR transmission spectra measured at $T = 2\text{ K}$ and frequencies ranging from 280.3 GHz to 440.8 GHz on a frozen solution of **c**. All spectra were background and phase mixing corrected, normalised to the absolute of the lowest value and shifted along y . ■, ●, ▲ and ★ mark the resonance features. Some of the spectra were measured with a higher resolution and therefore in a limited magnetic field range.

The remaining resonance features ■, ▲ and ★ are attributed to molecular species including Gd^{3+} -ions, described by the Hamiltonians in eq.(8.3) and eq.(8.4). Their resonance branches correspond to effective g -factors that are consistent with each other within the scope of their uncertainties. This effective g -factor is found to be consistent with $g = 2$ for a free Gd^{3+} -ion [24] within the errorbars.

In order to ascertain the origin of the different contributions to the shape of the measured spectra, simulations were performed utilizing the Hamiltonian in eq.(8.1). Interactions between the molecular species described by eq.(8.3) and eq.(8.4) are generally excluded for all of the following simulations, as are interactions between two Gd^{3+} -ions each described by eq.(8.4). This assumption is based on the expectation that the Gd^{3+} -ions described by eq.(8.4) are diluted equally over the entire frozen solution. Consequently, there are only a few Gd^{3+} -ions described by eq.(8.4) whose distance to the molecular species described by eq.(8.3) is small enough, that

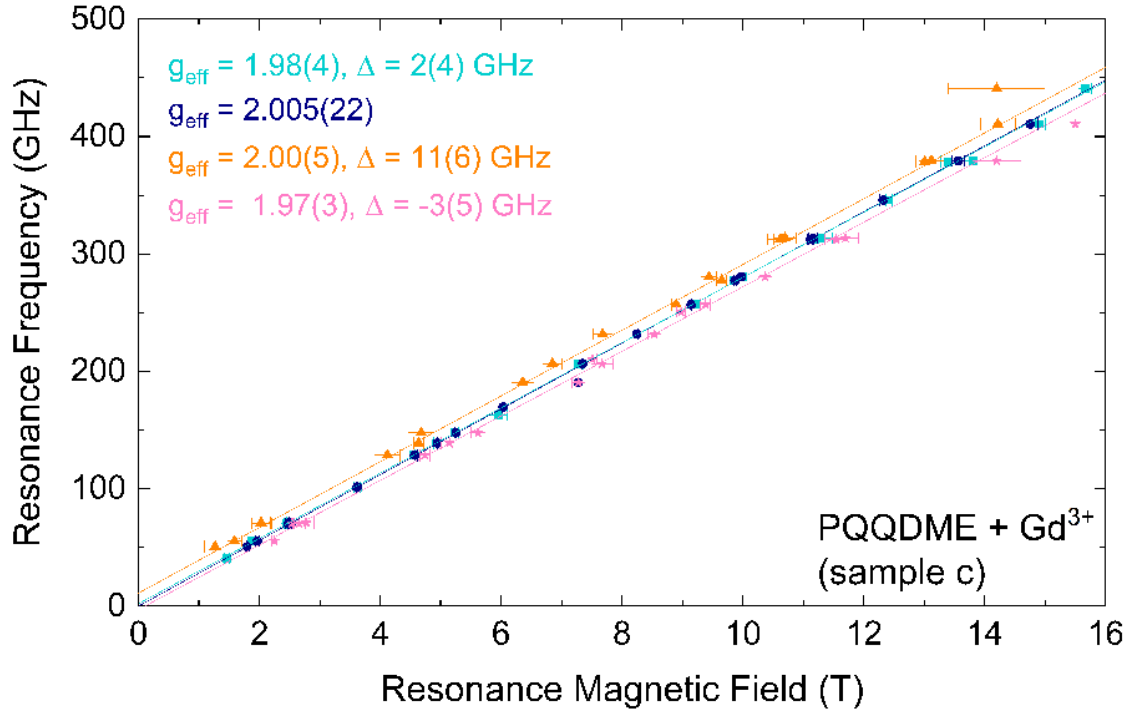


Fig. 8.13: Resonance magnetic field positions obtained from the transmission spectra measured at $T = 2$ K for various frequencies for **c** (Figs. 8.10, 8.11 and 8.12). ■, ●, ▲ and ★ correspond to the resonance features as explained in the text, respectively. The solid lines represent linear fits to the resonance positions with the parameters indicated in the upper left of the figure. In the case of the light and dark blue line, the fit was performed with the y -intersection fixed to zero.

the interaction strength between these two molecular species significantly influences the sample averaged spectrum.

The minimal model which describes the data best consists of the three distinct molecular species described by the Hamiltonian in eq. (8.1), where $\hat{H}_2$ is changed to

$$\hat{H}_2 = \mu_B \mathbf{B}^T \mathbf{g}_{e-} \hat{\mathbf{S}}_{e-,2} + \mu_B \mathbf{B}^T \mathbf{g}_{\text{Gd}^{3+}} \hat{\mathbf{S}}_{\text{LGd}^{3+},2} + D \left(\hat{\mathbf{S}}_{\text{z,Gd}^{3+},2}^2 - \frac{S_{\text{Gd}^{3+},2} (S_{\text{Gd}^{3+},2} + 1)}{3} \right) + E \frac{\hat{\mathbf{S}}_{+, \text{Gd}^{3+},2}^2 + \hat{\mathbf{S}}_{-, \text{Gd}^{3+},2}^2}{2}. \quad (8.6)$$

The magnetic moments of the radical and the Gd^{3+} -ion of the same PQQDME molecule do not interact in this model. In Fig. 8.15 the HF-EPR transmission spectrum measured at $T = 2$ K and $f = 312.2$ GHz alongside the simulation, of eq.(8.1) with $\hat{H}_2$ being equal to $\hat{H}_2$ in eq.(8.6), are displayed. The simulation fits the data well. The principle value of the isotropic g -tensor of the radical was determined by selecting the g -value that yielded the best fit to the measured spectra ($f = 50.5$ GHz, 147.6 GHz, 206.4 GHz, 231.6 GHz, and 312.2 GHz, see Fig. 8.15 and Fig. B.5) within the uncertainty range of the g -value resulting from the linear fit to the resonance branch ● (Fig. 8.13). The resulting g -value is $g_{e-} = 2.006(3)$. Similarly, the principle value of the isotropic g -tensor for the Gd-ions was determined to

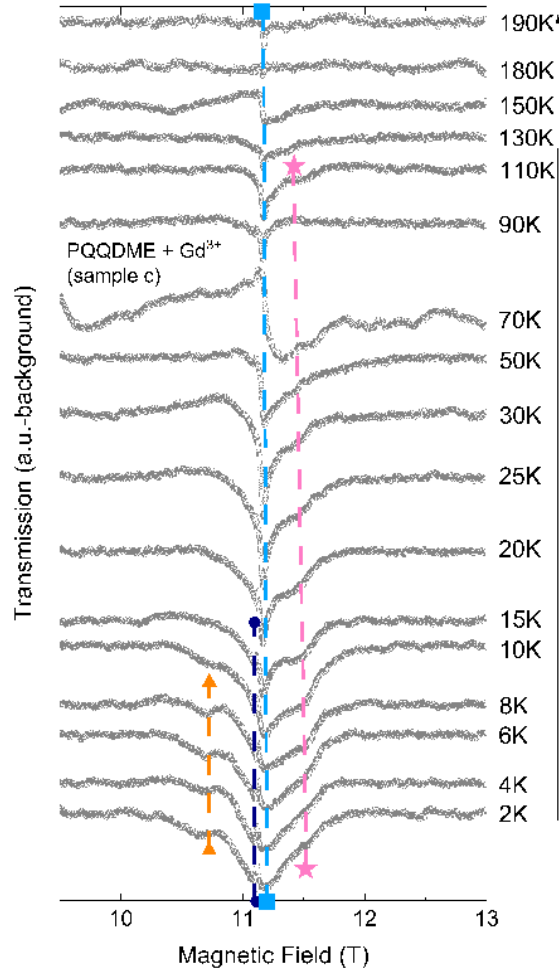


Fig. 8.14: HF-EPR spectra of **c** measured at $f = 312.2$ GHz for different temperatures ranging from 2 K to 190 K. ■, ●, ▲ and ★ and corresponding dashed lines mark the resonance features.

a value of $g_{\text{Gd}^{3+}} = 1.995(3)$. Furthermore, the best fit to the spectra ($f = 50.5$ GHz, 147.6 GHz, 206.4 GHz, 231.6 GHz, and 312.2 GHz, see Fig. 8.15 and Fig. B.5) yield the following parameters: $D = -3500(100)$ MHz, $E = -350(250)$ MHz. The uncertainty was determined by varying each of the fitting parameters until the simulation just barely matches the measured spectra ⁶.

The total spectrum is a sum of the spectra simulated for $\hat{H}_1$, $\hat{H}_2$ and $\hat{H}_3$ individually where each of them is weighted by its contribution to the total spectrum. Furthermore, a different degree of phase mixing and line width is used for each contribution in order to ensure that the total spectrum fits the data measured at $f = 50.5$ GHz, 147.6 GHz, 206.4 GHz, 231.6 GHz, and 312.2 GHz. This suggests that the sample itself comprises a mixture of at least the three different species described by eq.(8.1),

⁶Changes in the spectral shape of the spectra obtained from up- and down-field-sweeps, as well as differences in the resonance positions resulting from the remanence of the superconducting magnet, were also taken into account during the fitting process.

where $\hat{H}_2$ is given by eq.(8.6). Furthermore, the term describing the electron in $\hat{H}_2$ is necessary, as the line width and the degree of phase mixing of the spectrum simulated for $\hat{H}_2$ have to be chosen differently than for the simulated spectrum of $\hat{H}_1$ to fit the data properly. In Fig. 8.15 not only the total spectrum but also the contribution of each individual spectrum of the respective molecular species described by $\hat{H}_1$ in eq.(8.2), $\hat{H}_2$ in eq.(8.6) and $\hat{H}_3$ in eq.(8.4), are displayed. The contribution of the molecular species described by eq.(8.2) to the total simulation results in the resonance feature ●, shown as pink line in Fig. 8.15. The shoulder features ▲ and ★ are reproduced by the molecular species described by eq.(8.6), shown as dark blue line in Fig. 8.15. The Gd^{3+} -ions of this molecular species are influenced by the CF. This is the origin of the shoulder features in the simulated spectrum. The spectrum of the molecular species described by eq.(8.4), depicted as a light blue line in Fig. 8.15, shows a single resonance feature without shoulders. The resonance position of this spectrum is the main contribution to the main resonance ■.

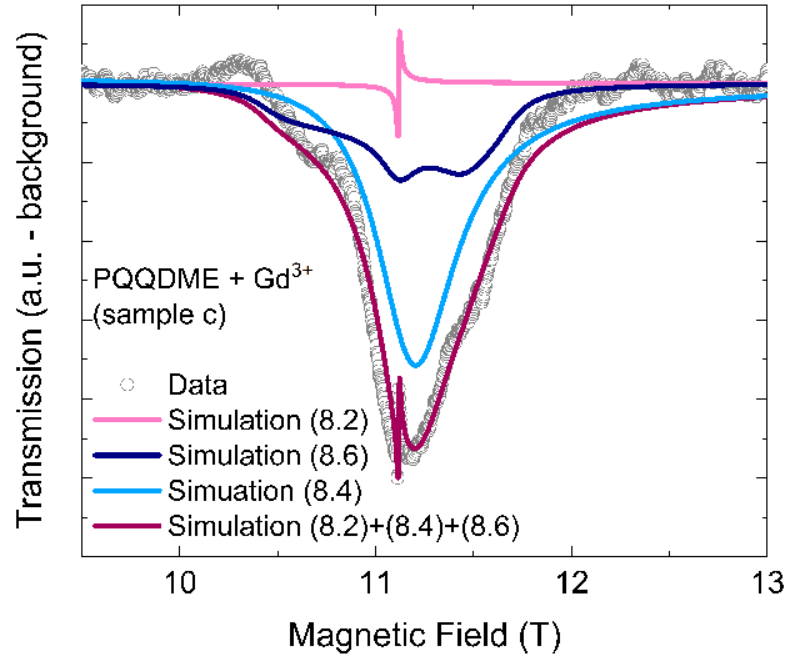


Fig. 8.15: HF-EPR transmission spectrum of **c** measured at $T = 2\text{ K}$ at $f = 312.2\text{ GHz}$. The spectrum is shown with open grey points, and has been background corrected and is normalised to the absolute of the lowest value. The solid lines represent spectral simulations using the indicated Hamiltonians as described in the text.

In Fig. 8.16(a) the evolution of the overall resonance feature with increasing temperature together with spectral simulations using the previously obtained parameters are depicted. The spectral simulations fit the temperature evolution of the resonance features well. For each temperature, the line width and the contributions of the different molecular species in eq. (8.1), were adjusted in order to achieve the optimal fit. In Fig. 8.16(b) the relative spectral weight of the total simulated spectrum (the sum of the contributions of all species) as a function of temperature

is shown. The data indicates a tendency for the spectral weight to decrease with increasing temperature up to 25 K, after which it appears to decrease. Due to the large relative uncertainties of the data points in the vicinity of 25 K an explanation of the data solely by a decay with increasing temperature cannot be ruled out.

The evolution of the line width with increasing temperature, obtained from the spectral simulations for the contributions of the molecular species described by eq.(8.4) and eq.(8.6), are shown in Fig. 8.16(c). The line width decreases with increasing temperature for both molecular species. One hypothesis for this decrease of the line width with increasing temperature is that all molecules are randomly distributed throughout the entire sample. They create a local field for neighbouring species. This local field is temperature-dependent: with increasing temperature the total magnetic moment decreases and the moments tend to be more evenly distributed over the entire sample due to thermal fluctuations. This implies that the local field at a neighbouring species is highly uniform across the entire sample at high temperatures. Therefore, the magnetic moments of a given species experience comparable local fields. Consequently, the resonance positions of the ions and molecules of each species are less disparate from one another. Therefore, the resonance feature narrows at higher temperatures. However, this was not addressed in the spectral simulations, as only the spectrum for each species was calculated individually and then added up. Such a change in the line width with increasing temperature is referred to as exchange narrowing or broadening and has been observed in the literature [97–100].

Other Simulation Models

Other models, for which the values of g_{e-} and $g_{Gd^{3+}}$ were fixed to the ones obtained for the aforementioned simulation, were also tested: For example, the free Gd^{3+} -ions were neglected together with the electron in $\hat{H}_2$. Furthermore an interaction of the Gd^{3+} -ions of neighbouring molecules was added. The Hamiltonian in eq.(8.1) therefore changes to:

$$\begin{aligned}
 \hat{H} &= \hat{H}_1 + \hat{H}_2 \\
 &= \mu_B \mathbf{B}^T \mathbf{g}_{e-} \hat{\mathbf{S}}_{e-,1} + \mu_B \mathbf{B}^T \mathbf{g}_{Gd^{3+}} \hat{\mathbf{S}}_{Gd^{3+}(1),2} + \mu_B \mathbf{B}^T \mathbf{g}_{Gd^{3+}} \hat{\mathbf{S}}_{Gd^{3+}(2),2} \\
 &\quad + \hat{\mathbf{S}}_{Gd^{3+}(1),2}^T \mathbf{J} \hat{\mathbf{S}}_{Gd^{3+}(2),2} \\
 &+ D \left(\hat{\mathbf{S}}_{z,Gd^{3+}(1),2}^2 - \frac{S_{Gd^{3+}(1),2} (S_{Gd^{3+}(1),2} + 1)}{3} \right) + E \frac{\hat{\mathbf{S}}_{+,Gd^{3+}(1),2}^2 + \hat{\mathbf{S}}_{-,Gd^{3+}(1),2}^2}{2} \\
 &+ D \left(\hat{\mathbf{S}}_{z,Gd^{3+}(2),2}^2 - \frac{S_{Gd^{3+}(2),2} (S_{Gd^{3+}(2),2} + 1)}{3} \right) + E \frac{\hat{\mathbf{S}}_{+,Gd^{3+}(2),2}^2 + \hat{\mathbf{S}}_{-,Gd^{3+}(2),2}^2}{2}.
 \end{aligned} \tag{8.7}$$

Simulated spectra using eq.(8.7) is shown in Figs. 8.17(a) and (b). For these simulations two different AFM interaction strengths were used. Both simulated spectra do not describe the spectral weight of the shoulder features $\blacktriangle$ and $\blackstar$.

Adding an isotropic AFM interaction of the magnetic moments of the electron

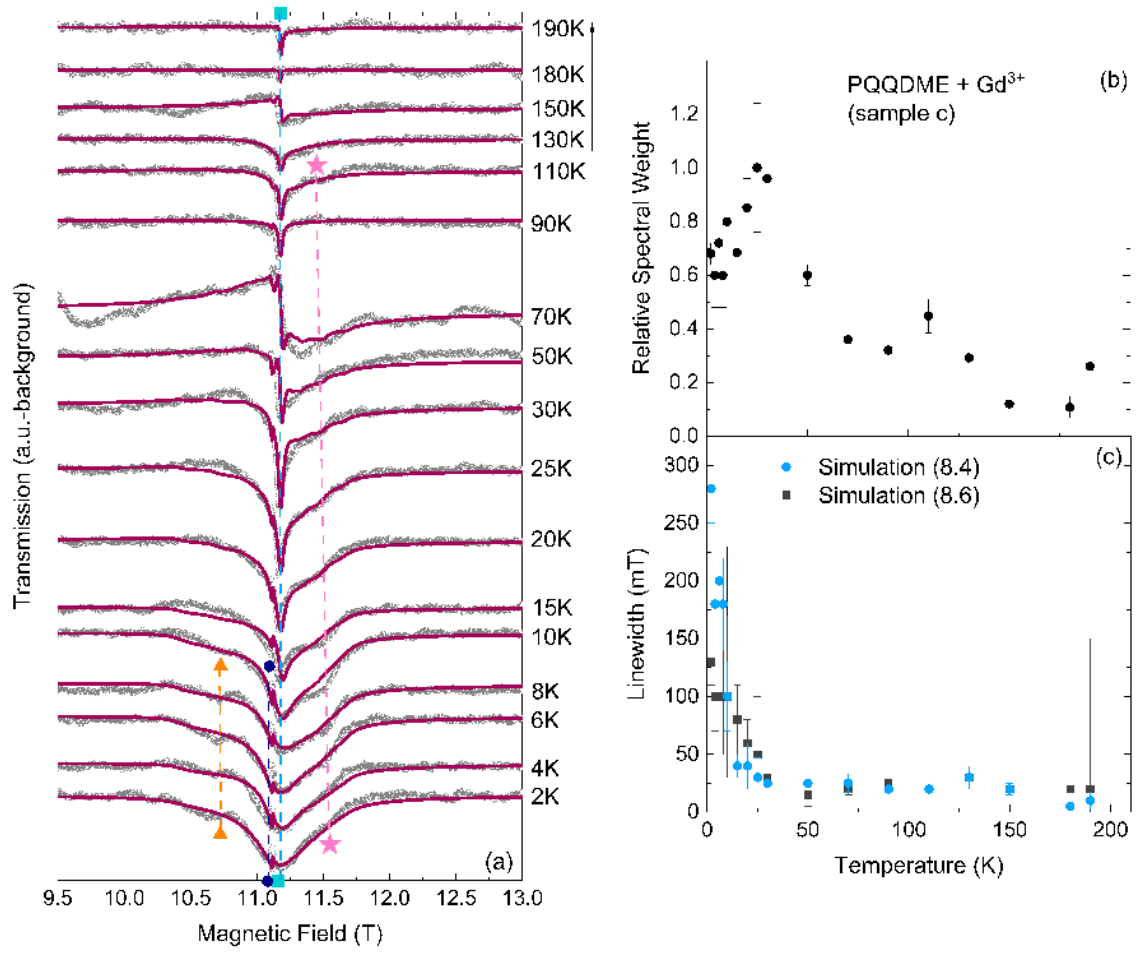


Fig. 8.16: (a) HF-EPR spectra of **c** measured at $f = 312.2$ GHz for different temperatures ranging from 2 K to 190 K, represented by open grey points. Red solid lines display spectral simulations as described in the text. $\blacksquare$, $\bullet$, $\blacktriangle$ and $\star$ and corresponding dashed lines mark the resonance features. (b) Relative spectral weight of the spectral simulations at $f = 312.2$ GHz using the Hamiltonian in eq.(8.1), where $\hat{H}_1, \hat{H}_2$ and $\hat{H}_3$ are given by eq.(8.2), eq.(8.6) and eq.(8.4), as a function of temperature. (c) Line width of the spectral simulations at $f = 312.2$ GHz using the Hamiltonians in eq.(8.6) and eq.(8.4) as a function of temperature.

and Gd^{3+} -ion (which are described by eq.(8.3)) - meaning that the Hamiltonian in eq.(8.1) without changes in eq.(8.2), eq.(8.3) and eq.(8.4) is used for the simulations - also fails to describe the measured spectra, as shown in Fig. 8.17(c): There are additional resonance features that are not observed in the measurement.

Using the Hamiltonian in eq.(8.1) without changes in eq.(8.2), eq.(8.3) and eq.(8.4) with an anisotropic interaction strength of $J = (0, 0, 4)$ GHz, describes the measured spectrum well, see Fig. 8.17(d). When comparing to the simulation in Fig. 8.15, the feature represented by $\star$ is better reproduced by the simulation with an anisotropic interaction strength. However, there is no physical explanation for such an anisotropic interaction strength between the magnetic moment of the radical of PQQDME and the Gd^{3+} -ion.

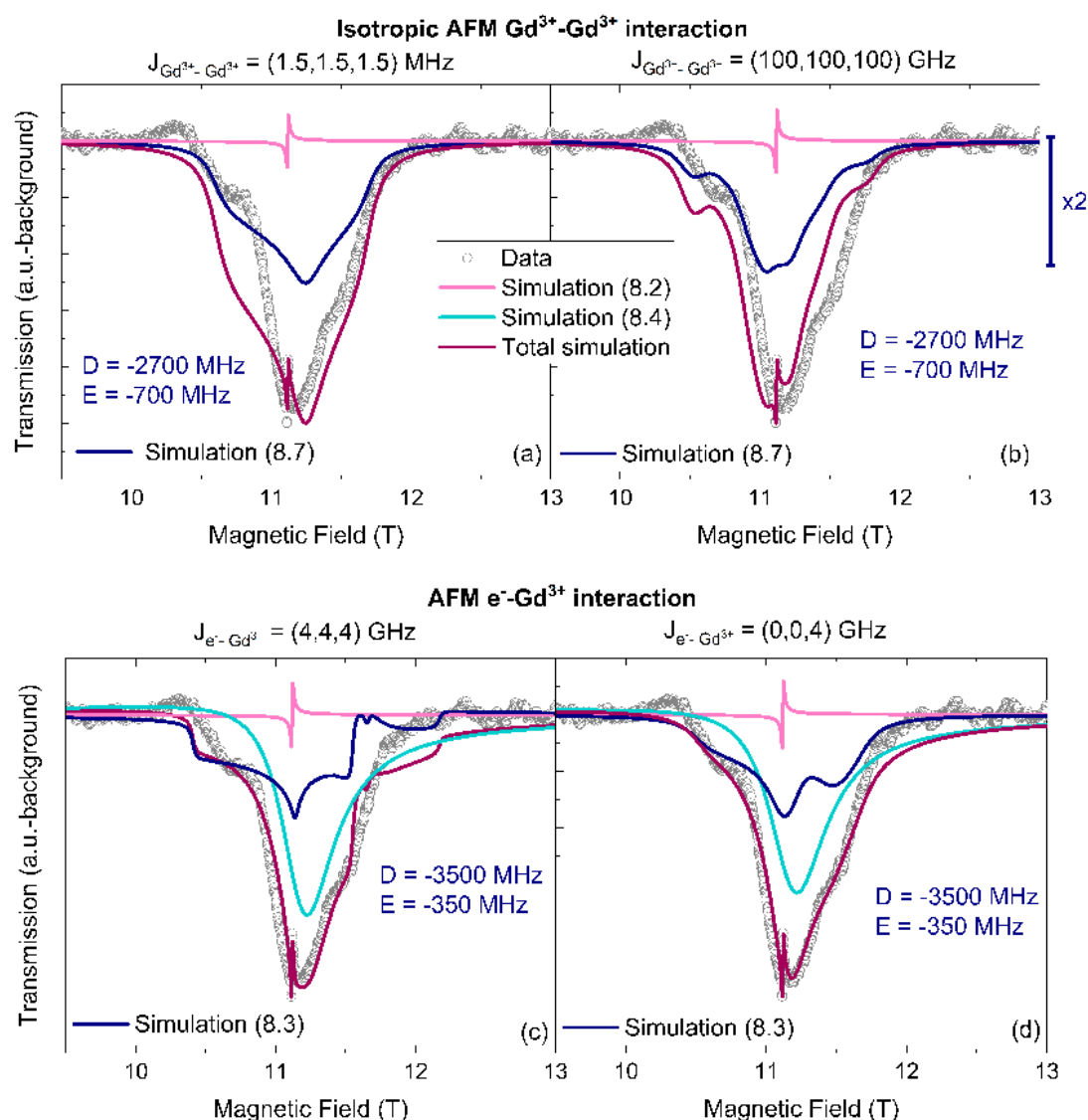


Fig. 8.17: HF-EPR transmission spectrum of **c** measured at $T = 2$ K at $f = 312.2$ GHz. The spectrum is shown with open grey points, and has been background corrected and is normalised to the absolute of the lowest value. The solid lines represent spectral simulations using the indicated Hamiltonians as described in the text. The non-shared parameters of the simulations are indicated in the corresponding figures. Selected simulated spectra are scaled as indicated.

Comparison of the HF-EPR Spectra of **c** to other Gd-containing Molecules

The width of the overall resonance feature of **c** and the presence of two shoulders are similar to those observed for a Gd^{3+} -ion in [101] and a Gd_2^{3+} complex in [102]. For the latter compound, the shoulder features can be described by zero-field interaction parameters of $D = 3000(50)$ MHz and $E = 700(50)$ MHz for each Gd^{3+} -ion [102]. The absolute values of D and E obtained in [102] are comparable in size with the

ones obtained for **c**, namely $D = -3500(100)$ MHz and $E = -350(250)$ MHz. Moreover, the evolution of the overall resonance feature (composed of ,  and ) with increasing temperature (Fig. 8.14), is analogous to the one observed for the weakly AFM coupled ($J = 1.5(1)$ GHz) Gd^{3+} -ions in [102].

Other studies on a frozen sample of $[\text{Gd}(\text{DOTA})(\text{H}_2\text{O})]^-$ dissolved in water showed a similarly sharp feature as , in addition to a broad overall feature [101], similar to the one obtained for **c**. In [101] the overall feature, including the sharp feature was described by two transitions within two Kramers doublets, which are separated in energy due to anisotropy. The sharp feature was attributed to a transition from $m_S = -1/2$ to $m_S = 1/2$ of the Gd^{3+} -ion, whereas the broader feature was assigned to a transition from $m_S = -7/2$ to $m_S = -5/2$ [101]. For **c** it was not possible to describe  with this description.

Chapter 9

Summary and Conclusion

Electron paramagnetic resonance and magnetisation measurements were performed on various molecular-scale magnetic systems to investigate the mechanisms that influence the interaction of magnetic moments, local anisotropies and other microscopic properties within these systems.

Magnetisation studies on monoindeno-diazatetracene-dimer-diradicals (MDDD)s have been conducted to assess the interaction strength between the spins of two unpaired electrons formed by the MDDDs. Two distinct samples were analysed, which differ by the material used in column chromatography for processing (refurbishing) post-synthesis. Neutron magnetic resonance measurements indicated that the interaction strength in MDDDs is weaker compared to a reference substance, namely Haley’s diindenoanthracene, as reported in previous studies [48, 49]. In the present work magnetisation measurement on the MDDDs corroborate the NMR findings by demonstrating the presence of diradicals with an AFM interaction of $J_{e-e} \simeq 120$ K between the spins of the unpaired electrons. The reduced interaction strength is attributed to a longer exchange path for the radical interaction in MDDDs compared to Haley’s diindenoanthracene. Additionally, the measurements revealed the presence of monoradicals, with their fraction being adjustable based on the material used for column chromatography during sample processing.

Magnetisation measurements were conducted on dinuclear Fe_2^{3+} -complexes of the family $[\text{X}(\text{L}^{\text{N7H}})\text{Fe}^{\text{III}} - \text{O} - \text{Fe}^{\text{III}}(\text{L}^{\text{N7H}})\text{X}]$ ($\text{X} = \text{Br}, \text{Cl}$) to determine the microscopic parameters of these complexes in order to validate a proposed mechanism for a halogenation process [52, 53]. The data revealed the presence of dinuclear Fe_2^{3+} -complexes and mononuclear Fe^{2+} -complexes in both samples. Isothermal magnetisation was found to be dominated by the Fe^{2+} -ions in the high-spin state and is accurately described by an isotropic g -tensor with $g = 2.30(2)$ for $\text{X} = \text{Br}$ and $g = 2.24(2)$ for $\text{X} = \text{Cl}$ along with second order crystal field parameters of $|D| = 55(5)$ GHz, $|E| = 17(3)$ GHz for $\text{X} = \text{Br}$ and $|D| = 37(3)$ GHz, $|E| = 5.4(46)$ GHz for $\text{X} = \text{Cl}$. Static magnetic susceptibility measurements revealed an AFM coupling between the Fe^{3+} -ions of the Fe_2^{3+} -complex with $J_{\text{Fe-Fe}}^{\text{Br}} = 288(3)$ K for $\text{X} = \text{Br}$ and $J_{\text{Fe-Fe}}^{\text{Cl}} = 312(24)$ K for $\text{X} = \text{Cl}$. These results demonstrate, that the crystal field is

influenced by the Br and Cl atoms in the sense that it is more axial for $X = \text{Cl}$ than for $X = \text{Br}$. However, the interaction between the magnetic moments of the Fe^{3+} -ions via the oxygen atom is not significantly influenced by the Br and Cl atoms.

Magnetisation measurements conducted on a muffin-shaped phenanthroline-pyridine-triazole (PPT) Er^{3+} -complex $([\text{Er}(\text{PPTMP})_2(\text{MeOH})][\text{OTf}]_3 \times 3\text{MeOH})$, revealed two field-induced slow magnetic relaxation processes of the magnetisation in this complex. The temperature dependent behaviour of the relaxation time of the slower process is well described by a combination of the direct, Orbach and Raman process. The determined Raman barrier $W = 24.0(3) \text{ K}$, corresponding to the barrier to the next optical phonon [35], is about half of the thermal Orbach barrier $U_{\text{eff}} = 54.9(14) \text{ K}$. HF-EPR measurements indicated that the field-induced slow magnetic relaxation in the Er^{3+} -complex can be explained by an energetically well-isolated ground state Kramers doublet. The ground state Kramers doublet is well-isolated, as the energy gap to the next excited Kramers doublet was determined to be larger than 550 GHz. Analysis of the HF-EPR spectra using a pseudo-spin- $1/2$ Heisenberg model to describe the ground state Kramers doublet, revealed an easy-plane-type magnetic anisotropy with effective g -tensor principle values of $g_x = 8.9(14)$, $g_y = 8.9(14)$, $g_z = 2.0(4)$ for the $m_J = \pm 7/2$ ground state Kramers doublet. As a consequence of the large energy gap to the next excited Kramers doublet, the probability for thermally assisted quantum tunnelling is small. Furthermore, the planar g -anisotropy of the ground state Kramers doublet could in principle reduce the probability for direct quantum tunnelling.

HF-EPR measurements on a Nd-methanol dehydrogenase (Nd-MDH) enzyme revealed a magnetic interaction between the magnetic moments of an unpaired electron, originating from the pyrroloquinoline quinone (PQQ) molecule in the active site of MDH, and the Nd^{3+} -ion with an interaction energy of 54(5) GHz. The spectra were analysed under the assumption that the Nd^{3+} -ions $|m_J|$ -value is equal to the absolute of the total spin, namely $m_J = \pm 9/2$, in combination with a pseudo-spin- $1/2$ -model to describe the Nd^{3+} magnetic moment. The results suggest a ferromagnetic (FM) interaction between the magnetic moments of the unpaired electron and the Nd^{3+} -ion. Whereas assuming $|m_J| < 9/2$ for the Nd^{3+} -ion does not allow a straightforward determination whether the interaction is of the AFM or FM type. Additionally, HF-EPR measurements also revealed the presence of non-interacting unpaired electrons, potentially originating from the buffer solution. For future research, it may be beneficial to improve magnetisation measurements for solutions with low concentrations, to allow for the determination of the Nd^{3+} ground state. The knowledge of the Nd^{3+} ground state might also allow to ascertain whether the observed interaction is FM or AFM.

Combined magnetic and EPR studies were performed on biomimetics of $\text{Ln}^{3+}/\text{Ca}^{2+}$ -methanol-dehydrogenase-enzymes ($\text{Ln} = \text{Nd, La, Gd, Dy, Lu}$) in order to study the role of metal centres and the localisation of unpaired electrons in the active sites of MDH enzymes. X-Band and HF-EPR measurements on $\text{Ln}_x^{3+}\text{-PQQDME}$ ($x = 0, 1$ and $\text{Ln} = \text{La, Gd, Dy}$) and $\text{La}^{3+}\text{-PQQTME}$ evidenced the presence of unpaired elec-

trons and revealed hyperfine interactions in PQQDME with a coupling constant of $A_{\text{iso}} = 5.8(9)$ mT between the spin of the unpaired electrons and a nitrogen nuclear spin. This finding indicates that the radical is localised at a nitrogen or neighbouring atom of the nitrogen atom in PQQDME.

HF-EPR measurements on Gd^{3+} -PQQDME revealed a complex resonance feature, which can be explained by the presence of three non-interacting molecular species: unpaired electrons, uncoordinated Gd^{3+} -ions and Gd^{3+} -ions coordinated to PQQDME. The coordination of the Gd^{3+} -ions to PQQDME leads to a local anisotropy of the coordinated Gd^{3+} -ions, with second order crystal field parameters of $D = -3500(100)$ MHz and $E = -350(250)$ MHz. Furthermore, the data revealed a line-width narrowing with increasing temperature, which might be explained by exchange narrowing.

Local anisotropy was also suggested for the Dy^{3+} -ions of Dy^{3+} -PQQDME through magnetisation measurements. Moreover, X-Band EPR for Dy^{3+} -PQQDME revealed a resonance feature that can either be explained by a transition within the $|m_J| = 9/2$ Kramers doublet of the Dy^{3+} -ion or by a magnetic transition within an interacting system of the magnetic moment of Dy^{3+} -ion and the unpaired electron.

All the performed measurements on the biomimetic samples have in common that interactions between the magnetic moments of the unpaired electrons and Ln-ions cannot be excluded, but their presence was also not evidenced by the measurements. For future research, the utilisation of alternative X-band sample tubes (which do not exhibit a resonance feature in the vicinity of $g = 2$) may assist in investigating the influence of the presence of distinct Ln-ions on the observed hyperfine coupling between the unpaired electron spin and the nitrogen nuclear spin. Improving magnetisation measurements on liquid solutions may allow for the determination of the influence of different metal-ions on the fraction of radical-hosting PQQTME molecules. Additionally, X-Band EPR measurements performed at other frequencies may provide further insight into the origin of the observed resonance feature of the sample containing PQQDME and Dy^{3+} -ions.

This work successfully determined the microscopic parameters of metal-organic complexes, polymers and bioinspired systems. The obtained parameters provided insights into the mechanisms influencing interactions between the magnetic moments of unpaired electrons and metal ions, as well as the origins of local anisotropy and its consequences, such as slow magnetic relaxation. Additionally, the precise localisation of an unpaired electron in a biomimetic system was identified.

Appendix A

Additional Information on the Nd-MDH Enzyme

A.1 Further Details on SQUID Measurements of Nd-MDH

SQUID measurements were performed using the following sample preparation method for Nd-MDH and blank, immediately following sample synthesis: As illustrated in Fig. A.1, initially, 10 μL of sample was poured into one of the open ends of the VSM Powder Sample Holders (QDC-4096-388) from *Quantum Design*. The position of the solution in the capsule is indicated by the yellow arrow in Fig. A.1a. In the next step, the capsule is closed by sliding the second capsule part into the first one in such a way that the solution is in the open space marked with a yellow arrow in Fig. A.1b, and most of the remaining air is pushed out. The capsule was then sealed with Teflon tape, as shown in Fig. A.1c. The capsule containing the sample was cooled subsequently.

The brass sample holder for MPMS was cooled in liquid nitrogen before inserting the capsule containing the frozen solution. The cooled sample holder along with the sample was then rapidly inserted into the MPMS at 300 K. Prior to pumping vacuum, the sample chamber was flushed with helium to cool it to a temperature of 267 K in order to prevent the sample from warming up during the pumping process.

To ascertain the magnetic ground state of the Nd^{3+} -ion, and to investigate potential interactions between the magnetic moments of Nd and radical, isothermal magnetisation and static magnetic susceptibility were measured for both the blank and Nd-MDH sample. The obtained voltage versus position curves for each data point of the Nd-MDH sample were then background corrected with the curves obtained for each data point for the blank. The resulting voltage versus position curves were then fitted by the dipole response function.

However, multiple problems arose: The first issue is that the signal from the Nd-

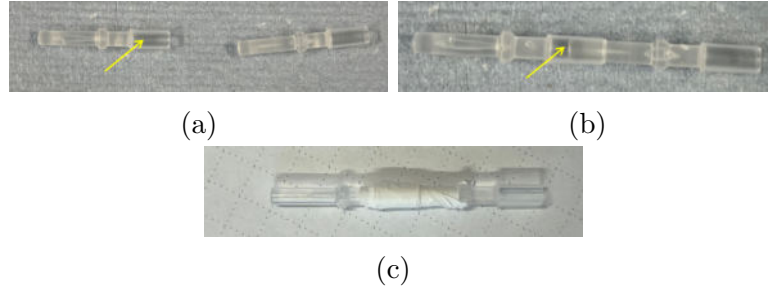


Fig. A.1: Preparation of the VSM Powder Sample Holders (QDC-4096-388) from *Quantum Design* for measuring solutions in MPMS. (a) Space for the solution in the open end of one of the capsule parts. (b) Closing of the capsule. (c) Sealing of the capsule with Teflon tape.

MDH sample is small compared to the devices measurement precision due to the limited quantity of Nd-MDH present in the sample. This results in noisy background-corrected voltage versus position curves, which in turn hinders the convergence of the fit. This can be observed in the form of jumps in the resulting magnetisation versus magnetic field curves, which are not observed in the absence of background correction (the raw signal is large in comparison to the corrected signal, as it is dominated by the diamagnetic contribution of PIPES and water. Consequently, the voltage versus position curve can be well fitted). Furthermore, an attempt was made to correct the measurement for the background by first fitting the dipole response function to the Nd-MDH and blank voltage versus position curves individually, and then subtracting the resulting magnetisation values from each other. An issue in this case was that although the fits and the subtraction were satisfactory, the resulting magnetisation (in the order of $1 \cdot 10^{-4} \text{ erg G}^{-1}$) was approximately three orders of magnitude larger than the signal the Nd-ion and radicals could contribute (in the order of $1 \cdot 10^{-7} \text{ erg G}^{-1}$). Furthermore, the presence of a surplus of water in the Nd-MDH sample in comparison to the blank should not result in such a large magnetisation value, given that the diamagnetic constant of water results in a magnetisation value in the order of $1 \cdot 10^{-6} \text{ erg G}^{-1}$ at 1 T [51]. The difference in the contribution to magnetisation between two different VSM capsules is in the order of $1 \cdot 10^{-9} \text{ erg G}^{-1}$. Consequently, the signal appears to be dominated by the difference in Teflon tape wrapped around the VSM capsules (which would result in a diamagnetic signal of the order of about $1 \cdot 10^{-5} \text{ erg G}^{-1}$ to $1 \cdot 10^{-4} \text{ erg G}^{-1}$ (depending on the amount of Teflon tape used) at 1 T [103]). It can therefore be concluded that this kind of sample preparation is not applicable to the sample under investigation.

A sealed liquid sample holder (QDC-8505-013) from *Quantum Design* was also tested. However, the diamagnetic signal it produces is too large to permit the observation of any contribution of the sample itself to the resulting magnetisation.

A.2 HF-EPR Spectra up to 60K

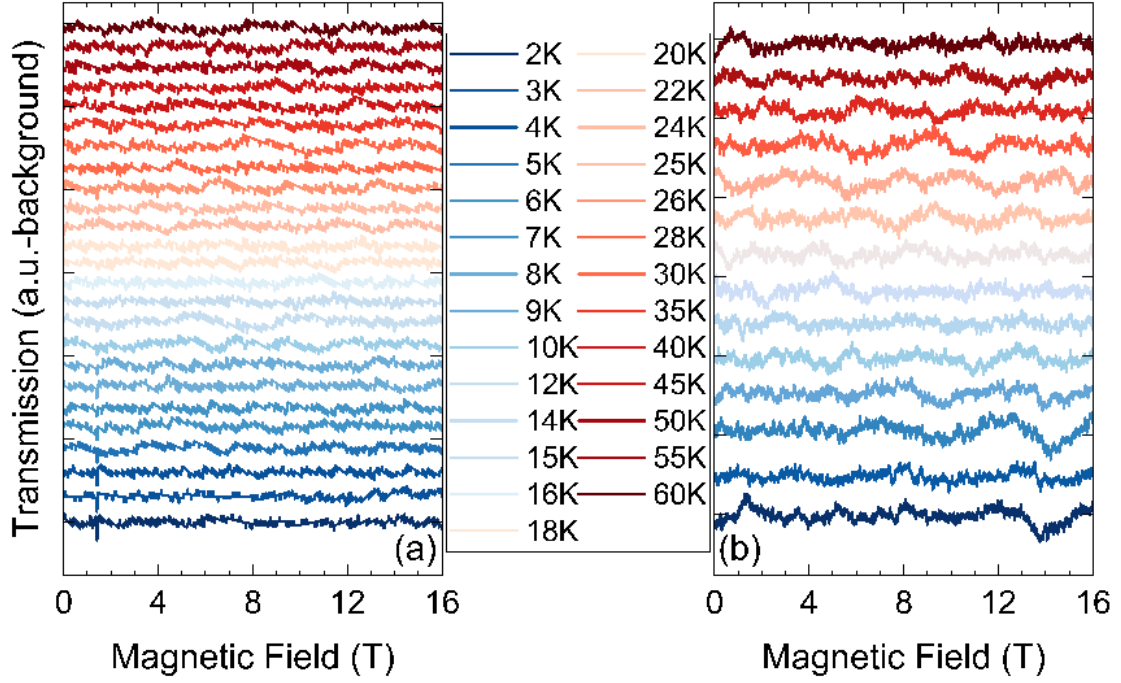


Fig. A.2: (a) HF-EPR spectra of Nd-MDH measured at $f = 40.2$ GHz for different temperatures ranging from 2 K to 60 K. (b) HF-EPR spectra of Nd-MDH measured at $f = 439.3$ GHz for different temperatures ranging from 2 K to 60 K.

Appendix B

Additional Information on the Biomimetic Samples

B.1 Further Details on SQUID Measurements of PQQTME Samples f-i

The samples **e-h** were prepared as shown in Fig. B.1: 100(3) μL of sample solution was poured into the larger part of polycarbonate capsules (QDC-AGC3) from *Quantum Design*. Subsequently, the capsule was closed by sliding the second smaller part of the capsule over the larger one. The capsule was then glued into a straw sample holder, as illustrated in the top of Fig. B.1, using GE Vanish and was dried over night.

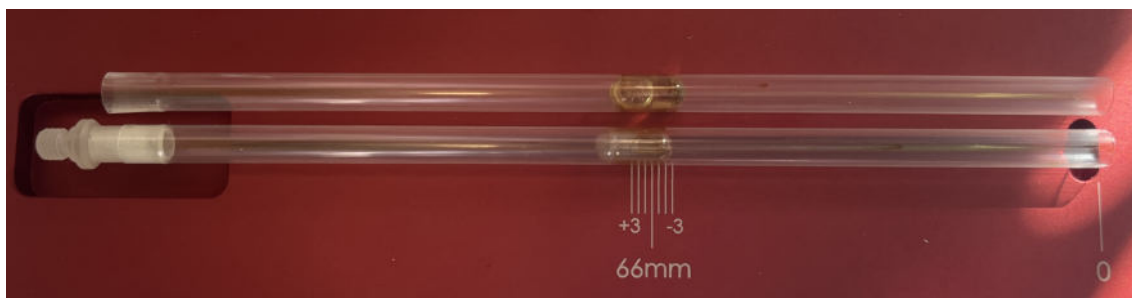


Fig. B.1: Sample preparation in the polycarbonate capsules (QDC-AGC3) from *Quantum Design* for measuring solutions in MPMS. Bottom: An empty capsule is glued into a straw sample holder with GE Vanish. Top: A capsule filled with a sample (yellow) glued into a straw sample holder with GE Vanish.

For background correction both an empty capsule, as illustrated in the bottom of Fig. B.1, and a capsule filled with acetonitrile were measured. In Fig. B.2 the voltage versus position curves obtained for sample **i** at 1.8 K and 7 T¹ are shown. The

¹It should be noted that the non-corrected and background-corrected signals of the other samples exhibited comparable signal size and curve shape to that shown in Fig. B.2.

measured voltage versus position curves of acetonitrile and sample **i** are similar to each other in the shape and signal amplitude, resulting in the background-corrected voltage versus position shown as the red curve in Fig. B.1. The background-corrected curve does not exhibit a maximum or minimum at the midpoint of the sample position (indicated as dashed vertical line), indicating that the resulting signal is not dominated by the sample. The grey curve in Fig. B.1 represents the measurement of an empty capsule. The maximum of this curve is displaced in relation to the sample position. In other measurements, it was observed that the difference in signal size between two polycarbonate capsules can be of the order of 40% of the signal of the capsule itself. The dashed grey line represents the negative of the voltage versus position curve of the empty capsule multiplied by 0.14. The background-corrected signal and this curve exhibit the same features. This indicates that the background-corrected signal is dominated by the difference in capsules used for the measurement of sample **i** and acetonitrile.

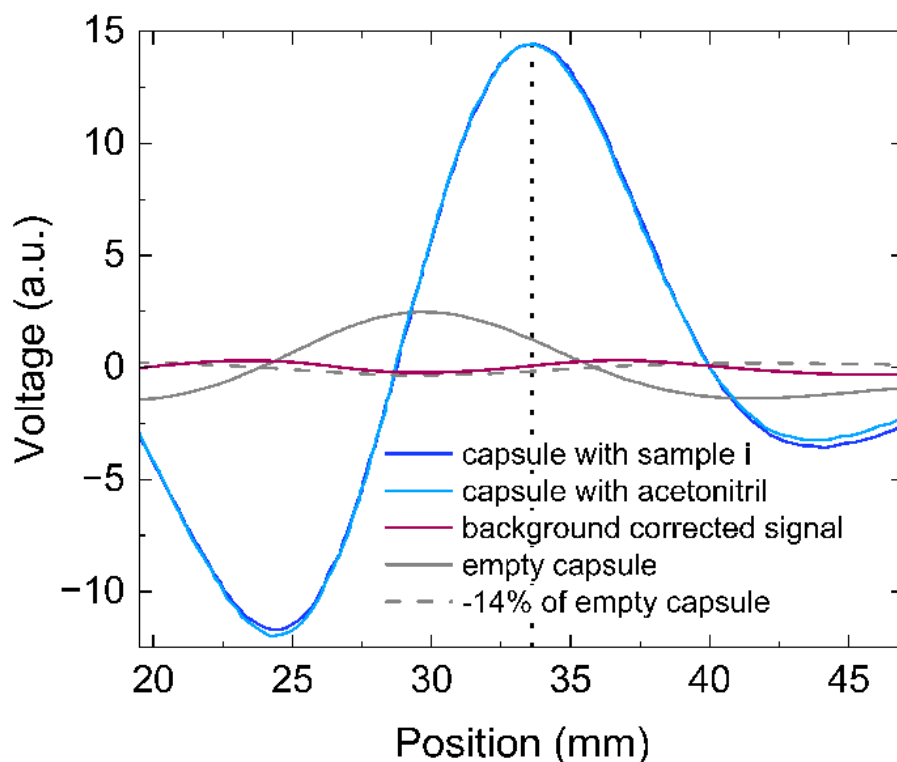


Fig. B.2: Voltage versus position curves measured at 1.8 K and 7 T in MPMS using polycarbonate capsules ((QDC-AGC3) from *Quantum Design*).

Finally, it can be concluded that the used sample preparation in the polycarbonate capsules is unsuitable for the measurement of radical concentration in the samples **e-h**. In order to accurately measure the radical concentration of the samples, it is necessary to use a sample container with less pronounced features (meaning that the signal is constant around the sample position) and a smaller signal, such that background-to-signal-ratio reduces.

B.2 Additional HF-EPR Spectra for Sample a

B.2.1 HF-EPR Spectra up to 60K for Sample a within the full Magnetic Field Range

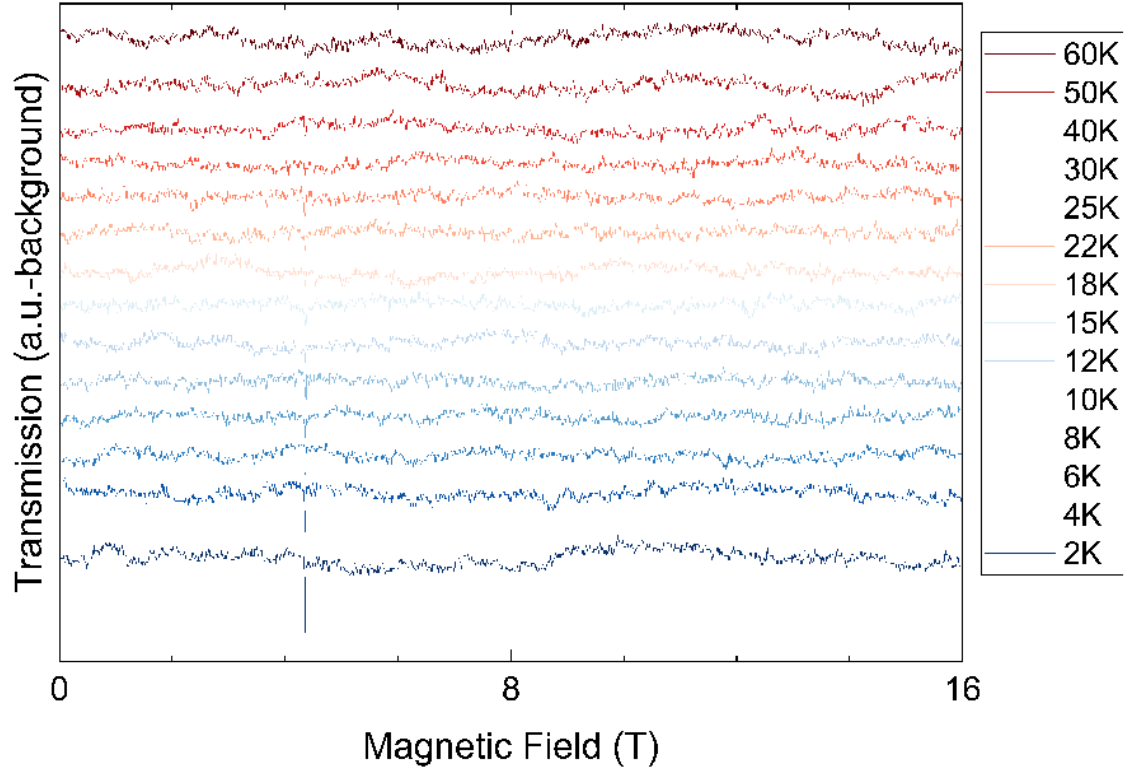


Fig. B.3: HF-EPR spectra of **a** measured at $f = 123.1$ GHz for different temperatures ranging from 2 K to 60 K.

B.2.2 HF-EPR Spectra with High Resolution for Sample a

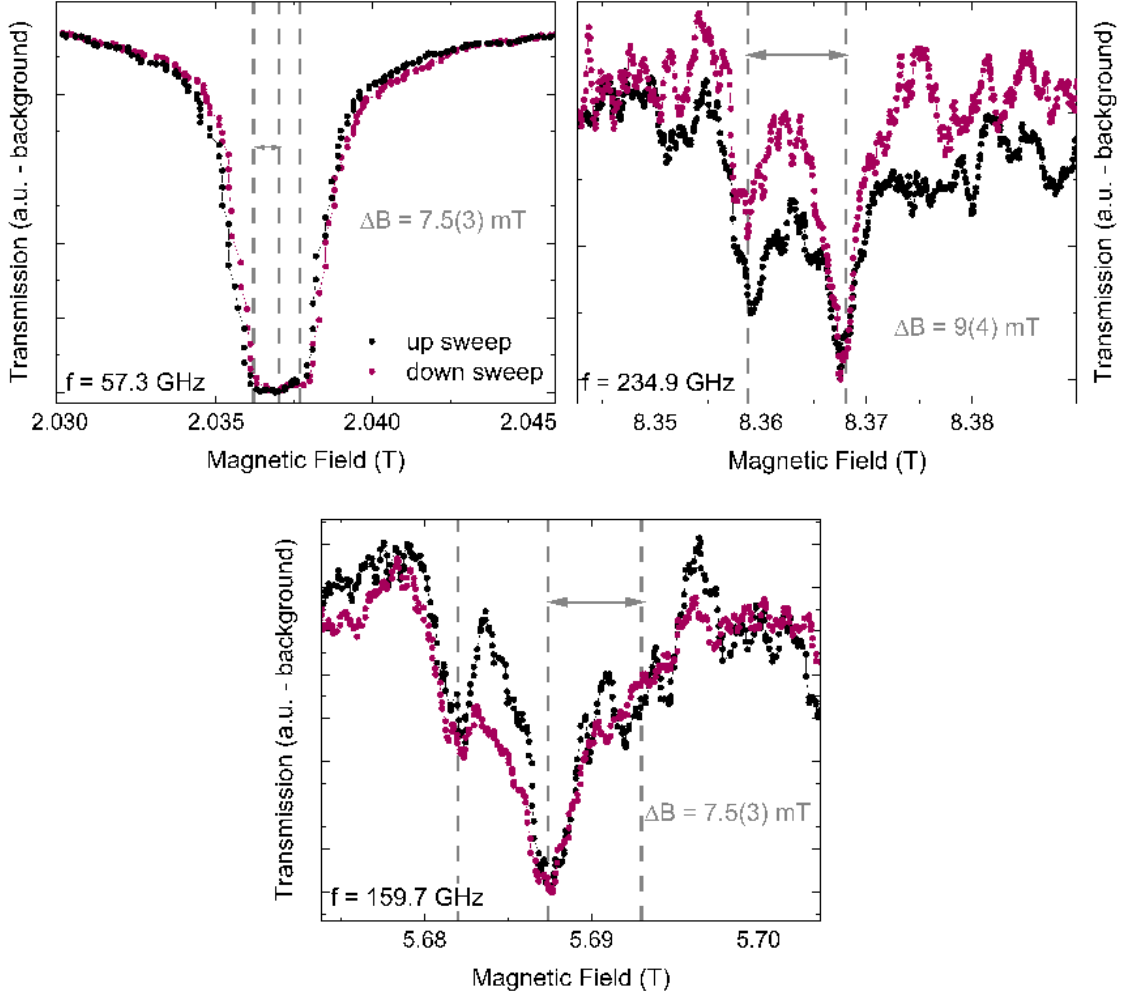


Fig. B.4: HF-EPR transmission spectra measured at $T = 2$ K at various frequencies for **a**. All spectra are background and phase mixing corrected and furthermore corrected for the remanence of the superconducting magnet of the device, as described in the text in subsection 8.4.1. The difference in resonance magnetic field between the shoulders and the middle feature, calculated as described in the text in subsection 8.4.1, is included as ΔB . Vertical dashed lines depict the resonance positions of the two shoulder and middle features. Note that for $f = 234.9$ GHz the shoulder feature at high magnetic fields was not observed. Therefore, ΔB for this frequency corresponds to the difference in resonance positions between the middle feature and the shoulder feature, observed at low magnetic fields.

B.3 Additional Spectral Simulations for Sample c

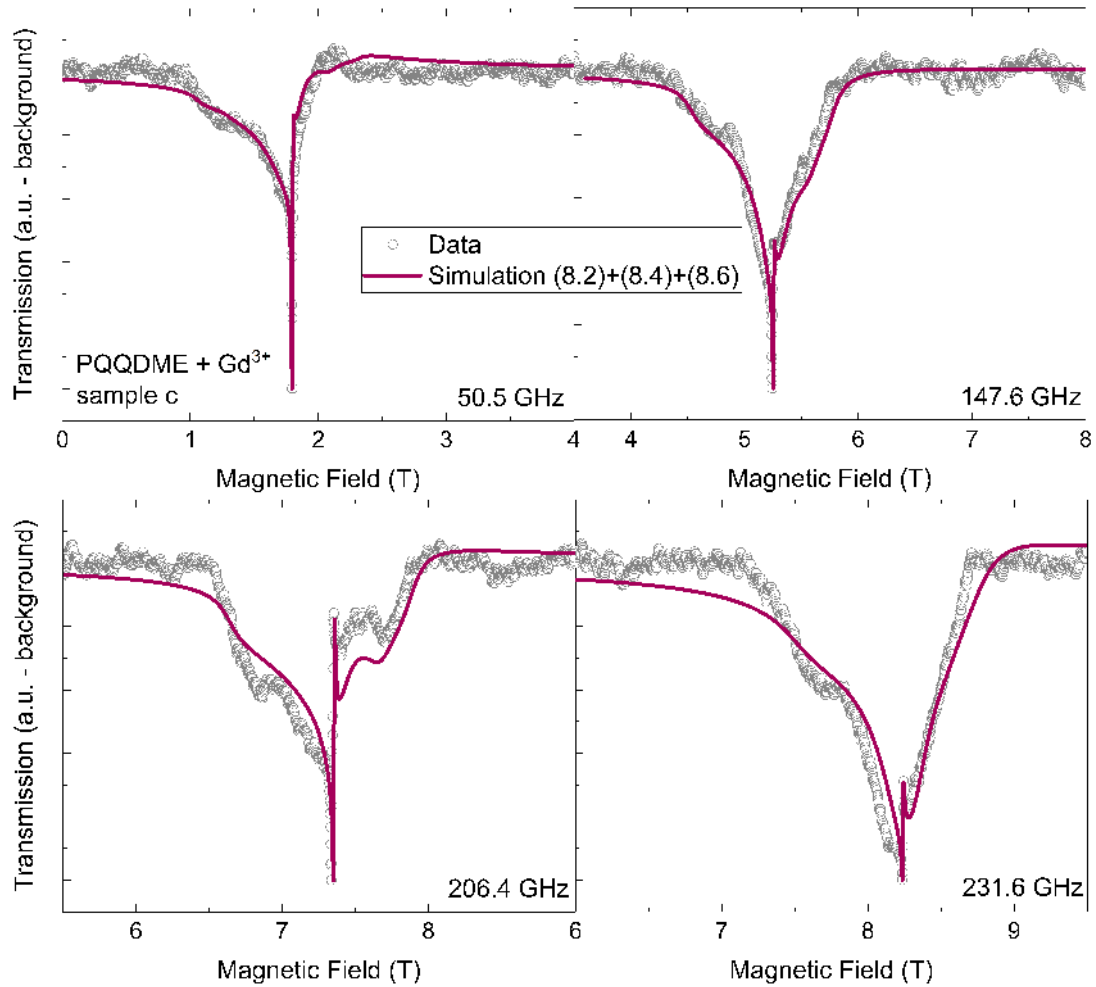


Fig. B.5: Exemplary HF-EPR transmission spectra measured at $T = 2$ K at $f = 50.5$ GHz, $f = 147.6$ GHz, $f = 206.4$ GHz and $f = 231.6$ GHz. The spectra are shown as grey open points, have been background corrected and are normalised to the absolute of the lowest value. The solid lines represent spectral simulations using the indicated Hamiltonians as described in subsection 8.4.2.

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Note of gratitude

I would like to express my gratitude to Prof. Dr. Rüdiger Klingeler for the excellent supervision, the helpful discussions, the open-door policy, and the trust you have placed in me.

I am also grateful to Prof. Dr. Peter Comba for serving as the second examiner of my thesis and for the excellent collaboration.

Furthermore, I thank our collaborators Prof. Dr. Uwe Bunz and Pascal Merten (Group of Prof. Dr. Uwe Bunz, Heidelberg University), Prof. Dr. Milan Kivala and Leon Martins (Group of Prof. Dr. Milan Kivala, Heidelberg University), Rejith Radhamani (Group of Prof. Dr. Peter Comba, Heidelberg University), Prof. Dr. Peter Roesky and Gerlinde Greif (Group of Prof. Dr. Peter Roesky, KIT), Prof. Dr. Lena Daumann, Ioana Ciubutaro and Dr. Manh Tri Phi (Group of Prof. Dr. Lena Daumann, LMU Munich) for the sample synthesis, the excellent collaboration, and the interesting and helpful discussions. I also thank Prof. Dr. Florian Weigend and Florian Bruder (Group of Prof. Dr. Florian Weigend, Philipps-Universität Marburg) for their theory support.

Additionally, my thanks go to all the members of the group of Prof. Dr. Klingeler for their energetic support, many exciting discussions, enjoyable break conversations, and pleasant working atmosphere. Thank you Luca Bischof, Leon Carstens, Bowen Dong, Dr. Ahmed Elghandour, Lukas Gries, Waldemar Hergett, Jonah-Gabriel Homm, Tobias König, Dr. Lennart Singer, Tillmann Stork, Tom Wickenhäuser, Ning Yuan, Jieyuan Zheng, Peng Guo, Kevin Ackermann, Martin Reitenbach, Timo Kleinbek and Marius Säubert for the wonderful time with you all!

I would especially like to thank Jan Arneth for the supervision, the fruitful discussions, and for explaining the measurement setups. Thank you for always having time for me.

I also thank Dr. Changhyun Koo for being an excellent office neighbour. The science-related conversations with you were very enlightening and our break conversations were always a great joy.

Additionally, I want to thank Beatrice Schwöbel for the organisational assistance.

Thank you Rudolph Eitel for always providing liquid helium.

I would also like to thank Janina Vogelgesang for her linguistic support with this work.

I am grateful to Hannah Bohnert for her support with questions on chemical topics, both in this work and throughout my studies.

I thank the people of my study group during my studies. I learned much from our shared learning sessions.

To my friends: Thank you for your understanding of my studies and the resulting time constraints. Thank you for always supporting and believing in me.

A special thanks goes to my family. Thank you for supporting me throughout my studies, for making my studies possible and for always believing in me.

Finally, a big thanks goes to Erik Walendy. Thank you for the countless discussions and the shared learning sessions throughout our studies. Thank you for always having time for me and believing in me!

Declaration

I declare that I have written this thesis independently and have not used any sources and aids other than those indicated.

Heidelberg, June 6, 2024