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**Spin dynamics and relaxation
in a dysprosium-based
single-ion magnet**

**Dinamica di spin in un magnete molecolare
a singolo ione di disprosio**

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Sinossi

Il presente lavoro si colloca nel contesto dello studio dei magneti molecolari e, in particolare, dei composti a singolo ione di lantanide. In particolare, la tesi si concentra sull'analisi di un complesso di disprosio, indicato di seguito come Dy-SQ, con l'obiettivo di analizzarne le proprietà magnetiche e di utilizzarle come strumento per ottenere informazioni sulla struttura elettronica microscopica del sistema. La presenza di uno ione Dy^{3+} in un ambiente molecolare contenente un radicale semiquinonato rende il composto particolarmente interessante, poiché la sua risposta magnetica riflette sia l'anisotropia di singolo ione indotta dal campo cristallino sia l'interazione di scambio tra il momento magnetico del disprosio e uno spin radicalico.

Lo studio è stato effettuato attraverso diverse tecniche sperimentali e metodi computazionali. La magnetometria SQUID fornisce una descrizione della risposta magnetica macroscopica, mentre la risonanza magnetica nucleare e la spettroscopia di spin del muone agiscono come sonde locali dell'ambiente magnetico e del rilassamento della magnetizzazione. Parallelamente, sono stati utilizzati calcoli di campo cristallino basati su un modello a cariche puntiformi per stimare lo schema dei livelli elettronici dello ione Dy^{3+} . L'integrazione di questi risultati permette di discutere il comportamento magnetico di Dy-SQ alla luce della sua struttura elettronica e delle interazioni microscopiche che lo caratterizzano.

Abstract

This thesis investigates the magnetic properties of a dysprosium-based single-ion magnet, hereafter referred to as Dy-SQ, with the aim of extracting information on its microscopic electronic structure. The system is characterized by the presence of a Dy^{3+} ion embedded in a molecular ligand environment and coupled to a semiquinonato radical. This makes the overall magnetic response the combination of crystal-field effects, magnetic anisotropy, and the exchange interaction between the rare-earth ion and the radical.

The work combines different experimental and computational approaches. SQUID magnetometry is used to characterize the bulk magnetic response, nuclear magnetic resonance and muon spin spectroscopy are employed as local probes of the magnetic environment and spin dynamics, while crystal-field calculations provide a microscopic description of the Dy^{3+} electronic level scheme. The comparison between these complementary techniques is used to build a coherent physical picture of the investigated molecular complex and to relate its measured magnetic behaviour to the underlying electronic structure.

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Introduction

Molecular magnetism provides a privileged framework for studying how magnetic behaviour emerges from well-defined microscopic units. In conventional magnetic solids, the macroscopic response is governed by collective phenomena extending throughout the crystal lattice. Molecular magnets, on the other hand, make it possible to investigate magnetic anisotropy, exchange interactions, relaxation processes, and quantum effects starting from discrete coordination complexes. In this sense, they lie at the interface between chemistry and condensed-matter physics: the magnetic properties of the material are not only determined by the magnetic ion itself, but also by the symmetry, geometry, and electronic structure imposed by the molecular environment. This dual character gives molecular magnets both fundamental and applicative relevance. On the one hand, they provide systems in which intrinsically quantum phenomena, such as magnetization tunnelling, can be detected through macroscopic magnetic measurements. On the other hand, their discrete and chemically tunable nature makes them promising candidates as elementary units for molecular spintronics and quantum-information architectures.

Lanthanide-based single-ion magnets are particularly interesting within this context. Lanthanide ions are characterized by strong spin-orbit coupling and by a partially shielded $4f$ electronic shell, whose interaction with the surrounding ligands gives rise to a crystal-field splitting of the ground multiplet. This produces highly anisotropic electronic states, which strongly influence the low-temperature magnetic response. Such anisotropy is generally much more pronounced than in clusters based on transition-metal ions, making lanthanide complexes especially attractive for the design of molecular magnets with large magnetic barriers.

The present thesis focuses on a dysprosium-based single-ion magnet, Dy-SQ, in which the Dy^{3+} ion is coordinated within an organic ligand environment containing a semiquinonato radical. This system is particularly interesting because its magnetic properties are expected to arise from the combination of two ingredients: the single-ion anisotropy of the dysprosium centre and the magnetic interaction between the lanthanide ion and the radical spin. From a broader perspective, this situation is also relevant for the possible use of molecular magnetic units in quantum-information schemes. An isolated dysprosium magnetic moment can, in principle, provide a highly anisotropic two-level system, but magnetic interactions with the surrounding environment generally represent an important source of decoherence. At the same time, controlled interactions are necessary if such a magnetic unit is to be addressed, manipulated, or coupled to other quantum objects. Introducing an additional spin degree of freedom in a chemically controlled

way, as in Dy–SQ, therefore provides a useful model system for investigating how magnetic interactions modify the electronic structure and relaxation properties of a lanthanide-based molecular magnet. The central purpose of this work is to study the magnetic properties of Dy–SQ and to use them as indirect probes of its underlying electronic structure.

This objective requires the combination of techniques that are sensitive to different aspects of the same physical problem. SQUID magnetometry gives access to the macroscopic magnetic response of the sample, allowing to investigate the field and temperature dependence of the magnetization. Nuclear magnetic resonance probes the local magnetic environment through the response of nuclear spins, providing information on the electronic spin dynamics and relaxation processes. Muon spin spectroscopy offers a complementary local probe, sensitive to internal magnetic fields and magnetic fluctuations on a different time scale. Finally, crystal-field calculations based on a point-charge description are used to obtain a microscopic estimate of the Dy³⁺ level scheme and of the magnetic anisotropy associated with the coordination environment. The aim of the thesis is not to treat these methods as independent characterizations, but to use them as complementary perspectives on the same system. The bulk magnetic response, the local relaxation channels, and the calculated crystal-field spectrum are therefore interpreted together in order to obtain a more complete physical picture of Dy–SQ. In this sense, the magnetic measurements are used as a route toward the electronic structure of the molecule, rather than as purely phenomenological observables.

The thesis is organized as follows. Chapter 1 introduces the theoretical background needed to frame the problem. It begins with the basic concepts of localized magnetism, magnetic anisotropy, and exchange interactions, and then discusses the emergence of molecular nanomagnets, single-molecule magnets, and single-ion magnets. Particular attention is devoted to lanthanide-based systems, Kramers ions, Stevens operators, and crystal-field effects, before introducing the Dy–SQ complex, the role of the semiquinonato radical, and the motivation for the present investigation.

Chapter 2 is devoted to nuclear magnetic resonance (NMR). The chapter first presents the basic physical principles of the technique, including nuclear magnetization, Larmor precession, radiofrequency excitation, and the rotating frame. It then introduces the quantum mechanical description of NMR, the Bloch equations, relaxation mechanisms, pulsed sequences, and frequency-domain spectroscopy. This provides the conceptual basis for the interpretation of the NMR measurements performed on Dy–SQ.

Chapter 3 introduces muon spin spectroscopy (μ SR) as a local probe of magnetism. After describing the properties of the muon and the experimental principle of the technique, the chapter discusses the main relaxation models relevant for the present work. Zero-field, longitudinal-field, and transverse-field configurations are presented in order to clarify how μ SR can distinguish between static internal fields, dynamic fluctuations, and field-induced decoupling effects.

Chapter 4 presents the experimental results obtained on Dy–SQ. The SQUID magnetometry, NMR, and μ SR data are reported and organized according to the different

techniques and experimental conditions, with the aim of providing a clear overview of the measured magnetic response.

Chapter 5 is devoted to the analysis and interpretation of the acquired data. The chapter first addresses the magnetization data through a computational modelling of the magnetic response, aimed at extracting information on the anisotropy and on the interaction between the Dy^{3+} ion and the radical spin. The relaxation data are then analysed independently, with particular attention to the estimate of the energy separation between the electronic states, especially between the ground state and the first excited state. The chapter concludes by combining these results in order to discuss the microscopic picture of the magnetic behaviour of Dy-SQ.

Unless otherwise stated, magnetic quantities throughout this thesis are expressed in the CGS-emu system of units. Accordingly, magnetic moments are reported in emu, magnetic fields in Oe or kOe, and magnetic susceptibilities in the corresponding CGS units.

Language-support tools were used during the writing process to assist with translation, sentence formulation, and stylistic refinement. Their use was limited to improving the clarity and readability of the text. The scientific content, data analysis, interpretation of the results, selection of the bibliographic references, and final decisions on the manuscript remain entirely the author's responsibility.

Chapter 1

Molecular Magnetism

Molecular magnetism lies at the intersection of coordination chemistry, condensed-matter physics, and quantum science, and investigates how magnetic behaviour can emerge from discrete molecular units. Unlike conventional magnetic solids, whose macroscopic properties are associated with collective interactions extending throughout a crystal lattice, molecular nanomagnets are governed primarily by the electronic structure, exchange interactions, and magnetic anisotropy of individual coordination complexes. Their discrete energy-level structure can give rise to magnetic bistability, thermally-activated magnetization reversal, quantum tunnelling, and environment-induced decoherence. Establishing the connection between these microscopic ingredients and the experimentally observable magnetic response is therefore essential both for understanding magnetic memory effects at the molecular scale and for assessing the potential of molecular spins in quantum technologies. This framework also provides the physical basis for the investigation of the Dy-based single-ion magnet presented in this thesis.

The chapter is organized as follows. Section 1.1 introduces the microscopic foundations of localized magnetism, including the magnetic response of individual ions, exchange interactions, magnetic ordering, and hysteresis in conventional materials. Section 1.2 then describes the emergence of molecular nanomagnets and single-molecule magnets, focusing on magnetic anisotropy, the anisotropy barrier, thermally-activated magnetization reversal, and quantum tunnelling of magnetization. Section 1.3 discusses magnetic relaxation and quantum decoherence, together with the limitations that these processes impose on the use of molecular spins for information storage and quantum computation. Section 1.4 introduces single-ion magnets and examines the properties of lanthanide ions, Kramers degeneracy, and the Stevens-operator description of crystal-field effects. Finally, Section 1.5 applies this theoretical framework to the investigated compound by presenting its molecular structure, and the magnetic properties previously reported in the literature.

The theoretical framework adopted throughout this chapter follows primarily the treatment of molecular nanomagnetism presented by Gatteschi, Sessoli, and Villain in *Molecular Nanomagnets* [1], unless otherwise stated. Additional references are provided where specific experimental results, historical developments, or more specialized theoretical treatments are discussed.

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1.1 Generalities on Bulk Magnetism

Before introducing molecular nanomagnets, it is useful to recall the microscopic origin of localized magnetic moments and the interactions responsible for the magnetic response of conventional materials.

1.1.1 Microscopic Foundations and Single-Ion Properties

From a quantum mechanical perspective, a magnetic material can be viewed as a collection of interacting electronic angular momenta arranged on atomic or molecular sites. While classical macroscopic magnetism arises from moving electric charges (currents), quantum magnetism is an intrinsic property of electrons, originating from both their spin and orbital angular momenta (S and L , respectively).

In condensed matter physics, magnetic behaviors are generally classified into two distinct regimes based on the nature of the electrons involved: the itinerant model, typical of conducting metals where magnetic electrons flow freely through energy bands, and the localized model, characteristic of insulators and molecular complexes where electrons remain tightly bound to specific atomic or molecular sites. Throughout this work, the discussion will focus on localized magnetic systems, since this framework provides the appropriate basis for describing molecular magnets.

Within the Russell–Saunders coupling scheme, the orbital and spin angular momenta of the individual electrons belonging to the magnetic ion at site i are first combined to define the total orbital and spin angular momenta

$$\mathbf{L}_i = \sum_j \mathbf{l}_{ij} \quad (1.1)$$

$$\mathbf{S}_i = \sum_j \mathbf{s}_{ij} \quad (1.2)$$

where the index j runs over the electrons of the atom. The total angular momentum associated with the site is then obtained by coupling these two contributions

$$\mathbf{J}_i = \mathbf{L}_i + \mathbf{S}_i \quad (1.3)$$

Within a given J_i multiplet, the corresponding magnetic dipole moment is related to the total angular momentum through the Landé factor g_{J_i}

$$\mu_i = -g_{J_i} \mu_B \mathbf{J}_i \quad (1.4)$$

where μ_B is the Bohr magneton and g_J is the dimensionless Landé g -factor, which takes into account the different gyromagnetic ratios of spin and orbital motions. For a free atom or ion, it is defined as:

$$g_J = 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)} \quad (1.5)$$

In molecular magnets and coordination complexes, the magnetic ions are embedded in a crystalline or coordination environment. The electrostatic potential generated by the surrounding ligands, known as the crystal electric field (CEF), breaks the spherical symmetry of the free ion. This interaction frequently leads to the phenomenon of *orbital angular momentum quenching*. In a free, isolated ion, the approximate spherical symmetry of the electrostatic potential preserves the degeneracy of states corresponding to different spatial orientations of the orbital angular momentum. Consequently, the orbital contribution to the magnetic moment is not suppressed by any preferred direction imposed by the surrounding environment. When the ion is placed within a molecular complex, the electrical charges of the surrounding ligands interact with the electron clouds, splitting the originally equivalent orbitals into different energy levels based on their spatial orientation.

As a result of this energy splitting, the electrons become energetically trapped in specific, fixed directional orbital pathways. Since they can no longer freely rotate or transition between these split levels without a significant energy input, their net orbital circulation is effectively frozen. Therefore, the orbital angular momentum is locked by the structural environment and cannot readily reorient under an external magnetic field. The orbital angular momentum is no longer a good quantum number and its contribution to the magnetic moment becomes strongly reduced and, in many transition-metal complexes, can be approximated as partially or even fully quenched ($L \approx 0$).

In such cases, L can be neglected, the total angular momentum simplifies to the spin-only contribution ($J_i \approx S_i$), and the Landé factor reduces to the free-electron spin g -factor ($g_J \approx g_s \approx 2.0023$, usually approximated to 2). Thus, equation 1.4 can be re-written in its spin-only form:

$$\mu_i \approx -g_s \mu_B S_i \quad (1.6)$$

Beyond merely quenching the orbital momentum, the CEF interaction defines the entire single-ion energy landscape. By lifting the degeneracy of the electronic states, the CEF Hamiltonian establishes a strong preference for the spatial orientation of the remaining magnetic moments. This mechanism generates the single-ion magnetic anisotropy, a key ingredient for the magnetic bistability observed in single-molecule magnets [2]. The crystal-field description will be discussed in greater detail in Section 1.4.2.

1.1.2 Single-Ion Magnetic Response

The macroscopic magnetic response of a material is fundamentally dictated by how its localized electronic moments interact both with external magnetic fields and with one another. Depending on the electronic configuration of the constituent sites and the quantum mechanical nature of their coupling, materials can exhibit a wide variety of magnetic phases [3].

The most universal, albeit often weakest, response to an external field is diamagnetism. This property is inherent to all matter, though it is frequently masked by stronger magnetic phenomena. When an external magnetic field $\mathbf{H}$ is applied, the orbital motion of the electrons is perturbed. According to Lenz's law, this perturbation induces a weak magnetic moment that opposes the applied field. Mathematically, this linear response is described by the Langevin equation for the diamagnetic susceptibility:

$$\chi_{\text{dia}} = -\frac{Ne^2}{6m_e c^2} \sum_i \langle r_i^2 \rangle \quad (1.7)$$

where N is the number of atoms per unit volume, m_e is the electron mass, and $\langle r_i^2 \rangle$ represents the mean square radius of the electron orbits, where the summation extends over all electrons belonging to each atom (or molecule). Thus diamagnetic materials exhibit a small, negative, and temperature-independent magnetic susceptibility ($\chi < 0$), causing them to be weakly repelled by magnetic fields.

If the constituent atoms or molecules possess unpaired electrons instead, the system exhibits permanent local magnetic moments. In the simplest scenario, where these localized moments are sufficiently far apart or structurally isolated such that they do not interact with each other, the system behaves as a conventional paramagnet. At finite temperatures, thermal fluctuations dominate the system, causing the individual spins to point in random, uncorrelated directions, which leads to a net zero macroscopic magnetization. An external magnetic field can break this thermal randomness, forcing the spins to align parallel to the field lines. For a system of independent spins, this competing mechanism between thermal fluctuations and magnetic alignment is quantified by Curie's law:

$$\chi_C = \frac{C}{T} = \frac{N g_j^2 \mu_B^2 J(J+1)}{3k_B T} \quad (1.8)$$

where C is the Curie constant, k_B is the Boltzmann constant, and J is the quantum number corresponding to total angular momentum and is reduced to S within the spin-only approximation.

While Curie paramagnetism originates from the thermal population of magnetic energy levels, a different paramagnetic contribution may arise when an external magnetic field couples a non-magnetic ground state $|0\rangle$ to an excited state $|1\rangle$. Known as Van Vleck paramagnetism, through this field-induced mixing, the ground-state energy acquires a second-order dependence on the applied field, producing a finite positive susceptibility even when the excited state is not thermally populated.

Considering a single relevant excited state separated from the ground state by an energy gap $\Delta = E_1 - E_0$, the molar Van Vleck susceptibility in CGS units is

$$\chi_{\text{VV}} = 2\mu_B^2 \frac{|\langle 0 | (L_z + 2S_z) | 1 \rangle|^2}{\Delta} \quad (1.9)$$

the angular-momentum operators are expressed in units of $\hbar$. This contribution is approximately temperature independent only in the low-temperature limit

$$k_B T \ll \Delta \quad (1.10)$$

for which the excited state remains negligibly populated. At higher temperatures, thermal occupation of the excited state introduces a Curie-like temperature dependence. Van Vleck paramagnetism is particularly relevant in coordination complexes possessing a non-magnetic ground state that can be polarized through field-induced mixing with nearby excited states [4].

1.1.3 Exchange Interactions and Magnetic Ordering

While the phenomena discussed so far originate from the properties of individual magnetic centers, collective magnetic phases emerge only when interactions between neighboring moments become significant. The origin of this coupling is not magnetic dipole-dipole interaction, which is generally too weak to explain the experimentally observed ordering temperatures. Collective ordering is driven instead by exchange interactions, which are purely quantum mechanical in nature, arising from the combined effects of the Pauli exclusion principle and Coulomb electrostatic repulsion.

When the wavefunctions of neighboring magnetic orbitals overlap directly, this interaction is referred to as direct exchange. However, in molecular magnets and transition metal oxides, the magnetic cations are typically separated by diamagnetic bridging ligands (such as O^{2-} or organic linkers). In these systems, the coupling is mediated indirectly through the ligand orbitals via a mechanism known as superexchange [5]. Regardless of the specific pathway, these interactions are conventionally described by the phenomenological Heisenberg exchange Hamiltonian:

$$\mathcal{H}_{\text{ex}} = - \sum_{\langle i,j \rangle} J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j \quad (1.11)$$

where $\langle i, j \rangle$ denote nearest-neighbor pairs in the lattice, and J_{ij} is the exchange integral. The sign and magnitude of the exchange constant J dictate the magnetic ground state of the system as the thermal energy decreases below a critical phase-transition threshold.

When the exchange coupling is positive ($J > 0$), the system minimizes its total energy when neighboring spins align strictly parallel to one another, resulting in a ferromagnetic order. Below the Curie temperature, exchange interactions overcome thermal agitation establishing long-range parallel spin alignment.

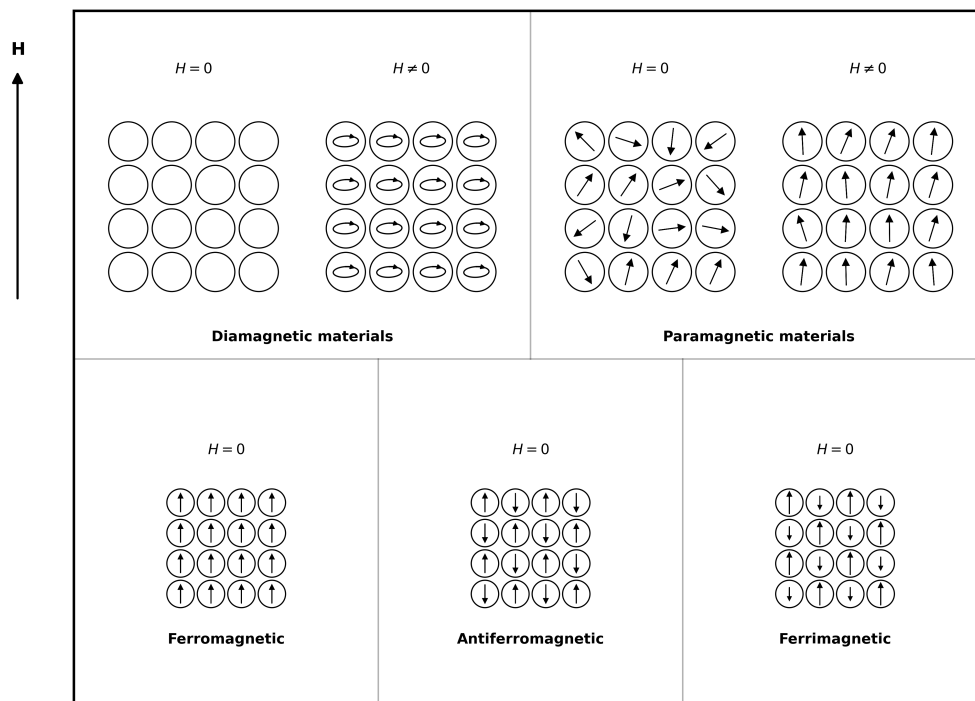


Figure 1.1: Schematic representation of the main magnetic responses and ordering states. Diamagnetic and paramagnetic materials are shown both in the absence and in the presence of an external field, while ferromagnetic, antiferromagnetic, and ferrimagnetic configurations are illustrated at zero field.

A negative exchange coupling ($J < 0$) favors an antiparallel spin arrangement typical of antiferromagnets. In the simplest antiferromagnets, the lattice can be conceptualized as two interpenetrating, high-symmetry sublattices, A and B . Sublattice A consists of spins aligned along one direction, while sublattice B contains an identical set of spins aligned in the opposite direction. Because the magnetic ions occupying both sublattices are identical in nature and number, their net magnetic moments perfectly cancel out ($\mathbf{M}_A + \mathbf{M}_B = 0$). Macroscopically, an antiferromagnet yields no spontaneous magnetization below its critical Néel temperature (T_N), despite preserving long-range magnetic order at the microscopic scale.

A closely related yet distinct phase arises when the exchange coupling is negative ($J < 0$) but the two sublattices are chemically or structurally asymmetric, a state known as ferrimagnetism. This asymmetry can stem from the sublattices being occupied by different magnetic ions (e.g., a transition metal and a lanthanide) or containing an unequal number of magnetic sites per unit cell. Because the opposing magnetic moments of sublattice A and B are unequal in magnitude ($|\mathbf{M}_A| \neq |\mathbf{M}_B|$), they do not perfectly cancel out. Ferrimagnets behave macroscopically much like ferromagnets, exhibiting a net spontaneous magnetization below a critical ordering temperature.

The primary magnetic states resulting from these microscopic interactions and symmetry constraints are schematically summarized in Figure 1.1.

Finally, real molecular and crystalline architectures may deviate from strictly parallel or antiparallel collinear spin arrangements, giving rise to non-collinear magnetic structures. One microscopic mechanism that can promote such configurations is the antisymmetric Dzyaloshinskii–Moriya exchange interaction, which originates from spin–orbit coupling when the local symmetry does not allow an inversion centre between two interacting magnetic sites. Its contribution to the spin Hamiltonian can be written as

$$\mathcal{H}_{\text{DM}} = \sum_{\langle i,j \rangle} \mathbf{D}_{ij} \cdot (\mathbf{S}_i \times \mathbf{S}_j) \quad (1.12)$$

where $\mathbf{D}_{ij}$ is the Dzyaloshinskii–Moriya vector. Unlike symmetric exchange, which favours parallel or antiparallel alignment depending on the sign of the coupling constant, this antisymmetric term favours a finite angle between neighbouring spins and can therefore produce canted or more generally non-collinear magnetic configurations [6, 7].

A distinct origin of non-collinearity is geometric frustration, which occurs when the topology of the magnetic lattice, as in triangular or tetrahedral arrangements, prevents all exchange interactions from being simultaneously minimized. In frustrated systems, several magnetic configurations may remain energetically equivalent or nearly equivalent, leading to a highly degenerate ground-state manifold, complex magnetic structures, and enhanced fluctuations [3, 8].

1.1.4 Hysteresis in Conventional Magnetism

The existence of a spontaneous, parallel alignment of spins ($J > 0$) does not automatically imply that a bulk ferromagnetic material will act as a permanent magnet. In the absence of an external magnetic field, a macroscopic sample minimizes its magnetostatic energy by dividing itself into many mesoscopic ordered regions known as magnetic domains. Within each individual domain, the spins are perfectly locked parallel to one another; however, the net magnetization vectors of different domains point in random directions, canceling each other out.

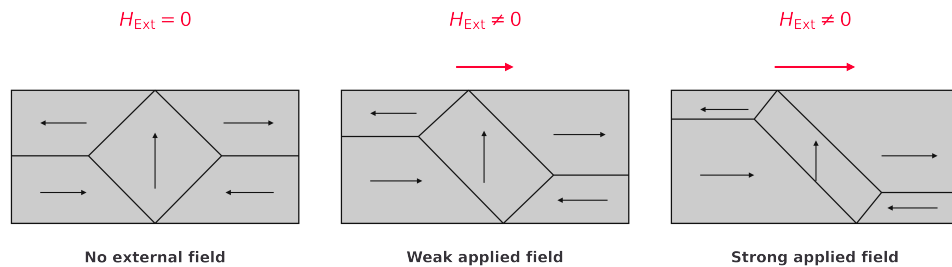


Figure 1.2: *Evolution of ferromagnetic domains under an increasing external magnetic field. The enlargement of the domain aligned with the field demonstrates the microscopic origin of bulk magnetization until magnetic saturation is achieved. Adapted from [9]*

When an external magnetic field (H) is applied, these domains begin to interact with the field. The domains whose internal magnetization aligns parallel to the applied field begin to expand, swallowing adjacent domains through the motion of domain walls. If the external field is strong enough, all domains eventually merge, bringing the sample into a state of magnetic saturation (M_{sat}) where all the microscopic spins are forced to point in the same direction (see Figure 1.2)

The hallmark of conventional ferromagnetism is what happens when the external magnetic field is then gradually removed. Instead of the spins randomizing and the magnetization dropping back to zero (as expected in a paramagnet), the material resists this change. The displacement of domain walls is an irreversible process, pinned by atomic defects, impurities, and grain boundaries within the crystal lattice, giving rise to the phenomenon of magnetic hysteresis. When the external field is reduced to zero, the material retains a finite, spontaneous magnetization known as the remanent magnetization (M_{rem}).

To completely demagnetize the material and force the macroscopic magnetization back to zero, a specific magnetic field of opposite polarity must be applied. This necessary reverse field is defined as the coercive field (H_{coerc}). Plotting the magnetization M as a function of the sweeping field H yields the well-known closed hysteresis loop. The area inside this loop is directly proportional to the energy dissipated as heat when the domain walls are forced to move back and forth or rotated [10]. This is shown in Figure 1.3, where B is the field that acts inside the sample.

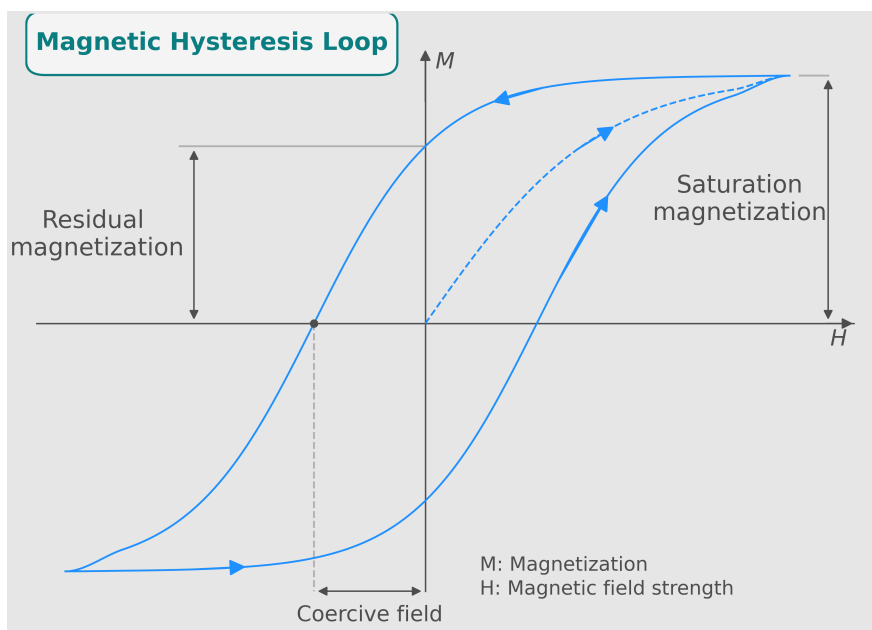


Figure 1.3: *Magnetic hysteresis loop showing the path-dependent nature of magnetization. The discrepancy between the ascending and descending branches highlights the energy dissipation due to domain wall pinning and rotational impediments.*

Beyond its fundamental significance, magnetic hysteresis is of enormous technological importance because it provides a mechanism for storing information in a

stable and non-volatile manner. The existence of a finite remanent magnetization and coercive field implies that a magnetic material can remain trapped in one of two distinct magnetization states even after the external magnetic field has been removed. These two stable states, conventionally identified as "up" and "down" magnetization, constitute a magnetic bistability that can be naturally associated with the binary logic states 1 and 0.

This property forms the physical foundation of magnetic data storage technologies. In conventional hard-disk drives and other magnetic memory devices, information is encoded in the orientation of small magnetic domains whose magnetization can be switched by an external field while remaining stable against thermal fluctuations over long periods of time. The continuous demand for higher storage densities has motivated the search for progressively smaller magnetic units capable of preserving this bistable behavior.

From this perspective, single-molecule magnets represent the ultimate limit of magnetic miniaturization. Remarkably, they can exhibit magnetic hysteresis and bistability at the level of an individual molecule, without requiring the long-range magnetic ordering or domain structures characteristic of conventional bulk ferromagnets. Understanding how such molecular systems reproduce the essential features of magnetic memory therefore constitutes one of the central themes of modern molecular magnetism [2, 11, 12].

1.2 The Emergence of Molecular Nanomagnets

Unlike conventional bulk magnetic materials, whose macroscopic response arises from collective interactions extending throughout the crystal lattice, molecular magnetism is based on discrete, non-interacting molecular units that act as individual magnetic entities.

A molecular magnetic crystal is composed of molecules containing one or more magnetic centres, typically transition-metal or lanthanide ions, embedded within an organic ligand framework. The low-energy magnetic properties of each molecule are mainly determined by the intramolecular exchange interactions between the magnetic ions and by the crystal electric field generated by the surrounding ligands [12]. The exchange interactions couple the individual magnetic moments and may produce a well-defined molecular spin ground state, whereas the ligand environment determines the crystal-field splitting and the resulting magnetic anisotropy. Consequently, the magnetic response of the molecule can often be described in terms of an effective molecular magnetic moment arising from the combined contributions of its magnetic centres.

The organic ligands surrounding the magnetic core also tend to increase the separation between neighbouring molecules, strongly reducing direct intermolecular exchange interactions. At sufficiently low temperatures, when the lowest molecular spin multiplet becomes predominantly populated, the crystal can therefore often be

treated as an ensemble of nearly independent molecular magnetic moments.

Among the polynuclear transition-metal clusters described by this framework, some compounds exhibit magnetic bistability and hysteresis of molecular origin and are therefore classified as single-molecule magnets (SMMs). Unlike conventional ferromagnets, where hysteresis is associated with the formation and motion of magnetic domains, each SMM behaves as an individual magnetic unit capable of retaining the orientation of its magnetic moment. This behaviour originates from the combination of a well-defined molecular spin ground state and strong magnetic anisotropy, which generates an energy barrier between oppositely oriented magnetic states. The microscopic origin of this barrier and the mechanisms through which the molecular magnetization can reverse will be discussed in the following sections [12].

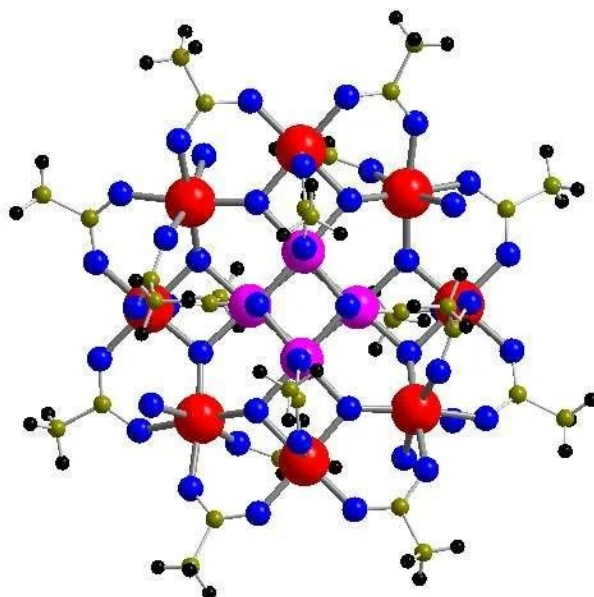


Figure 1.4: Molecular structure of the Mn_{12} -acetate cluster. Adapted from [13].

Historically, the development of molecular nanomagnetism was largely driven by the study of polynuclear transition-metal clusters. One of the most prominent examples is the Mn_{12} -acetate cluster (see Figure 1.4), first investigated as a molecular magnetic system by Sessoli, Gatteschi, and co-workers in the early 1990s [14, 15]. The molecule contains twelve manganese ions coupled through intramolecular exchange interactions, resulting in a high-spin ground state, while the surrounding ligand environment produces the magnetic anisotropy required for bistable behaviour.

Mn_{12} -acetate became a landmark system because it provided one of the earliest clear demonstrations of magnetic bistability and hysteresis originating from individual molecular units. It is therefore regarded as the prototypical SMM and has served as a model system for investigating the relationship between exchange in-

teractions, magnetic anisotropy, and quantum spin dynamics [13, 14].

1.2.1 The Zero-Field Splitting Hamiltonian and the Anisotropy Barrier

The magnetic anisotropy of a SMM originates from the combined effects of spin-orbit coupling and the electrostatic crystal field generated by the surrounding ligands. Within the giant-spin approximation, these interactions are incorporated into an effective spin Hamiltonian that acts on the ground spin multiplet of total spin S . In the absence of an external magnetic field, the magnetic anisotropy lifts the degeneracy of the spin multiplet, a phenomenon known as zero-field splitting. The most general second-order anisotropy contribution can be written as

$$\mathcal{H}_{ZFS} = \mathbf{S} \cdot \mathbf{D} \cdot \mathbf{S} \quad (1.13)$$

where $\mathbf{S} = (S_x, S_y, S_z)$ is the spin operator vector and $\mathbf{D}$ is the zero-field splitting (ZFS) tensor. The tensor $\mathbf{D}$ contains the information about the magnetic anisotropy induced by the molecular environment. Since $\mathbf{D}$ is a real symmetric tensor, it can always be diagonalized by choosing an appropriate set of principal magnetic axes. In this reference frame, the Hamiltonian assumes the form

$$\mathcal{H}_{ZFS} = D_{xx}S_x^2 + D_{yy}S_y^2 + D_{zz}S_z^2 \quad (1.14)$$

The isotropic contribution of the tensor merely shifts all energy levels by the same amount and therefore does not contribute to magnetic anisotropy. Thus, only the traceless part of the tensor is retained, imposing the condition

$$D_{xx} + D_{yy} + D_{zz} = 0 \quad (1.15)$$

It is convenient to express the anisotropy in terms of two phenomenological parameters: the axial anisotropy parameter D and the rhombic anisotropy parameter E , defined as

$$D = D_{zz} - \frac{D_{xx} + D_{yy}}{2} \quad ; \quad E = \frac{D_{xx} - D_{yy}}{2}. \quad (1.16)$$

Using the identity

$$S^2 = S_x^2 + S_y^2 + S_z^2 \quad (1.17)$$

and neglecting the constant term proportional to S^2 , the ZFS Hamiltonian can be rewritten in its conventional form which is widely employed in the description of molecular nanomagnets [1]:

$$\mathcal{H}_{ZFS} = DS_z^2 + E(S_x^2 - S_y^2) \quad (1.18)$$

The parameter D quantifies the axial magnetic anisotropy, whose sign determines whether the molecule prefers to align its magnetic moment along a specific axis (easy-axis anisotropy) or within a plane perpendicular to it (easy-plane anisotropy), while E describes deviations from perfect axial symmetry.

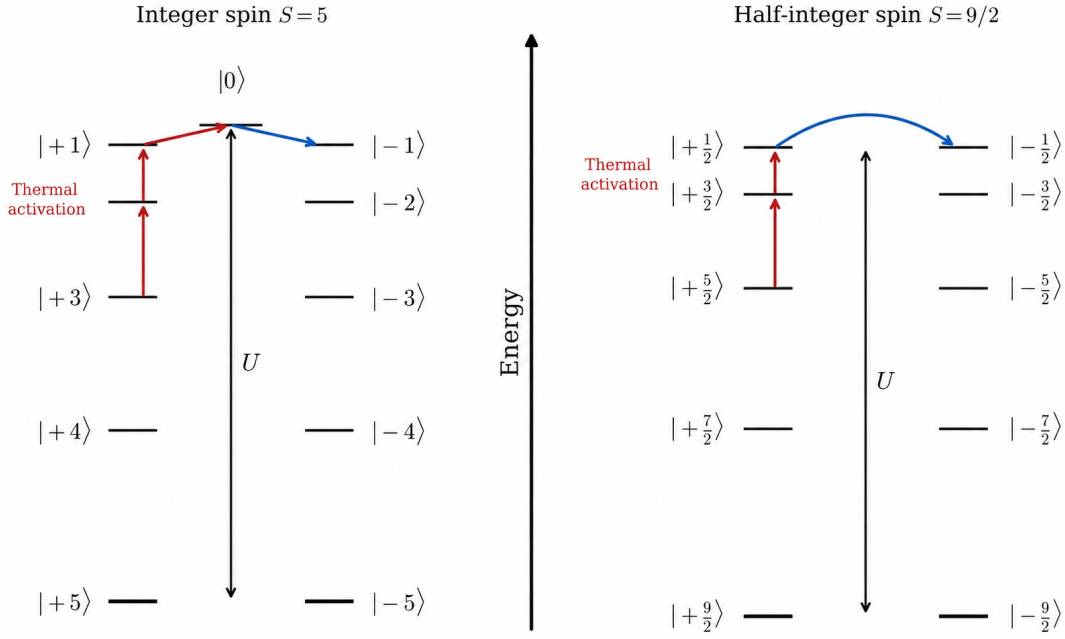


Figure 1.5: Energy level schemes generated by the axial zero-field splitting Hamiltonian ($E = 0$) for integer- and half-integer-spin systems with negative axial anisotropy ($D < 0$). The red arrows illustrate the thermally activated population of higher-lying spin states, whereas the blue arrows represent the subsequent transition between the two sides of the anisotropy barrier, corresponding to the magnetization reversal step.

For the moment, the discussion will be restricted to the ideal axial case ($E = 0$), which captures the essential physics of the anisotropy barrier. In this case, the system exhibits purely axial anisotropy and the spin projection quantum number m_S remains a good quantum number. In this case, the energy spectrum is simply given by:

$$E(m_S) = Dm_S^2 \quad (1.19)$$

For $D > 0$, the system exhibits easy-plane anisotropy and the lowest-energy states correspond to the smallest values of $|m_S|$. Such a level structure does not support magnetic bistability and is therefore generally unfavorable for SMM behavior.

Of particular interest for SMMs is the case $D < 0$, corresponding to easy-axis anisotropy. In this situation, the states with the largest spin projection along the quantization axis, $|+S\rangle$ and $|-S\rangle$, become the lowest-energy states of the spin multiplet. States with progressively smaller values of $|m_S|$ lie at higher energies, while the highest-energy state is found at $m_S = 0$ for integer spins or $m_S = \pm 1/2$ for half-integer spins. This distinction between integer and half-integer spin systems has important consequences for the degeneracy of their energy levels and their behaviour under time-reversal symmetry, as will be discussed in Section 1.4.1. The resulting energy level scheme is illustrated in Figure 1.5.

The anisotropy barrier corresponds approximately to the energy difference between the ground states $|+S\rangle$ and the top of the anisotropy-split spin multiplet. For

integer-spin systems, the anisotropy barrier approximately equals to [16–18]

$$U \simeq |D|S^2 \quad (1.20)$$

while for half-integer spin systems the barrier becomes

$$U \simeq |D|\left(S^2 - \frac{1}{4}\right) \quad (1.21)$$

In this framework, magnetization reversal can only occur by thermally overcoming the anisotropy barrier. Starting from one of the ground states, for example $|\pm S\rangle$, the molecule must absorb energy from lattice phonons and undergo a sequence of transitions through progressively higher-energy spin states. In the simplest approximation, spin–phonon interactions predominantly connect neighboring m_S levels ($\Delta m_S = \pm 1$) resulting in a sequential climb over the anisotropy barrier.

$$|+S\rangle \rightarrow |+S-1\rangle \rightarrow \cdots \rightarrow |0\rangle \quad (1.22)$$

After reaching the highest-energy region of the multiplet, the system can relax through the opposite branch of states,

$$|0\rangle \rightarrow |-1\rangle \rightarrow \cdots \rightarrow |-S\rangle \quad (1.23)$$

thereby reversing the direction of its magnetization. However, the discrete quantum nature of the spin system introduces additional relaxation pathways that bypass the energy barrier altogether, allowing magnetization reversal even when thermal activation is insufficient. These purely quantum processes form the basis of quantum tunneling of magnetization and will be discussed in the following section [12].

1.2.2 Quantum Tunneling

To appreciate the physics of SMMs, one must first reconcile the fundamental difference between how objects behave in our everyday classical world versus the subatomic quantum world.

Imagine a ball resting in a valley, separated from an adjacent valley by a steep hill. To move the ball to the other side, one must physically push it up and over the hill. If the ball is not given enough kinetic energy to reach the peak, it is strictly forbidden from crossing; it will simply roll back down and remain trapped in its original valley. In a conventional macroscopic magnet, this "push over the hill" is supplied by heat (thermal energy), which allows the magnetic moments to climb the anisotropy barrier and flip their orientation. In the quantum world, however, particles do not behave like hard, localized objects; they behave as delocalized probability waves.

Because of this wave-like nature, a quantum particle does not always need to climb over the energy hill to reach the adjacent valley. Instead, there is a finite, calculable probability that the particle can simply tunnel straight through the barrier, vanishing from one side and instantly reappearing on the other without ever occupying the peak of the hill (see Figure 1.6).

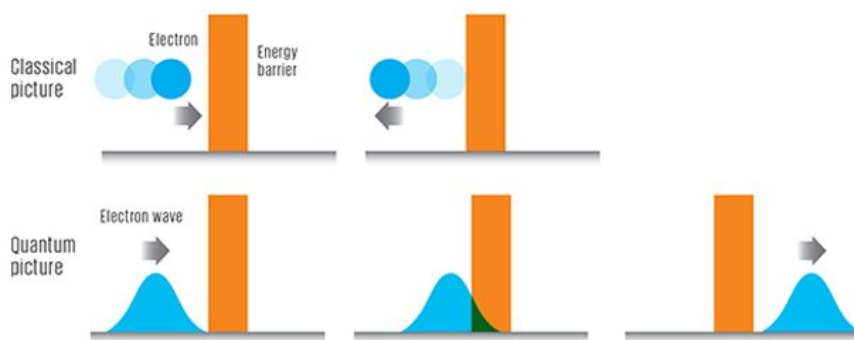


Figure 1.6: Schematic representation of the quantum tunneling effect. A particle with energy E encounters a potential barrier V_0 where $E < V_0$. According to classical mechanics, the particle would be reflected; however, the quantum mechanical wavefunction $\psi(x)$ decays exponentially within the barrier and maintains a non-zero amplitude on the opposite side, allowing for a finite probability of transmission.

When applied to molecular magnetism, the two valleys do not represent physical locations in space, but rather the two magnetic orientations of the molecule. The "hill" separating them is the magnetic anisotropy barrier (U). While a classical view predicts that a single-molecule magnet will remain indefinitely trapped in the "up" state at absolute zero temperature (where no thermal energy exists to climb the hill), the quantum reality is quite different. Through a phenomenon known as quantum tunneling of magnetization (QTM), the magnetic moment can cheat the barrier, tunneling directly through the energy hill to flip its orientation. This purely quantum mechanical leakage is the defining feature and, simultaneously, the central engineering dilemma of modern molecular magnetism [12, 15].

1.2.3 Transverse Anisotropy and Quantum Tunneling

The picture discussed in the previous section assumes purely axial anisotropy ($E = 0$), for which the spin projection quantum number m_s remains a good quantum number and the eigenstates of the system coincide with the states $|m_s\rangle$. In real molecules, however, perfect axial symmetry is rarely achieved. Small distortions of the coordination environment introduce a transverse anisotropy described by the rhombic term $E(S_x^2 - S_y^2)$. Using the spin ladder operators,

$$S_+ = S_x + iS_y \quad S_- = S_x - iS_y \quad (1.24)$$

this contribution can be rewritten as

$$E(S_x^2 - S_y^2) = \frac{E}{2} (S_+^2 + S_-^2) \quad (1.25)$$

The operators S_+^2 and S_-^2 connect states differing by two units of spin projection ($\Delta m_s = \pm 2$). As a consequence, the rhombic anisotropy couples states belonging to different m_s manifolds and mixes the eigenstates of the purely axial Hamiltonian [12]. In molecules possessing exact axial symmetry ($E = 0$), such couplings

vanish and tunneling between opposite magnetization states is strongly suppressed.

In the presence of this transverse interaction, m_S is no longer a conserved quantum number and the eigenstates of the system become quantum superpositions of different spin projections. The degeneracies predicted by the purely axial model are lifted and small energy gaps, known as tunnel splittings (Δ_T), appear between states that were previously degenerate. In most SMMs though, the transverse anisotropy is significantly smaller than the axial contribution ($|E| \ll |D|$), so the eigenstates remain largely dominated by a single spin-projection component and can still be conveniently labeled by the corresponding m_S value. Throughout the following discussion, the $|m_S\rangle$ basis will therefore be used as an approximate but physically meaningful description of the spin states even with the assumption of $E \neq 0$.

The appearance of these tunnel splittings opens a new magnetization relaxation channel. Instead of reaching the opposite magnetic orientation through thermal activation over the anisotropy barrier, the spin can undergo a direct quantum transition between states of opposite magnetization (QTM). This process allows magnetic reversal even when the available thermal energy is insufficient to overcome the barrier.

From a technological perspective, intrinsic QTM plays a dual role. For classical information storage it represents a detrimental leakage mechanism, since it enables spontaneous magnetization reversal and limits the magnetic memory lifetime. For quantum technologies, the same state mixing provides coherent superpositions of spin states, forming the physical basis for quantum manipulation and qubit implementations based on molecular nanomagnets [11, 19].

1.2.4 Field-Induced Resonant Quantum Tunneling

While transverse anisotropy provides the microscopic mechanism responsible for state mixing and tunnel splitting, an external magnetic field H_z applied along the easy axis can tune the energies of the spin states and bring them into resonance. When two levels become degenerate or nearly degenerate, the transverse anisotropy can efficiently couple them, leading to a dramatic enhancement of the tunneling probability. In this framework the full Hamiltonian must incorporate the Zeeman interaction:

$$\mathcal{H} = DS_z^2 + E(S_x^2 - S_y^2) + g\mu_B H_z S_z \quad (1.26)$$

The Zeeman term removes the degeneracy between states with opposite spin projections and shifts their energies linearly with the applied magnetic field. For $|E| \ll |D|$, the spin projection quantum number m_S remains a useful approximate quantum number and the energy levels can be written as

$$E(m_S) = Dm_S^2 + g\mu_B H_z m_S \quad (1.27)$$

As the magnetic field is varied, levels corresponding to different spin projections shift at different rates. Resonant tunneling is strongly enhanced whenever two levels satisfy the condition:

$$E(m_S) = E(m'_S) \quad (1.28)$$

which yields

$$D(m_S^2 - m'^2_S) + g\mu_B H_z(m_S - m'_S) = 0 \quad (1.29)$$

For $m_S \neq m'_S$, the resonance fields are therefore

$$H_z = -\frac{D}{g\mu_B}(m_S + m'_S) \quad (1.30)$$

The approximately regular spacing of these resonance fields gives rise to the equally spaced magnetization steps observed experimentally in many SMMs. Thus, level crossings occur only at discrete values of the applied field, generating a series of tunneling resonances characteristic of SMMs [12, 15].

Since the structural design of SMMs ensures that intermolecular interactions are negligible, this field-induced tunneling is a purely individual, single-molecule phenomenon. However, because the molecules within the crystal are structurally equivalent, they satisfy the resonance condition at nearly the same values of the applied field. It is this perfectly synchronized occurrence of independent quantum events across the entire non-interacting ensemble that allows the tunneling to manifest as a distinctly observable step in the macroscopic magnetization dynamics.

Instead of a smooth hysteresis curve typical of bulk ferromagnets, SMMs subjected to a swept magnetic field exhibit a characteristic discontinuous loop. The flat plateaus on the hysteresis loop represent regions where the spin is kinetically trapped and classical behavior dominates. The sharp, vertical steps correspond to resonance fields at which QTM is strongly enhanced, producing an abrupt, non-thermal relaxation of the magnetization. Thus, QTM can be systematically mapped and manipulated not only through synthetic chemistry (tuning the E parameter) but also through external physical perturbations.

This behavior was reported for the Mn_{12} -acetate cluster [15] (see the original hysteresis curve in Figure 1.7).

1.2.5 Mn_{12} -Acetate: The Prototypical Single-Molecule Magnet

The theoretical frameworks of zero-field splitting and quantum tunneling converge perfectly in the study of the Mn_{12} -acetate cluster, widely considered the prototypical SMM. First studied in depth by Sessoli et al. [14, 15] in the early 1990s, the complex – whose chemical formula is $[\text{Mn}_{12}\text{O}_{12}(\text{CH}_3\text{COO})_{16}(\text{H}_2\text{O})_4] \cdot 2\text{CH}_3\text{COOH} \cdot 4\text{H}_2\text{O}$ – provided the first direct experimental evidence of a purely molecular origin for the magnetic hysteresis.

The magnetic core of the molecule consists of 12 manganese ions: an inner tetrahedron of four Mn^{4+} ions (spin $S = 3/2$) antiferromagnetically coupled to an outer

ring of eight Mn^{3+} ions (spin $S = 2$). This specific topology and exchange couplings stabilize a collective ground state with a large ground-state spin of $S = 10$. The Mn^{3+} ions experience a strong Jahn-Teller distortion due to the surrounding ligand field, which imparts a strong axial, easy-axis magnetic anisotropy ($D < 0$) to the entire molecule. The combination of a large ground state spin and strong axial anisotropy produces a significant energy barrier for spin reversal, which in the axial approximation is approximately given by $U_{\text{eff}} \simeq |D|S^2$ [13, 14].

When this system is studied at very low temperatures, the thermal energy in the lattice is insufficient for the magnetization to climb this barrier. Instead, the magnetization relaxation dynamics are dominated by field-induced resonant QTM [15].

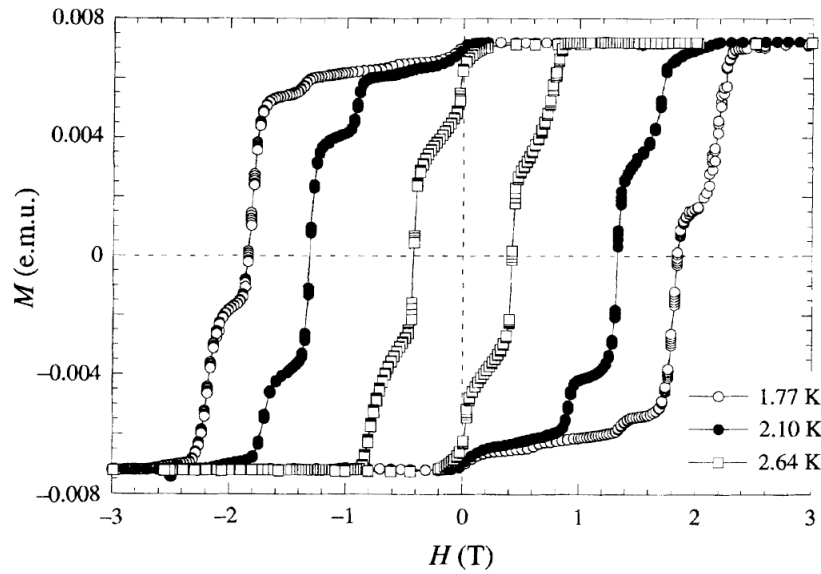


Figure 1.7: Low-temperature $M - H$ loop for a single crystal of Mn_{12} -acetate. Unlike the smooth curves of bulk ferromagnets, the sharp transitions (steps) indicate that the magnetization relaxes via discrete quantum tunneling events rather than purely classical thermal activation. Adapted from [15].

As shown in Figure 1.7, the $M - H$ hysteresis loop of a Mn_{12} -acetate single crystal does not exhibit the smooth curve typical of bulk ferromagnets. Instead, it features a series of sharp discontinuities occurring at regular field intervals of approximately 0.44 T. These discontinuities correspond to the resonant transition fields where the quantum spin levels on opposite sides of the anisotropy barrier are brought into energetic alignment by the Zeeman effect [15, 20].

1.3 Quantum Decoherence in Single-Molecule Magnets

The SMMs are ideal candidates for the creation of a qubit system. Quantum superposition of their spin states can be exploited to implement logic operations, while their well-defined energy levels provide a useful platform for quantum coherence

manipulation. Although a classical memory only requires a bistable magnetic state to encode binary information, the realization of a functional qubit requires instead the preservation of quantum coherence and the ability to perform precise control over superpositions of these states [11, 19, 21].

The main sources of quantum decoherence are the spurious interactions between the core and the nuclear spins of the surrounding ligand matrix and the influence of fluctuating magnetic environments, which lead to a rapid loss of phase information. Even if a molecule is chemically isolated from other molecules, its spin can interact with phonons and lose coherence. This phenomenon can be broken down as the sum of several phenomena [11, 22, 23].

- Hyperfine interaction: the nuclear spins within the molecule create an environment of magnetic noise that acts as a decoherence source, coupling the electronic spin to the nuclear spin bath [22, 23].
- Dipolar interaction: long-range magnetic interactions between neighboring molecular units in the crystal lattice create a fluctuating dipolar field that accelerates the dephasing process, thereby limiting the operational lifetime of quantum states [22–24].
- Spin-lattice relaxation: phonons within the crystal lattice induce transitions between magnetic levels, causing energy dissipation that shortens the phase coherence time of the molecular spin system [25, 26]. This spin–phonon coupling introduces significant energy relaxation and phase decoherence channels, fundamentally constraining the coherence times necessary for high-fidelity quantum information processing.

The decoherence mechanisms described above ultimately manifest themselves through the relaxation dynamics of the molecular spin system. In particular, interactions with lattice vibrations provide one of the principal pathways through which the spin exchanges energy with its environment, leading to the loss of magnetic memory and quantum coherence. A quantitative description of these processes is therefore essential for understanding the performance limits of SMMs. The relaxation rate can be expressed as the sum of several independent contributions, each associated with a distinct microscopic mechanism [25, 26].

Spin-lattice relaxation rate

Among the decoherence channels discussed above, spin-lattice interactions play a central role in determining the magnetic relaxation dynamics of SMMs. A quantitative description of these processes is therefore essential for understanding the loss of magnetic memory and quantum coherence. Following the framework proposed by Liddle and van Slageren [25], the relaxation rate τ^{-1} can be expressed as the sum of several independent contributions arising from different microscopic mechanisms. The general equation used to fit experimental data is:

$$\tau^{-1} = \underbrace{\tau_{\text{QTM}}^{-1}}_{\text{QTM}} + \underbrace{AH^{n_1}T}_{\text{Direct}} + \underbrace{CT^{n_2}}_{\text{Raman}} + \underbrace{\tau_0^{-1} \exp(-\Delta_{CF}/k_B T)}_{\text{Orbach}} \quad (1.31)$$

Here A , C and τ_0^{-1} are parameters that can be particularly difficult to compute by first-principles, so are usually taken as free fit parameters [25, 26].

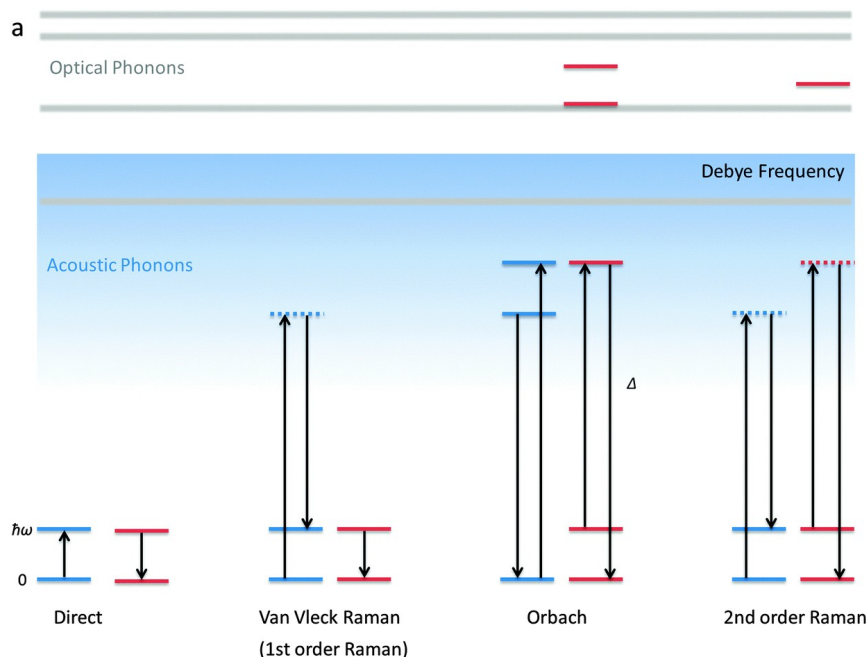


Figure 1.8: *Schematic representation of the multiple phonon-related relaxation pathways available in a single-molecule magnet. Adapted from [25].*

Let us now focus on each term and describe it in detail. All the processes involving phonons are represented in Figure 1.8.

- The direct process is a one-phonon absorption process leading to a transition between spin levels subject to the overall conservation of energy. It has a linear dependence on temperature. For ions with integer total spin $n_1 = 2$ if the levels are degenerate in zero-field, while for ions with half-integer total spin $n_1 = 4$ due to "Van Vleck cancelation", which states that the transition matrix element must be zero for time-reversal conjugate states unless a magnetic field is applied [25, 26].
- The Raman process is a two-phonon process involving a virtual intermediate state in which one phonon is absorbed and another is emitted, with the frequency difference matching the spin transition energy. The exponent n_2 varies depending on the nature of the metallic ion: $n_2 = 7$ for ions with integer total spin and $n_2 = 9$ for ions with half-integer total spin [25, 26].
- The Orbach process is yet another two-phonon process, but it occurs via a real, excited crystal field state. The spin absorbs a phonon to reach an excited state and then it emits a phonon to fall into the other ground-state well. Δ represents the energy gap to the first excited state, and τ_0 is the attempt time (typically 10^{-7} to 10^{-12} s) [26]. This process dominates at higher temperatures where enough thermal energy exists to climb over the barrier [25, 26].

- Unlike the previous three processes, QTM is not governed by phonons. In its simplest form at very low temperatures, it is temperature-independent. It is highly sensitive to external factors like dipolar couplings and nuclear spins. When it occurs via an excited state, it is dubbed thermally-assisted QTM [1, 12, 25].

While decoherence and magnetic relaxation represent fundamental limitations to the preservation of quantum information, they are not the only obstacles preventing the practical implementation of SMMs as qubits. Even in the ideal case of long coherence times, a functional quantum device requires the ability to selectively initialize, manipulate, and read the quantum state of an individual molecule within a macroscopic ensemble. These requirements form part of the broader DiVincenzo criteria for the physical implementation of quantum computation, which also include scalability, well-characterized qubits, universal quantum control, and coherence times sufficiently long compared with the duration of quantum operations [27]. In the specific context of molecular spin qubits, Coronado and Bogani emphasize the central role of coherent control and quantum-state readout [11]. Addressing an individual molecule within a macroscopic ensemble requires its spin transitions to be spectroscopically distinguishable from those of the surrounding molecules. However, small variations in the local environment can shift and broaden the resonance frequencies, making selective manipulation and readout more difficult [11, 22, 23].

Reading the state of a single molecular qubit remains a significant challenge. Techniques such as micro-SQUID and scanning tunneling microscopy have demonstrated single-molecule sensitivity in laboratory settings, but their integration into scalable solid-state architectures remains difficult because of the need to interface organic molecules with conventional semiconductor technology.

Likewise, coherent control of molecular spin states requires the ability to selectively manipulate individual qubits. Although magnetic fields are routinely employed for this purpose, they are difficult to localize and to switch rapidly. Consequently, considerable effort is being devoted to developing electrically addressable molecular qubits, where spin states can be controlled through electric-field pulses [11, 28].

Furthermore, the integration of molecular spins with superconducting circuits or nanophotonic cavities offers a promising pathway to bridge the gap between individual molecular control and scalable quantum device architectures. In this context, the quantum tunneling effect can be seen as a double-edged sword [11, 12, 21]:

- It allows the implementation of quantum gates in molecular nanomagnets by enabling coherent transitions between spin states, even when direct transitions are forbidden by selection rules.
- If the tunneling rate is not precisely controlled, it induces uncontrollable transitions between spin levels, which accelerates the loss of phase memory and compromises the stability of stored quantum information.

The actual challenge of molecular magnetism is not only to increase the blocking temperature of our samples but also to engineer molecules that are magnetically silent in respect to the surrounding bath of nuclear spins, thereby minimizing decoherence and enabling longer phase-memory times [22, 23].

1.4 Single-Ion Magnets

The discussion presented so far has mainly focused on polynuclear single-molecule magnets, in which several magnetic ions are coupled through intramolecular exchange interactions to generate a collective molecular spin. Within the broader class of SMMs, a conceptually distinct approach is represented by single-ion magnets (SIMs). These are mononuclear coordination complexes in which slow magnetic relaxation and magnetic bistability originate predominantly from the magnetic anisotropy of a single metal ion [25, 26].

The development of SIMs marked an important change in the design strategy of molecular nanomagnets. In conventional polynuclear SMMs, a large molecular spin is obtained by coupling several transition-metal ions. However, a large total spin does not by itself guarantee a high barrier to magnetization reversal [16, 18, 29]. Although the barrier is often expressed within the giant-spin approximation as $U \simeq |D|S^2$, the molecular anisotropy parameter D is not independent of S . In exchange-coupled clusters, it results from the projection of the local single-ion anisotropies onto the collective ground-state multiplet and may be reduced by non-collinear local anisotropy axes [16, 17].

Furthermore, finite exchange interactions can mix states belonging to different spin multiplets, while low-lying excited states may provide additional pathways for magnetization reversal. These effects make the relationship between molecular nuclearity, total spin, and the effective relaxation barrier considerably more complex than suggested by the simple $|D|S^2$ expression [17].

In a SIM, by contrast, the magnetic moment and the anisotropy are concentrated at a single metal centre. The absence of a polynuclear magnetic core removes the need to engineer exchange interactions between several ions and allows the magnetic energy-level structure to be controlled more directly through the coordination environment. Mononuclearity alone does not necessarily produce stronger magnetic behaviour; rather, its main advantage is that the intrinsic properties of a highly anisotropic ion can be exploited without requiring the formation of a collective exchange-coupled spin state [25, 29, 30].

This approach is particularly effective for complexes containing lanthanide ions. In contrast to many transition-metal ions, the orbital angular momentum of the 4f electrons is largely unquenched. The strong spin-orbit coupling therefore combines the spin and orbital contributions into a total angular momentum $\mathbf{J}$, which can assume a large value and consequently generate a large magnetic moment. At the same time, the interaction between the anisotropic 4f-electron density and the

surrounding crystal field can produce a pronounced preference for the orientation of the magnetic moment [25, 26, 30].

The shielding of the $4f$ orbitals by the filled $5s$ and $5p$ shells largely preserves the free-ion character of the lanthanide, while the coordination environment still produces a splitting of the different m_J components of the ground-state multiplet [25, 26]. For an appropriate ion and coordination geometry, a favourable crystal field can stabilize a doubly degenerate ground state characterized by a large value of $|m_J|$ and separate it substantially from the first excited states. The combination of a large ground-state magnetic moment, strong axial anisotropy, and a large energy separation from the excited states is particularly favourable for suppressing magnetization reversal [30, 31].

The historical emergence of lanthanide SIMs can be traced to the work of Ishikawa and co-workers, who reported in 2003 that mononuclear bis(phthalocyaninato) complexes exhibit slow magnetic relaxation [32]. These compounds consist of a single lanthanide ion located between two approximately parallel phthalocyanine ligands, forming a double-decker or sandwich-like coordination geometry. The ligand environment generates a strongly axial crystal field, which favours high- $|m_J|$ states for ions with an oblate $4f$ -electron density, particularly Tb^{3+} and Dy^{3+} [30, 32].

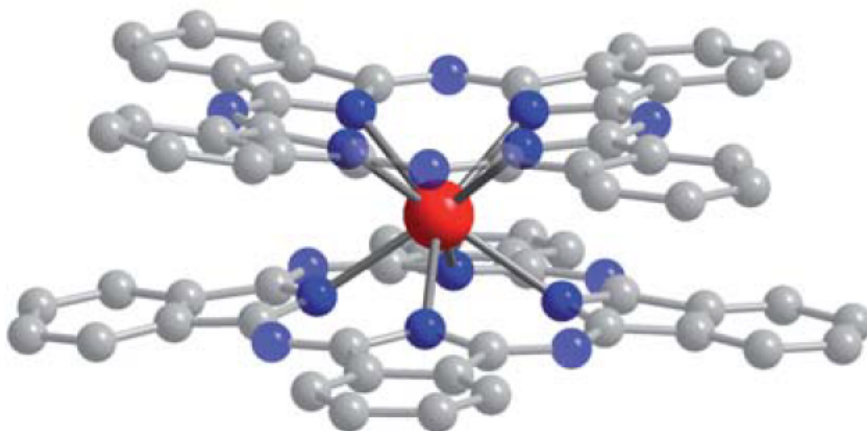


Figure 1.9: *Molecular structure of the terbium bis(phthalocyaninato) complex $[\text{TbPc}_2]^-$, belonging to the first family of lanthanide-based single-ion magnets reported by Ishikawa and co-workers [32]. Adapted from [30].*

These complexes are widely regarded as the first lanthanide-based SIMs and demonstrated that a substantial anisotropy barrier could originate from an individual metal ion without requiring a polynuclear high-spin cluster. Their discovery redirected a significant part of molecular-magnetism research towards the rational design of the coordination environment surrounding a single lanthanide centre [26, 30, 32].

Among the lanthanides, Dy^{3+} is particularly attractive for the realization of SIM behaviour. Its ground multiplet is described by the term symbol $^6H_{15/2}$, corresponding

to $J = 15/2$, and combines a large magnetic moment with a strongly anisotropic $4f$ -electron density. Moreover, Dy^{3+} is a Kramers ion, so that every crystal-field level remains at least doubly degenerate in the absence of an applied magnetic field [26, 30, 31]. The role of Kramers degeneracy and of the crystal-field environment in determining the magnetic properties of lanthanide SIMs will therefore be examined before introducing the specific dysprosium complexes investigated in this thesis.

1.4.1 Kramers Theorem and Kramers Ions

Talking about the relaxation time in previous paragraphs, it was made clear that some properties and behaviors depend on whether the metal ion in our sample is characterized by an even or an odd number of electrons occupying the active electronic shell. This leads straightforwardly to the definition of Kramers ions. In order to introduce them, it is necessary to state Kramers' theorem and to show the consequences of its statements:

"For a quantum system with an odd number of fermions (half-integer total spin) that is invariant under time-reversal symmetry, every energy eigenstate is at least doubly degenerate, provided no magnetic field is present"

The fundamental proof of Kramers' theorem rests on the properties of the time-reversal operator, Θ . For any electronic system, Θ can be written as the product of a unitary operator U and the complex conjugation operator K (i.e., $\Theta = UK$). A standard property of angular momentum dictates that applying time-reversal twice to a state $|\psi\rangle$ yields:

$$\Theta^2|\psi\rangle = (-1)^{2S}|\psi\rangle \quad (1.32)$$

For a system with an odd number of electrons (a half-integer total spin, S), $2S$ is an odd integer, yielding the identity:

$$\hat{\Theta}^2 = -1 \quad (1.33)$$

Now, consider a time-reversal symmetric Hamiltonian $\mathcal{H}$ in the absence of an external magnetic field, such that $[\mathcal{H}, \Theta] = 0$. Let $|\psi\rangle$ be a non-zero eigenstate of $\mathcal{H}$ with a real energy eigenvalue E :

$$\mathcal{H}|\psi\rangle = E|\psi\rangle \quad (1.34)$$

Because the Hamiltonian and the time-reversal operator commute, the time-reversed state $\Theta|\psi\rangle$ is also an eigenstate with the exact same energy E :

$$\mathcal{H}(\Theta|\psi\rangle) = \Theta\mathcal{H}|\psi\rangle = \Theta E|\psi\rangle = E(\Theta|\psi\rangle) \quad (1.35)$$

To prove that the energy level E is at least doubly degenerate, one must prove that $|\psi\rangle$ and $\Theta|\psi\rangle$ are physically distinct, orthogonal states. Assuming they are the same state leads to the conclusion that they must be proportional to each other by some complex scalar c :

$$\Theta|\psi\rangle = c|\psi\rangle \quad (1.36)$$

Applying the time-reversal operator a second time to both sides yields:

$$\Theta^2|\psi\rangle = \Theta(c|\psi\rangle) \quad (1.37)$$

Because Θ is anti-unitary and contains the complex conjugation operator K , it conjugates the scalar c when applied to its eigenstates:

$$\Theta^2|\psi\rangle = c^*\Theta|\psi\rangle \quad (1.38)$$

Substituting the initial assumption ($\Theta|\psi\rangle = c|\psi\rangle$) into the right-hand side gives:

$$\Theta^2|\psi\rangle = c^*c|\psi\rangle = |c|^2|\psi\rangle \quad (1.39)$$

Equating this to the fundamental identity for fermions ($\Theta^2 = -1$):

$$-|\psi\rangle = |c|^2|\psi\rangle \quad \Rightarrow \quad |c|^2 = -1 \quad (1.40)$$

Since the absolute square of a complex number cannot be negative, this is a mathematical contradiction. Therefore, the initial assumption is false: the state $|\psi\rangle$ and its time-reversed partner $\Theta|\psi\rangle$ cannot be the same state. They are distinct orthogonal states that share the same energy E . Hence, every energy level for an odd-electron system is at least doubly degenerate leading to the generation of the so-called Kramers' doublet.

Ions can now be split into two different groups [25, 26, 30]:

- Kramers' ions (half-integer overall spin): even in the presence of a strong electric crystalline field with a non-zero rhombic term, the energy levels remain coupled. In doublets a magnetic field will split them, and a microwave radiation will find the right frequency to induce transitions. QTM at zero field ($H = 0$) is theoretically prohibited but a small hyperfine magnetic interaction from the nucleus could be enough to make transitions possible.
- Non-Kramers' ions (integer overall spin): Since the levels can be split by the crystalline field, a microwave radiation could not be sufficient to induce the transition due to the high energy difference between the ground state and the first excited state. Since the states can easily mix, this makes QTM highly efficient, often leading to a rapid loss of magnetization at zero field.

1.4.2 Stevens Operators and Total Angular Momentum J

While the magnetism of transition metal clusters, such as the Mn_{12} complex, can be effectively described using the total spin operator S , the physics of lanthanide-based SIMs requires a shift to the total angular momentum representation J .

In 3d transition metals, the valence electrons are spatially extended and interact strongly with the surrounding ligands, leading to a crystal field effect that is much

larger than the spin-orbit coupling (SOC). This results in the partial or even complete quenching of the orbital angular momentum ($L \approx 0$), making the spin-only Hamiltonian a useful approximation for many transition-metal complexes [25, 26, 30].

In contrast, the $4f$ electrons in lanthanides like Dy^{3+} are deeply buried and shielded by the filled $5s^2$ and $5p^6$ outer shells. This shielding ensures that the SOC ($\lambda L \cdot S$) is significantly stronger than the crystal field interaction. L and S are no longer independent; they couple to form a total angular momentum $J = L + S$ [25, 26, 30].

For Dy^{3+} , the ground state multiplet is defined by Hund's rules as ${}^6H_{15/2}$, giving a total $J = 15/2$ [30, 31]. Mathematically, the Hamiltonian for such a system must be expressed using Stevens operator equivalents (O_k^q) rather than the simple S_z^2 terms used for Mn_{12} [1, 33].

$$\mathcal{H}_{\text{CF}} = \sum_{k,q} B_k^q O_k^q(J) \quad (1.41)$$

Stevens operators are polynomial functions of the total angular momentum operators (J_z, J_+, J_-). They are used to replace the complex electrostatic potential energy terms of the crystal field with equivalent quantum mechanical operators that act directly on the $|J, m_J\rangle$ states of the ground multiplet [1, 33].

The indices k and q represent the rank and order of the operator:

Rank (k): For lanthanides, k is limited to even integers ($k = 2, 4, 6$) due to the parity of the f -orbitals. The higher the rank, the more fine-grained the interaction between the electron density and the ligands.

Order (q): This describes the angular symmetry. $q = 0$ terms represent axial interactions, while $q \neq 0$ terms represent transverse (rhombic) interactions [1, 30].

The most powerful aspect of Stevens operators is that they are strictly governed by the point group symmetry of the molecule:

- High axial symmetry. In a perfectly axial environment (like a linear or high-order rotation axis), most $q \neq 0$ terms are forced to zero by symmetry. This minimizes state-mixing and suppresses quantum tunneling of magnetization, leading to a higher energy barrier.
- Geometric distortions. Any deviation from ideal symmetry (rhombic distortion) activates transverse operators like O_2^2 or O_4^4 . Mathematically, these operators have non-zero off-diagonal matrix elements, meaning they mix states with different m_J values (e.g., mixing $|+15/2\rangle$ with $|+11/2\rangle$). This mixing creates shortcuts through the anisotropy barrier, facilitating QTM and accelerating the relaxation of magnetization [1, 30, 31].

By determining the Stevens parameters (B_k^q) through experimental techniques like EPR, magnetometry, luminescence or via *ab-initio* calculations, we can directly correlate the physical shape of any complex with its magnetic performance [26, 31].

1.5 The Dysprosium–Semiquinonate Complex

1.5.1 Molecular Structure and Coordination Environment

The molecular compound investigated in the present work is $\text{Dy}(\text{DTBSQ})(\text{HBPz}_3)_2$ (see Figure 1.10), hereafter denoted as Dy–SQ. In this formula, HBPz_3 denotes the hydrotris(pyrazolyl)borate ligand, whereas DTBSQ denotes the 3,5-di-*tert*-butyl-semiquinonato ligand. Dy–SQ is a mononuclear dysprosium complex whose magnetic response is strongly influenced by the single-ion anisotropy of the Dy^{3+} centre. However, the molecule also contains a ligand-centred paramagnetic radical, and its low-energy magnetic properties cannot therefore be described solely in terms of an isolated dysprosium ion [34, 35].

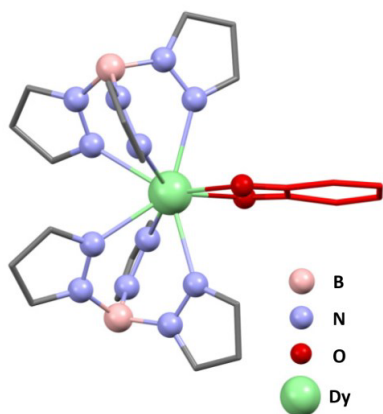


Figure 1.10: *Molecular structure of Dy–SQ. Adapted from [35].*

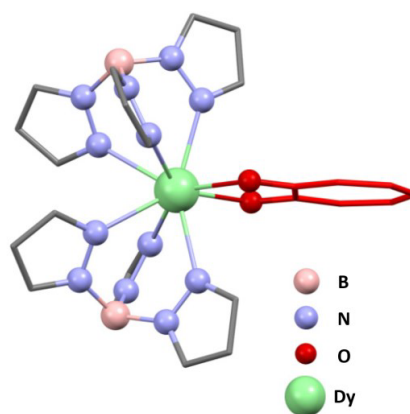


Figure 1.11: *Molecular structure of Dy–Trp. Adapted from [35].*

Previous crystallographic investigations showed that the lanthanide semiquinonato derivatives belong to a homologous series that is isomorphous with the structurally characterized yttrium analogue [34]. In this molecular structure, the metal ion is eight-coordinate: six nitrogen atoms are provided by two tridentate hydrotris-(pyrazolyl)borate ligands, while the remaining two coordination sites are occupied by the oxygen atoms of the bidentate semiquinonato ligand. The resulting coordination environment was described as a slightly distorted square antiprism (see Figure 1.13) [34].

The crystallographic analysis also revealed relatively large separations between neighbouring molecular magnetic centres. In the structural model of the homologous series, the shortest metal–metal distance is approximately 9.84 Å, while the distance between parallel semiquinonato planes is approximately 12.2 Å [34]. These large intermolecular separations support a description in which the most relevant magnetic interaction is the intramolecular coupling between the dysprosium ion and the radical ligand, rather than a direct exchange interaction between neighbouring molecules [34, 35].

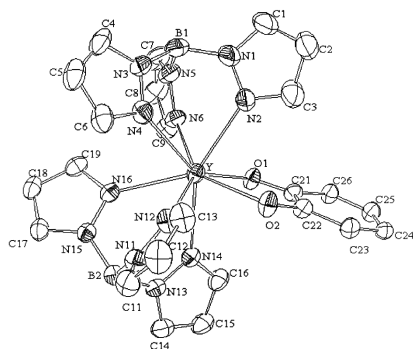


Figure 1.12: Representation of the molecular structure of Y-SQ. Adapted from [34].

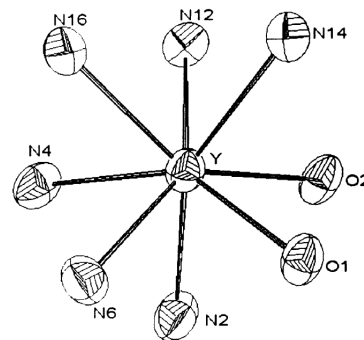


Figure 1.13: Eight-coordinate environment of the yttrium ion. Adapted from [34].

1.5.2 The Semiquinonato Radical and the Dy-Radical Interaction

The semiquinonato ligand is not merely a structural component of the coordination sphere. It is a paramagnetic radical carrying one unpaired electron with spin $s = 1/2$. The radical spin can interact with the strongly anisotropic magnetic moment of Dy^{3+} through an intramolecular exchange interaction. The magnetic response of Dy-SQ therefore results from the interplay between the crystal-field splitting of the dysprosium ground multiplet and the coupling between the lanthanide magnetic moment and the ligand-centred spin [34, 35].

Although Dy-SQ is naturally discussed in the context of SIMs because it contains a single metallic magnetic centre with strong single-ion anisotropy, it is not an ideal isolated single-ion system. The additional spin carried by DTBSQ modifies the molecular energy-level structure and introduces magnetic relaxation pathways that would not be present in a complex containing only the crystal-field-split states of Dy^{3+} [25, 35].

The interpretation of the magnetic interaction is particularly complex in lanthanide compounds. The strong orbital contribution and spin-orbit coupling of Dy^{3+} produce a highly anisotropic magnetic moment, while the energy scale of the exchange interaction may be comparable to that of the crystal-field splitting. As a consequence, changes in magnetic susceptibility may originate from exchange coupling, thermal depopulation of crystal-field levels, or a combination of both effects. The two contributions cannot generally be separated quantitatively using magnetic measurements on polycrystalline samples alone [34, 35].

1.5.3 Dysprosium–Tropolonate as a Diamagnetic Reference

To address this difficulty, previous investigations introduced the structurally related compound $\text{Dy}(\text{Trp})(\text{HBPz}_3)_2$, hereafter denoted as Dy-Trp [35] (see Figure 1.11). In this complex, the paramagnetic semiquinonato ligand is replaced by a diamagnetic tropolonate ligand. The term diamagnetic refers only to the tropolonate lig-

and, since the complete Dy–Trp molecule remains paramagnetic because it still contains a Dy³⁺ ion.

Dy–SQ and Dy–Trp exhibit closely related molecular coordination environments around the lanthanide centre, although differences in their crystal packing and small geometrical distortions are present [34, 35]. Since Dy–Trp does not contain an additional ligand-centred spin, its magnetic response can be used as an experimental reference for estimating the contribution associated with the crystal-field-split dysprosium ion.

This comparison is an example of the diamagnetic-substitution method. Within this approach, the magnetic properties of the radical-containing complex are compared with those of a structurally similar complex in which the radical has been replaced by a diamagnetic ligand. The difference between the two magnetic responses can then be attributed, at least qualitatively, to the radical spin and to its exchange interaction with the lanthanide ion [34, 35]. Dy–Trp was not investigated experimentally in the present thesis, but the data previously reported for this compound provide an important reference for the interpretation of Dy–SQ.

1.5.4 Magnetic Properties Reported in the Literature

The magnetic properties of Dy–SQ and Dy–Trp were previously investigated through temperature-dependent susceptibility and field-dependent magnetization measurements [35] (see Figure 1.14). The contribution associated with the radical was examined by considering the difference

$$\Delta(\chi T) = (\chi T)_{\text{Dy-SQ}} - (\chi T)_{\text{Dy-Trp}} \quad (1.42)$$

At high temperatures, $\Delta(\chi T)$ was found to be approximately

$$\Delta(\chi T) \simeq 0.38 \text{ emu K mol}^{-1} \quad (1.43)$$

This value is in good agreement with the Curie contribution expected for an approximately uncoupled spin-1/2 radical. Furthermore, the difference remained nearly constant down to approximately 100 K. Within the assumptions of the diamagnetic-substitution method, this behaviour indicates that the crystal-field contributions in Dy–SQ and Dy–Trp are sufficiently similar in this temperature range and that the dysprosium and radical magnetic moments behave approximately as independent contributions [35].

Below approximately 100 K, $\Delta(\chi T)$ progressively decreases from the value expected for an isolated radical. This deviation indicates that the interaction between the semiquinonato spin and the dysprosium magnetic moment becomes increasingly relevant as the thermal population of the excited crystal-field levels is reduced. The observed decrease was interpreted as evidence for a dominant antiferromagnetic contribution to the Dy–radical exchange interaction [35].

Independent evidence for the sign of the interaction was obtained from low-temperature magnetization measurements. At 2.5 K, the magnetization curve of Dy–SQ was found to remain below that of Dy–Trp throughout the investigated field range. If the radical and dysprosium moments were independent, the presence of the additional spin-1/2 radical would instead be expected to increase the total magnetization. The experimentally observed reduction therefore supports an antiferromagnetic alignment between the dysprosium magnetic moment and the semiquinonato spin [35].

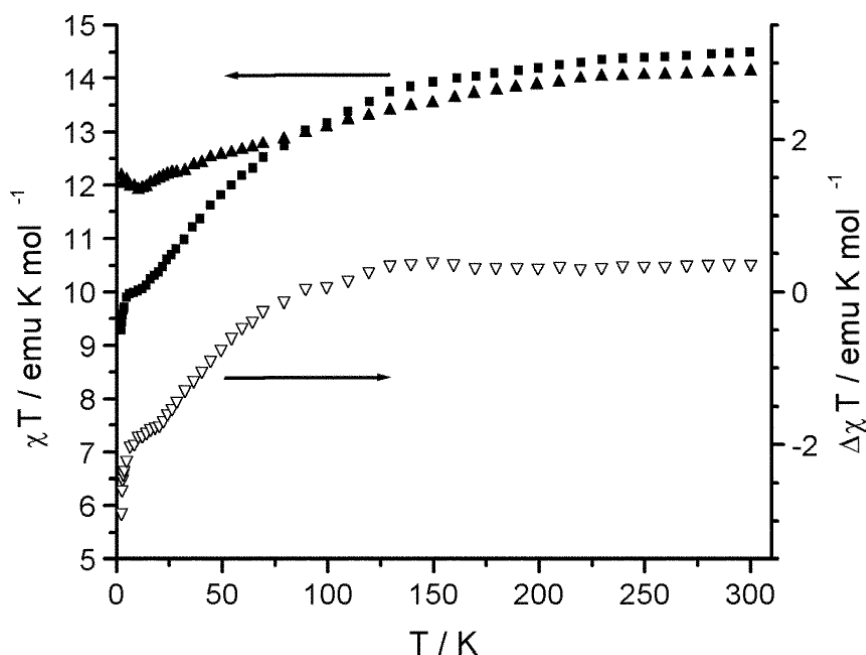


Figure 1.14: χT vs. T curves for $\text{Dy}(\text{DTBSQ})(\text{HBPz}_3)_2$ (■) and $\text{Dy}(\text{Trp})(\text{HBPz}_3)_2$ (▲), and corresponding $\Delta\chi T = (\chi T)_{\text{DySQ}} - (\chi T)_{\text{DyTrp}}$ curve (▽). Adapted from [35].

The antiferromagnetic contribution observed in the semiquinonato series was reported to be more pronounced than in several rare-earth complexes containing nitronyl-nitroxide radicals. This difference was associated with the stronger donor character of the semiquinonato oxygen atoms and with the comparatively larger covalent contribution to the lanthanide–ligand interaction [34, 35]. A stronger overlap between the ligand magnetic orbital and the orbitals of the metal centre may enhance the antiferromagnetic exchange pathway.

This microscopic interpretation should nevertheless be regarded as qualitative. The magnetic response of an anisotropic lanthanide complex depends simultaneously on the crystal-field eigenstates, the orientation of their magnetic moments, and the isotropic and anisotropic components of the exchange interaction. In the absence of single-crystal anisotropic measurements or an independent determination of the crystal-field parameters, the susceptibility and magnetization data do not allow a unique exchange tensor or exchange constant to be extracted [34, 35].

1.5.5 Motivation for the Present Investigation

Previous magnetometric and spectroscopic investigations therefore establish two central features of Dy–SQ. First, the Dy³⁺ centre retains a strongly anisotropic, crystal-field-split magnetic response. Second, the semiquinonato radical is an active magnetic component that modifies the low-energy behaviour of the molecule through a predominantly antiferromagnetic intramolecular interaction [34, 35].

Bulk magnetic measurements provide evidence for the sign of the Dy–radical interaction and characterize the macroscopic magnetic response of the system, but they offer limited information on the spatial distribution of the local magnetic fields and on the characteristic timescales of the electronic fluctuations. For this reason, the present work combines DC SQUID magnetometry with two complementary local-probe techniques, namely nuclear magnetic resonance (NMR) and muon spin spectroscopy (μ SR).

SQUID magnetometry provides the temperature and field-dependent bulk magnetic response of Dy–SQ and establishes a macroscopic reference for the interpretation of its magnetic ground state and anisotropy. NMR probes the static and time-dependent local magnetic fields experienced by the protons in the ligand environment, providing information on the electronic spin dynamics through the nuclear resonance and relaxation processes [36, 37]. Muon spin spectroscopy provides an additional microscopic probe of the internal magnetic-field distribution and of the electronic fluctuations over a complementary dynamical range [38–40].

The combined analysis of SQUID, NMR, and μ SR measurements therefore enables a more comprehensive investigation of the static and dynamic magnetic properties of Dy–SQ than could be obtained from any single technique. All original experimental results presented in the following chapters refer exclusively to Dy–SQ and aim to clarify how the anisotropic dysprosium moment and its interaction with the semiquinonato radical determine the bulk magnetic response, the local magnetic environment, and the spin-relaxation dynamics.

Concluding Remarks

This chapter established the theoretical framework required to describe molecular magnetic systems, beginning with the microscopic origin of localized magnetic moments and the interactions responsible for conventional magnetic behaviour. The discussion then moved to single-molecule magnets and single-ion magnets, highlighting the roles of exchange interactions, crystal-field effects, magnetic anisotropy, magnetization reversal, and quantum decoherence. These concepts were finally applied to the Dy–SQ complex, whose magnetic properties are determined by the interplay between the anisotropic Dy³⁺ ion and the semiquinonato radical. Having introduced the physical system investigated in this work, the following chapter presents the theoretical and experimental foundations of nuclear magnetic resonance, one of the local-probe techniques employed to investigate its magnetic environment and spin dynamics.

Chapter 2

Nuclear Magnetic Resonance

Nuclear magnetic resonance is a local-probe technique that investigates condensed-matter systems through the response of nuclear magnetic moments to externally applied magnetic fields. Although the measured degrees of freedom are nuclear spins, their resonance frequencies, spectral lineshapes, and relaxation rates are strongly influenced by the surrounding electronic and magnetic environment through dipolar and hyperfine interactions. Nuclear magnetic resonance can therefore provide microscopic information on both the static distribution of local magnetic fields and their temporal fluctuations. In a molecular magnet such as Dy–SQ, proton nuclei act as local probes of the magnetic fields generated by the anisotropic Dy³⁺ ion and by the semiquinonato radical, making the technique particularly suitable for investigating the magnetic environment and spin dynamics of the compound introduced in the previous chapter.

The chapter is organized as follows. Section 2.1 introduces the fundamental magnetic interactions governing the nuclear-spin system and clarifies how the nuclear response is connected to the local electronic and magnetic environment. Section 2.2 provides a concise overview of the principal components of a pulsed nuclear magnetic resonance experiment. Section 2.3 develops the theoretical description of the technique through the classical vector model, the rotating frame of reference, and the quantum-mechanical treatment of nuclear spins, before introducing the Bloch equations and the spectral-density formalism employed to relate the relaxation times T_1 and T_2 to microscopic magnetic fluctuations. Section 2.4 then describes the generation, acquisition, and processing of the signal, beginning with the free induction decay and quadrature detection and proceeding through Fourier transformation, spectral integration, radiofrequency-pulse calibration, spin-echo formation, and the experimental determination of the transverse and longitudinal relaxation times. Section 2.5 examines the frequency-domain representation of the nuclear magnetic resonance response, the origins of homogeneous and inhomogeneous line broadening, the finite excitation bandwidth of rectangular radiofrequency pulses, and the frequency-stepped procedure used to reconstruct spectra whose width exceeds the bandwidth of a single pulse. Finally, Section 2.6 presents the spectrometer, magnetic-field sources, probe, and cryogenic systems employed during the experimental campaign.

The theoretical framework and the description of pulsed nuclear magnetic resonance presented in this chapter follow primarily the comprehensive treatments by Slichter, Levitt, Fukushima and Roeder, and Carretta and Lascialfari [36, 37, 41, 42]. The discussions of magnetization dynamics, nuclear relaxation, and spin-echo formation also draw on the foundational works of Bloch, Bloembergen, Purcell and Pound, Redfield, and Hahn [43–46], unless otherwise specified.

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2.1 Fundamentals of Nuclear Magnetic Resonance

Nuclear magnetic resonance (NMR) spectroscopy is a non-destructive experimental technique employed for the investigation of condensed matter systems. Its peculiarity and strength resides in the ability of probing information about the electronic dynamics of a system through the indirect observation of its effect on the nuclear spin dynamics.

The connection between the nuclear and electronic degrees of freedom is primarily established by magnetic interactions. For a system of nuclear spins coupled to an electronic spin, a minimal nuclear spin Hamiltonian relevant to the present discussion can be written as

$$\mathcal{H} = \mathcal{H}_Z + \mathcal{H}_{n-n} + \mathcal{H}_{n-e} + \mathcal{H}_{\text{EFG}} \quad (2.1)$$

where $\mathcal{H}_Z$ describes the nuclear Zeeman interaction, $\mathcal{H}_{n-n}$ the dipole–dipole interaction between nuclear spins, $\mathcal{H}_{n-e}$ the hyperfine interaction between nuclear and electronic spins, and $\mathcal{H}_{\text{EFG}}$ the interaction between the nuclear electric quadrupole moment and the local electric-field gradient.

Nuclear Zeeman Interaction

The Zeeman term describes the interaction between the nuclear magnetic moments and the externally applied static magnetic field. It is responsible for the removal of the degeneracy between the nuclear spin states and it defines the characteristic resonance frequency of the nuclei. It can be written as

$$\mathcal{H}_Z = -\hbar \sum_i \gamma_i \mathbf{I}_i \cdot \mathbf{H} \quad (2.2)$$

where:

- γ_i is the gyromagnetic ratio of the i -th nucleus, a constant specific to each isotope, which defines how sensitive they are to magnetic fields. Typical values fall within the range $10^7 - 10^8 \text{ rad s}^{-1} \text{ T}^{-1}$. In the particular case of the proton one has $\gamma_p \simeq 2.675 \cdot 10^8 \text{ rad s}^{-1} \text{ T}^{-1}$ which is the highest value among all nuclei. This implies that the characteristic resonant frequency for protons when $H = 1 \text{ T}$ is around 42.5 MHz.
- $\mathbf{I}_i$ is the spin angular momentum operator of the i -th nucleus.
- $\mathbf{H}$ is the applied magnetic field.

Nuclear Dipole-Dipole Interaction

The term $\mathcal{H}_{n-n}$ describes the direct magnetic interaction between pairs of nuclear magnetic moments. Each nuclear spin generates a local dipolar magnetic field that is experienced by the surrounding nuclei. The nuclear dipole-dipole interaction can be expressed as

$$\mathcal{H}_{n-n} = \sum_{i < j} \frac{\gamma_i \gamma_j \hbar^2}{r_{ij}^3} [\mathbf{I}_i \cdot \mathbf{I}_j - 3(\mathbf{I}_i \cdot \hat{\mathbf{r}}_{ij})(\mathbf{I}_j \cdot \hat{\mathbf{r}}_{ij})] \quad (2.3)$$

where $\mathbf{r}_{ij}$ is the vector connecting nuclei i and j and r_{ij} is the distance between the two nuclei.

This interaction is strongly dependent on the internuclear distance, since its magnitude decreases as r_{ij}^{-3} . It is also anisotropic, as it depends on the orientation of the internuclear vector with respect to the applied magnetic field.

In solid-state NMR, nuclear dipole-dipole interactions contribute to the broadening and shape of the resonance line. They can also allow nuclear magnetization to be transferred through the sample by means of nuclear spin diffusion [36, 37].

Nuclear-Electron Hyperfine Interaction

The term $\mathcal{H}_{n-e}$ describes the magnetic coupling between the nuclear spins and the electronic magnetic moments. This interaction represents the fundamental connection between the quantities directly measured by NMR and the electronic properties of the investigated system. The nuclear-electron interaction can be written in tensorial form as

$$\mathcal{H}_{n-e} = -\gamma_N \hbar \sum_{i,k} \mathbf{I}_i \cdot \tilde{\mathbf{A}}_{ik} \cdot \mathbf{S}_k \quad (2.4)$$

where $\mathbf{S}_k$ is the spin operator associated with the k -th electronic magnetic moment and $\tilde{\mathbf{A}}_{ik}$ is the hyperfine coupling tensor connecting the i -th nuclear spin to the k -th electronic spin.

The hyperfine tensor generally contains both isotropic and anisotropic contributions and may therefore be decomposed as

$$\mathbf{A}_{ik} = A_{ik}^{\text{iso}} \mathbf{1} + \mathbf{A}_{ik}^{\text{dip}} \quad (2.5)$$

where A_{ik}^{iso} is the isotropic hyperfine coupling constant and A_{ik}^{dip} is the anisotropic dipolar contribution.

The isotropic contribution is associated with the presence of electronic spin density at the nuclear site. The dipolar contribution originates from the magnetic dipole-dipole interaction between the nuclear and electronic magnetic moments and depends on their relative position and orientation.

When an external magnetic field is applied, the electronic system develops a finite magnetization. Through $\mathcal{H}_{n-e}$, this magnetization produces an additional local magnetic field at the nuclear sites. The static component of this local field modifies the nuclear resonance frequency, giving rise to the NMR shift making it possible to probe and estimate the electronic susceptibility. On the other hand its time-dependent fluctuations induce transitions between the nuclear energy levels and are responsible for nuclear spin relaxation.

The analysis of the resonance shift and of the nuclear relaxation rates therefore provides information on the static magnetic susceptibility and on the characteristic electronic spin dynamics of the system [36, 37].

Nuclear Quadrupolar Interaction

The term $\mathcal{H}_{\text{EFG}}$ describes the interaction between the electric quadrupole moment of a nucleus and the electric-field gradient generated by the surrounding electronic charge distribution.

This interaction is present only for nuclei with spin quantum number $I > 1/2$. Such nuclei possess a non-spherical nuclear charge distribution and consequently a non-zero electric quadrupole moment.

In the principal-axis reference frame of the electric-field-gradient tensor, the quadrupolar Hamiltonian can be written as

$$\mathcal{H}_{\text{EFG}} = \sum_i \frac{eQ_i V_{zz,i}}{4I_i(2I_i - 1)} \left[3I_{iz}^2 - I_i(I_i + 1) + \eta_i (I_{ix}^2 - I_{iy}^2) \right] \quad (2.6)$$

where:

- Q_i is the electric quadrupole moment of the i -th nucleus;
- $V_{zz,i}$ is the largest principal component of the electric-field-gradient tensor at the i -th nuclear site;
- η_i is the asymmetry parameter of the electric-field gradient defined as $\eta_i = (V_{xx} - V_{yy})/V_{zz}$;
- I_{ix} , I_{iy} , and I_{iz} are the components of the nuclear spin operator in the principal-axis reference frame.

The quadrupolar interaction is highly sensitive to the local charge distribution and to the symmetry of the nuclear environment. It can therefore provide information on structural distortions, local symmetry, and charge redistribution. It can contribute to the relaxation processes and in NMR spectra, it may produce shifts, line

splittings, and additional broadening.

The measurements considered in the present work are performed on ^1H nuclei. Since the proton has nuclear spin $I = 1/2$, its electric quadrupole moment is identically zero. Consequently, the contribution $\mathcal{H}_{\text{EFG}}$ vanishes and will not be considered further.

2.2 Experimental Setup in a Nutshell

The following description of the experimental apparatus is deliberately concise and is intended only to introduce the essential components, geometry, and operating principles required to understand the discussion that follows. A more detailed account of the detection process, radiofrequency excitation, pulse sequences, and specific experimental equipment will be provided in the subsequent sections of this chapter.

A typical NMR apparatus is designed to provide integrated and precise control over the sample's physical environment, specifically its temperature and the magnetic fields applied to it.

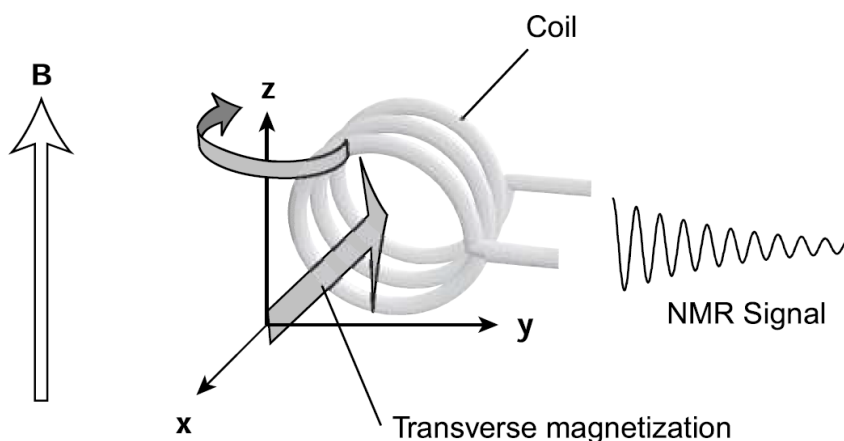


Figure 2.1: *Schematic representation of inductive NMR signal detection. The precessing transverse magnetization produces a time-dependent magnetic flux through the receiving coil, whose winding axis is perpendicular to the static magnetic field, thereby inducing an oscillating voltage at the nuclear resonance frequency. Adapted from [41].*

The technique requires at least two magnetic fields: a static field, H_0 , and an oscillating field, $H_1(t)$. To facilitate studies across a range of temperatures, the sample is placed inside a cryostat positioned at the very center of the static field, which can be generated by a large electromagnet or by a superconducting solenoid. The second oscillating field is produced within the cryostat itself, where the sample is held at the center of a smaller solenoid. This second coil operates as an integrated radiofrequency transceiver, serving as the primary electromagnetic interface for both the perturbation of nuclear spins and the subsequent acquisition of data [41, 42].

To start a measurement, an advanced spectrometer delivers a short, controlled burst of radiofrequency (RF) energy to the solenoid. This allows for microsecond precision in controlling the magnitude, duration, and specific waveform of the H_1 pulse, ensuring the nuclear spins are perturbed with the exact energy and timing.

Immediately after the excitation pulse has ended, the spectrometer rapidly switches the radiofrequency coil from the transmission circuit to the receiving electronics. The precessing transverse nuclear magnetization of the sample produces a time-dependent magnetic flux through the coil and therefore induces an electromotive force according to Faraday's law. Since the NMR signal is detected through this induced voltage, this conventional experimental approach is commonly referred to as *inductively detected NMR*. Immediately after the electronic switching, however, the signal cannot be recorded reliably because of probe ringing and the finite recovery time of the receiving electronics. This brief interval is known as the receiver dead time, after which the transient response of the nuclear-spin system can be acquired [41, 42].

Throughout the end of this chapter, a more detailed presentation of the experimental apparatus will be given.

2.3 Theory of Nuclear Magnetic Resonance

2.3.1 The Classical Vector Model

As the name suggests, one of the main quantities investigated by NMR is the nuclear magnetization. For a crystalline sample of volume V , the nuclear magnetization is defined as the total nuclear magnetic moment per unit volume:

$$\mathbf{M} = \frac{1}{V} \sum_{j=1}^N \boldsymbol{\mu}_j \quad (2.7)$$

where the index j runs over the N nuclei considered within the sample, and $\boldsymbol{\mu}_j$ is the magnetic moment of the j -th nucleus. In the present work, which focuses on proton NMR, the sum extends over all the ^1H nuclei contained in the sample.

When the sample is placed in a strong and static external magnetic field H_0 , the direction of the field conventionally defines the z -axis of the laboratory frame. A nuclear magnetic moment that is not aligned with H_0 experiences a torque given by

$$\boldsymbol{\tau}_j = \boldsymbol{\mu}_j \times H_0 \quad (2.8)$$

This torque causes the nuclear magnetic moments, and therefore any transverse component of the macroscopic magnetization, to precess around the direction of H_0 . This motion is known as Larmor precession, and its angular frequency depends on the magnitude of the static magnetic field and on the gyromagnetic ratio of the nuclear species.

In order to perturb the equilibrium nuclear magnetization, an additional time-dependent magnetic field must be applied perpendicular to the static field H_0 . This oscillating magnetic field, conventionally denoted as H_1 , is usually applied in the transverse xy -plane. However, the presence of a transverse field alone is not sufficient to produce an efficient interaction with the nuclear spin system. The frequency of the oscillating field must match the Larmor frequency of the nuclei:

$$\omega_{\text{RF}} = \omega_L = \gamma_N H_0 \quad (2.9)$$

This condition is known as magnetic resonance.

When the resonance condition is satisfied, the oscillating field can efficiently exchange energy with the nuclear spin system and exert a torque on the magnetization. In the laboratory reference frame, the magnetization continues to precess rapidly around the direction of H_0 , which defines the z -axis, while simultaneously being driven away from its equilibrium orientation by the transverse field H_1 .

The resulting motion consists of a precession around the z -axis combined with a progressive rotation of the magnetization towards the transverse plane. This second motion is commonly referred to as nutation. The effect becomes particularly simple in a reference frame rotating around the z -axis at the angular frequency ω_{RF} (see Figure 2.2).

In an NMR experiment, the transverse field is not normally applied continuously, but for a controlled and finite time interval. Such a finite burst of radiofrequency radiation is referred to as a radiofrequency pulse. For a rectangular pulse of duration t_p and constant amplitude H_1 , the angle through which the magnetization is rotated is given, under resonance conditions, by

$$\theta = \gamma_N H_1 t_p = \omega_1 t_p \quad (2.10)$$

The angle θ is known as the pulse angle or flip angle. By adjusting the amplitude and duration of the radiofrequency pulse, the magnetization can therefore be rotated by a selected angle [41, 42].

- A $\pi/2$ pulse, or 90° pulse, rotates the equilibrium magnetization from the longitudinal direction into the transverse plane.
- A π pulse, or 180° pulse, reverses the orientation of the magnetization with respect to the rotation axis defined by the phase of the radiofrequency field.

Once a transverse component of the magnetization has been generated, it continues to precess around the direction of the static field H_0 . This precession corresponds to a continuous rotation of the transverse magnetization vector.

The rotating transverse magnetization produces a time-dependent magnetic field at the position of the radiofrequency coil and therefore generates a time-dependent magnetic flux through its windings. According to Faraday's law of electromagnetic induction, the variation of this magnetic flux induces a voltage across the coil:

$$V_{\text{ind}}(t) = -\frac{d\Phi(t)}{dt} \quad (2.11)$$

where $\Phi(t)$ is the magnetic flux through the receiving coil produced by the nuclear magnetization. The quantity directly detected by the spectrometer is therefore not the magnetization itself, but the oscillating voltage induced in the coil by the precessing transverse component of the magnetization.

The longitudinal component M_z , being approximately stationary and parallel to H_0 , does not produce a time-dependent magnetic flux and is therefore not detected directly.

During the signal acquisition, the radiofrequency coil is connected to the receiver electronics, and the induced voltage is amplified and converted into a time-dependent electrical signal [41, 42].

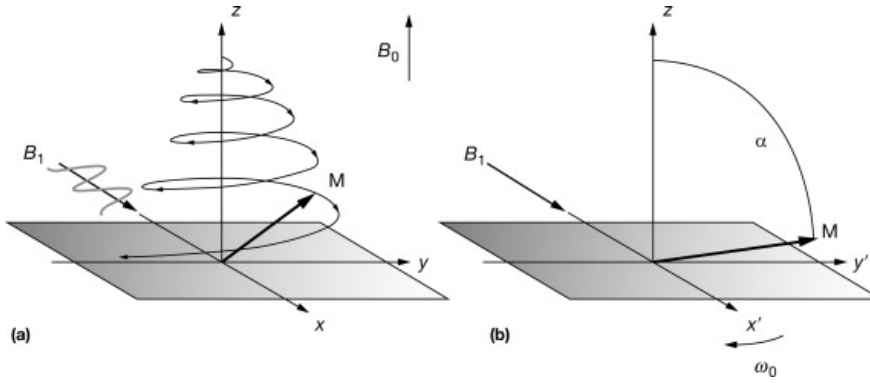


Figure 2.2: Trajectory of the total magnetization vector in both the rotating frame (b) and the laboratory frame (a).

2.3.2 The Rotating Frame of Reference

The movement of the magnetization during the RF pulse was described as a combination of precession and relaxation in the laboratory frame. The equation of motion for μ_j in the laboratory frame is:

$$\frac{\partial \mu}{\partial t} = \gamma \mu \times (\mathbf{H}_0 + \mathbf{H}_1) \quad (2.12)$$

To simplify the analysis of the system, in particular the one on the effects of the radiofrequency pulse and subsequent relaxation, a rotating frame of reference can be used to describe the system [36, 41]. Rewriting the previous equation using a rotating frame of frequency ω , the equation of motion becomes:

$$\frac{\partial \mu}{\partial t} = \gamma \mu \times \left[\mathbf{H}_1 + \left(\frac{\omega - \omega_L}{\gamma} \right) \hat{z} \right] \quad (2.13)$$

Choosing the rotation frequency $\omega = \omega_L$, the term $[(\omega - \omega_L)/\gamma]\hat{z}$ becomes zero. This effectively removes the large static field H_0 from the description in the rotating frame, making the rapid precession around the z -axis (due to H_0) invisible to

an observer within the rotating frame. This allows the observer to focus the analysis on the movements induced by the RF pulse and, especially, on the relaxation phenomena.

2.3.3 Quantum Mechanical Description of Nuclear Magnetic Resonance

To gain further knowledge and a better understanding of NMR technique, one has to study it using quantum mechanics. Resuming from formula 2.7 one can view the magnetic moment μ_j as a quantum operator that can be expressed as:

$$\mu_j = \gamma \hbar \mathbf{I} \quad (2.14)$$

The operator $\mathbf{I}$ obeys the usual angular momentum commutation relations and is characterized by the spin quantum number I . Its squared modulus and its z component satisfy

$$I^2 |I, m\rangle = \hbar^2 I(I+1) |I, m\rangle \quad (2.15)$$

and

$$I_z |I, m\rangle = \hbar m |I, m\rangle \quad (2.16)$$

where $m = -I, -I+1, \dots, I$. In this thesis, only proton (^1H) NMR experiments are considered. Since the proton has spin quantum number $I = 1/2$ only two spin states are allowed, corresponding to

$$m = \pm \frac{1}{2} \quad (2.17)$$

Therefore, in the presence of an external magnetic field, the proton behaves as a two-level quantum system. Once an isolated proton is subject to a static magnetic field H_0 , defining the z direction, the degeneracy of the two spin states $m = \pm \frac{1}{2}$ is lifted by the Zeeman interaction. The Hamiltonian related to this system is the Zeeman Hamiltonian:

$$\mathcal{H} = -\gamma \hbar I_z H_0 \quad (2.18)$$

As shown in Figure 2.3, this Hamiltonian is characterized by a ground state and an excited state corresponding to the two possible spin orientations relative to the external field. These two energy levels differ by: $\Delta E = \hbar \omega_L$, where ω_L is the Larmor frequency and corresponds to $\omega_L = \gamma H_0$.

Up to this point, the discussion has concerned the energy levels and dynamics of a single nuclear magnetic moment. An NMR experiment, however, probes a macroscopic statistical ensemble of nuclei subjected to the same static magnetic field. The observable magnetization therefore depends on how the nuclear spins are distributed between the two Zeeman levels. At thermal equilibrium, their populations follow the Boltzmann distribution

$$\frac{N_+}{N_-} = \exp\left(\frac{\Delta E}{k_B T}\right) \quad (2.19)$$

where N_+ and N_- denote the populations of the lower- and higher-energy states, respectively. Since $\Delta E \ll k_B T$ under typical NMR conditions, the population imbalance is very small but sufficient to produce a measurable net magnetization along the z direction.

When an oscillating magnetic field H_1 is applied perpendicular to H_0 at an angular frequency matching the Larmor frequency, $\omega = \omega_L$, the corresponding perturbation Hamiltonian is

$$\mathcal{H}_{\text{pert}} = -\gamma \hbar I_x H_1 \cos(\omega t) \quad (2.20)$$

couples the two Zeeman levels and induces transitions between them. The RF field therefore transfers population from the lower-energy state to the higher-energy state. The transition probability depends on the amplitude and duration of the RF pulse.

As the populations of the two levels evolve under the action of the RF field, a quantum superposition of the spin states is created. In the macroscopic description, this corresponds to the appearance of a transverse magnetization component. For a suitable pulse duration, known as a $\pi/2$ pulse, the longitudinal magnetization is converted entirely into transverse magnetization, while a π pulse inverts the populations of the two Zeeman levels.

2.3.4 The Bloch Equations and Magnetization Relaxation

Once the field H_0 is active and the Zeeman levels are split, the energy level of the sample can be schematized as in Figure 2.3.

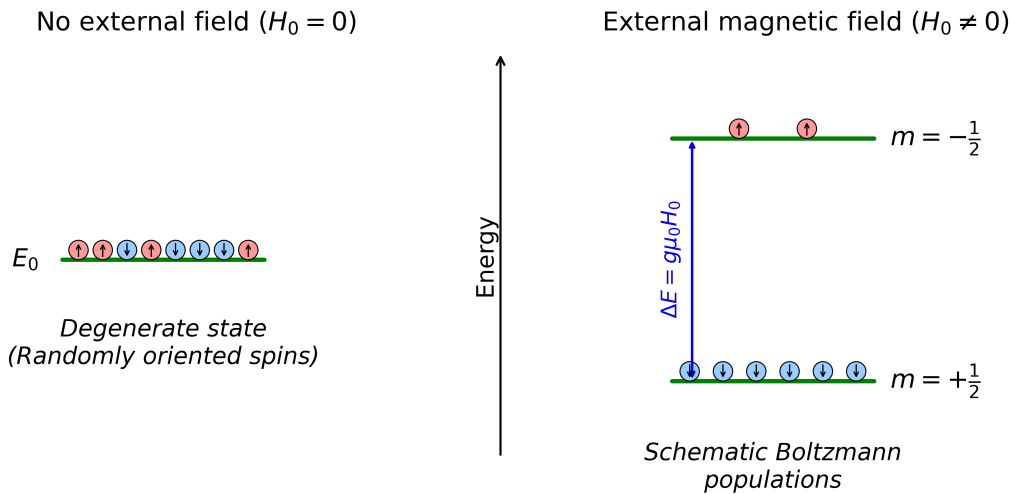


Figure 2.3: Energy level diagram showing the degeneracy lifting (Zeeman effect) of a $I = 1/2$ system induced by an applied magnetic field.

Defining the population of those levels as N_+ and N_- and trying to model how they will behave once a magnetic pulse interacts with the system, a set of differential equations emerges:

$$\frac{dN_+}{dt} = N_-W_{\rightarrow+} - N_+W_{+\rightarrow-} \quad (2.21)$$

$$\frac{dN_-}{dt} = N_+W_{+\rightarrow-} - N_-W_{\rightarrow+} \quad (2.22)$$

Here $W_{x \rightarrow y}$ represents the probability to have a transition from x to y in the time unit. These probabilities are influenced by the strength of the oscillating magnetic field H_1 and the proximity of its frequency to the Larmor frequency, driving transitions between the spin states.

Defining $N = N_+ + N_-$ and $n = N_+ - N_-$, and expressing the rate equations in terms of the population difference n (which is directly proportional to the z -component of the macroscopic magnetization of the sample), the previous set of differential equations changes into:

$$\frac{dn}{dt} = \frac{n_0 - n}{T_1} \quad (2.23)$$

$$n_0 = N \left(\frac{W_{+\rightarrow-} - W_{\rightarrow+}}{W_{+\rightarrow-} + W_{\rightarrow+}} \right) \quad (2.24)$$

This differential equation describes the recovery of longitudinal magnetization, represented by the population difference n , back to its equilibrium value n_0 with a time constant $T_1 = (W_{\rightarrow+} + W_{+\rightarrow-})^{-1}$, known as the longitudinal relaxation time.

This process involves the transfer of energy from the excited spins to the surrounding lattice, bringing the nuclear population back into thermal equilibrium with the lattice.

The M_z component of the magnetization can be directly correlated to the population difference. On the other hand, after the magnetic pulse the M_x and M_y component become non-zero, and due to various effects (such as field inhomogeneity and spin-spin interactions) they tend to decay back to zero.

This behavior can be summarized by the Bloch equations [36, 43], which can be derived by imagining the total magnetization vector as affected by a torque caused by the external magnetic field and also subject to a series of relaxation behaviors with different time constants:

$$\frac{dM_z}{dt} = \gamma(\mathbf{M} \times \mathbf{H}_0)_z + \frac{M_0 - M_z}{T_1} \quad (2.25)$$

$$\frac{dM_x}{dt} = \gamma(\mathbf{M} \times \mathbf{H}_0)_x - \frac{M_x}{T_2} \quad (2.26)$$

$$\frac{dM_y}{dt} = \gamma(\mathbf{M} \times \mathbf{H}_0)_y - \frac{M_y}{T_2} \quad (2.27)$$

T_1 represents the spin-lattice relaxation time and governs the recovery of the longitudinal magnetization towards its equilibrium value. This process involves an exchange of energy between the nuclear-spin system and its surrounding environment.

T_2 represents the intrinsic transverse relaxation time and governs the irreversible decay of the transverse magnetization. This loss of coherence originates from microscopic interactions between the nuclear spins and from fluctuating local magnetic fields within the sample. These interactions progressively modify the relative phases of the nuclear magnetic moments and cannot be reversed by the application of an RF pulse sequence.

In a real NMR experiment, an additional loss of transverse coherence is produced by macroscopic inhomogeneities of the static magnetic field H_0 generated by the experimental apparatus. Nuclei located in different regions of the sample may therefore experience slightly different values of H_0 and consequently precess at different Larmor frequencies. Even if the individual nuclear spins have not lost their intrinsic coherence, their transverse magnetic moments progressively move out of phase, causing a faster decay of the total transverse magnetization.

The effective transverse decay time observed in a directly acquired signal is denoted by T_2^* . This quantity accounts for the combined effect of the intrinsic transverse relaxation described by T_2 and the additional dephasing caused by macroscopic inhomogeneities of the laboratory magnetic field. Consequently, the measured transverse signal generally decays more rapidly than it would under intrinsic relaxation alone.

The dephasing produced by static magnetic-field inhomogeneities is reversible because each nucleus continues to precess coherently at its own approximately constant frequency. A suitable sequence can therefore refocus this contribution and recover the corresponding loss of signal. By contrast, the intrinsic and stochastic processes responsible for T_2 produce an irreversible loss of phase coherence and cannot be recovered.

2.3.5 Relaxation Times and Spectral Density Function

The Bloch equations provide a phenomenological description of the recovery of the nuclear magnetization towards equilibrium through the relaxation times T_1 and T_2 . Although this formalism correctly describes the macroscopic evolution of the magnetization, it does not identify the microscopic mechanisms responsible for relaxation or explain the dependence of the relaxation times on temperature, magnetic field, and the properties of the investigated material.

A microscopic interpretation requires the time-dependent local magnetic fields experienced by the nuclei to be considered. These fields arise from fluctuations of the magnetic interactions acting at the nuclear sites and may contain components over a broad range of frequencies. Only the frequency components that overlap with the

characteristic frequencies of the nuclear spin system can efficiently affect its evolution. In particular, transverse fluctuations with a significant spectral component at the nuclear Larmor frequency ω_L can induce transitions between the Zeeman levels and therefore contribute to longitudinal relaxation. Longitudinal fluctuations, especially at low frequency, modulate the instantaneous precession frequency and contribute mainly to transverse dephasing and relaxation.

It is useful to distinguish these stochastic local fields from the coherent radiofrequency field used to manipulate the nuclear magnetization. A coherent field applied near the Larmor frequency produces a controlled rotation of the magnetization, whereas randomly fluctuating fields lead to an irreversible loss of energy and phase coherence when averaged over the nuclear ensemble. Possible microscopic sources of such fluctuations include electronic spin dynamics, nuclear dipole–dipole interactions, lattice vibrations, molecular reorientations, and time-dependent modulations of the hyperfine or dipolar couplings [36, 37].

In a rigid molecular magnet such as Dy–SQ, large-scale molecular reorientation is expected to be strongly suppressed, particularly at low temperature. The dominant fluctuating fields are therefore more likely to originate from the dynamics of the electronic magnetic moments associated with the Dy^{3+} ion and the semiquinonato radical, transmitted to the proton nuclei through hyperfine and dipolar interactions [34, 35, 37].

The following discussion introduces the correlation function $G(\tau)$, which describes how rapidly the fluctuating local fields lose memory of their initial value, and the corresponding spectral density function $J(\omega)$. These quantities provide the microscopic connection between the magnetic fluctuations and the phenomenological relaxation times introduced in the Bloch equations.

Let $h_q(t)$ denote the q -th Cartesian component of the fluctuating local magnetic field at a nuclear site. Its temporal autocorrelation function is defined as

$$G_q(\tau) = \overline{h_q(t)h_q(t + \tau)} \quad (2.28)$$

where the overline denotes an ensemble average. The correlation function measures how strongly the local field at time $t + \tau$ remains related to its value at time t . At zero delay it can be written as

$$G_q(0) = \overline{h_q^2} \quad (2.29)$$

which represents the mean-squared amplitude of the fluctuating field. As τ increases, the correlation function decreases as the system progressively loses memory of its previous magnetic configuration. The characteristic timescale of this loss of memory is described by the correlation time τ_c , which can be defined as

$$\tau_c = \frac{1}{G_q(0)} \int_0^{+\infty} G_q(\tau) d\tau \quad (2.30)$$

A short correlation time corresponds to rapidly varying local fields, whereas a long correlation time indicates slowly evolving or nearly static fluctuations.

In the present context, τ_c should not necessarily be interpreted as the reorientation time of the entire molecule. For a rigid molecular magnet, it more generally characterizes the dynamics of the microscopic magnetic degrees of freedom responsible for the local field, such as fluctuations of the electronic moments associated with the Dy^{3+} ion and the semiquinonato radical. The frequency distribution of these fluctuations is described by the spectral density function. Using the convention adopted by Slichter [36], it is defined as the cosine Fourier transform of the correlation function:

$$J_q(\omega) = \int_0^{+\infty} G_q(\tau) \cos(\omega\tau) d\tau \quad (2.31)$$

The spectral density $J_q(\omega)$ therefore quantifies the amplitude of the fluctuating local field available at the angular frequency ω . To obtain an explicit expression for $J_q(\omega)$, a functional form must be assumed for the correlation function. One of the simplest and most widely employed approximations is the single-exponential correlation function:

$$G_q(\tau) = \overline{h_q^2} \exp\left(-\frac{|\tau|}{\tau_c}\right) \quad (2.32)$$

This model assumes that the fluctuations are characterized by a single correlation time and that the system loses memory exponentially. It is the standard approximation employed in the Bloembergen–Purcell–Pound description of nuclear relaxation [36, 44], but it is not the only possible choice. More complex systems may require sums of exponentials, stretched-exponential functions, or other correlation functions describing distributions of characteristic timescales.

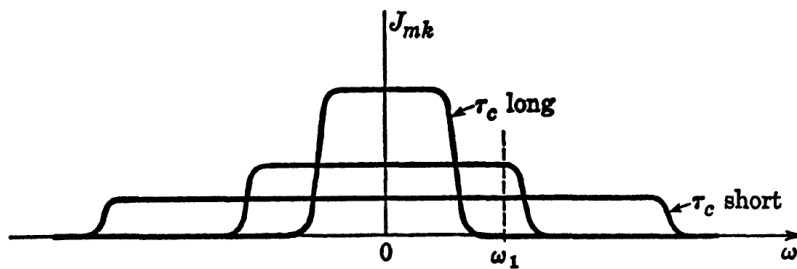


Figure 2.4: Typical behavior for the spectral density obtained for different values of the correlation time τ_c . As τ_c increases, the spectral weight becomes progressively concentrated at low frequencies. Adapted from [36].

For the single-exponential model, the corresponding spectral density has the Lorentzian form

$$J_q(\omega) = \overline{h_q^2} \frac{\tau_c}{1 + \omega^2 \tau_c^2} \quad (2.33)$$

The quantity $\overline{h_q^2}$ determines the overall intensity of the fluctuations, whereas τ_c determines how their spectral weight is distributed in frequency. For short correlation times, the spectral density is broad and extends over a wide frequency range. For long correlation times, the spectral density becomes progressively narrower and is concentrated near zero frequency.

The microscopic connection with the relaxation times introduced in the Bloch equations is established through the standard perturbative treatment of fluctuating magnetic fields presented by Slichter [36]. A complete derivation of these relations is beyond the scope of the present discussion and can be found in the cited reference. Adopting the notation and the weak-fluctuation approximation used in that treatment, the longitudinal relaxation rate is determined by the transverse components of the fluctuating local field evaluated at the nuclear Larmor frequency:

$$\frac{1}{T_1} = \gamma_N^2 [J_x(\omega_L) + J_y(\omega_L)] \quad (2.34)$$

Transverse fluctuations can induce transitions between the nuclear Zeeman levels only when they possess a significant spectral component at ω_L . The transverse relaxation rate also contains a contribution from longitudinal fluctuations close to zero frequency and within the same formalism, and is written as

$$\frac{1}{T_2} = \frac{1}{2T_1} + \gamma_N^2 J_z(0) \quad (2.35)$$

The first term describes the loss of transverse coherence associated with transitions between the Zeeman levels, whereas the second term represents pure dephasing caused by slow fluctuations of the longitudinal local field [36].

At a fixed observation frequency ω_L , the Lorentzian spectral density reaches its maximum when

$$\omega_L \tau_c = 1 \quad (2.36)$$

Consequently, a maximum in the longitudinal relaxation rate is expected when the characteristic timescale of the magnetic fluctuations becomes comparable to the inverse nuclear Larmor frequency. The spectral density formalism thus provides the microscopic connection between the fluctuating local fields experienced by the nuclei and the phenomenological relaxation times T_1 and T_2 .

2.4 Radiofrequency Pulsed Sequences

The previous sections introduced the physical principles governing the nuclear magnetization, its interaction with radiofrequency fields, and its return towards equilibrium through the relaxation times T_1 and T_2 . The discussion now turns to the experimental procedures through which the nuclear response is generated, detected, and processed.

The most elementary time-domain response observed in a pulsed NMR experiment

is the free induction decay. Its acquisition provides the starting point for understanding both the operation of the receiver and the construction of more complex pulse sequences. The following subsection first describes how an RF pulse generates a detectable transverse magnetization and how the resulting signal evolves after the pulse. The quadrature-acquisition procedure is then introduced to explain how the complete amplitude and phase information contained in this signal is preserved and transformed into the frequency domain. Once the relation between the applied pulse and the measured NMR response has been established, pulse calibration can be discussed as the experimental procedure used to determine the pulse durations that produce the desired rotations of the nuclear magnetization.

2.4.1 The Free Induction Decay

Before the application of a radiofrequency pulse, the equilibrium nuclear magnetization M_0 is directed along the static magnetic field H_0 . A resonant RF pulse rotates the magnetization away from this equilibrium direction by a flip angle θ . Immediately after the pulse, the magnitude of the transverse component is

$$M_{\perp}(0) = M_0 \sin \theta \quad (2.37)$$

A detectable transverse response is therefore generated whenever the pulse leaves a non-zero component of the magnetization in the xy -plane. An ideal π pulse reverses the longitudinal magnetization from $+z$ to $-z$ but does not, by itself, leave a transverse component and consequently does not generate a FID. By contrast, a $\pi/2$ pulse rotates the equilibrium magnetization entirely into the transverse plane and produces the maximum possible initial FID amplitude.

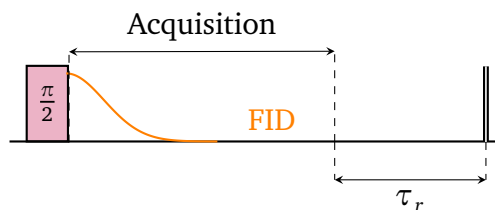


Figure 2.5: Pulse sequence timing diagram for a FID signal acquisition.

Once the RF pulse has ended, the transverse magnetization continues to precess around H_0 in the laboratory frame. Its rotation produces a time-dependent magnetic flux through the receiving coil and therefore induces the voltage recorded by the spectrometer. This transient signal is known as the free induction decay (FID) because its amplitude decreases progressively after the external excitation has been removed.

The oscillation frequency of the recorded signal is determined by the difference between the nuclear resonance angular frequency and the reference angular frequency of the receiver. Its decay reflects the progressive loss of phase coherence within the nuclear ensemble. For a directly acquired FID, the characteristic decay time is generally denoted by T_2^* , since it includes both the intrinsic transverse

relaxation and the reversible dephasing produced by quasistatic magnetic-field inhomogeneities.

In practice, the signal obtained from a single acquisition may have an insufficient signal-to-noise ratio (SNR). The same pulse-and-acquisition procedure is therefore repeated several times and the resulting signals summed. The coherent NMR response adds reproducibly from one scan to the next, whereas uncorrelated noise increases only statistically, producing an improvement in the SNR proportional to $\sqrt{N}$, where N is the number of scans [41, 42].

Successive scans are separated by a recycle delay τ_r , during which the longitudinal magnetization recovers towards its thermal-equilibrium value. The recycle delay must be sufficiently long compared with the relevant longitudinal relaxation time to ensure a reproducible initial magnetization at the beginning of each acquisition.

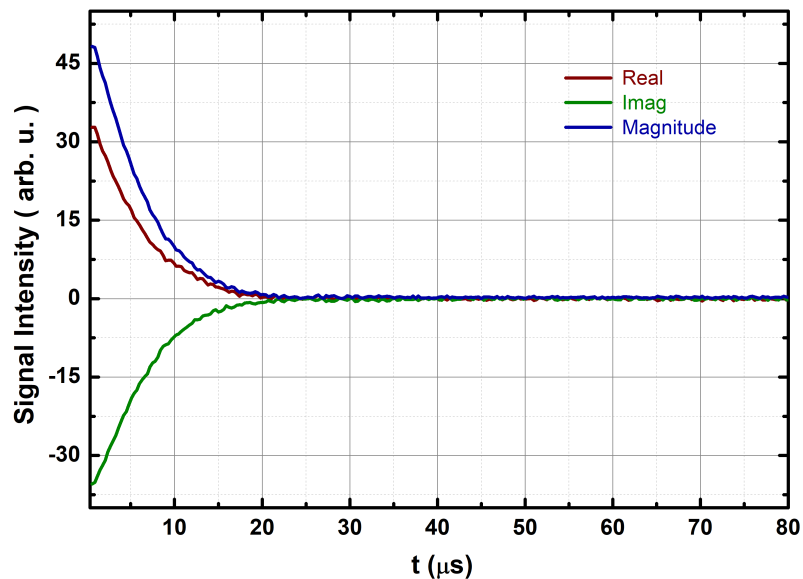


Figure 2.6: Time-domain representation of an averaged FID signal. The quadrature components, M_x (red) and M_y (green), exhibit a constant phase offset. The blue curve represents the quadrature magnitude (envelope), illustrating the pure T_2^* relaxation of the transverse magnetization.

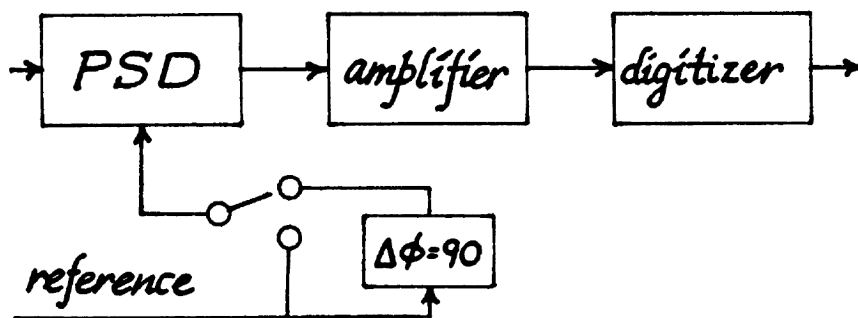
Figure 2.6 shows a typical raw FID signal, the y-axis represents the Intensity of the signal, while the x-axis represents the time elapsed in seconds.

The FID is therefore the primary time-domain signal generated by the freely precessing transverse magnetization. However, the voltage measured by a single receiver channel does not retain all the information required to determine both the amplitude and the phase evolution of this rotating magnetization. The complete experimental signal is obtained through quadrature acquisition, as discussed in the following subsection.

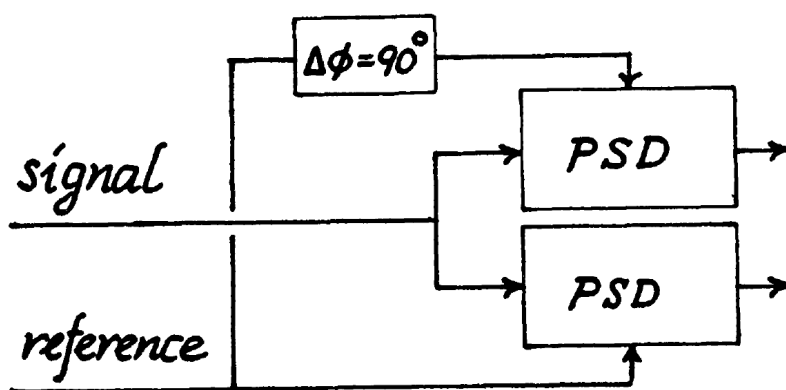
Quadrature Detection

The voltage induced in the receiver coil by the precessing transverse magnetization is a real radiofrequency signal oscillating close to the reference frequency of the spectrometer. A single phase-sensitive detector (PSD) compares this voltage with a sinusoidal reference signal and therefore measures only the component that is in phase with the selected reference. As a consequence, one phase-sensitive channel alone does not contain sufficient information to determine the complete motion of the transverse magnetization in the rotating frame.

As described by Fukushima and Roeder [42], quadrature detection overcomes this limitation by demodulating the same NMR signal with two reference signals shifted by 90° with respect to one another. The two resulting outputs are conventionally called the in-phase and quadrature channels, denoted by $I(t)$ and $Q(t)$, respectively.



(a) Sequential acquisition of the two quadratures using one phase-sensitive detector and a switchable reference phase.



(b) Simultaneous quadrature acquisition using two phase-sensitive detectors supplied with reference signals differing by 90° .

Figure 2.7: Schematic representations of quadrature phase-sensitive detection. The two output channels retain the amplitude and phase information required to determine the direction of rotation of the transverse magnetization. Adapted from [42].

Figure 2.7 illustrates two possible implementations. In the first scheme, a single PSD is alternately connected to reference signals differing in phase by 90° , so that the two quadratures are acquired in successive measurements. In the second scheme, two PSDs operate in parallel and acquire the two quadratures simultaneously.

To illustrate the operation of the receiver, consider a signal whose angular frequency differs from the receiver reference frequency by an offset Ω . After demodulation and low-pass filtering, the two ideal quadrature signals can be expressed as

$$I(t) = S_0 e^{-t/T_2^*} \cos(\Omega t + \phi_0) \quad ; \quad Q(t) = S_0 e^{-t/T_2^*} \sin(\Omega t + \phi_0) \quad (2.38)$$

where ϕ_0 is the initial phase of the signal relative to the receiver reference. The two channels are combined into the complex time-domain signal

$$s(t) = I(t) + iQ(t) \quad (2.39)$$

which, with the convention used above, becomes

$$s(t) = S_0 e^{-t/T_2^*} e^{i(\Omega t + \phi_0)} \quad (2.40)$$

The use of both quadrature channels makes it possible to distinguish positive and negative frequency offsets. A single detector would produce only a cosine-like signal, and since

$$\cos(\Omega t) = \cos(-\Omega t) \quad (2.41)$$

it could not determine on which side of the reference frequency the resonance lies. In the complex representation, instead,

$$s_+(t) \propto e^{+i|\Omega|t} \quad ; \quad s_-(t) \propto e^{-i|\Omega|t} \quad (2.42)$$

so that positive and negative offsets correspond to opposite directions of rotation in the complex (I, Q) plane. Quadrature acquisition therefore preserves the sign of the frequency offset relative to the carrier.

The frequency-domain response can be related to the complex magnetic susceptibility. Following Slichter [36], and adopting the harmonic time dependence $e^{i\omega t}$, the susceptibility is written as

$$\chi(\omega) = \chi'(\omega) - i\chi''(\omega) \quad (2.43)$$

The coefficient $\chi'(\omega)$ describes the dispersive response and is associated with the component of the magnetization that is in phase with the applied radiofrequency field. The coefficient $\chi''(\omega)$ describes the absorptive response, is in quadrature with the applied field, and determines the power transferred from the radiofrequency field to the spin system. Although the mathematical imaginary part of χ is $-\chi''$ with the convention written above, χ'' is traditionally referred to as the imaginary or absorptive susceptibility.

For a single resonance characterized by an exponential transverse decay, the two corresponding line shapes may be written, apart from an overall amplitude and convention-dependent signs, as

$$\chi'(\omega) \propto \frac{\Delta\omega T_2^*}{1 + (\Delta\omega T_2^*)^2} \quad ; \quad \chi''(\omega) \propto \frac{1}{1 + (\Delta\omega T_2^*)^2} \quad (2.44)$$

where

$$\Delta\omega = \omega - \omega_0 \quad (2.45)$$

Thus, $\chi'(\omega)$ has an antisymmetric dispersive line shape and crosses zero at resonance, whereas $\chi''(\omega)$ has a symmetric absorptive Lorentzian line shape centred at ω_0 . This Lorentzian form applies specifically to an exponentially decaying resonance; more general FID decay functions may produce different spectral line shapes.

For the following discussion, the complex frequency-domain signal is represented using the reference convention

$$S_{\text{ref}}(\omega) = D(\omega) + iA(\omega) \quad (2.46)$$

where

$$D(\omega) \propto \chi'(\omega) \quad (2.47)$$

is the dispersive component and

$$A(\omega) \propto \chi''(\omega) \quad (2.48)$$

is the absorptive component. In this convention, dispersion is assigned to the real axis and absorption to the imaginary axis.

The two output channels of the quadrature receiver do not, however, correspond automatically to pure dispersion and pure absorption. The receiver directly measures two orthogonal quadratures of the voltage induced in the detection coil. Their relative phase may be altered by the phase setting of the receiver reference and by the finite phase response and propagation delays of the probe, cables, preamplifiers, filters, and mixers. These effects generally produce a frequency-independent, or zero-order, phase offset.

In addition, a delay between the RF pulse and the effective beginning of acquisition, including the receiver dead time, shifts the time origin of the FID. This introduces a phase error that varies with frequency and therefore contributes to a first-order phase distortion. Consequently, the two measured channels generally contain mixtures of the dispersive component $D(\omega)$ and the absorptive component $A(\omega)$ [41, 42]. A frequency-independent phase offset ϕ_0 produces

$$S_{\text{raw}}(\omega) = e^{i\phi_0} S_{\text{ref}}(\omega) \quad (2.49)$$

Using Euler's relation, this becomes

$$S_{\text{raw}}(\omega) = [D(\omega) \cos \phi_0 - A(\omega) \sin \phi_0] + i[D(\omega) \sin \phi_0 + A(\omega) \cos \phi_0] \quad (2.50)$$

Consequently, the real and imaginary raw channels are not pure physical responses, but projections of the same complex spectrum onto axes rotated by the angle ϕ_0 .

A zero-order phase correction consists of applying the opposite phase rotation to the measured spectrum:

$$S_{\text{corr}}(\omega) = e^{-i\phi_0} S_{\text{raw}}(\omega) \quad (2.51)$$

The corrected dispersive and absorptive components are then obtained by taking the real and imaginary parts of the rotated spectrum:

$$D(\omega) = \text{Re}[e^{-i\phi_0} S_{\text{raw}}(\omega)] \quad ; \quad A(\omega) = \text{Im}[e^{-i\phi_0} S_{\text{raw}}(\omega)] \quad (2.52)$$

Writing the raw spectrum as

$$S_{\text{raw}}(\omega) = S_{\text{real,raw}}(\omega) + iS_{\text{imag,raw}}(\omega) \quad (2.53)$$

the two corrected components are explicitly

$$D(\omega) = S_{\text{real,raw}}(\omega) \cos \phi_0 + S_{\text{imag,raw}}(\omega) \sin \phi_0 \quad (2.54)$$

$$A(\omega) = S_{\text{imag,raw}}(\omega) \cos \phi_0 - S_{\text{real,raw}}(\omega) \sin \phi_0 \quad (2.55)$$

The phase correction therefore forms new linear combinations of the two measured quadratures, corresponding geometrically to a rotation of the complex spectrum. By selecting the appropriate value of ϕ_0 , the absorptive and dispersive responses are aligned with the chosen numerical axes. No spectral information is removed.

A phase rotation of 90° illustrates explicitly how the two numerical channels can be interchanged. For example,

$$e^{-i\pi/2} [D(\omega) + iA(\omega)] = A(\omega) - iD(\omega) \quad (2.56)$$

Thus, after a 90° rotation, absorption appears in the real channel and dispersion in the imaginary channel, with a possible reversal of the sign of the dispersive component.

During the processing of the experimental data presented in this thesis, the zero-order phase was chosen so that the absorptive component appears in the real numerical channel. The displayed spectra therefore follow the convention

$$S_{\text{lab}}(\omega) = A(\omega) + iD_{\text{lab}}(\omega) \quad (2.57)$$

where $D_{\text{lab}}(\omega)$ denotes the dispersive component displayed by the acquisition software. Its sign depends on the adopted quadrature, frequency-axis, and Fourier-transform conventions. This display convention differs by a fixed phase rotation

from the reference convention $S_{\text{ref}} = D + iA$, but it does not alter the physical identification of χ' with dispersion and χ'' with absorption, it only changes the numerical axes onto which the two responses are projected [41, 42].

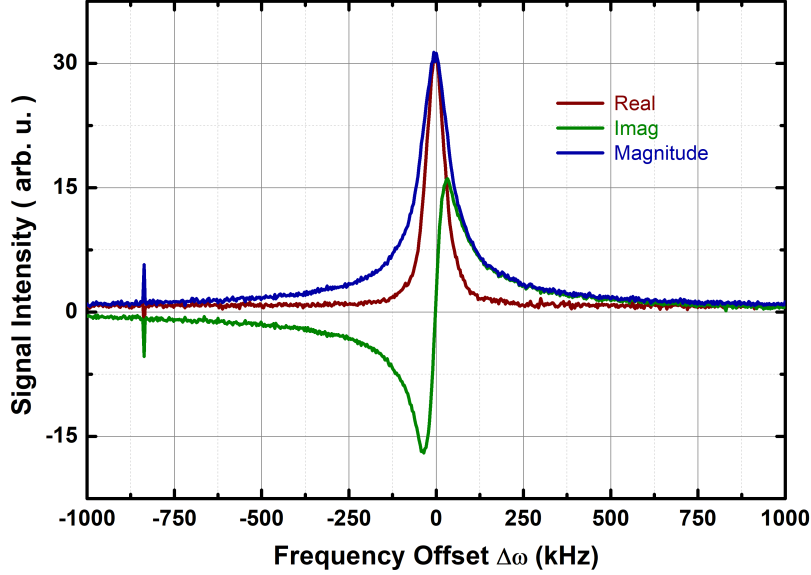


Figure 2.8: Frequency-domain representation of a phase-adjusted free induction decay. According to the display convention adopted for the experimental data in this thesis, the real channel (red) contains the symmetric absorption-mode component, while the imaginary channel (green) contains the antisymmetric dispersion-mode component. The blue curve represents the magnitude spectrum.

Figure 2.8 shows the complex frequency-domain spectrum after Fourier transformation and phase adjustment of a measured FID signal. According to the experimental display convention used here, the real channel contains the symmetric absorption-mode signal, whereas the imaginary channel contains the corresponding antisymmetric dispersion-mode component.

Once the complex time-domain signal has been Fourier transformed and the phase has been corrected, the absorptive component of the NMR spectrum can be isolated. A quantitative measure of the detected response is then obtained by integrating this component over the angular-frequency interval containing the resonance line

$$I_{\text{NMR}} = \int_{\omega_1}^{\omega_2} A(\omega) d\omega \quad (2.58)$$

where $A(\omega)$ denotes the absorptive spectral component and the integration limits are chosen to include the complete resonance signal. Provided that the acquisition and processing parameters are kept unchanged, the resulting integrated intensity is proportional to the transverse nuclear magnetization generated by the RF pulse. This quantity is therefore used in pulse-calibration measurements to determine the pulse duration that produces the maximum detectable NMR response.

2.4.2 Radiofrequency-Pulse Calibration

The preceding subsection established that the strength of the detected NMR response can be quantified through the integrated area of the absorptive spectrum. Pulse calibration therefore consists of measuring this integrated intensity while systematically varying the duration of the RF pulse, with the aim of identifying the pulse conditions that maximize the transverse magnetization. Under resonance conditions, the flip angle generated by a rectangular RF pulse is

$$\theta = \gamma_N H_1 t_p \quad (2.59)$$

where H_1 is the amplitude of the radiofrequency field and t_p is the pulse duration. Combining this relation with Equation 2.37, the initial transverse magnetization produced by the pulse is

$$M_{\perp}(0) = M_0 \sin(\gamma_N H_1 t_p) \quad (2.60)$$

The amplitude of the FID, and consequently the intensity of its Fourier-transformed spectrum, therefore varies periodically as the pulse duration is increased. The maximum detectable response is obtained for a $\pi/2$ rotation, whereas an ideal π pulse reverses the longitudinal magnetization and produces no transverse signal immediately after the pulse.

In an ideal experiment, the pulse duration corresponding to a selected flip angle could be calculated directly from the nominal value of H_1 . In practice, however, the effective RF field experienced by the sample depends on the tuning and matching of the probe, the geometry and quality factor of the coil, the applied RF power, and the electromagnetic properties and position of the sample. The required pulse duration must therefore be determined experimentally [41, 42].

A pulse-calibration measurement is performed by repeating the same FID acquisition while systematically varying t_p . Each acquired signal is processed using the same quadrature, Fourier-transform, and phase-correction procedures, and a consistent measure of its intensity is extracted, such as the integrated absorptive spectral component. The resulting signal intensity exhibits an oscillatory dependence on the pulse duration as the magnetization undergoes progressive nutation around the RF-field direction.

The first maximum of the calibration curve identifies the pulse duration $t_{\pi/2}$ corresponding to a $\pi/2$ rotation. The first subsequent zero identifies, under ideal conditions, the duration t_{π} of a π pulse, with

$$t_{\pi} = 2t_{\pi/2} \quad (2.61)$$

Once the relevant pulse durations have been calibrated, combinations of excitation, inversion, refocusing, and detection pulses can be used to prepare selected non-equilibrium states and investigate the longitudinal and transverse evolution of the nuclear magnetization. The following subsections introduce the principal pulse sequences employed for these purposes.

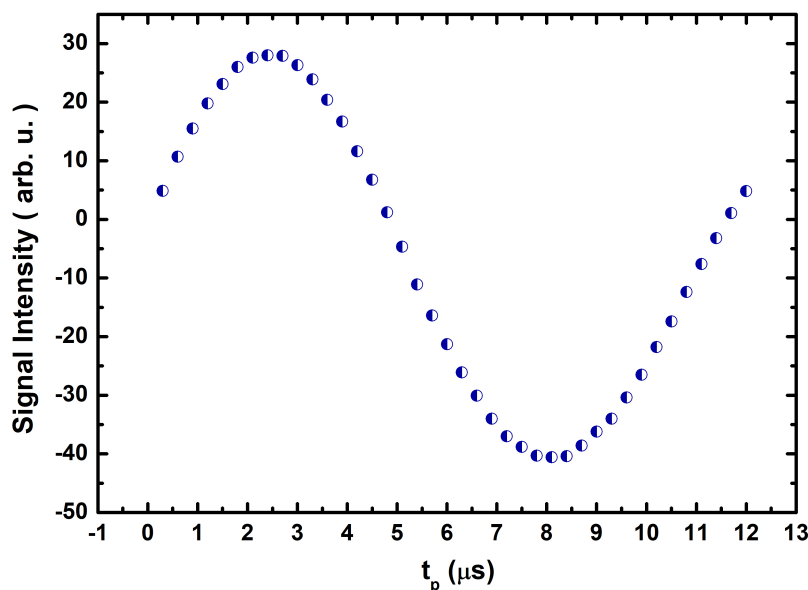


Figure 2.9: *Experimental RF-pulse calibration obtained by recording the processed NMR signal intensity as a function of the pulse duration t_p . The oscillatory behaviour reflects the nutation of the nuclear magnetization under the action of H_1 . The first signal maximum identifies the duration of the $\pi/2$ pulse, whereas the first subsequent zero corresponds ideally to a π pulse.*

2.4.3 The Spin-Echo Sequence

Sometimes the FID signal of a sample cannot be detected because the transverse magnetization dephases on a timescale comparable to, or shorter than, the receiver dead time. In this case, a substantial fraction of the signal decays before the receiving electronics become operational, leading to a significant loss and distortion of the measured FID. When this rapid decay is mainly caused by static magnetic-field inhomogeneities, a spin-echo sequence can be employed to refocus the corresponding reversible dephasing.

The characteristic time describing the decay of the transverse magnetization observed in a directly acquired FID is denoted by T_2^* . This decay arises from two different contributions. The first is associated with intrinsic microscopic interactions and fluctuating local magnetic fields within the sample, which produce an irreversible loss of phase coherence characterized by T_2 . The second originates from macroscopic inhomogeneities of the static magnetic field H_0 generated by the experimental apparatus. Nuclei located in different regions of the sample consequently precess at slightly different Larmor frequencies, causing an additional but reversible loss of phase coherence.

By refocusing the reversible dephasing caused by static magnetic-field inhomogeneities, a spin-echo sequence can recover the corresponding loss of transverse signal. The effective transverse decay time measured from the FID can be phenomenologically expressed as

$$\frac{1}{T_2^*} = \frac{1}{T_2} + \gamma \Delta H_0 \quad (2.62)$$

where ΔH_0 represents the spatial inhomogeneity of the static magnetic field across the sample. In a spin-echo experiment, the contribution associated with $\gamma \Delta H_0$ is refocused, allowing the intrinsic transverse relaxation time T_2 to be determined.

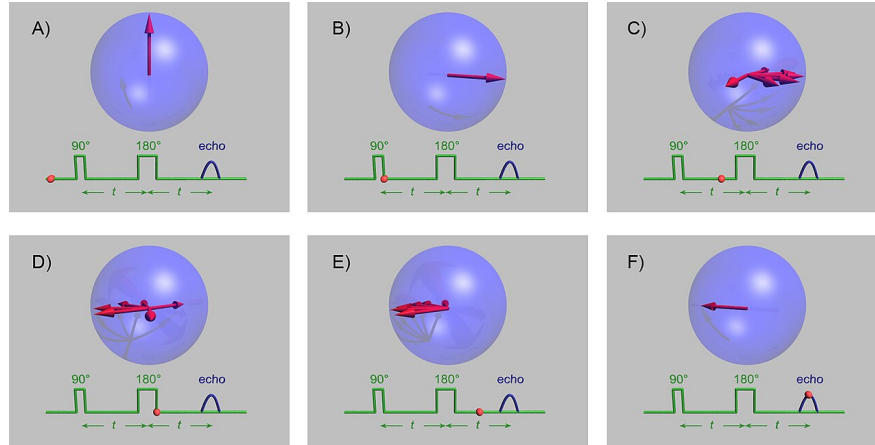


Figure 2.10: *Timing diagram of the Hahn spin-echo pulse sequence. Adapted from Gavin W. Morley, HahnEcho GWM.gif, Wikimedia Commons.*

The evolution of the nuclear magnetization during a Hahn spin-echo sequence is illustrated in Figure 2.10. An initial $\pi/2$ pulse rotates the equilibrium magnetization into the transverse plane [B]. The nuclear magnetic moments then begin to dephase due to the distribution of local static magnetic fields, causing nuclei with higher and lower precession frequencies to separate progressively in phase [C]. After a delay τ , a refocusing π pulse is applied [D]. This pulse reverses the relative orientation of the transverse magnetic moments without changing the local precession frequencies. During the subsequent evolution interval, the phase dispersion accumulated before the pulse is progressively compensated [E]. After a second delay of equal duration, the transverse magnetic moments rephase and generate a spin echo [F]. The maximum of the echo therefore occurs at the echo time

$$TE = 2\tau \quad (2.63)$$

The spin echo recovers the signal lost through reversible dephasing caused by static field inhomogeneities, but it cannot recover the irreversible loss of coherence associated with the intrinsic transverse relaxation. Consequently, by measuring the echo amplitude for different values of TE , the intrinsic relaxation time T_2 can be determined [36, 41, 46].

As in a conventional FID acquisition, the sequence may be repeated over several scans, separated by a sufficiently long recycle delay. The coherent echo signals are then summed to improve the SNR and allow a more accurate extraction of the spectral information.

2.4.4 Quantum Mechanical Formalism of the Spin-Echo

To avoid the limitations inherent in classical interpretations of quantum-mechanical systems, the evolution of the spin system is now discussed within a fully quantum mechanical framework. For an exhaustive derivation of the density matrix formalisms involved, the reader is referred to the foundational text of Slichter [36].

Consider the sample in the rotating frame subject to the Hahn echo pulse sequence shown in Figure 2.11.

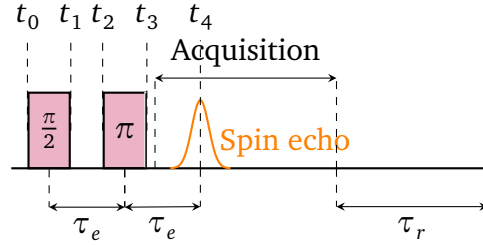


Figure 2.11: Pulse-sequence timing diagram for a Hahn spin-echo experiment used for the measurement of T_2 . The labels t_0 , t_1 , t_2 , t_3 , and t_4 identify the key stages discussed in the quantum-mechanical description of the sequence.

The relevant times appearing in the pulse sequence are defined as follows. The first RF pulse begins at $t = t_0 = 0$ and ends at $t = t_1$, while the refocusing pulse begins at $t = t_2$ and ends at $t = t_3$. The spin echo reaches its maximum amplitude at $t = t_4$. The two free-evolution intervals, extending from t_1 to t_2 and from t_3 to t_4 , respectively, are chosen to have the same duration τ . In the ideal-pulse approximation adopted in the following derivation, the durations of the RF pulses are neglected. The $\pi/2$ and π rotations are therefore treated as instantaneous operations applied at $t = 0$ and $t = \tau$, respectively, while the maximum of the spin echo occurs at $t = t_4 = 2\tau$.

Consider the nuclear-spin ensemble in a reference frame rotating around the z -axis at the carrier angular frequency ω_{RF} . The effective Hamiltonian describing the action of the static local field and of an RF pulse applied along the x direction can be written as

$$H = -\gamma\hbar(h_0I_z + H_1I_x) \quad (2.64)$$

Here, H_{loc} denotes the static local magnetic field experienced by a given nucleus. This field includes the externally applied field H_0 together with any static local contribution arising from the microscopic magnetic environment and from spatial inhomogeneities of the applied field. The quantity h_0 is defined as the effective field offset in the rotating frame

$$h_0 = H_{\text{loc}} - \frac{\omega_{\text{RF}}}{\gamma} \quad (2.65)$$

Equivalently, the corresponding angular-frequency offset is

$$\Delta\omega = \omega_L - \omega_{\text{RF}} = \gamma h_0 \quad (2.66)$$

where $\omega_L = \gamma H_{\text{loc}}$ is the local Larmor angular frequency. Therefore, h_0 does not represent the absolute static magnetic field, but the detuning of a given nucleus from the carrier frequency expressed in magnetic-field units.

Since different nuclei may experience slightly different static local fields, the ensemble is characterized by a distribution of offsets $p(h_0)$ satisfying

$$\int p(h_0) dh_0 = 1 \quad (2.67)$$

When the carrier angular frequency is chosen at the centre of the resonance line, the distribution $p(h_0)$ is centred approximately at $h_0 = 0$. During free evolution, nuclei characterized by different values of h_0 accumulate phase at different rates, producing the reversible dephasing that is subsequently refocused by the π pulse.

The operators I_α , with $\alpha = x, y, z$, represent the components of the nuclear spin angular momentum. During an RF pulse, and for the nuclei lying within the effectively excited spectral interval, the condition $H_1 \gg |h_0|$ allows the offset term to be neglected. Between the pulses, $H_1 = 0$, and the evolution is governed exclusively by the local static-field offset. In the time intervals $(0, t_1)$ and (t_2, t_3) , during which the RF pulses act on the system, the Hamiltonian can therefore be approximated as

$$H = -\gamma \hbar H_1 I_x \quad (2.68)$$

When no RF pulse is acting on the system, namely during the intervals (t_1, t_2) and (t_3, t_4) , the Hamiltonian becomes

$$H = -\gamma \hbar h_0 I_z \quad (2.69)$$

If the starting wave function is $\psi(0)$, its time evolution is then

$$\psi(t_1) = e^{i\gamma H_1 t_1 I_x} \psi(0) \quad (2.70)$$

$$\psi(t_2) = e^{i\gamma h_0 (t_2 - t_1) I_z} \psi(t_1) \quad (2.71)$$

The following operators can be defined:

- $T(t, h_0) = e^{i\gamma h_0 t I_z}$ describes the free evolution of the system under the local static field
- $X(\theta) = e^{i\theta I_x}$ describes a rotation around the x -axis in the right-handed direction

The state evolved from $\psi(0)$ at a generic time after both pulses can then be described as

$$\psi(t) = T(t - \tau, h_0) X(\pi) T(\tau, h_0) X(\pi/2) \psi(0) \quad (2.72)$$

The observable NMR signal is proportional to the total transverse magnetization. In the rotating frame, this corresponds to the ensemble average of the I_y operator

$$\langle I_{y,\text{total}}(t) \rangle = N \int p(h_0) dh_0 \int \psi^*(h_0, t) I_y \psi(h_0, t) d\tau_I \quad (2.73)$$

By inserting the propagation operators and using the commutation relations of the $SU(2)$ algebra, specifically the rotation of operators $X^{-1}(\theta)I_yX(\theta)$ and the phase-accumulation properties of T , the expectation value at the echo time $t = t_4 = 2\tau$ simplifies significantly. At this instant, the two free-evolution intervals have the same duration, and the phase evolution accumulated before the π pulse is exactly reversed during the interval following it

$$\begin{aligned} \langle I_{y,\text{total}}(t) \rangle &= -N \int p(h_0) dh_0 \times \\ &\times \int \psi^*(0) X^{-1}(\pi/2) T^{-1}(\tau, h_0) T(t - \tau, h_0) I_y T^{-1}(t - \tau, h_0) T(\tau, h_0) X(\pi/2) \psi(0) d\tau_I \end{aligned} \quad (2.74)$$

At the echo time $t = 2\tau$, one has $t - \tau = \tau$. Consequently, the free-evolution operators appearing on either side of I_y cancel according to

$$T^{-1}(\tau, h_0) T(t - \tau, h_0) = T^{-1}(\tau, h_0) T(\tau, h_0) = \mathbb{1} \quad (2.75)$$

The phase factors depending on the local field h_0 therefore disappear from the integrand. The transverse magnetization at the echo maximum is thus independent of the static distribution of local fields represented by $p(h_0)$, and the integral over h_0 reduces to the normalization condition

$$\int p(h_0) dh_0 = 1 \quad (2.76)$$

Thus, the final expression for the echo amplitude is

$$\langle I_{y,\text{total}}(2\tau) \rangle = -N \int \psi^*(0) X^{-1}(\pi/2) I_y X(\pi/2) \psi(0) d\tau_I \quad (2.77)$$

Using the transformation $X^{-1}(\pi/2)I_yX(\pi/2) = I_z$, this becomes

$$\langle I_{y,\text{total}}(2\tau) \rangle = -N \int \psi^*(0) I_z \psi(0) d\tau_I = -N \langle I_z(0^-) \rangle \quad (2.78)$$

The signal amplitude following the refocusing pulse is congruent with the post-initial-pulse state. Specifically, for any time t after the π pulse, the transverse magnetization follows a trajectory equivalent to the period t' after the $\pi/2$ pulse, subject to a sign inversion. This behaviour illustrates the time-reversal property of the refocusing pulse within the rotating frame and can be seen in Figure 2.12.

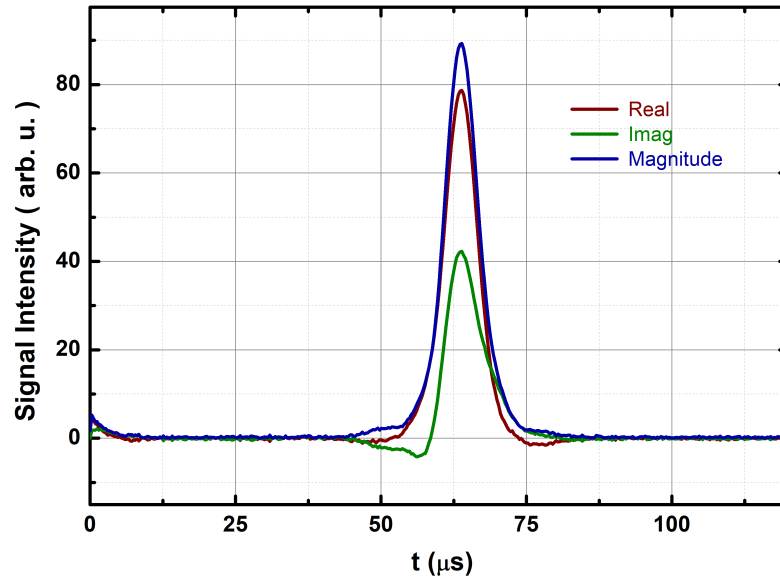


Figure 2.12: Time-domain representation of a spin-echo signal. Following the application of refocusing sequence, the transverse magnetization requires an additional interval τ to reach maximum coherence, at which point the echo signal is generated.

2.4.5 Transverse Relaxation (T_2) Measurement

The Hahn spin-echo sequence described in the previous subsection can be directly employed to measure the transverse relaxation time T_2 , which characterizes the irreversible decay of the magnetization component in the plane perpendicular to the static magnetic field. By refocusing the reversible dephasing caused by static magnetic-field inhomogeneities, the spin echo makes it possible to isolate the intrinsic loss of transverse coherence associated with T_2 [36, 41, 46].

Following Figure 2.10, the sequence consists of an initial $\pi/2$ -perturbation pulse, which flips the longitudinal magnetization into the transverse plane. After a variable time period τ , a π -refocusing pulse is applied. This pulse acts as a refocusing mechanism, reversing the dephasing caused by static field inhomogeneities and leading to the formation of a spin echo at time 2τ after the initial $\pi/2$ -pulse.

To measure T_2 , this spin-echo sequence is repeated multiple times, systematically varying the separation time (by changing τ) for each acquisition. For each time τ , the signal intensity of the generated spin echo is recorded. The signal intensity is obtained by taking the Fourier transform of the echo signal and then integrating along the frequency axis.

The intensity of the signal decreases as the echo time increases. This decrease in echo amplitude is precisely due to the intrinsic, irreversible relaxation time T_2 . Although the spin echo successfully recovers the signal lost from static field inhomogeneities, it cannot recover the signal lost due to the random, fluctuating spin-spin interactions that constitute the true T_2 decay.

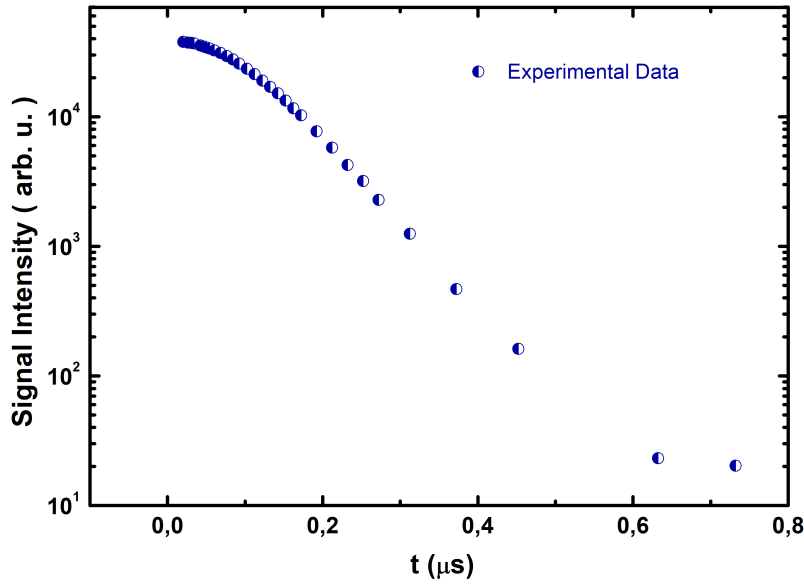


Figure 2.13: Measurement of the transverse relaxation time (T_2) using a series of spin echo acquisitions. Each point represents a refocused signal at different separation between the pulses.

Therefore, by plotting the measured echo signal intensity versus the corresponding separation time, an exponential/gaussian decay curve as the one shown in Figure 2.13 is recorded. This curve allows for the precise determination of the T_2 relaxation time by fitting to an exponential decay model:

$$I = A \cdot \exp(-(tR_1)^\beta) \cdot \exp(-0.5 \cdot (tR_2)^2) \quad (2.79)$$

This specific form is physically justified by the Redfield framework, as detailed in Slichter's formalization [36]. Within this framework, the total intrinsic transverse relaxation rate ($1/T_2$) is partitioned into contributions from different physical regimes:

$$\frac{1}{T_2} = \frac{1}{T_2'} + \frac{1}{2T_1} \quad (2.80)$$

$1/T_2'$ accounts for the 'pure dephasing', the $1/2T_1$ term represents the fundamental broadening due to the finite lifetime of the spin states. T_2' represents the broadening introduced by the spread in the local z -field produced by internal nuclear interactions.

The physics of the fitting model can be explained utilizing the theory of random frequency modulation, which describes how a nuclear spin system loses coherence through stochastic fluctuations of local magnetic fields. This specific hybrid form is necessary for a spin echo experiment because it accounts for the fact that a nucleus often exists in a complex environment where multiple relaxation mechanisms operate on vastly different time scales.

The Gaussian component originates from the nearly static limit of fluctuations. In this regime, the local magnetic fields (primarily generated by neighboring nuclear dipoles) vary at a rate significantly slower than the experimental observation time. Given that these microscopic fields are stochastic and follow a Gaussian probability distribution, the resulting phase accumulation by the spins grows quadratically over time. The parameter R_2 is therefore linked to the secular part of the transverse relaxation ($1/T_2'$).

The exponential is rooted in motional the narrowing limit, occurring when local field fluctuations are sufficiently rapid to average out the local magnetic environment. This physical state is typically driven by dynamic processes, such as molecular reorientation. In this fast-motion limit, the quadratic phase growth transitions into a linear dependence on time, resulting in a purely exponential decay profile.

The parameter R_1 is linked to the longitudinal relaxation (T_1) contribution within the transverse decay measurement. Following the Redfield framework, the total transverse relaxation rate incorporates a broadening term ($1/2T_1$). High-frequency fluctuations occurring at the Larmor frequency provide the necessary energy transitions for this longitudinal relaxation to take place.

The inclusion of the stretching exponent β takes into account that the system may not have a single, uniform correlation time, but rather a distribution of rates caused by structural or dynamic inhomogeneities in the environment.

Using this combined model for a single-ion magnet experiment is essential because it allows to separate the slow dipolar interactions from the fast dynamic fluctuations. Without both terms, the fit would fail to capture the transition between these two physical regimes, leading to an inaccurate determination of the relaxation rates as the system's internal dynamics change with external parameters like temperature.

2.4.6 Inversion Recovery Sequence (T_1)

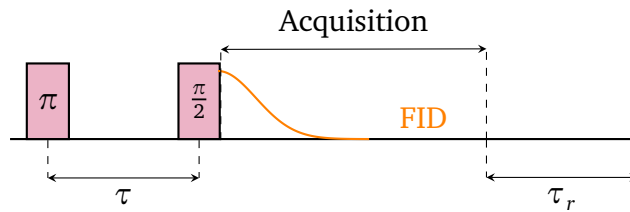


Figure 2.14: Pulse sequence timing diagram for a T_1 FID measurement.

Having established how the Hahn spin-echo sequence can be used to determine the transverse relaxation time T_2 , the discussion now turns to the measurement of the longitudinal relaxation time T_1 . In an inversion-recovery experiment, an additional π pulse is applied before the detection sequence in order to invert the equilibrium longitudinal magnetization. When the recovered magnetization is detected through a spin echo, the resulting sequence therefore contains three RF pulses: an initial π inversion pulse followed, after a variable recovery delay τ , by the $\pi/2$ and π pulses

of the Hahn echo sequence. Alternatively, when the FID can be acquired directly, the recovered magnetization may be detected using only a $\pi/2$ reading pulse.

As shown in Figure 2.14, the measurement sequence consists of an initial π -perturbation pulse to invert the magnetization along the z-axis and, after a variable τ , a $\pi/2$ -reading pulse to read the information encoded in the system. The reading pulse has the function of switching the value of the longitudinal magnetization making it transversal, as the transverse magnetization is the only component that can induce a voltage into the coil and thus the only component that can be measured. By repeating this sequence for various values of τ and plotting the intensity of the signal against τ , a graph that resembles the one in Figure 2.15 can be obtained.

After the magnetization is inverted by the π -pulse, the subsequent transverse magnetization component upon excitation will vary depending on the time that separates the pulses.

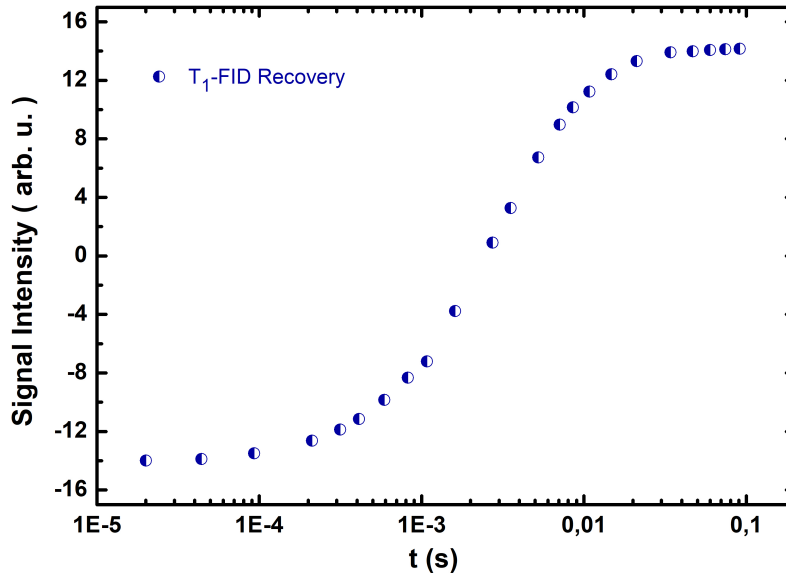


Figure 2.15: Measurement of T_1 relaxation time through a series of FID acquisitions. Each point represents a signal recorded after a specific time τ between pulses.

For short values of τ , the inverted magnetization will have recovered only slightly, leading to a high, yet negative, transverse component after the reading $\pi/2$ pulse. With intermediate values of τ , the magnetization will have recovered partially, resulting in a smaller, near zero, transverse component that could be positive or negative. Finally, for sufficiently long values of τ , the inverted magnetization will be fully recovered, ensuring that after the $\pi/2$ pulse the maximum possible transverse component will be observed.

The signal intensity can be obtained by taking the Fourier transform of the FID signal and then integrating along the frequency axis. This comprehensive set of measurements, when fitted to an appropriate exponential recovery model, allows a

precise determination of the relaxation time T_1 [36, 41]. Mathematically, the signal intensity $I(\tau)$ as a function of the recovery time follows an exponential growth law:

$$I(\tau) = y_0 + A \left[1 - \exp \left(- \left(\frac{\tau}{T_1} \right)^\beta \right) \right] \quad (2.81)$$

To get a good estimate of T_1 one will need a sufficiently broad range of values of τ , ensuring that both the initial inverted state and the fully recovered state are adequately sampled.

Whenever the FID signal cannot be read, the reading sequence can be modified by adding a π -pulse. By adding this pulse, instead of the FID the spin-echo signal will be measured [41, 42]. This sequence can be seen in Figure 2.16

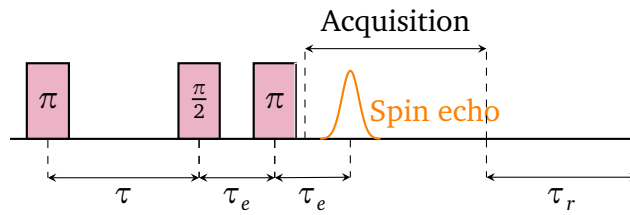


Figure 2.16: *Pulse sequence timing diagram for a T_1 -Echo measurement.*

Another useful approach for determining the longitudinal relaxation time T_1 is the saturation-recovery sequence shown in Figure 2.17. This method is particularly advantageous when the NMR spectrum of the sample is broader than the excitation bandwidth of a single RF pulse.

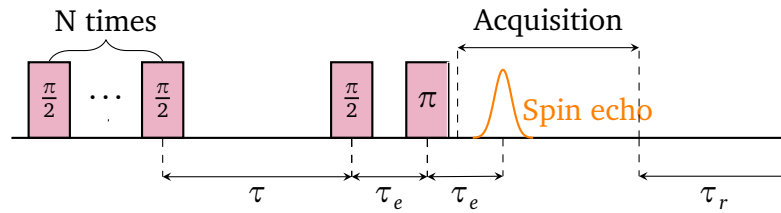


Figure 2.17: *Pulse sequence timing diagram of a saturation comb for T_1 measurement.*

Under these conditions, an individual $\pi/2$ pulse cannot act uniformly on all the nuclei contributing to the spectrum, but directly excites only the fraction whose resonance frequencies lie within the spectral bandwidth of the pulse, typically around the carrier frequency.

To overcome this limitation, a saturation comb consisting of a rapid series of closely spaced $\pi/2$ pulses is applied. The first pulse directly perturbs the nuclei lying within its excitation bandwidth and reduces the corresponding longitudinal polarization. During the interval separating two successive pulses, polarization can be exchanged between dipolar-coupled nuclei through nuclear spin diffusion. This process is mediated by mutual spin flip-flops and transfers the perturbation from the directly

excited nuclei to neighbouring nuclei having sufficiently similar resonance frequencies.

Each subsequent pulse acts again on the nuclei within the directly excited region, while spin diffusion redistributes the loss of polarization throughout a progressively larger fraction of the nuclear-spin system. Provided that the pulses are repeated at sufficiently short intervals compared with the longitudinal recovery time, the combined action of repeated excitation and spin diffusion progressively equalizes the populations of the nuclear Zeeman levels. The saturation comb therefore produces an approximately vanishing longitudinal magnetization over a spectral range broader than that directly covered by a single pulse

$$M_z(0) \simeq 0 \quad (2.82)$$

This saturated state provides a reproducible initial condition for the subsequent recovery measurement. After the pulse train, the system is allowed to evolve for a variable delay τ , during which the longitudinal magnetization returns towards its equilibrium value M_0 through spin-lattice relaxation. At the end of this interval, the recovered longitudinal magnetization is converted into a measurable transverse component using either a single $\pi/2$ reading pulse or a Hahn spin-echo detection sequence [36, 41].

A practical advantage of saturation recovery over inversion recovery is that the initial state is actively prepared by the pulse train at the beginning of each measurement. Consequently, it is not necessary for the magnetization to return completely to thermal equilibrium before the following scan, which can reduce the total acquisition time. The effectiveness of the method nevertheless depends on the ability of the pulse train and nuclear spin diffusion to produce a sufficiently uniform saturation across the complete NMR line. The number of pulses, their separation, and the applied RF power must therefore be chosen so that the residual longitudinal magnetization after the saturation comb is negligible over the spectral region of interest.

The finite excitation bandwidth that motivates the use of a saturation comb is also a central consideration in the acquisition of broad NMR spectra, as discussed in the following section.

2.5 The Frequency Spectrum

Having introduced the Fourier transformation and phase-sensitive processing of the acquired signal, the discussion now focuses on the relation between the spectral width of the sample and the excitation bandwidth of the RF pulse. The complex NMR spectrum is obtained by applying a Fourier transform to the acquired signal:

$$S(\omega) = \int_0^{+\infty} s(t) \exp(-i\omega t) dt \quad (2.83)$$

where $s(t)$ is the complex time-domain signal obtained through quadrature acquisition. The Fourier transform decomposes the temporal evolution of the transverse

magnetization into its angular-frequency components. Each spectral contribution therefore corresponds to a group of nuclei precessing at a particular resonance angular frequency. For a nucleus experiencing a local magnetic field H_{loc} , the corresponding Larmor angular frequency is

$$\omega_0 = \gamma_N H_{\text{loc}} \quad (2.84)$$

where γ_N is the nuclear gyromagnetic ratio. The position of an NMR line therefore reflects the average local magnetic field experienced by the nuclei, while its width and shape provide information about the spatial distribution and temporal evolution of these fields.

For an ideal ensemble of identical, non-interacting nuclei precessing indefinitely at a single angular frequency, the spectrum would consist of a delta function centred at ω_0 . In a real condensed-matter system, the transverse magnetization has a finite coherence time and the nuclei generally experience a distribution of local magnetic environments. The observed resonance consequently has a finite width and a characteristic lineshape.

The sources of spectral broadening are conventionally divided into homogeneous and inhomogeneous contributions. Homogeneous broadening describes mechanisms that give the same intrinsic linewidth to all nuclei belonging to an equivalent ensemble. For example, an exponential transverse decay characterized by the intrinsic relaxation time T_2 produces a Lorentzian resonance whose full width at half maximum, expressed in angular-frequency units, is

$$\Delta\omega_{\text{hom}} \simeq \frac{1}{T_2} \quad (2.85)$$

Inhomogeneous broadening instead arises when different nuclei experience different quasistatic local magnetic fields and therefore precess at different resonance angular frequencies. Possible contributions include spatial inhomogeneities of the applied field, inequivalent nuclear sites, distributions of hyperfine fields, anisotropic magnetic interactions, and the different orientations of crystallites in a powder sample. The measured linewidth may therefore contain both intrinsic information about the sample and contributions associated with the experimental apparatus [36, 41].

In a molecular magnet such as Dy-SQ, the proton spectrum can be particularly broad because the nuclei experience different dipolar and hyperfine fields generated by the anisotropic electronic magnetic moments. The resulting angular-frequency distribution constitutes a microscopic fingerprint of the static magnetic environment of the proton sites [34, 35, 37].

Spectral Profile and Excitation Bandwidth of a Rectangular Radiofrequency Pulse

The NMR spectrum of the sample must be distinguished from the angular-frequency profile of the radiofrequency pulse used to excite it. A rectangular RF pulse con-

sists of an oscillating carrier wave at an angular frequency ω_{RF} , selected close to the expected nuclear resonance frequency, modulated by a rectangular envelope of duration t_p . The pulse can be represented in the laboratory frame as

$$H_1(t) = A(t) \cos(\omega_{\text{RF}}t + \phi) \quad (2.86)$$

where ϕ is the phase of the pulse and the rectangular envelope is

$$A(t) = \begin{cases} H_1, & |t| \leq t_p/2 \\ 0, & |t| > t_p/2 \end{cases} \quad (2.87)$$

Since the pulse has a finite duration, it cannot contain only a single angular-frequency component. Considering the co-rotating component of the RF field, its spectral amplitude around ω_{RF} is proportional to

$$|\tilde{H}_1(\omega)| \propto H_1 t_p \left| \frac{\sin[(\omega - \omega_{\text{RF}}) t_p/2]}{(\omega - \omega_{\text{RF}}) t_p/2} \right| \quad (2.88)$$

The angular-frequency profile of a rectangular pulse therefore has a sinc shape centred at the carrier angular frequency. The quantity $|\tilde{H}_1(\omega)|$ represents the spectral amplitude of the RF field, whereas a quantity proportional to the spectral power would be given by $|\tilde{H}_1(\omega)|^2$. The first zeros of the central lobe occur at

$$\omega - \omega_{\text{RF}} = \pm \frac{2\pi}{t_p} \quad (2.89)$$

and the corresponding zero-to-zero angular-frequency width is

$$\Delta\omega_{\text{exc}} = \frac{4\pi}{t_p} \quad (2.90)$$

A short pulse therefore possesses a broad angular-frequency profile and can excite a wide range of resonance frequencies. Conversely, a longer pulse is more frequency-selective.

The sinc profile provides a useful first-order representation of the spectral content and approximate excitation bandwidth of a rectangular pulse. The exact rotation produced for spins away from resonance also depends on the direction and magnitude of the effective magnetic field in the rotating frame and must, in general, be obtained from the equations of motion of the magnetization [41, 42].

Receiver Reference Frequency and Angular-Frequency Offsets

Before analyzing specific spectral scenarios, it is essential to define the nature of the data captured by a pulsed spectrometer. As described in the discussion of quadrature detection, the high-frequency voltage induced in the receiving coil is demodulated with respect to the spectrometer reference angular frequency ω_{RF} . The Fourier transform of the demodulated time-domain signal therefore produces a spectrum expressed in terms of the angular-frequency offset

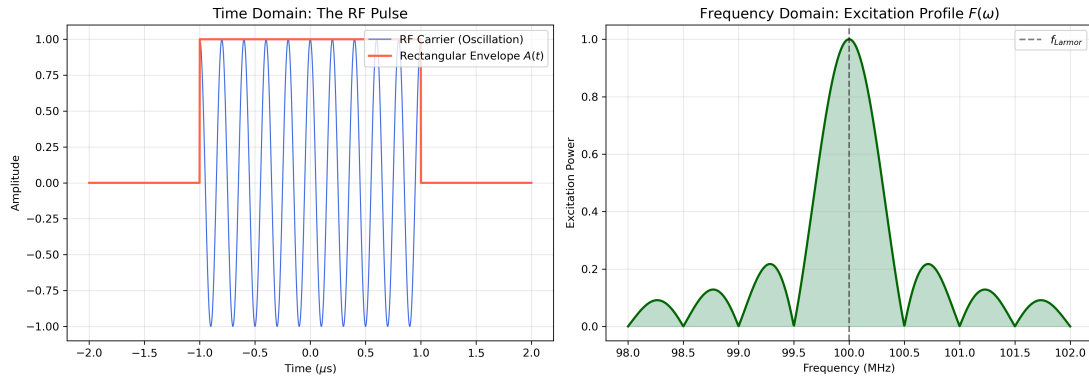


Figure 2.18: Time-domain representation of a rectangular radiofrequency pulse and corresponding sinc-shaped spectral amplitude. The central lobe is centred at the carrier angular frequency ω_{RF} , and its first zeros occur at $\omega - \omega_{\text{RF}} = \pm 2\pi/t_p$. A shorter pulse produces a broader excitation profile.

$$\omega_{\text{off}} = \omega_0 - \omega_{\text{RF}} \quad (2.91)$$

rather than directly in terms of the absolute resonance angular frequency. The carrier angular frequency consequently defines the origin of the rotating-frame spectrum. A resonance exactly at the carrier angular frequency appears at $\omega_{\text{off}} = 0$, whereas a resonance above or below the carrier appears at a positive or negative offset, respectively. The absolute resonance angular frequency is recovered through

$$\omega_{\text{abs}} = \omega_{\text{RF}} + \omega_{\text{off}} \quad (2.92)$$

Changing the carrier angular frequency therefore changes the apparent position of a given resonance in the rotating-frame spectrum but does not change its absolute physical angular frequency. Two acquisitions performed using different carrier angular frequencies can consequently be compared only after their angular-frequency axes have been mapped onto the same absolute laboratory-frame scale [41, 42].

The Frequency-Stepped Point-by-Point Reconstruction

The necessity of a frequency-stepped acquisition protocol arises from the possible mismatch between the excitation bandwidth of the RF pulse and the spectral width of the sample. In an ideal situation in which the sample exhibits a narrow resonance, the distribution of local resonance frequencies is significantly smaller than the central lobe of the RF pulse and a single acquisition is sufficient. As shown in Figure 2.19, the excitation bandwidth encompasses the complete resonance, allowing the whole line to be detected under approximately uniform excitation conditions.

However, in systems such as molecular magnets or magnetic solids, inhomogeneous broadening may extend over an angular-frequency range considerably larger than the excitation bandwidth of a standard rectangular pulse. In this regime, a single pulse does not uniformly excite the complete resonance but probes only a restricted

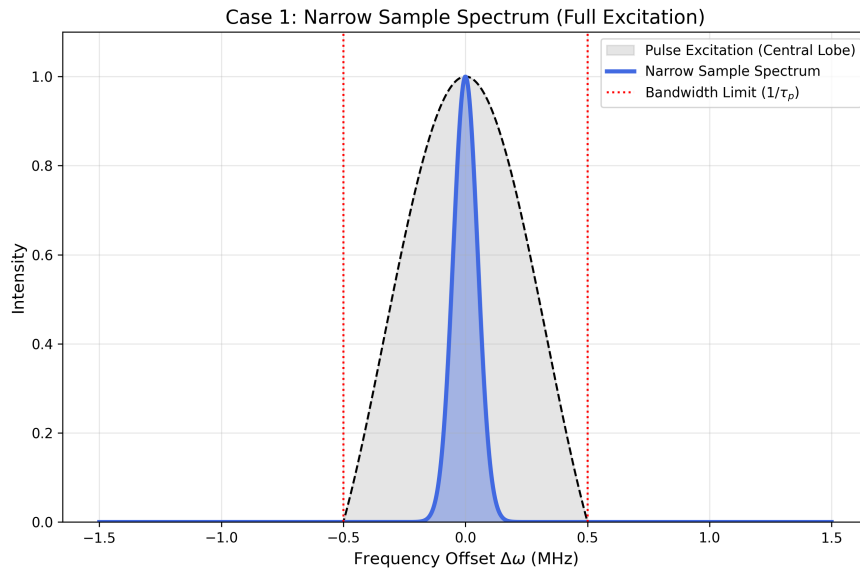


Figure 2.19: *Excitation of a narrow resonance. The excitation bandwidth of the RF pulse exceeds the spectral width of the sample, allowing the complete resonance to be detected in a single acquisition.*

spectral interval of the total nuclear spin ensemble. When the carrier angular frequency ω_{RF} is displaced from a given resonance frequency, the detected contribution appears at a non-zero rotating-frame offset and is excited with a lower efficiency because it lies away from the centre of the pulse profile, as illustrated in Figure 2.20.

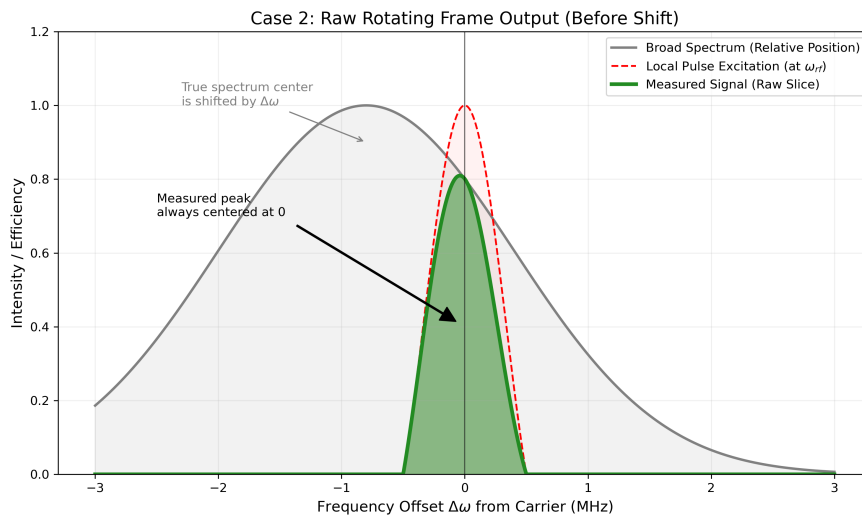


Figure 2.20: *Local excitation of an inhomogeneously broadened spectrum. Since the excitation bandwidth of the RF pulse is smaller than the spectral width of the sample, only a restricted spectral interval of the total spin distribution contributes significantly to a single acquisition.*

To map the complete lineshape of a broad resonance, the carrier angular frequency is incremented in discrete steps across the expected spectral range. At each step,

a complete NMR acquisition is performed using the same pulse amplitude, pulse duration, receiver gain, number of scans, echo time, and recycle delay, so that the measured intensities remain directly comparable. The reconstruction procedure can be summarized as follows.

Discrete Stepping: The carrier angular frequency $\omega_{\text{RF},n}$ is incremented in discrete steps across the expected resonance interval. At each step, a local time-domain NMR signal is acquired and Fourier transformed.

Selective Windowing: Only the central part of each local spectrum is retained because this is the region in which the RF excitation amplitude and phase are most uniform. Spectral regions associated with the side lobes of the pulse profile are excluded or given a lower statistical weight.

Laboratory-Frame Mapping: Each local spectrum, initially expressed as a function of ω_{off} , is mapped onto the absolute angular-frequency scale according to equation 2.92.

Combination of the Spectral Windows: After the coordinate transformation, adjacent spectral windows occupy different and partially overlapping regions of the absolute angular-frequency axis. The overlapping regions are combined by averaging or by using weights based on the signal-to-noise ratio and excitation efficiency of each acquisition.

The reconstruction should therefore be regarded as a mapping and weighted combination of overlapping spectral windows rather than as a coherent summation, unless the relative complex phases of all acquisitions are explicitly preserved and corrected. The spacing between successive carrier angular frequencies must be sufficiently small to ensure partial overlap between adjacent windows and to avoid unsampled regions of the resonance.

This method allows the complete NMR lineshape to be reconstructed even when its total width substantially exceeds the excitation bandwidth of a single pulse. The resulting spectrum represents the distribution of local resonance angular frequencies within the sample, provided that the experimental conditions remain constant throughout the frequency sweep and that the frequency dependence of the probe sensitivity is negligible or appropriately corrected.

The Narrow Spectrum: From Misalignment to Restoration

In the case of a narrow resonance, whose spectral width is smaller than the central lobe of the pulse profile, the experimental result depends on the difference between the carrier angular frequency and the resonance angular frequency. When ω_{RF} coincides with ω_0 , the resonance lies at the centre of the RF excitation profile and the transverse magnetization is generated with maximum efficiency. The resulting rotating-frame spectrum therefore displays a high-intensity peak at $\omega_{\text{off}} = 0$.

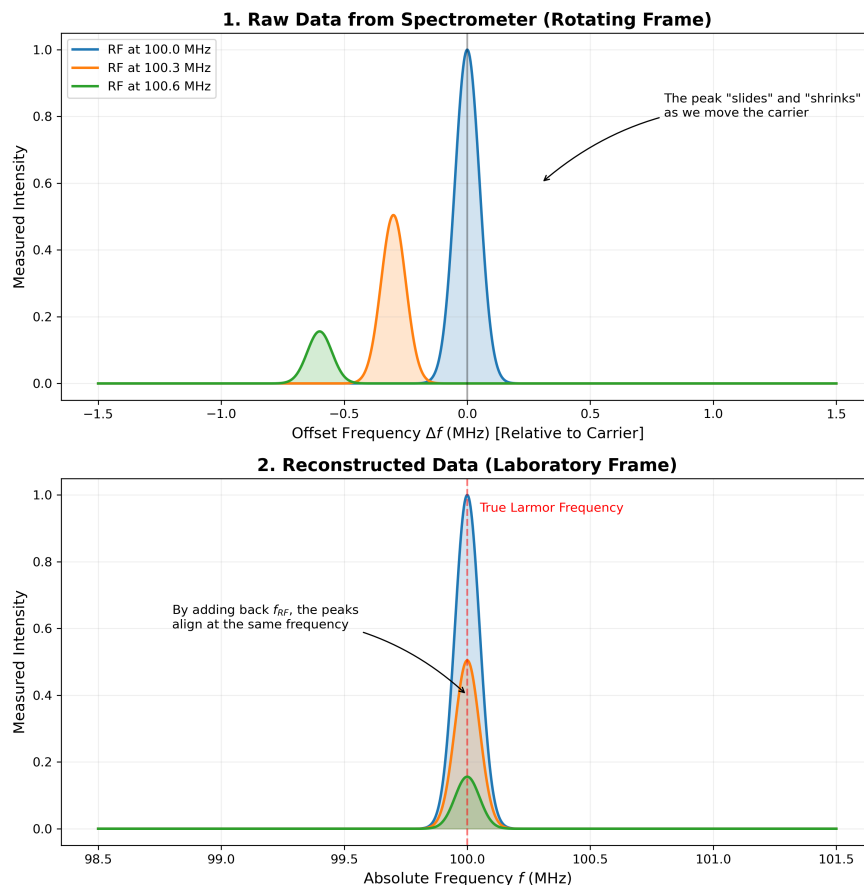


Figure 2.21: Comparison of a narrow resonance acquired using different carrier angular frequencies. The rotating-frame spectra show different frequency offsets and excitation amplitudes, whereas mapping onto the absolute angular-frequency scale restores the common physical resonance position.

When the carrier angular frequency is displaced from the resonance, the same physical peak appears at a non-zero offset and its amplitude may be reduced because the excitation efficiency decreases away from the centre of the RF pulse profile. This apparent displacement does not correspond to a modification of the microscopic magnetic environment of the sample but results from the choice of the receiver reference frequency.

The absolute resonance position is recovered by applying the coordinate transformation given in Equation 2.92. After this mapping, acquisitions performed using different carrier angular frequencies coincide at the same value of ω_{abs} , while any remaining difference in amplitude reflects the different off-resonance excitation conditions. This behaviour is illustrated in Figure 2.21.

The Broad Spectrum: Synthesis of the Complete Lineshape

The situation changes when the inhomogeneous spectral width substantially exceeds the excitation bandwidth of the RF pulse. In this regime, a single acquisition can detect only the fraction of the nuclear spin ensemble whose resonance frequen-

cies fall within the efficiently excited interval around ω_{RF} . The carrier-frequency sweep therefore becomes the principal experimental procedure used to sample the different regions of the broad resonance.

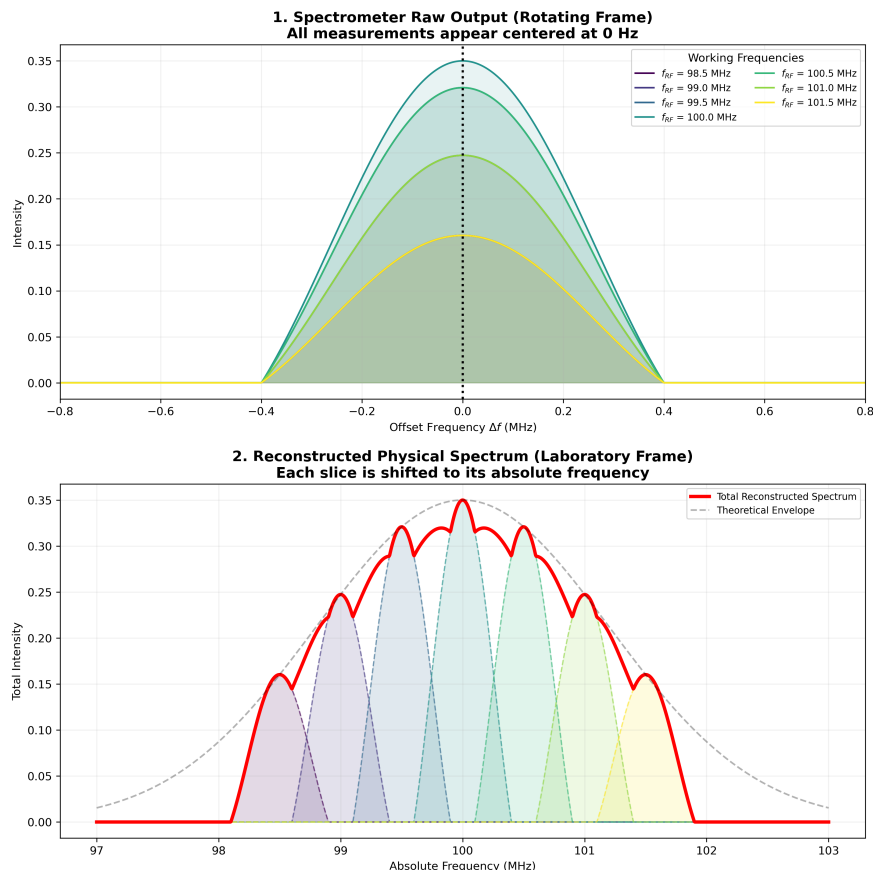


Figure 2.22: Reconstruction of a broad NMR spectrum using a frequency-stepped acquisition protocol. Individual spectral windows, initially expressed relative to their respective carrier angular frequencies, are mapped onto the absolute angular-frequency scale and combined to recover the complete lineshape.

During a frequency-stepped experiment, the spectrometer records a series of local spectra. Each acquisition is initially represented as a function of the offset angular frequency relative to its own carrier $\omega_{\text{RF},n}$. The positions of the detected contributions in the rotating frame depend on the difference between their physical resonance frequencies and the carrier angular frequency used for that acquisition. They are therefore not necessarily centred at zero offset. Before the different acquisitions can be combined, each local spectrum must be mapped onto the absolute angular-frequency scale using equation 2.92.

After this transformation, each spectral window occupies the correct interval of the global resonance. Only the central and most uniformly excited part of each acquisition is retained, while overlapping regions are averaged or appropriately weighted.

The complete broad lineshape is obtained by combining these mapped spectral win-

dows across the full angular-frequency range. Each acquisition therefore acts as a local observation window of the nuclear spin distribution, while the final reconstructed spectrum provides a global representation of the static magnetic environments experienced by the nuclei, as illustrated in Figure 2.22.

2.6 Experimental Setup and Cryogenic Systems

A brief overview of the basic components of an NMR apparatus was given at the beginning of this chapter. In this section, the experimental setup used for the measurements on Dy-SQ is described in more detail. A schematic representation of the full apparatus is shown in Figure 2.23.

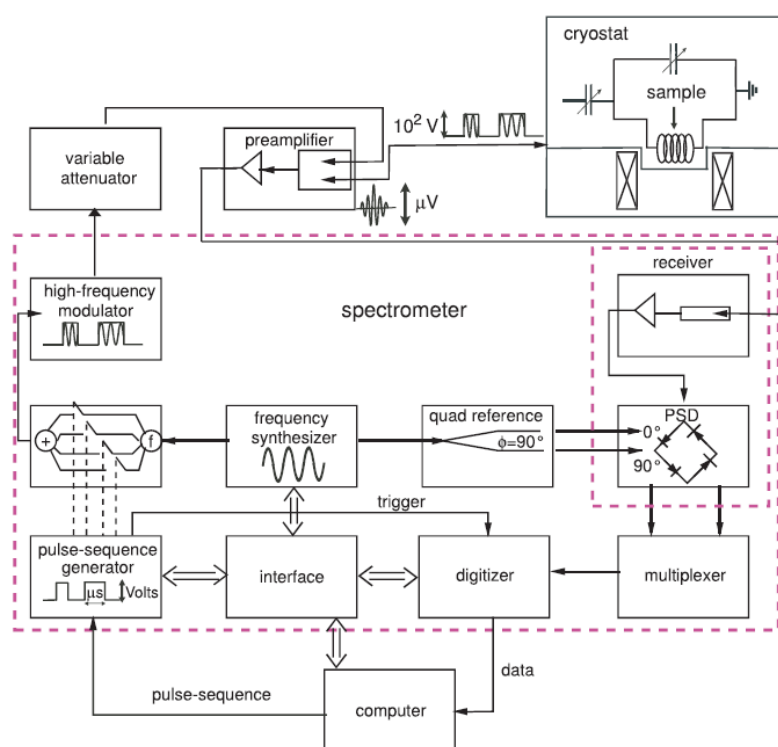


Figure 2.23: Schematic representation of a pulsed NMR experimental apparatus. The spectrometer generates the radio-frequency pulse sequence, which is amplified and delivered to the RF coil surrounding the sample inside the cryostat. After excitation, the weak NMR signal induced in the same coil is routed through the preamplifier and receiver chain, phase-sensitive detected in quadrature, digitized, and finally processed by the computer. Adapted from [47].

The Spectrometer

The spectrometer is the central electronic unit of the NMR setup. Its role is twofold: it generates the radio-frequency pulses used to excite the nuclear spin system and it detects the weak electromagnetic signal produced by the sample response after excitation.

During the excitation stage, the spectrometer synthesizes a radio-frequency carrier close to the Larmor frequency of the selected nucleus. This signal is shaped into pulses of controlled duration, amplitude, and phase, according to the pulse sequence required by the experiment. The generated RF pulse is then sent to a power amplifier, which increases its power before delivering it to the probe circuit and, ultimately, to the RF coil surrounding the sample.

Immediately after the excitation pulse, the setup must switch from transmission to reception. The NMR signal emitted by the sample is several orders of magnitude weaker than the applied RF pulse, and the receiver electronics must therefore be protected from the high-power excitation stage. This separation is achieved through the duplexer, which isolates the sensitive receiver chain during transmission and redirects the weak free-induction decay or spin-echo signal toward the preamplifier during acquisition.

In the detection stage, the spectrometer acts as a phase-sensitive receiver. The signal amplified by the preamplifier is mixed with the reference frequency, digitized through an analog-to-digital converter, and stored as a time-domain complex signal. This signal is then processed to reconstruct the NMR spectrum or to extract the relaxation times, depending on the pulse sequence employed.

Cryogenic Systems and Magnetic Fields

The cryogenic system allows the sample temperature to be controlled during the NMR measurements. This is essential in the present work, since the magnetic response of Dy-SQ was investigated over a broad temperature range. Cooling was achieved using either liquid nitrogen or liquid helium, depending on the temperature interval required by the experiment. The final temperature of the sample was controlled by regulating the flow of cryogenic fluid and by using a resistive heater placed close to the cold region of the cryostat.

Two different cryogenic configurations were used during the experimental campaign. The first set of measurements, performed at low field with $H_0 = 1.3$ T, was carried out using an exchange-gas cryostat. In this configuration, the sample is not in direct contact with the cryogenic liquid. Instead, it is placed in an inner chamber filled with an inert exchange gas, which provides thermal contact between the sample and the colder external region of the cryostat. This configuration allows the sample to thermalize in a controlled and relatively homogeneous environment.

The second set of measurements, performed at high field with $H_0 = 3.8$ T, was carried out using a flow cryostat. In this case, the cooling medium is directly guided through the cryostat region containing the sample. The temperature is controlled by adjusting the cryogenic flow and the power dissipated by the heater placed near the entrance of the cryostat. This configuration provides efficient cooling and was used for the high-field measurements.

The magnetic field was generated by different systems in the two experimental campaigns. For the measurements at $H_0 = 1.3$ T, the static field was generated by a water-cooled resistive electromagnet. In this setup, the magnetic field is produced by high-current coils wound around a ferromagnetic yoke, which concentrates the magnetic flux in the gap between the pole pieces. The sample and the RF coil were positioned in this central gap, where the field is sufficiently homogeneous for the NMR measurement. Since the coils dissipate heat during operation, a continuous water-cooling circuit was used to stabilize the magnet and prevent overheating during long acquisition times.

For the measurements at $H_0 = 3.8$ T, the required field was produced by a superconducting magnet manufactured by Cryogenic Ltd, with a nominal maximum field of approximately 9 T. In contrast to the water-cooled resistive electromagnet used for the low-field measurements, this system relies on superconducting coils kept below their critical temperature by a liquid-helium cryogenic environment. Under these conditions, the coils can sustain large persistent currents with negligible resistive dissipation, allowing the generation of intense and temporally stable magnetic fields. This stability is particularly advantageous for high-field NMR experiments. In addition to temporal stability, NMR measurements also require a high degree of spatial field homogeneity over the sample volume. Residual inhomogeneities of the main static field H_0 can be compensated by means of shim coils, namely auxiliary coils placed around the magnet bore and designed to generate small corrective magnetic-field gradients. By driving controlled currents through these coils, the spatial profile of the magnetic field can be adjusted in order to reduce unwanted field variations across the sample region. This procedure is essential in NMR spectroscopy, since field inhomogeneities directly contribute to artificial line broadening and may affect the reconstruction of the absorption spectrum [41, 42]. In this configuration, the sample was placed inside the RF coil and positioned in the homogeneous central region of the magnet, where the NMR signal can be detected under well-defined field conditions.

Concluding Remarks

This chapter established the theoretical and experimental framework required for the proton nuclear magnetic resonance investigation presented in this work. The discussion began with the principal interactions governing the nuclear-spin system and with the mechanism through which the precessing transverse magnetization generates a detectable voltage in the receiving coil. The classical and quantum-mechanical descriptions of nuclear magnetic resonance were then introduced, together with the Bloch equations and the spectral-density formalism connecting microscopic fluctuations of the local magnetic field to the longitudinal and transverse relaxation times T_1 and T_2 . Particular attention was subsequently devoted to pulsed nuclear magnetic resonance, including the generation of the free induction decay, quadrature acquisition, Fourier transformation, spectral integration, radiofrequency-pulse calibration, and the formation of the Hahn spin echo. These concepts provided the basis for the description of the pulse sequences employed to

determine T_2 and T_1 through spin-echo, inversion-recovery, and saturation-recovery measurements. Finally, the chapter examined the relation between the spectral width of the sample and the excitation bandwidth of a finite radiofrequency pulse, introducing the frequency-stepped procedure required to reconstruct the broad proton NMR spectra characteristic of molecular magnetic systems.

Nuclear magnetic resonance therefore provides microscopic information on both the static distribution and the temporal fluctuations of the magnetic fields experienced by the nuclear probes. The following chapter introduces muon spin spectroscopy, a complementary local-probe technique in which spin-polarized positive muons are implanted directly into the sample. Although the nature and detection of the probe are different, the evolution of the muon polarization is likewise governed by the local magnetic environment and its fluctuations. The concepts of spin precession, relaxation, field distributions, correlation functions, and spectral density developed in the present chapter will therefore provide a useful foundation for the discussion of zero-field, longitudinal-field, and transverse-field muon spin spectroscopy measurements.

Chapter 3

Muon Spin Spectroscopy

Muon spin spectroscopy is a local-probe technique that investigates magnetic systems through the time evolution of the spin polarization of implanted positive muons. In analogy with nuclear magnetic resonance, the basic physical principle is the precession and relaxation of a magnetic moment in the local magnetic field generated by the sample. The distinctive feature of muon spin spectroscopy is that the probe is not a nucleus already present in the material, but an externally implanted spin-polarized muon. After thermalization, the muon senses the magnetic environment at its stopping site and subsequently decays, emitting a positron preferentially along the instantaneous direction of its spin. By reconstructing the time-dependent positron asymmetry, muon spin spectroscopy provides direct access to the distribution and dynamics of local magnetic fields on the microsecond timescale.

This chapter introduces the physical principles and experimental methodology required to interpret the muon spin spectroscopy measurements discussed in this work. Section 3.1 presents the properties of the positive muon, the production and implantation of a polarized muon beam, the origin of the experimental asymmetry, and the connection between Larmor precession and local magnetic sensing. Section 3.2 then develops the main polarization functions used to interpret the data in zero-field, longitudinal-field, and transverse-field geometries, emphasizing the distinction between static field distributions and dynamical magnetic fluctuations. The aim is not to provide an exhaustive review of the technique, but to establish the theoretical and experimental tools needed for the analysis of the Dy-SQ measurements presented in the following chapters.

The theoretical framework and the description of muon spin spectroscopy presented in this chapter follow primarily the treatments by Cox, Blundell, Dalmas de Réotier and Yaouanc, Hillier *et al.*, Amato, and Carretta and Lascialfari [37–40, 48, 49], unless otherwise specified. The discussion of dynamic longitudinal relaxation and spectral-density effects also follows the Redfield framework [45].

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3.1 Fundamentals of Muon Spin Spectroscopy

Muon spectroscopy (μ SR) is an experimental technique that uses spin-polarized positive muons (μ^+) to study a variety of phenomena, including magnetism, superconductivity and molecular dynamics [38, 48].

3.1.1 The Muon as a Microscopic Magnetic Probe

The positive muon (μ^+) is a spin-1/2 lepton. Its mass is approximately 207 times higher than the electron's mass and 9 times smaller than the proton's mass. For a charged spin-1/2 particle, the magnetic moment and the gyromagnetic ratio are inversely related to the particle mass, although the precise value also depends on its gyromagnetic factor. As a consequence the muon's magnetic moment is approximately 3.18 times higher than the proton's magnetic moment and for its gyromagnetic ratio one has [38, 39, 48]

$$\frac{\gamma_\mu}{2\pi} \simeq 135.54 \text{ MHz T}^{-1} \quad (3.1)$$

This value is more than three times larger than the proton gyromagnetic ratio and is higher than that of conventional nuclear spin probes. The positive muon is therefore exceptionally sensitive to weak magnetic fields: even small local fields produce a sizeable precession of the muon spin within its finite lifetime. This makes μ SR a powerful local probe of both the magnitude and the spatial distribution of internal magnetic fields.

The usefulness of the muon as a microscopic probe also relies on the fact that it is implanted directly into the material. After entering the sample, the muon rapidly loses its kinetic energy and generally comes to rest at an interstitial site, where its spin evolves under the action of the local magnetic field generated by nuclear magnetic moments, electronic moments, and externally applied fields.

The subsequent decay products are detected and used to reconstruct the time evolution of the muon spin polarization, thereby providing information about the static and dynamic magnetic environment at the muon stopping site.

Unlike scattering techniques, which probe spatially averaged correlations through particles leaving the sample, μ SR measures the magnetic response locally from within the material. The muon should not, however, be regarded as a completely non-interacting probe, since its positive charge may locally perturb the electronic or crystallographic environment. It is therefore more appropriate to describe it as a highly sensitive local magnetic probe whose degree of perturbation depends on the investigated material [38, 39].

	charge	spin	mass	moment	$\gamma / 2\pi$ (kHz G ⁻¹)	lifetime (μ s)
e	$\pm e$	1/2	m_e = 0.51 MeV	$657 \mu_p$	2800	∞
μ	$\pm e$	1/2	$207 m_e$ = 105.7 MeV	$3.18 \mu_p$	13.5	2.19
p	$\pm e$	1/2	$1836 m_e$ = 938 MeV	μ_p	4.26	∞

Figure 3.1: Comparison of fundamental properties for the electron (e), muon (μ), and proton (p). The muon's intermediate mass and distinct gyromagnetic ratio (γ_μ) allow it to probe magnetic environments with a unique sensitivity if compared with conventional NMR or ESR. Adapted from [48].

3.1.2 Experimental Set-up

Muon spin spectroscopy cannot be performed using a conventional laboratory-scale spectrometer alone. In addition to the detector system and the sample environment, the experiment requires an intense beam of spin-polarized muons, together with a particle accelerator and a dedicated beamline capable of producing, selecting, and transporting the particles to the sample.

The short lifetime of the muon and the technological complexity associated with its production restrict μ SR experiments to a small number of large-scale accelerator facilities worldwide. The four long-established international facilities routinely associated with condensed-matter μ SR are the Paul Scherrer Institute in Switzerland, TRIUMF in Canada, the ISIS Neutron and Muon Source in the United Kingdom, and J-PARC in Japan [38]. The measurements reported in this thesis were performed at the Paul Scherrer Institute in Villigen, Switzerland, using the General Purpose Surface-Muon instrument.

The following sections describe the production of the muon beam, the origin of its spin polarization, and the experimental apparatus used to implant the muons into the sample and detect their subsequent decay.

From Proton Acceleration to Pion Production

The generation of a muon beam at the Paul Scherrer Institute begins with the acceleration of a high-intensity proton beam to 590 MeV by means of an 8-sector cyclotron with a generated current of approximately 2.2 mA. When these protons collide with a stationary graphite target, they trigger nuclear spallation reactions that produce positive pions (π^+). The pions are short-lived (lifetime of ≈ 26 ns) mesons whose decay is governed by the weak nuclear interaction, which introduces the fundamental symmetries necessary for the μ SR [38, 51].

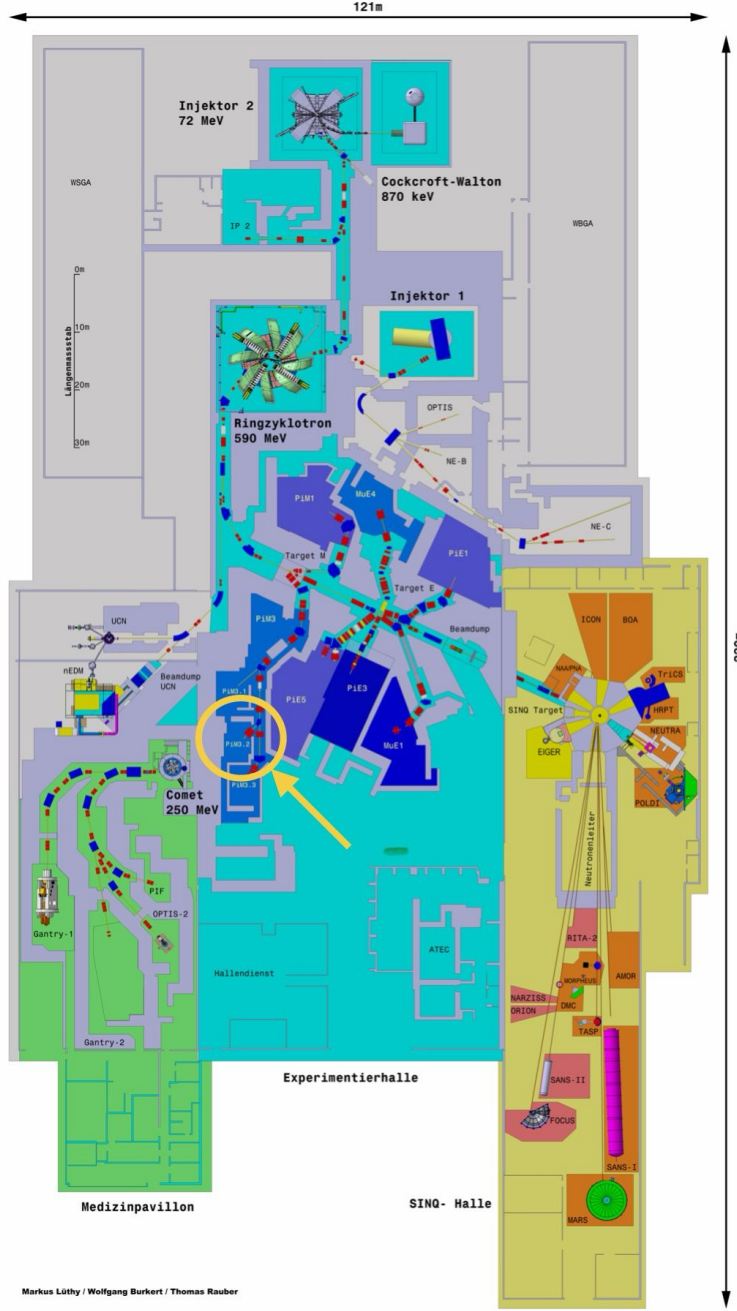


Figure 3.2: A map of the $S\mu S$ facility at the Paul Scherrer Institute for muon spectroscopy experiments. The arrow points at the GPS Laboratory. Adapted from [50].

Kinematics of Two-Body Pion Decay and Beam Polarization

The utility of the muon in the spectroscopic investigation of condensed matter is rooted in the specific kinematics of the pion decay process. A positive pion decays in a positive muon and a muon-neutrino through a two-body process (see Figure 3.3) described by the following decay law:

$$\pi^+ \rightarrow \mu^+ + \nu_\mu \quad (3.2)$$

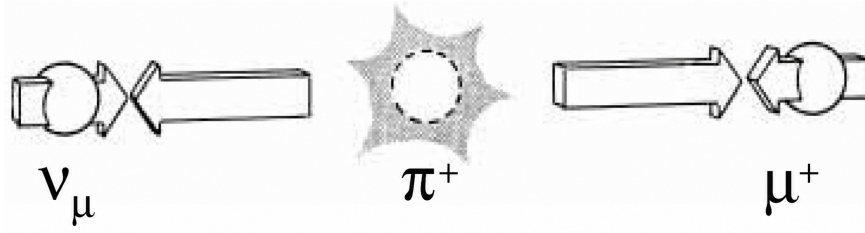


Figure 3.3: Sketch of the two-body process describing the decay of the pion. Adapted from [39].

Because the pion is a spin-zero particle, the conservation of angular momentum requires that the resulting muon and neutrino possess opposite spin orientations. The weak interaction is characterized by a maximal violation of parity, meaning that neutrinos are exclusively left-handed, with their spin always oriented antiparallel to their linear momentum. To satisfy the conservation of both momentum and angular momentum in the rest frame of the pion, the muon is forced into a state where its spin is also oriented strictly antiparallel to its momentum.

This kinematic constraint results in a muon beam that is naturally almost fully spin-polarized, eliminating the need for external polarizing fields or cryogenic temperatures [38, 39]. This represents a major advantage of μ SR over conventional NMR, where the nuclear polarization is established by thermal equilibrium in an applied magnetic field and is therefore typically very small [36, 38].

Implantation and the Experimental Environment

The measurements were performed on the π M3.2 beamline using the GPS, or General Purpose Surface-Muon instrument. The standard helium-4 flow cryostat of the instrument allows measurements to be performed at temperatures down to approximately 1.6 K. At the experimental station, the surface-muon beam has a kinetic energy of approximately 4 MeV and a linear momentum of approximately 28 MeV/c [51–53]. The transverse intensity distribution of the beam is approximately Gaussian.

Under the collimation conditions employed in the present experiment, its full width at half maximum was approximately 5 mm. The finite transverse dimensions of the beam must be considered when mounting the sample, since muons falling outside the sample may stop in the sample holder or in other surrounding materials and produce an additional background contribution to the measured signal.

After entering the sample, the muons rapidly lose their kinetic energy through successive interactions with the electrons and nuclei of the material. These processes are dominated by the Coulomb interaction and include electronic excitation, ionization, and elastic scattering. They reduce the translational energy of the muon

until it reaches thermal energies and comes to rest, generally at an interstitial position within the crystal lattice, on a timescale shorter than approximately 1 ns.

Since the slowing-down processes are predominantly electrostatic and do not couple significantly to the muon spin, very little depolarization occurs during thermalization. The muon therefore retains most of the spin polarization acquired during pion decay when it reaches its stopping site [38, 39].

The identification of the muon stopping site represents an important aspect of the interpretation of μ SR experiments. Unlike NMR, where the crystallographic position of the probed nucleus is known from the chemical structure of the sample, the implanted muon is an external probe whose final position is determined by the electrostatic potential of the crystal. The preferred stopping regions therefore depend on the crystallographic structure, on the charge distribution generated by the ions, and on the local minima of the electrostatic potential experienced by the positive muon.

This represents a complication of μ SR with respect to conventional NMR, since the local magnetic field sensed by the muon can be interpreted microscopically only if the corresponding stopping site is known. Moreover, the implanted muon is not a passive probe from the structural point of view: because it carries a positive charge, it can locally distort the surrounding lattice and modify the electrostatic environment. For this reason, the determination of the muon stopping site often requires dedicated first-principles calculations, typically based on density-functional theory, in which the muon is explicitly included in the simulated crystal structure [38, 39, 49].

It should also be emphasized that a single crystallographic stopping site is not always guaranteed. In complex or low-symmetry materials, several inequivalent local minima of the electrostatic potential may exist, and muons can therefore occupy more than one stopping site. In such cases, the measured asymmetry reflects an average over different local magnetic environments, which must be taken into account when interpreting the relaxation functions.

Three-Body Muon Decay and the Origin of Asymmetry

The observation of the local magnetic environment is made possible by the subsequent decay of the muon after a mean lifetime of $2.197 \mu\text{s}$. The main decay channel is a three-body process (see Figure 3.4) described by the following decay law:

$$\mu^+ \rightarrow e^+ + \nu_e + \bar{\nu}_\mu \quad (3.3)$$

Unlike the two-body pion decay, the energy of the resulting positron is not fixed but it follows a continuous distribution up to a maximum of 52.8 MeV [38, 39].

The spatial distribution of the decay positrons (described in Figure 3.5) provides the fundamental link between the microscopic muon spin and the macroscopic experimental signal. This distribution is intrinsically linked to the energy of the emitted

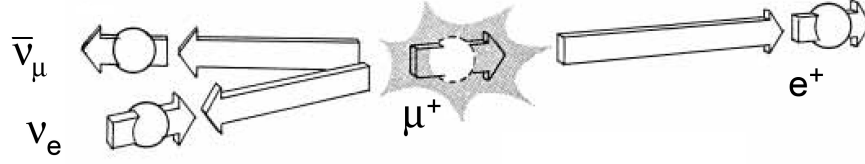


Figure 3.4: sketch of the three-body process describing the decay of the muon. Adapted from [39].

positron, as the weak interaction dictates a stronger correlation between the spin direction and the emission path for higher-energy particles. Mathematically, the probability of a positron being emitted at an angle θ with respect to the muon spin vector at the moment of the decay is defined by the asymmetry function:

$$A(E, \theta) \propto 1 + a(E) \cos(\theta) \quad (3.4)$$

In this expression, the asymmetry parameter a is a function of the positron energy. For the highest energy positrons, those emitted at the maximum of the spectrum ($E_{e^+} \simeq 52.8$ MeV), the asymmetry is maximal with $a = 1$. This theoretical limit results in a cardioid-shaped distribution, where no positrons are emitted in the direction strictly opposite to the muon spin.

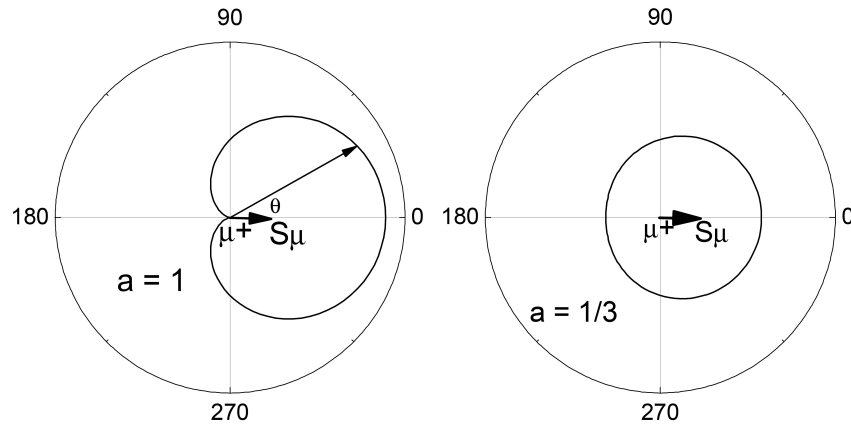


Figure 3.5: Angular distribution of the positron emission following the positive muon decay. The plot illustrates the parity-violating nature of the weak interaction. The left panel displays the theoretical maximum asymmetry corresponding to positrons emitted at the highest possible energy, the right panel illustrates the experimental reality representing the statistical average over the entire positron energy spectrum. Adapted from [39].

However, in a laboratory setting, the detectors are sensitive to a wide range of positron energies. Because the asymmetry parameter is significantly lower for low-energy positrons, the total observed signal is a statistical average over the entire energy spectrum. When this integration is performed, the effective asymmetry a reduces to a value of $1/3$ for a perfectly polarized muon beam. This leads to a distribution that is more isotropic than the high-energy limit but retains a distinct preference for the forward direction along the spin axis [39].

In practice, factors such as detector efficiency and positron scattering further refine this experimental asymmetry, typically resulting in measured $A(0)$ values between 0.25 and 0.28. This is essential for the accurate calibration of the μ SR spectrometers and the subsequent interpretation of internal magnetic field strengths.

The discussion above shows that the weak decay of the positive muon is not only the process that limits the observation time of a μ SR experiment, but also the mechanism that makes the measurement possible. Since the emitted positron is preferentially detected along the instantaneous direction of the muon spin, the angular distribution of the decay positrons carries information on the muon polarization at the moment of decay. The experimental task is therefore to convert this anisotropic positron emission into a time-resolved signal.

For this reason, a μ SR spectrometer requires both a detector that identifies the arrival of each implanted muon and a set of positron detectors arranged around the sample. The first detector defines the implantation time, while the positron detectors record the time and direction of the decay products. By collecting a large number of muon-decay events, the time-dependent positron count rates can be reconstructed and used to determine the evolution of the muon spin polarization inside the sample [38, 49].

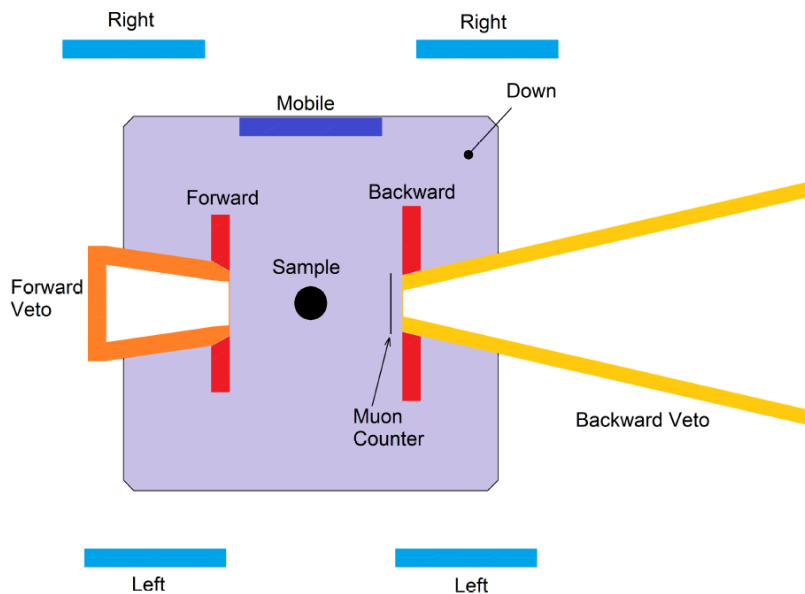


Figure 3.6: Schematic representation of the sample chamber and detector arrangement of the GPS instrument. The forward and backward positron detectors are positioned along the beam axis, while the left and right detector banks are arranged along the perpendicular direction. The muon and veto counters are used to define the arrival of an accepted muon and to reject events in which the particle does not stop within the selected sample region. Adapted from [52].

In practice, this is achieved through a system of plastic scintillation detectors and

dedicated timing electronics. An upstream muon counter detects the passage of an incoming muon and defines the initial time $t = 0$ of the measurement. The subsequent detection of a decay positron stops the corresponding timing interval, allowing the positron counts to be accumulated as a function of the time elapsed after implantation.

The veto system improves the fraction of accepted muons that stop inside the sample. Events associated with muons that miss the selected sample area, traverse the sample without stopping, or reach surrounding components can be identified through coincidences with the appropriate veto detectors and excluded from the final histograms.

The acquisition electronics also applies pile-up rejection conditions. If another muon enters the apparatus within the time window assigned to a previously implanted muon, the event may be rejected because the detected decay positron could not be assigned unambiguously to either particle. The accepted dataset therefore consists predominantly of events for which a single incoming muon can be reliably associated with its corresponding decay positron.

Figure 3.6 shows the sample chamber and the arrangement of the detector banks around the sample position. The forward and backward detectors measure the positron emission along the principal detector axis, whereas the left and right detectors provide additional angular coverage. Part of the backward detector assembly also operates as an active veto, allowing events associated with muons that pass through or miss the sample to be rejected [52, 53].

Magnetic Sensing via Larmor Precession

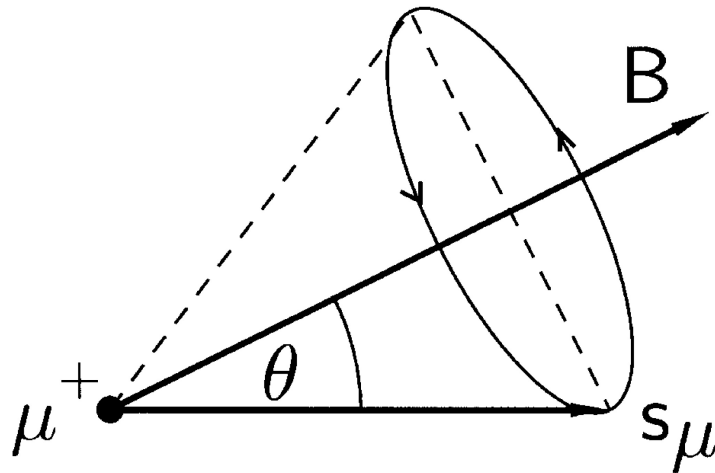


Figure 3.7: Sketch of a muon spin precession due to the action of an external magnetic field. Adapted from [48].

The connection between the observed positron emission and the internal physics of the material lies in the Larmor precession. Once a muon is localized within the

sample, its spin begins to precess around the local magnetic field H_{loc} at a frequency proportional to the field strength, as illustrated in Figure 3.7 [38–40].

This mechanism is conceptually analogous to the precession of nuclear spins in NMR. In both techniques, a magnetic moment evolves under the action of the local magnetic field, and the measured signal contains information on the magnitude, distribution, and dynamics of this field. The main difference is experimental: in NMR the precessing transverse nuclear magnetization is detected inductively through the voltage induced in a coil, whereas in μ SR the time evolution of the implanted muon spin is reconstructed from the anisotropic emission of decay positrons. Thus, despite the different probes and detection schemes, both techniques exploit spin precession as a local measurement of the magnetic environment.

This connection becomes quantitative through the Larmor equation, which relates the angular frequency of the muon-spin precession to the local magnetic field experienced at the muon stopping site:

$$\omega = \gamma_\mu H_{loc} \quad (3.5)$$

The constant $\gamma_\mu/2\pi \simeq 135.5$ MHz/T is the muon gyromagnetic ratio, which dictates the strict linear conversion between the observed oscillation frequency and the absolute magnetic flux density.

As the spin vector rotates, the direction of preferential positron emission rotates with it. By recording the time-dependent count rates in detectors positioned around the sample, it is possible to reconstruct the time evolution of the muon polarization. This allows for the precise determination of internal magnetic field distributions, phase transitions, and dynamical fluctuations within the studied material.

3.1.3 The Asymmetry Function

To extract physical information from the experiment, the spatial distribution of the detected positrons must be analyzed. The time-resolved countings in a single detector look like the ones in Figure 3.8 (b). The raw data obtained from an individual detector incorporates two superimposed effects: the exponential radioactive decay of the muon and the time-dependent physical modulation caused by the spin precession. Accordingly, the counting rate for a single detector is expressed as:

$$N(t) = N_0 e^{-t/\tau_\mu} [1 + A(t)] + B_{kg} \quad (3.6)$$

where N_0 is the initial count rate, τ_μ is the muon mean lifetime ($\simeq 2.2 \mu\text{s}$), and B_{kg} represents a constant background. $A(t)$ is the total observed asymmetry, which contains the relevant physics of the investigated system and can be expressed as $A(t) = A_0 P(t) + A_b$, where A_0 represents the initial asymmetry governed by detector efficiency and positron scattering, while A_b is the background contribution from muons that missed the sample.

To isolate the magnetic behavior and remove the inherent exponential decay factor,

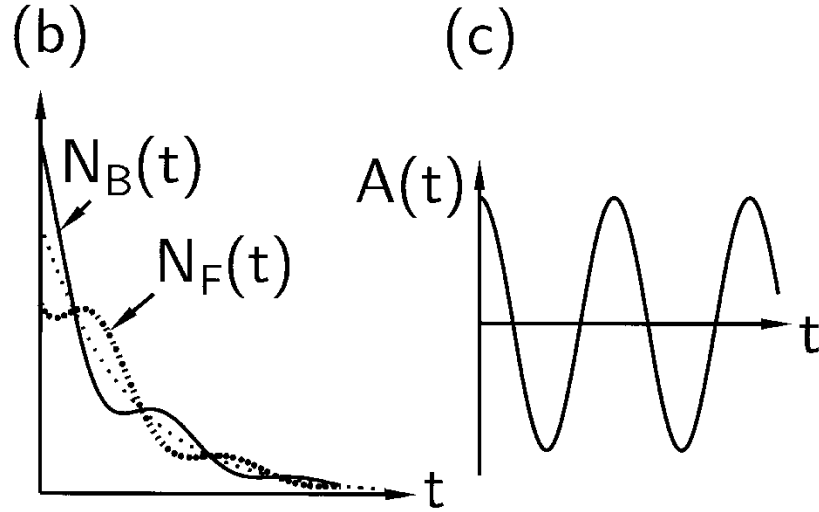


Figure 3.8: (b) *Positron Counts*: The detected positron histograms $N(t)$ follow an exponential decay, modulated by the muon spin precession. (c) *Asymmetry Function*: The normalized difference between detector counts produces the signal $A(t)$, whose oscillations reveal the local magnetic field properties. Adapted from [48].

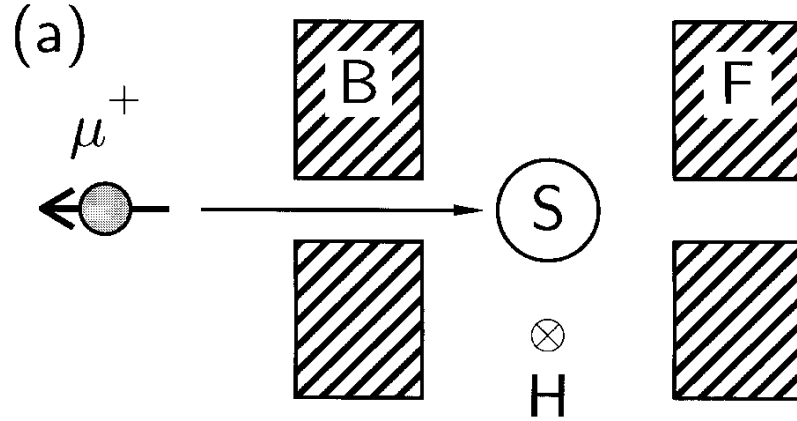


Figure 3.9: *Schematic arrangement of a conventional μ SR detector geometry*. The spin-polarized μ^+ beam is implanted into the sample S , while the backward and forward detectors, labelled B and F , record the emitted decay positrons. In the configuration shown, the magnetic field H is applied perpendicular to the initial muon-spin direction. Adapted from [48].

the experimental asymmetry function $A(t)$ is calculated by taking the normalized difference between two opposing detectors (e.g., forward and backward):

$$A(t) = \frac{N_F(t) - \alpha N_B(t)}{N_F(t) + \alpha N_B(t)} \quad (3.7)$$

Here, $N_F(t)$ and $N_B(t)$ are the positron counts at time t in the forward and backward detectors, respectively. The calibration parameter α accounts for differences in the intrinsic detection efficiency of the opposing counters [38–40, 48].

The time-dependent asymmetry $A(t)$ is directly related to the muon spin polarization function $P(t)$ through

$$A(t) = A_0 P(t) + A_b \quad (3.8)$$

where $P(t)$ represents the ensemble-averaged projection of the muon spin polarization along the detector axis, A_0 is the initial observable asymmetry, and A_b accounts for the background contribution.

The time evolution of $P(t)$ is determined by the local magnetic environment experienced by the implanted muons. In particular, it depends on the magnitude and orientation of the local magnetic fields, on their spatial distribution across the different muon stopping sites, and on whether these fields are static or fluctuating on the muon timescale.

A well-defined quasistatic local field produces a coherent precession of the muon polarization at the corresponding Larmor frequency. A distribution of static field values causes different muons to precess at slightly different frequencies, leading to a progressive dephasing and damping of the ensemble polarization. Time-dependent fluctuations of the local fields instead produce dynamical relaxation by continuously modifying the direction and magnitude of the field experienced by each muon.

The characteristic form of $P(t)$ therefore contains information about magnetic ordering, field inhomogeneity, magnetic volume fractions, multiple stopping sites, and the fluctuation rates of the electronic magnetic moments. The measured asymmetry function then provides a direct experimental probe of both the static and dynamic magnetic properties of the material [38, 40].

The following sections introduce the polarization functions and relaxation models appropriate to the zero-field, longitudinal-field, and transverse-field experimental configurations.

3.2 Relaxation Models

To interpret the experimental asymmetry $A(t)$ in complex magnetic systems, one must model the time-evolution of the muon spin ensemble as it probes the local magnetic landscape. The following subsections describe how specific experimental geometries — zero field (ZF), longitudinal field (LF), and transverse field (TF) — allow us to isolate different physical properties of the sample [38–40].

3.2.1 Zero-Field Mode: Spontaneous Order and Powder Averaging

In ZF configuration, no external magnetic field is applied, allowing the technique to serve as a highly sensitive probe for spontaneous magnetic moments. At the

fundamental level, a single muon implanted at a site with a local magnetic field $\mathbf{H}$ at an angle θ relative to the initial muon spin direction ($\mathbf{S}_0 \parallel \mathbf{z}$) follows a polarization evolution defined by [39, 40]:

$$P_z(t) = \cos^2 \theta + \sin^2 \theta \cos(\gamma_\mu H t) \quad (3.9)$$

This expression illustrates that the muon spin does not simply decay; it precesses. The $\cos^2 \theta$ term represents the longitudinal projection of the spin component parallel to the field, which remains static in the absence of fluctuations, while the $\sin^2 \theta$ term represents the transverse component that undergoes Larmor precession at a frequency $\omega = \gamma_\mu H$.

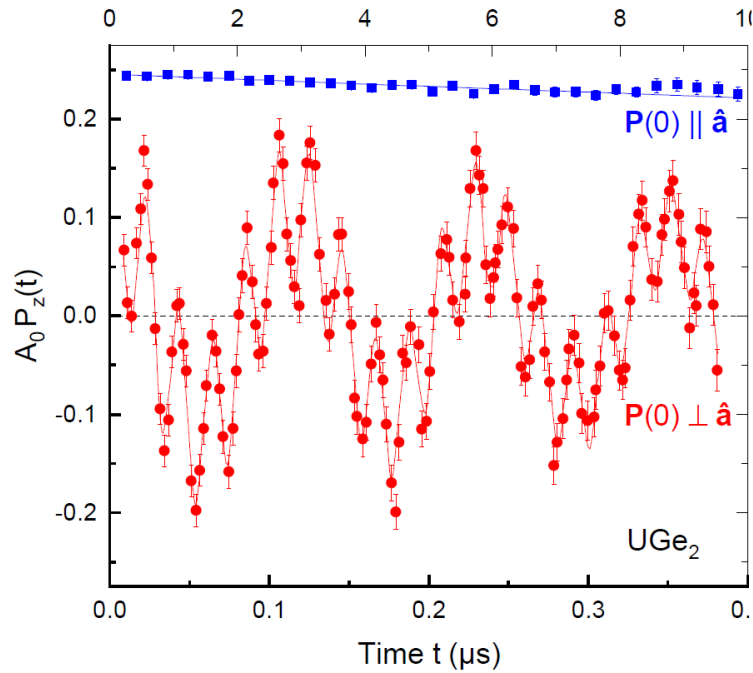


Figure 3.10: ZF- μ SR signal measured in single-crystalline UGe_2 . The spontaneous internal field is directed along the crystallographic a axis. When the initial muon polarization is parallel to this axis, no precession is observed. When the initial polarization is perpendicular to the a axis, spontaneous oscillations appear because the muon spins precess around the internal field. Adapted from [54].

The dependence of the ZF- μ SR signal on the relative orientation between the initial muon polarization and the spontaneous internal field is illustrated in Figure 3.10. In single-crystalline UGe_2 , the spontaneous internal field at the muon stopping site is directed along the crystallographic a axis. When the initial muon polarization is parallel to this direction, $P(0) \parallel \hat{a}$, the muon spins are initially aligned with the local field and no precession is observed. Conversely, when the initial polarization is perpendicular to the internal field, $P(0) \perp \hat{a}$, the muon spins precess around the local field and an oscillating signal appears. This example shows explicitly that coherent oscillations in ZF- μ SR are observed only when a transverse component of

the initial muon polarization exists with respect to a sufficiently well-defined internal magnetic field.

When extending this description to a macroscopic sample, especially one exhibiting magnetic phase transitions, phase coexistence and multi-site occupancy must be accounted for [37, 40]. The total normalized asymmetry $A_T(t)/A_0$ is thus modeled as [54, 55]:

$$\frac{A_T(t)}{A_0} = [1 - V_m(T)]e^{-\frac{\sigma^2 t^2}{2}} + \sum_i \zeta_i [a_i^{Tr}(T)F_i(t)D_i^{Tr}(t) + a_i^L(T)D_i^L(t)] \quad (3.10)$$

The total normalized asymmetry is modeled as a superposition of signals from paramagnetic and magnetically ordered volumes. In the paramagnetic (non-magnetic) fraction, $1 - V_m(T)$, the fast-fluctuating electronic moments average to zero on the muon timescale, leaving the muon sensitive only to the dense array of static nuclear moments. According to the central limit theorem, the sum of these random nuclear fields results in a Gaussian distribution, leading to the characteristic relaxation term $\exp(-\sigma^2 t^2/2)$ [40, 56].

The magnetically ordered fraction $V_m(T)$ is defined by the sum of contributions from all available muon stopping sites:

$$V_m(T) = \sum_i \zeta_i [a_i^{Tr}(T) + a_i^L(T)] \quad (3.11)$$

Here, ζ_i represents the site occupancy probability, while a_i^{Tr} and a_i^L are the transverse and longitudinal amplitudes. This summation acts as a normalization constraint, ensuring that the total magnetic signal is properly partitioned across the various interstitial positions within the unit cell.

In the general case of a single crystal, the amplitudes a_i are determined by the specific geometric projection of the initial muon spin $\mathbf{S}_0$ onto the local magnetic field vector $\mathbf{H}_i$. For each site i , the evolution of the polarization is further defined by two distinct functions, $F_i(t)$ and $D_i(t)$, which capture the static and dynamic properties of the local environment:

The Oscillatory Function $F_i(t)$: This term describes the coherent Larmor precession of the transverse component. In the case of a well-defined internal field, $F_i(t) = \cos(\gamma_\mu H_i t + \phi)$. It serves as a direct measure of the local magnetic field magnitude H_i . In commensurately ordered systems, this produces sharp frequencies, whereas in short-range ordered systems, $F_i(t)$ may be replaced by Bessel functions or more complex modulations.

The Damping Functions $D_i^{Tr}(t)$ and $D_i^L(t)$: These terms represent the loss of spin coherence. The transverse damping, D_i^{Tr} , typically originates from a static distribution of local fields (ΔH) across the sample (the T_2 -like effect), causing muons at the same crystallographic site to precess at slightly different rates and eventually dephase.

In contrast, the longitudinal damping D_i^L is a probe of spin-lattice relaxation (T_1).

Since the longitudinal component is parallel to the average field, it can only relax if the local fields are fluctuating in time [39, 40].

While in a single crystal these amplitudes vary with the sample's orientation, in a polycrystalline powder an average over all possible orientations must be done. Substituting the fundamental trigonometric relationships into the site-specific amplitudes:

$$a_i^L = \cos^2 \theta \quad ; \quad a_i^{Tr} = \sin^2 \theta \quad (3.12)$$

to find the powder values, the expectation value $\langle \dots \rangle$ can be calculated over a solid angle Ω [40, 56]:

$$\langle a^L \rangle = \frac{1}{4\pi} \int_0^{2\pi} d\phi \int_0^\pi \cos^2 \theta \sin \theta d\theta = \frac{1}{3} \quad (3.13)$$

$$\langle a^{Tr} \rangle = \frac{1}{4\pi} \int_0^{2\pi} d\phi \int_0^\pi \sin^2 \theta \sin \theta d\theta = \frac{2}{3} \quad (3.14)$$

Applying these averages to the general summation, the magnetic fraction of the asymmetry formula simplifies. Assuming the damping and oscillatory functions are uniform across the crystallites for site i , the site-specific term becomes:

$$\zeta_i \left[\frac{2}{3} F_i(t) D_i^{Tr}(t) + \frac{1}{3} D_i^L(t) \right] \quad (3.15)$$

Assuming a single dominant muon stopping site (where $\zeta_i = 1$) or that all sites i experience the same average field magnitude H , the geometric constants can be factored out. The total normalized asymmetry for a fully magnetic powder ($V_m = 1$) then collapses into the standard oscillatory powder-averaged function:

$$\frac{A_T(t)}{A_0} = \frac{2}{3} \cos(\gamma_\mu H t) D^{Tr}(t) + \frac{1}{3} D^L(t) \quad (3.16)$$

This expression represents the ideal powder-averaged response expected when the magnetically ordered state produces a well-defined internal field at the muon site. In this case, the transverse component gives rise to coherent oscillations, while the longitudinal component gives the characteristic non-oscillating contribution. However, the experimental observation of a magnetic state is not always accompanied by clearly resolved oscillations. If the magnetic order is spatially disordered, or if the muons experience a broad distribution of local fields, the transverse precession frequencies are strongly distributed and the oscillating signal can become overdamped.

This effect is illustrated in Figure 3.11, adapted from [54]. The figure shows ZF- μ SR depolarization curves for $\text{CeFe}_{1-x}\text{Co}_x\text{AsO}$ at different Co concentrations. In the less disordered samples, coherent oscillations are visible, reflecting a relatively well-defined spontaneous internal field. Upon increasing the disorder, the oscillations are progressively suppressed and the signal evolves towards a rapidly relaxing, non-oscillatory form. Therefore, the absence of a resolved oscillation does not

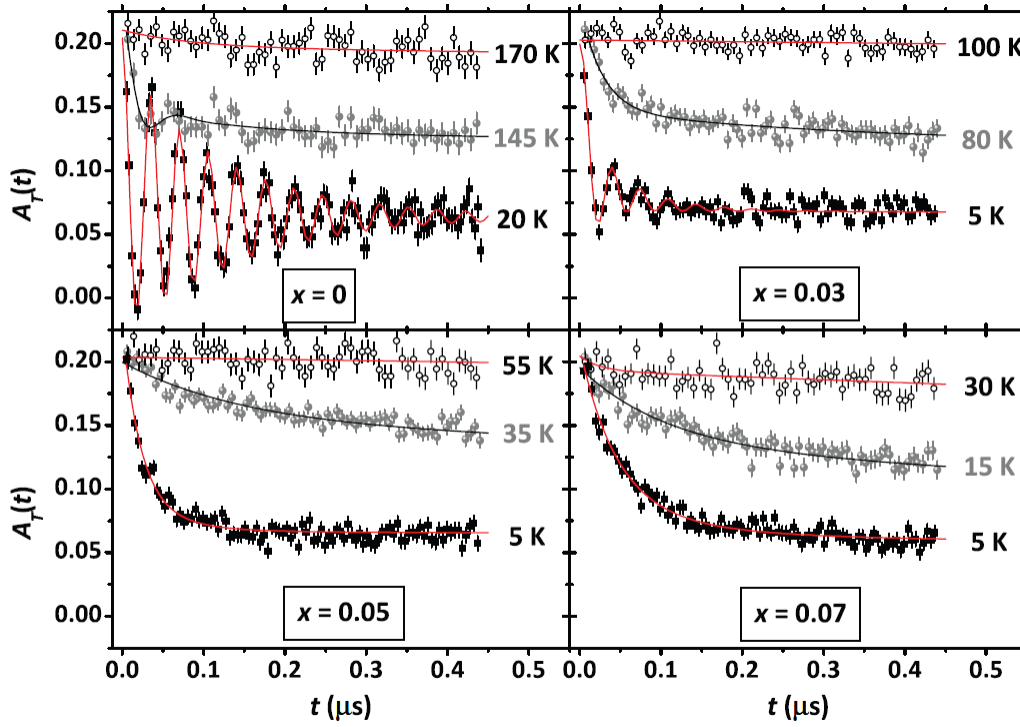


Figure 3.11: ZF- μ SR depolarization curves for $\text{CeFe}_{1-x}\text{Co}_x\text{AsO}$ at representative temperatures and different Co concentrations. The progressive overdamping of the oscillations illustrates how increasing magnetic disorder can transform a coherent precessing signal into a rapidly relaxing non-oscillatory response. Adapted from [54].

necessarily imply the absence of static magnetism; it may instead indicate a broad static distribution of internal fields.

This ambiguity motivates the use of longitudinal-field measurements. A rapidly relaxing ZF signal can originate either from a broad static distribution of local fields or from dynamic fluctuations of the electronic moments. Applying a longitudinal field helps to distinguish these scenarios: a static contribution can be partially decoupled by the external field, whereas a genuinely dynamic relaxation channel is not suppressed in the same way. LF measurements therefore provide an essential tool to discriminate between static magnetic disorder and fluctuating local fields.

3.2.2 Longitudinal-Field Mode: Static Decoupling and Dynamic Relaxation

A LF measurement addresses two conceptually distinct aspects of the local magnetic environment. The recovery of polarization with increasing field provides information on the quasistatic distribution of internal fields, whereas the residual time-dependent relaxation probes magnetic fluctuations [38, 40, 56]. The following discussion therefore first considers static longitudinal-field decoupling and then introduces the spectral-density description of dynamic relaxation. Finally, deviations from single-exponential behaviour are discussed in terms of a distribution of local

relaxation processes.

Static Longitudinal-Field Decoupling

The zero-field polarization function separates naturally into transverse and longitudinal contributions with respect to the local magnetic field. In a polycrystalline sample, the random orientation of the internal fields gives rise to the characteristic (2/3) transverse component and (1/3) longitudinal component as seen in formula 3.16

The transverse component contains the precession and dephasing associated with the quasistatic internal-field distribution. The longitudinal component is instead insensitive to a perfectly static field parallel to the local quantization axis. Any decay of this component therefore indicates that the local magnetic environment changes during the muon lifetime.

In the LF configuration, an external magnetic field H_{LF} is applied parallel to the initial muon-spin polarization, which defines the laboratory (z) axis. The total field acting on the muon is then

$$\mathbf{H}_{\text{tot}}(t) = H_{LF}\hat{\mathbf{z}} + \mathbf{H}_{\text{loc}}(t) \quad (3.17)$$

Here, $\mathbf{H}_{\text{loc}}(t)$ is the internal magnetic field generated by the surrounding nuclear and electronic magnetic moments.

The applied longitudinal field does not by itself produce an observable coherent precession, since the initial muon polarization is parallel to it. However, when H_{LF} becomes large compared with the transverse components of the quasistatic local field, the direction of $\mathbf{H}_{\text{tot}}$ becomes progressively aligned with the initial polarization. Equivalently, the angle θ_{tot} between the initial muon polarization and the total field approaches zero

$$\sin^2 \theta_{\text{tot}} \longrightarrow 0 \quad \cos^2 \theta_{\text{tot}} \longrightarrow 1 \quad (3.18)$$

The transverse precession amplitude and the associated dephasing are consequently suppressed, while the polarization lost in zero field is progressively recovered. This process is referred to as longitudinal-field decoupling.

The field scale required to produce static decoupling is determined by the width of the quasistatic local-field distribution. If ΔH denotes its characteristic width in magnetic-field units, substantial decoupling is expected when

$$H_{LF} \gg \Delta H \quad (3.19)$$

Equivalently, if the distribution width is expressed in angular-frequency units as

$$\Delta = \gamma_{\mu} \Delta H \quad (3.20)$$

the decoupling condition becomes

$$\gamma_{\mu} H_{\text{LF}} \gg \Delta \quad (3.21)$$

The expression “strong longitudinal field” therefore refers to the magnitude of the applied field relative to the internal-field distribution rather than to an absolute experimental value. In this limit, a quasistatic distribution of local fields can be progressively decoupled, and the corresponding muon depolarization is strongly suppressed.

This point is important because, as discussed in the previous section, the absence of a resolved oscillation in ZF- μ SR cannot be taken by itself as evidence for the absence of static magnetism. Coherent oscillations require a transverse component of the initial muon polarization with respect to a sufficiently well-defined internal magnetic field. If the internal field is broadly distributed, for example because of magnetic disorder, inequivalent muon stopping sites, or powder averaging over many local environments, the muon ensemble precesses with a broad distribution of frequencies. The resulting dephasing can overdamp the oscillatory signal, transforming a coherent precession into a rapidly relaxing non-oscillatory depolarization.

LF measurements are useful precisely in this situation, because the field dependence of the relaxation provides an additional criterion to distinguish a quasistatic distribution of local fields from genuinely dynamical magnetic fluctuations. In the former case, the relaxation is progressively suppressed by increasing H_{LF} , whereas in the latter case a residual relaxation may persist because it is driven by time-dependent fluctuations of the local field.

Dynamic Longitudinal Relaxation

The Zeeman interaction and the relation between longitudinal relaxation and transitions between the two levels of a spin-1/2 system were introduced in the NMR chapter. The same general formalism applies to the muon spin, with the muon gyromagnetic ratio replacing the nuclear gyromagnetic ratio.

An important experimental distinction must nevertheless be emphasized. In NMR, the initial population imbalance is established through thermal equilibrium in the applied magnetic field and is subsequently perturbed by a radiofrequency pulse. In μ SR, the incoming muon beam is already strongly spin polarized as a consequence of the parity-violating pion-decay process [38–40]. The initial muon polarization therefore does not originate from thermal equilibrium in H_{LF} .

The applied longitudinal field defines the muon quantization axis and the corresponding Larmor angular frequency

$$\omega_{\mu} = \gamma_{\mu} H_{\text{LF}} \quad (3.22)$$

In a perfectly static magnetic environment, no transitions occur between the muon Zeeman states and the initial longitudinal polarization remains constant. Time-dependent components of the local field perpendicular to H_{LF} can instead induce

transitions between the two states. These transitions reduce the initial population imbalance and therefore produce longitudinal muon-spin relaxation.

Under the temperature and field conditions relevant to the present measurements, the muon Zeeman splitting is much smaller than the thermal energy

$$\hbar\omega_\mu \ll k_B T \quad (3.23)$$

The equilibrium population difference is consequently negligible compared with the initially implanted polarization. For a homogeneous magnetic environment characterized by a single relaxation rate, the polarization can then be written as

$$P_z(t) = P_z(0) \exp(-\lambda_{\text{LF}} t) \quad (3.24)$$

The exponential form is obtained when the implanted muons experience statistically equivalent environments and the field fluctuations are sufficiently weak and rapid to be described within a Markovian approximation. It should therefore be regarded as a limiting case rather than as the universal form of longitudinal-field relaxation.

Spectral Density and the Redfield Limit

To relate the measured relaxation rate to the microscopic spin dynamics, the local magnetic field can be separated into an average and a fluctuating contribution

$$\mathbf{H}_{\text{loc}}(t) = \langle \mathbf{H}_{\text{loc}} \rangle + \delta \mathbf{H}(t) \quad (3.25)$$

Only the fluctuating components perpendicular to the longitudinal field can efficiently induce transitions between the muon Zeeman states. Their temporal correlations are described by the transverse field-correlation function

$$G_\perp(\tau) = \langle \delta H_x(0) \delta H_x(\tau) \rangle + \langle \delta H_y(0) \delta H_y(\tau) \rangle \quad (3.26)$$

The corresponding transverse spectral density is defined as

$$J_\perp(\omega) = \int_0^{+\infty} G_\perp(\tau) \cos(\omega\tau) d\tau \quad (3.27)$$

The correlation function describes how rapidly the transverse local field loses memory of its initial value, whereas the spectral density describes how the fluctuation power is distributed over frequency. The longitudinal relaxation rate is sensitive to the portion of this fluctuation spectrum located near the muon Larmor frequency.

Within the perturbative Redfield treatment, the longitudinal relaxation rate is determined by the transverse spectral density evaluated at the muon Larmor frequency [37, 40, 45]:

$$\lambda_{\text{LF}} \propto \gamma_\mu^2 J_\perp(\omega_\mu) \quad (3.28)$$

The precise numerical prefactor depends on the definitions adopted for the correlation function and the spectral density. The relevant physical result is that the

longitudinal field defines the frequency at which the magnetic fluctuation spectrum is sampled. Changing H_{LF} changes ω_μ and therefore allows different regions of the spectral density to be probed.

This interpretation is the direct μSR analogue of the spectral-density description introduced for the nuclear spin-lattice relaxation time T_1 in NMR. In both cases, the longitudinal relaxation of a spin probe is not determined simply by the total amplitude of the local magnetic fluctuations, but by the spectral weight of their transverse components at the probe Larmor frequency. The difference lies in the identity of the probe and in the detection scheme: in NMR the relaxing spin is a nucleus and the recovered magnetization is detected inductively, whereas in μSR the relaxing spin is the implanted muon and its polarization is reconstructed from the anisotropic emission of decay positrons. The underlying physical principle, however, is the same: the applied field fixes the Zeeman splitting of the probe and therefore selects the fluctuation frequencies that can efficiently induce spin transitions.

A commonly employed approximation assumes that the transverse field correlations decay exponentially with a single correlation time τ_c

$$G_\perp(\tau) = \Delta_\perp^2 \exp\left(-\frac{|\tau|}{\tau_c}\right) \quad (3.29)$$

Here, $\Delta_\perp^2$ is the mean-squared amplitude of the fluctuating transverse local field

$$\Delta_\perp^2 = \langle \delta H_x^2 \rangle + \langle \delta H_y^2 \rangle \quad (3.30)$$

The corresponding spectral density has a Lorentzian form

$$J_\perp(\omega) = \frac{\Delta_\perp^2 \tau_c}{1 + \omega^2 \tau_c^2} \quad (3.31)$$

The longitudinal relaxation rate is consequently described by the Redfield relation

$$\lambda_{\text{LF}}(H_{\text{LF}}) = \frac{2\gamma_\mu^2 \Delta_\perp^2 \tau_c}{1 + (\gamma_\mu H_{\text{LF}} \tau_c)^2} \quad (3.32)$$

The Redfield approximation requires the fluctuating local field to act as a weak perturbation. In the low-frequency or fast-fluctuation regime

$$\gamma_\mu H_{\text{LF}} \tau_c \ll 1 \quad (3.33)$$

the relaxation rate becomes approximately field independent

$$\lambda_{\text{LF}} \simeq 2\gamma_\mu^2 \Delta_\perp^2 \tau_c \quad (3.34)$$

In this regime, the relaxation rate increases as the fluctuations slow down and the correlation time becomes longer, provided that the fluctuating-field amplitude varies only weakly.

At a fixed longitudinal field, the relaxation rate reaches a maximum when the characteristic fluctuation time becomes comparable to the inverse muon Larmor frequency

$$\gamma_\mu H_{\text{LF}} \tau_c \simeq 1 \quad (3.35)$$

A maximum in $\lambda_{\text{LF}}(T)$ can therefore occur when a characteristic fluctuation time-scale crosses the experimental frequency window. Such a maximum does not necessarily coincide with a thermodynamic transition temperature. Similarly, the observation of more than one maximum may indicate the presence of several fluctuation processes or a broad distribution of correlation times, but does not by itself identify their microscopic origin.

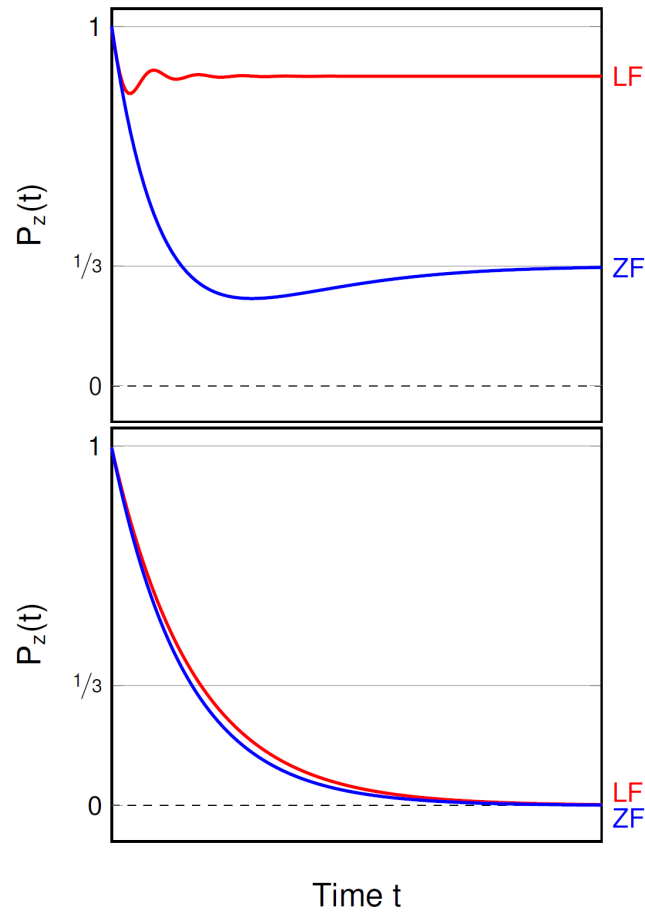


Figure 3.12: Schematic comparison between quasistatic and dynamic longitudinal-field relaxation. In the quasistatic case, shown in the upper panel, the longitudinal field suppresses the zero-field depolarization and recovers most of the initial polarization. In the dynamic case, shown in the lower panel, relaxation persists even in longitudinal field, indicating that time-dependent local magnetic fields remain active within the μSR time window. Adapted from [49].

The field dependence provides complementary information. Increasing H_{LF} suppresses the contribution of a quasistatic field distribution through longitudinal-field

decoupling. For a dynamic process described by the Redfield approximation, the relaxation rate also decreases when

$$\gamma_\mu H_{\text{LF}} \tau_c \gtrsim 1 \quad (3.36)$$

In this regime, the muon probes the decreasing high-frequency side of the spectral density. A field scan can therefore provide estimates of $\Delta_\perp$ and τ_c , provided that the magnetic dynamics can be represented by a single characteristic correlation time.

The experimental consequence of the distinction between quasistatic and dynamic relaxation is summarized schematically in Figure 3.12. In the quasistatic case, the application of a longitudinal field suppresses the zero-field depolarization by decoupling the muon spin from the static distribution of local fields. In the dynamic case, instead, relaxation persists even in longitudinal field because time-dependent transverse local fields continue to provide spectral weight at the muon Larmor frequency.

The recovery of the initial asymmetry with increasing field does not by itself demonstrate that all internal fields are static. Persistent relaxation after the quasistatic contribution has been decoupled indicates that dynamical magnetic fluctuations remain active within the muon frequency window.

Finally, the interpretation of the field-dependent relaxation rate as a direct sampling of $J_\perp(\omega)$ assumes that the applied longitudinal field does not substantially modify the underlying magnetic dynamics. In strongly anisotropic or molecular magnetic systems, the field may also alter electronic energy levels, tunnelling conditions, and fluctuation timescales. The measured field dependence of λ_{LF} may therefore reflect both a change in the muon observation frequency and a genuine field-induced modification of the spin dynamics.

Non-Exponential Longitudinal Relaxation

The exponential polarization function

$$P_z(t) = P_z(0) \exp(-\lambda_{\text{LF}} t) \quad (3.37)$$

represents an ideal limiting case in which all implanted muons experience statistically equivalent magnetic environments and relax with the same characteristic rate. This approximation may fail in materials containing inequivalent muon stopping sites, spatially disordered magnetic couplings, or a distribution of fluctuation timescales.

A non-exponential polarization can be represented generally as a superposition of exponential decays [37, 57]

$$P_z(t) = P_z(0) \int_0^{+\infty} \rho(W) \exp(-W t) dW \quad (3.38)$$

where $\rho(W)$ is a normalized distribution of local relaxation rates

$$\int_0^{+\infty} \rho(W) dW = 1 \quad (3.39)$$

If $\rho(W)$ is sharply concentrated around a single value W_0 , the polarization approaches a conventional exponential decay with $\lambda_{\text{LF}} = W_0$. A broad distribution of rates instead produces a non-exponential time dependence.

A widely employed phenomenological representation of such behaviour is the stretched-exponential function

$$P_z(t) = P_z(0) \exp[-(\lambda t)^\beta] \quad (3.40)$$

Equivalently, it may be written as

$$P_z(t) = P_z(0) \exp\left[-\left(\frac{t}{\tau}\right)^\beta\right] \quad (3.41)$$

with

$$\tau = \lambda^{-1} \quad (3.42)$$

The parameter τ is the time at which the polarization has decreased to $P_z(0)/e$, independently of the value of β . The stretching exponent β determines the shape of the relaxation function.

For $\beta = 1$ the conventional single-exponential relaxation is recovered. In this case, the polarization is characterized by a single relaxation rate and λ can be identified directly with the inverse longitudinal relaxation time.

For $0.5 < \beta < 1$ the relaxation is stretched and generally reflects a broad distribution of local relaxation rates. Smaller values of β correspond phenomenologically to increasingly broad and heterogeneous relaxation behaviour.

Such a distribution can originate from several microscopic situations, including inequivalent muon stopping sites, randomly distributed coupling strengths, structural or magnetic disorder, spatially inhomogeneous electronic moments, and a distribution of correlation times. A stretched-exponential decay does not, by itself, distinguish among these possibilities and should therefore not be assigned to a unique microscopic mechanism without additional evidence.

The stretched-exponential description is compatible with the spectral-density approach introduced above. Each local magnetic environment may be associated with a relaxation rate determined approximately by its own fluctuating-field amplitude and correlation time

$$W = \frac{2\gamma_\mu^2 \Delta_\perp^2 \tau_c}{1 + (\gamma_\mu H_{\text{LF}} \tau_c)^2} \quad (3.43)$$

If $\Delta_{\perp}$ or τ_c varies throughout the muon ensemble, the corresponding local rates are also distributed. The experimentally-measured polarization is then the ensemble average over these local responses and may no longer be described by a single exponential.

When $\beta \neq 1$, the parameter λ should therefore be interpreted as a characteristic relaxation scale rather than automatically as the inverse of a unique microscopic spin-lattice relaxation time. Values of λ obtained at different temperatures or magnetic fields should also be interpreted together with the corresponding values of β , since changes in both parameters may reflect an evolution of the distribution of local relaxation processes.

A decrease of β with temperature, for example, may indicate that the magnetic dynamics become increasingly heterogeneous or that the distribution of correlation times broadens. Conversely, a value of β approaching unity indicates that the relaxation becomes more homogeneous and closer to a single-rate process. These interpretations remain phenomenological and require comparison with the field dependence, temperature dependence, and other experimental observables.

The particular relaxation function used to analyse the measurements presented in this work will be introduced in the experimental chapter. The discussion above provides the theoretical basis for interpreting deviations from a single-exponential longitudinal polarization without assigning them prematurely to a specific microscopic model.

3.2.3 Transverse Field: Inhomogeneity and Precession

In the TF configuration, an external magnetic field is applied perpendicularly to the initial muon spin direction. In the present work, the weak-transverse-field configuration was used primarily to calibrate the instrumental asymmetry parameter, α , which accounts for the geometric and electronic discrepancies between the detector banks [38, 52].

By applying a weak transverse field (typically between 30-100 G) while the sample is in a paramagnetic state at room temperature, the muon spins are forced to precess in a plane that is perpendicular to the applied field and contains the axis defined by the forward and backward detector banks. As the muon ensemble precesses at the Larmor frequency, the spin vector periodically sweeps toward and away from each detector, creating a coherent oscillatory signal. Because α represents the ratio of the counting efficiencies and solid angles of the two detector sets, any imbalance will cause the resulting asymmetry oscillations to be vertically shifted from the zero-baseline.

By fitting this sinusoidal signal and adjusting the α parameter until the oscillations are perfectly centered around zero, the experimenter can calibrate the instrument to a high degree of precision. This ensures that the detector response is normalized, allowing for an accurate determination of the magnetic volume fraction and

relaxation rates in subsequent zero-field or longitudinal field measurements where such periodic normalization is not intrinsically available.

In the present work, TF measurements were mainly employed to calibrate the detector asymmetry parameter α . More generally, however, the transverse-field geometry is one of the most powerful μ SR configurations for the investigation of superconductors. In type-II superconductors, when the sample is in the mixed state, the applied magnetic field penetrates the material in the form of quantized vortices. The resulting flux-line lattice generates an inhomogeneous internal field distribution, which is directly sampled by the implanted muons through their Larmor precession. The damping of the transverse muon polarization therefore contains information on the width of this field distribution and can be used to extract microscopic superconducting parameters, such as the magnetic penetration depth. This makes TF- μ SR a particularly useful local probe of the vortex state and of the superconducting condensate [48].

Concluding Remarks

This chapter introduced the basic principles of muon spin spectroscopy needed for the interpretation of the experimental data presented in this thesis. The positive muon was described as an implanted local probe whose spin evolution can be reconstructed from the anisotropic emission of decay positrons. The measured asymmetry was then related to the local magnetic fields inside the sample through Larmor precession and relaxation.

The main μ SR geometries were discussed, with particular emphasis on zero-field and longitudinal-field measurements. These configurations provide information on static field distributions and dynamical magnetic fluctuations, making them especially relevant for the study of molecular magnetic systems. The longitudinal-field relaxation rate was also connected to the spectral density of transverse magnetic fluctuations, in analogy with the treatment of spin-lattice relaxation introduced in the NMR chapter.

The concepts developed here provide the framework for the next chapter, where the μ SR measurements on the Dy-SQ sample are analysed together with the complementary experimental results.

Chapter 4

Experimental Procedures

The primary focus of this chapter are the experimental results obtained in the study of the Dysprosium-Semiquinonate complex. The structural core of this coordination compound consists of a Dy^{3+} Kramers ion, characterized by a large magnetic moment and significant electronic anisotropy. This central ion is embedded within a specialized ligand matrix containing a semiquinonate paramagnetic radical, which introduces complex exchange interactions and modulates the overall magnetic dynamics of the system [34, 35].

To probe the properties of this complex, a complementary suite of experimental techniques was employed. While the theoretical foundations and basic principles of these methods have been established in the preceding chapters, the following sections provide a detailed dissertation on the specific laboratory settings, instrumental configurations, and experimental protocols adopted during the measurements. This includes the optimization of nuclear magnetic resonance (NMR) and muon spin spectroscopy (μSR) local probes, alongside macroscopic DC magnetometry, to ensure a comprehensive characterization of the Dysprosium-Semiquinonate magnetic ground state and relaxation pathways.

Section 4.1 presents the basic SQUID magnetometry protocols used for the magnetic characterization, discusses the specific direct-current measurements performed on the sample. Particular attention is devoted to the comparison between loose powder and resin-embedded powder, since this step was necessary to identify and correct experimental effects associated with field-induced grain motion. The local-probe measurements are described in the second part of the chapter. Section 4.2 presents the nuclear magnetic resonance protocols, including the calibration procedures and the strategies adopted to measure the relaxation times and reconstruct the broad spectra of the sample. Finally, Section 4.3 describes the muon spin spectroscopy measurements and the fitting strategy used to extract the temperature and field dependence of the relaxation rates.

Overall, this chapter provides the experimental basis for the analysis of the Dy-SQ magnetic response. The goal is to clarify how the data were acquired and treated before moving to the physical interpretation of the results in Chapter 5.

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4.1 DC SQUID Magnetometry

4.1.1 Generalities

The superconducting quantum interference device (SQUID) magnetometer is one of the most sensitive instruments available for measuring the macroscopic magnetic response of a material [58]. Unlike local probes such as NMR or μ SR, which provide information on a microscopic scale, the SQUID magnetometer measures the total magnetic moment of the sample.

In a standard DC magnetometry experiment, the SQUID magnetometer measures the magnetic moment induced in the sample by an external magnetic field H , typically up to 70 kOe, over a temperature range extending from 2 K to 340 K. The measured magnetic moment represents the sum of all magnetic contributions arising from the material placed inside the magnetometer. In this sense, SQUID magnetometry is sensitive to all the magnetic responses discussed in Chapter 1, including diamagnetic, paramagnetic, ferro/ferrimagnetic, and antiferromagnetic contributions, depending on the nature of the investigated system. At the same time, the instrument does not distinguish a priori between the intrinsic signal of the sample and additional contributions coming from the sample holder, such as the capsule or any other material introduced into the detection region. For this reason, background measurements and proper subtraction procedures are often required in order to isolate the magnetic response of the compound under investigation.

From the raw magnetic moment, typically measured in emu (1 emu = 1 erg/Oe), one can derive the magnetization M , defined as the magnetic moment per unit volume or per unit amount of sample, and the magnetic susceptibility $\chi = M/H$.

In order to compare measurements performed on different samples or with theoretical models, the raw magnetic moment measured by the SQUID must be properly normalized. Indeed, the measured moment depends not only on the intrinsic magnetic response of the material, but also on the amount of sample introduced into the magnetometer. For this reason, the raw moment must be converted into molar magnetization (M_{mol}) or molar susceptibility (χ_{mol}). These quantities can be expressed as:

$$M_{mol} = \frac{m \cdot MW}{m_{sample}} \quad ; \quad \chi_{mol} = \frac{M_{mol}}{H} \quad (4.1)$$

where m is the measured moment, MW is the molecular weight of the complex, H is the applied field, and m_{sample} is the mass of the measured sample. High precision

on the sample mass estimate is required. An error in the weight leads directly to an error in the final physical conclusion.

In addition to the molar magnetic susceptibility (χ_{mol}), the product of the susceptibility and temperature (χT) is a fundamental parameter used to evaluate the magnetic properties of molecular systems. The graphical representation of χT vs. T is significantly more informative than χ_{mol} vs. T for several reasons. First, for a system following ideal Curie law behavior ($\chi = C/T$), the χT plot results in a horizontal line equal to the Curie constant (C). This allows for an immediate visual assessment of the effective magnetic moment (μ_{eff}) and the oxidation state of the magnetic centers. The χT product is highly sensitive to the nature of magnetic interactions within the sample. A decrease in χT as temperature is lowered typically indicates the presence of antiferromagnetic exchange or the thermal depopulation of Stark levels (crystal field effects) in lanthanide ions like Dy^{3+} . An increase in the product instead suggests ferromagnetic coupling.

By removing the $1/T$ dependence that dominates the raw susceptibility, the χT plot acts as a view of the underlying spin dynamics and electronic structure, making it the best choice for interpreting the thermal evolution of the magnetic state [1, 37].

4.1.2 Measurement Configurations

Zero-Field Cooling and Field-Cooling Measurements

To investigate the magnetization dynamics and identify the possible presence of a magnetic blocking temperature (T_B), zero-field cooling (ZFC) and field-cooling (FC) measurements can be performed. These protocols study the magnetic memory of the Dy-SQ system by comparing its response under different thermodynamic histories.

- In the ZFC protocol, the sample is cooled to the base temperature in the absence of an external field ($H = 0$), forcing the molecular spins to freeze in random orientations dictated by local anisotropy or minimal stray fields. Upon the application of a probe field and subsequent warming, the magnetization initially increases as thermal energy allows spins to overcome internal barriers and align with the field, reaching a maximum at the blocking temperature.
- In the FC protocol, the sample is cooled under a constant applied field, ensuring that the spins are statistically weighted toward the field direction as they enter the blocked state.

The bifurcation between the ZFC and FC curves serves as a definitive signature of magnetic irreversibility within the sample [1, 12]. Usually a low-field measurement is standard for locating the intrinsic blocking temperature, as high fields can suppress the magnetic anisotropy barrier via the Zeeman effect. Meanwhile, a high-field measurement is typically conducted to reach the saturation regime, providing a baseline for the total magnetic moment and ensuring that the observed dynamics are representative of the bulk sample's electronic ground state.

Virgin Magnetization Branch

The field dependence of the magnetization at a fixed temperature can be investigated by recording the initial magnetization curve, often referred to as the virgin magnetization branch. In this configuration, the sample is quenched to the target temperature in a zero-field state to ensure a random distribution of magnetic domains or molecular spins. The external magnetic field (H) is then increased monotonically from zero to a maximum value while the resulting magnetic moment is recorded.

This measurement is primarily used to evaluate the approach to saturation and the nature of the magnetic ground state. As the field increases, the magnetic moments rotate away from their local anisotropy axes to align with the external field direction. The point at which the curve reaches a horizontal plateau defines the saturation magnetization (M_{sat}). Analyzing the slope and the curvature of this single branch allows for the determination of the magnetic susceptibility in the low-field limit and provides a quantitative measure of the magnetic anisotropy without the influence of the reversal mechanisms associated with a full hysteresis loop [3, 10].

4.1.3 SQUID Measurements of Dy–SQ

The magnetic characterization of the Dy–SQ molecular magnet was first performed on a 21.6 mg sample of unrestrained microcrystalline powder. The powder was carefully weighed, loaded into a small glass vial, sealed with Teflon tape to avoid contact with air or moisture, and fixed at the center of a clear plastic straw using a non-magnetic thread. This configuration was chosen to keep the sample in a well-defined position during the SQUID scan and to allow the measured magnetic moment to be normalized to the amount of magnetic material.

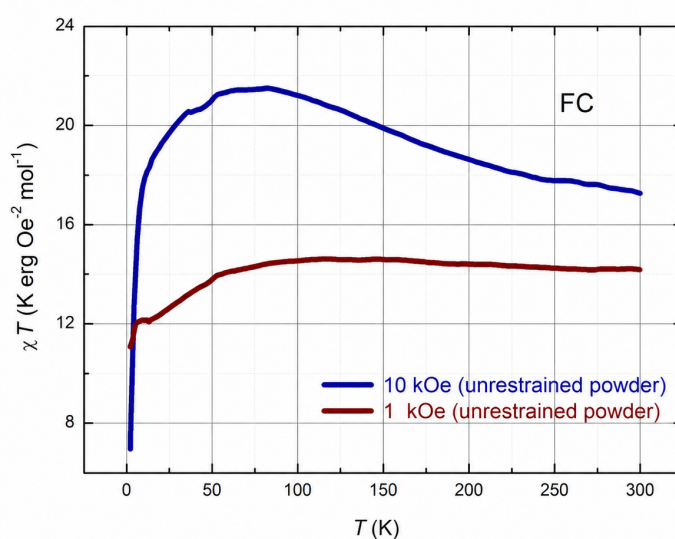


Figure 4.1: Field-cooled susceptibility product χT as a function of temperature for the unrestrained Dy–SQ powder, measured under applied fields of 1 kOe and 10 kOe.

Preliminary measurements were carried out following standard ZFC and FC protocols under applied fields of 1 kOe and 10 kOe. The analysis of the molar susceptibility product χT immediately revealed an unexpected behavior. As shown in Figure 4.1, the FC curves obtained at the two fields do not overlap. The 10 kOe curve reaches much larger χT values than the 1 kOe curve and displays a broad maximum at intermediate temperature, followed by a decrease on warming toward room temperature. This behavior is difficult to reconcile with a simple powder-averaged paramagnetic response and suggested that the measured signal could be affected by the experimental configuration of the loose powder.

To investigate whether these anomalies were intrinsic to the sample or related to the experimental setup, we blocked the powder sample within a non-magnetic epoxy matrix. By embedding the material in resin, we aimed to eliminate any potential sample instability and ensure a fixed, random orientation of the crystallites. During the encapsulation procedure, a small but unknown part of the original powder was lost. Consequently, the active mass of Dy–SQ inside the resin had to be recalculated based on published data [35], and all powder-in-epoxy data shown below were normalized using the corrected mass of 18.8 mg (see Figure 4.2 and 4.3).

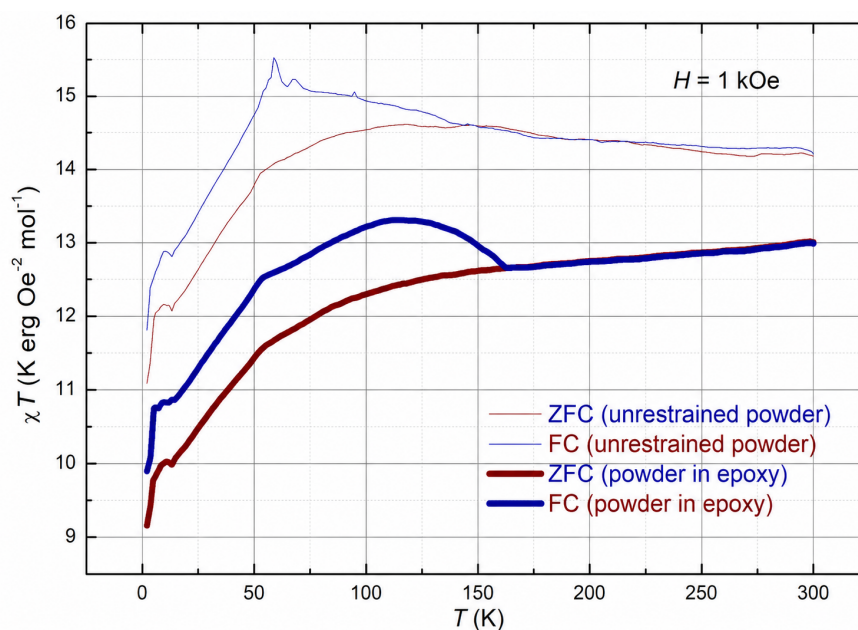


Figure 4.2: Temperature dependence of the ZFC and FC susceptibility product χT measured at 1 kOe for the unrestrained powder and for the powder embedded in epoxy. The powder-in-epoxy curves were corrected for the epoxy background and normalized using the corrected active mass.

Since the epoxy matrix became part of the measured sample environment, its magnetic contribution also had to be evaluated separately. Independent SQUID measurements performed on the resin alone showed a small but non-negligible signal. The intrinsic magnetic moment of the embedded Dy–SQ powder was therefore obtained by subtracting the epoxy contribution from the total measured signal

$$m_{\text{Dy-SQ}}(T, H) = m_{\text{tot}}(T, H) - m_{\text{epoxy}}(T, H) \quad (4.2)$$

The corrected moment was then used to calculate the molar susceptibility product χT of the powder-in-epoxy sample. This correction is particularly important at high temperature. Before subtraction, the resin contribution partially compensated the intrinsic temperature dependence of the Dy-SQ signal, making the high-temperature region appear almost flat. After subtraction, the corrected Dy-SQ response shows a weak increase of χT upon warming. The following comparison therefore takes into account both the corrected active mass and the subtraction of the epoxy background.

The effect of the resin embedding is first shown at 1 kOe and 10 kOe in Figure 4.2 and 4.3 respectively. The unrestrained powder displays larger χT values. In contrast, the powder-in-epoxy curves are lower and smoother, indicating that blocking the crystallites strongly reduces the anomalous contribution associated with the loose-powder configuration. The ZFC and FC branches are still not identical, suggesting the onset of a spurious contribution from an extrinsic magnetic phase ordering at around 160 K, but the overall response is much more consistent with a powder-averaged measurement of a paramagnetic sample.

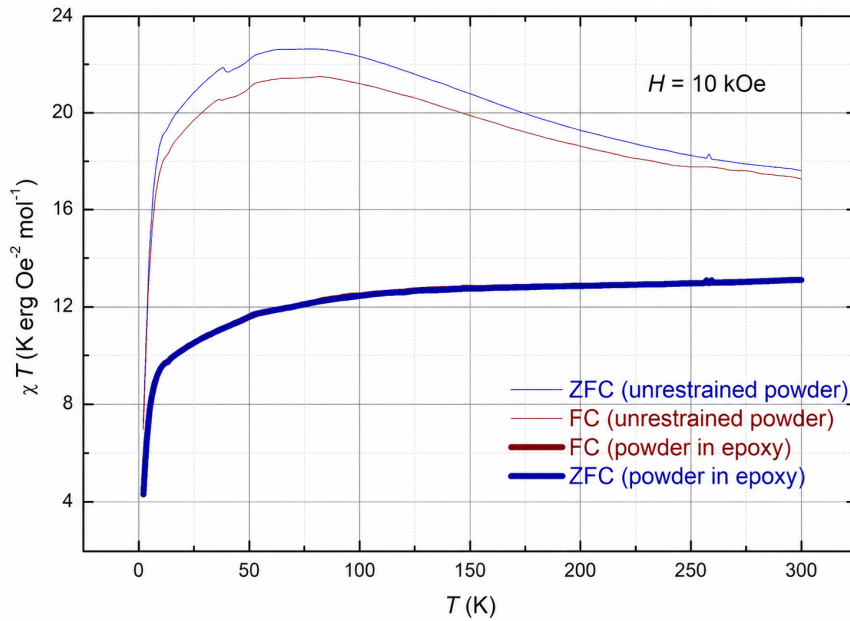


Figure 4.3: Temperature dependence of the ZFC and FC susceptibility product χT measured at 10 kOe for the unrestrained powder and for the powder embedded in epoxy.

Only by comparing the two datasets did the origin of the initial anomaly become clear: the unrestrained powder was subject to mechanical torqueing. Due to the strong magnetic anisotropy of the Dy^{3+} center, the external field exerted a torque on the loose microcrystals, physically rotating them toward their easy axis of magnetization during the warming cycle [30, 31]. This alignment caused the SQUID

magnetometer to measure the response along the most magnetic direction rather than a powder average, leading to the observed overestimation of χT . In this case, the measured response would no longer correspond to a reliable random powder average, but would contain an additional contribution associated with the mechanical reorientation of the grains.

The comparison at 10 kOe, reported in Figure 4.3, makes the effect even clearer. In the unrestrained powder, both ZFC and FC curves reach very large χT values, confirming that the high applied field enhances the anomalous response of the loose crystallites. After embedding the sample in epoxy, the absolute value of χT is strongly reduced and the ZFC and FC curves become much closer to each other. The absence of a sizeable separation between the two branches suggests a suppression of the spurious response upon increasing the applied field H . This observation supports the idea that the ZFC–FC splitting observed in the previous measurements is not an intrinsic feature of the magnetic response of the molecular system, but rather reflects an extrinsic contribution affecting the low-field data.

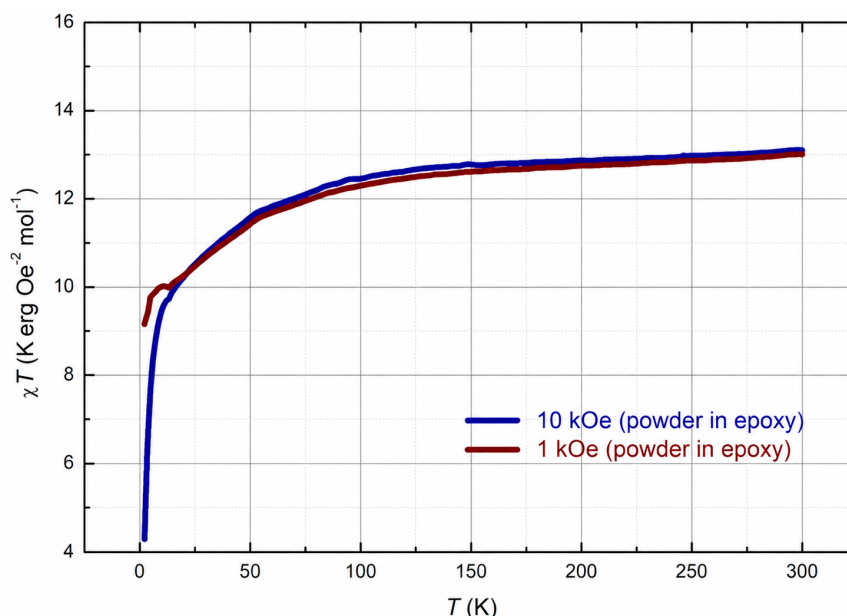


Figure 4.4: Corrected FC susceptibility product χT as a function of temperature for the powder-in-epoxy sample measured at 1 kOe and 10 kOe. The comparison shows that, after immobilization, mass renormalization and epoxy-background subtraction, the high-temperature response is no longer dominated by the anomalous behavior observed in the loose powder.

A final consistency check is provided in Figure 4.4, where the corrected FC curves of the powder-in-epoxy sample measured at 1 kOe and 10 kOe are directly compared. Unlike the unrestrained powder, the embedded sample shows a much weaker field dependence in the high-temperature region. The two curves are not perfectly identical, especially at low temperature where field effects and slow relaxation processes are expected to be more relevant, but their overall agreement confirms that the resin embedding and background subtraction provide a more reliable estimate of the intrinsic macroscopic response of the Dy–SQ powder.

4.1.4 Isothermal Magnetization Curves

To investigate the ground-state properties and the magnetic anisotropy of the complex, isothermal magnetization curves (M vs. H) were recorded at temperatures of 2 K, 3 K, and 5 K, with the external field swept up to 70 kOe.

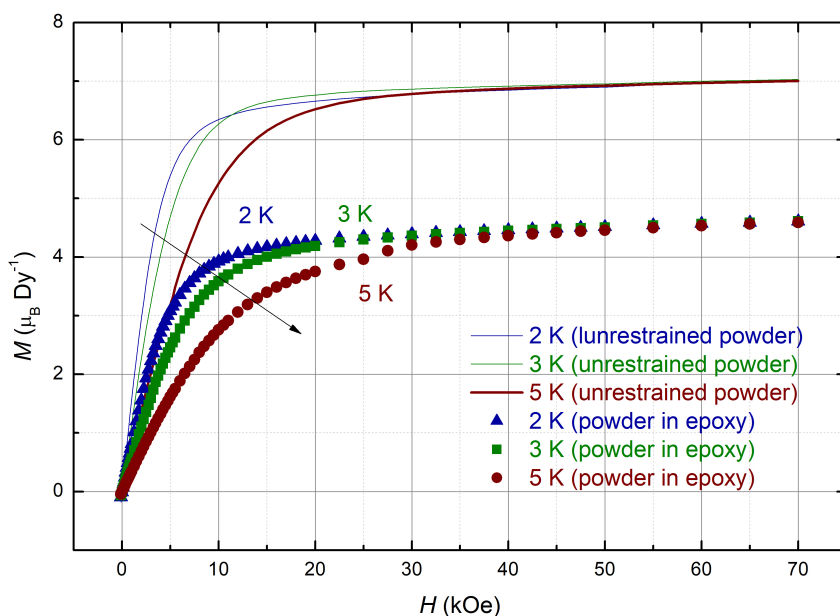


Figure 4.5: Isothermal magnetization (M) versus applied magnetic field (H) up to 70 kOe measured at 2 K, 3 K, and 5 K, comparing the unrestrained powder and epoxy-embedded configurations.

The magnetization data, shown in Figure 4.5, are normalized in Bohr magnetons per Dysprosium ion ($\mu_B \cdot \text{Dy}^{-1}$). Since the molecular structure contains a single magnetic center per formula unit, this normalization directly represents the molar magnetization of the complex. The comparison between the unrestrained powder and the resin-embedded sample provides further evidence of the magnetic anisotropy of the system.

In the unrestrained powder configuration, the magnetization rises sharply at low fields and reaches significantly higher values. This behavior is again a clear consequence of the mechanical reorientation of the microcrystals: the Dy^{3+} ions possess a strongly axial magnetic ground state, and under the influence of the external field, the loose grains physically rotate to align their easy axis of magnetization with the field direction.

The resin-embedded sample exhibits a more gradual approach to saturation. By immobilizing the crystallites in a random distribution, the epoxy matrix allows for the measurement of the true powder-average magnetization.

The fact that the magnetization does not reach the theoretical free-ion value of $10.6 \mu_B$ is consistent with the presence of a strong crystal field, which splits the J multiplet and leaves only the lowest energy Stark levels populated at cryogenic temperatures [30, 31].

4.2 Nuclear Magnetic Resonance

The investigated sample was provided in the form of a fine polycrystalline powder. In this solid-state configuration, the sample consists of a large number of randomly oriented microcrystallites, leading to a powder average of the magnetic response. To prevent degradation and ensure mechanical stability during the measurements, the powder was densely packed and sealed with Teflon inside a standard cylindrical NMR glass tube.

NMR measurements were performed at two different static magnetic fields, $H_0 = 13$ kOe and $H_0 = 38$ kOe. The low-field measurements were carried out using a conventional laboratory electromagnet, whereas the high-field measurements required a superconducting magnet. The corresponding cryogenic arrangements were those described in Section 2.6, with the sample housed in an exchange-gas cryostat for the low-field experiment and in a continuous-flow cryostat for the high-field experiment.

4.2.1 Probe Tuning and Pulse Calibration

Prior to the initiation of any experimental acquisition, it is strictly required to tune and match the radio-frequency (RF) probe circuit. The circuit must be precisely tuned to the Larmor frequency, which is the natural precessional frequency of the probed nuclei dictated by the external magnetic field.

Focusing on the ^1H nucleus (proton) as the primary local probe, the resonance condition is determined by the Larmor equation:

$$\nu_L = \frac{\gamma}{2\pi} H_0 \quad (4.3)$$

where $\gamma/2\pi$ is the characteristic gyromagnetic ratio of the proton, equal to 42.577 MHz/T. Consequently, for the applied static field of 13 kOe, the target resonance frequency is approximately 55.35 MHz, while for the stronger field of 38 kOe the target resonance frequency is 161.79 MHz.

Once the operating frequency was fixed by the Larmor condition, the RF circuit had to be tuned and matched at that frequency. The probe coil and the variable capacitors form a resonant circuit, whose resonance frequency must coincide with the NMR frequency of the experiment. At the same time, the impedance of the circuit as seen from the transmission line must be matched to the standard value of $50\ \Omega$. This impedance matching is essential to minimize reflected RF power during the excitation pulse and to ensure an efficient transfer of power from the spectrometer to the coil. It also improves the sensitivity during signal detection, since an unmatched circuit would reduce the voltage effectively transmitted from the coil to the receiver.

For this reason, different sets of variable capacitors and transmit/receive switch circuits were selected depending on the working frequency. The tuning procedure adjusted the resonance condition, while the matching procedure optimized

the impedance of the RF circuit close to $50\ \Omega$. In this way, the same probe could be adapted to the different experimental configurations used in the low-field and high-field NMR measurements.

After tuning and matching the RF circuit at the working frequency for each field configuration, the RF pulses were calibrated following the procedure described in Section 2.4.2. The purpose of this calibration is to determine the pulse length t_p required to rotate the macroscopic nuclear magnetization by a selected flip angle θ with respect to the static magnetic field H_0 . In the rotating-frame description, this nutation is governed by

$$\theta = \gamma H_1 t_p \quad (4.4)$$

where H_1 is the amplitude of the oscillating magnetic field generated by the RF coil.

Experimentally, the preliminary calibration was performed using a standard free induction decay (FID) sequence. A single RF pulse with systematically varied duration was applied, and the amplitude of the resulting FID signal was recorded. As discussed in Section 2.4.2, the signal intensity follows an oscillatory dependence on the pulse length, proportional to $\sin(\gamma H_1 t_p)$. This procedure allows the $\pi/2$ pulse condition to be identified, from which the corresponding π pulse length can be determined. An example of this calibration is shown in Figure 4.6.

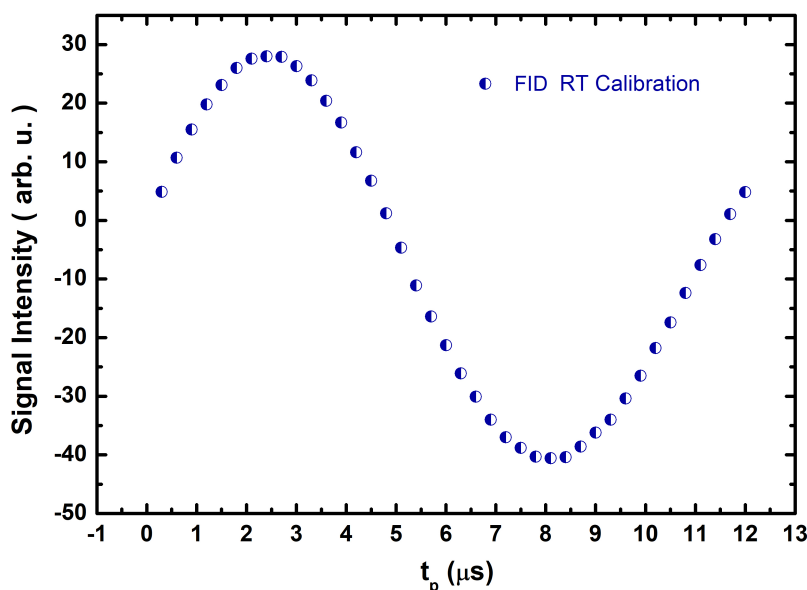


Figure 4.6: Calibration of the flip angle at room temperature. Each data point represents the integrated signal intensity for a given pulse width. The first maximum corresponds to a 90° rotation, while the subsequent null point indicates a 180° inversion of the longitudinal magnetization.

Consequently, the pulse length yielding the maximum positive signal amplitude corresponds to a $\pi/2$ (90°) excitation pulse, whereas the pulse length resulting in a zero-crossing of the signal (a null signal) corresponds to a π (180°) inversion pulse.

Subsequent to the determination of the nominal $\pi/2$ pulse length via the FID nutation experiment, a standard Hahn echo sequence ($\pi/2 - \tau - \pi$) was implemented. The purpose of this secondary calibration was to accurately refine the length of the π refocusing pulse and to optimize the overall spin-echo amplitude [41, 42, 46].

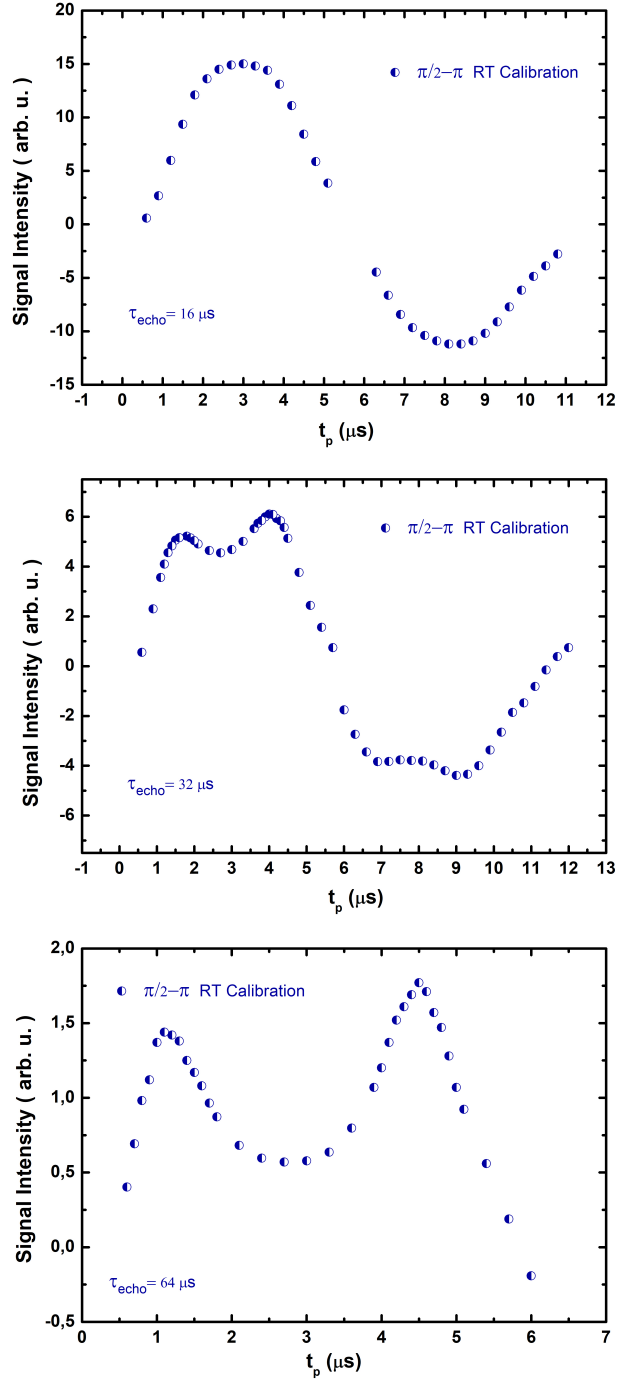


Figure 4.7: Spin-echo calibration for different values of τ (16, 32 and 64 μs).

However, during the execution of this echo-based calibration sequence, the resulting nutation profile yielded anomalous results. The echo amplitude as a function

of the refocusing pulse length, which theoretically follows a regular sinusoidal pattern, deviated significantly from the expected ideal behavior. Specifically, the signal maximum during the first half-period exhibited a pronounced flattening, strongly suggesting the superposition of two unresolved, distinct peaks. This anomaly persisted across different values of the inter-pulse delay τ (see Figure 4.7).

Since a reliable echo-based calibration is important for T_2 relaxation measurements, which rely on the systematic variation of τ , it was imperative to identify an alternative pulse configuration that could provide a clean, undistorted signal.

This distortion implies a complex spin dynamics, potentially arising from slightly different local magnetic environments or strong radio-frequency field (H_1) inhomogeneities across the powder sample. To mitigate this issue and achieve a reliable signal for the experimental campaign, alternative double-pulse configurations were tested and calibrated. Specifically, the standard sequence was substituted with $\pi/2 - \tau - \pi/2$ (solid echo) and $\pi/2 - \tau - \pi/4$ pulse sequences.

Following a comparative evaluation of the acquired profiles, the $\pi/2 - \pi/4$ sequence was identified as the optimal configuration. Unlike the previous attempts, this sequence showed no anomalous behavior at the reference delay of $\tau = 64 \mu\text{s}$, closely approximating the theoretical standards required for reliable data extraction (see Figure 4.8).

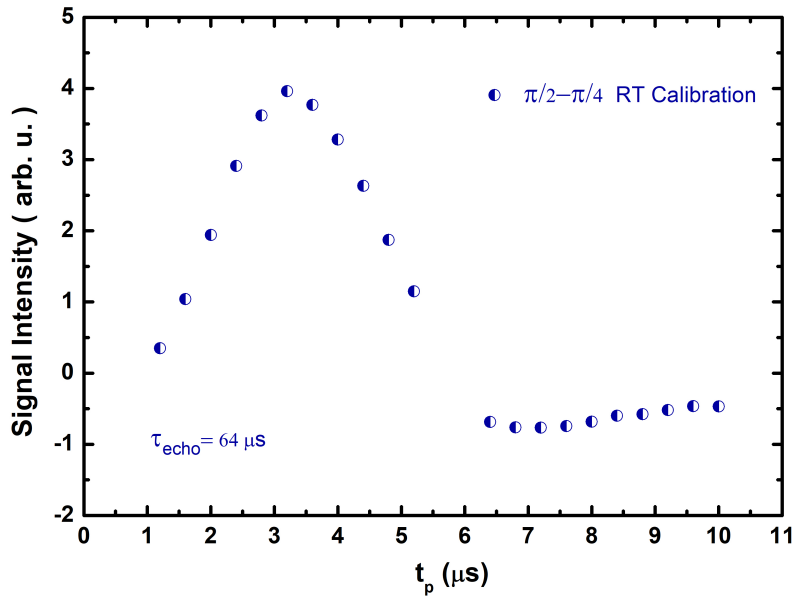


Figure 4.8: $\pi/2 - \pi/4$ calibration sequence ($\tau_{\text{echo}} = 64 \mu\text{s}$)

To ensure the highest possible fidelity in the measurements, this specific non-standard pulse configuration was strictly adopted for all subsequent nuclear relaxation investigations of the sample.

To ensure the continued validity of the excitation parameters throughout the extended duration of the experimental campaign, the pulse calibration procedures were periodically repeated at regular intervals. These checks were performed to

account for any potential drift in the spectrometer's performance or minor variations in the probe's tuning due to thermal cycling. Despite these frequent re-evaluations, no significant deviations from the initial optimal pulse lengths were observed. The consistency of these calibration results confirms the high stability of the radio-frequency setup and ensures that the excitation conditions remained uniform across all acquired datasets.

4.2.2 Optimization of T_1 Measurements

Following the calibration protocols, temperature-dependent FID and spin-echo measurements were systematically acquired. The initial experimental run for the low field configuration (13 kOe) started at a temperature of 305 K, with data collected upon cooling in discrete steps of 8 K. To achieve a higher thermal resolution, the measurement grid was densified during a subsequent experimental session the following week. Before initiating this finer temperature sweep, the sample was carefully heated back to the initial starting temperature of 305 K and allowed to fully thermalize. This rigorous procedure was strictly implemented to ensure data reproducibility and to preclude any potential spurious artifacts or relaxation anomalies arising from the thermal history of the sample.

The measurement of the longitudinal relaxation time (T_1) presented increasing technical challenges as the temperature was lowered. At a lower applied field of 13 kOe, the standard inversion recovery sequence using a FID readout became progressively unreliable. In the acquisition of T_1 relaxation curves, it became increasingly difficult to resolve the initial experimental points corresponding to the short-time limit (specifically, the first plateau and the early rising edge of the expected sigmoidal recovery function). This degradation in data quality (as seen in Figure 4.9) is primarily attributed to two factors: the significant broadening of the NMR resonance line, which causes the FID to decay faster than the spectrometer's dead time, and a rapid decrease in T_1 values.

To circumvent these limitations and extend the experimental range toward lower temperatures, a T_1 -Echo protocol was implemented, following the spin-echo-based detection strategy discussed in Section 2.4.3. By substituting the FID readout with a refocusing pulse to generate an echo, the signal could be acquired outside the dead time, partially mitigating the effects of spectral broadening. Although the refocusing of the transverse magnetization through the echo allowed for the extension of the measurement range toward lower temperatures, this compensation was not entirely optimal. The inherent dead time between the excitation pulses and the echo formation, combined with the extremely fast relaxation components of the Dysprosium-Semiquinonate complex, meant that a portion of the fastest relaxation dynamics remained inaccessible, even with the echo-based approach. At the higher field of 38 kOe, the signal-to-noise ratio (SNR) of the FID was found to be insufficient for any quantitative analysis. Even the standard echo-based inversion recovery sequence proved ineffective as the temperature decreased.

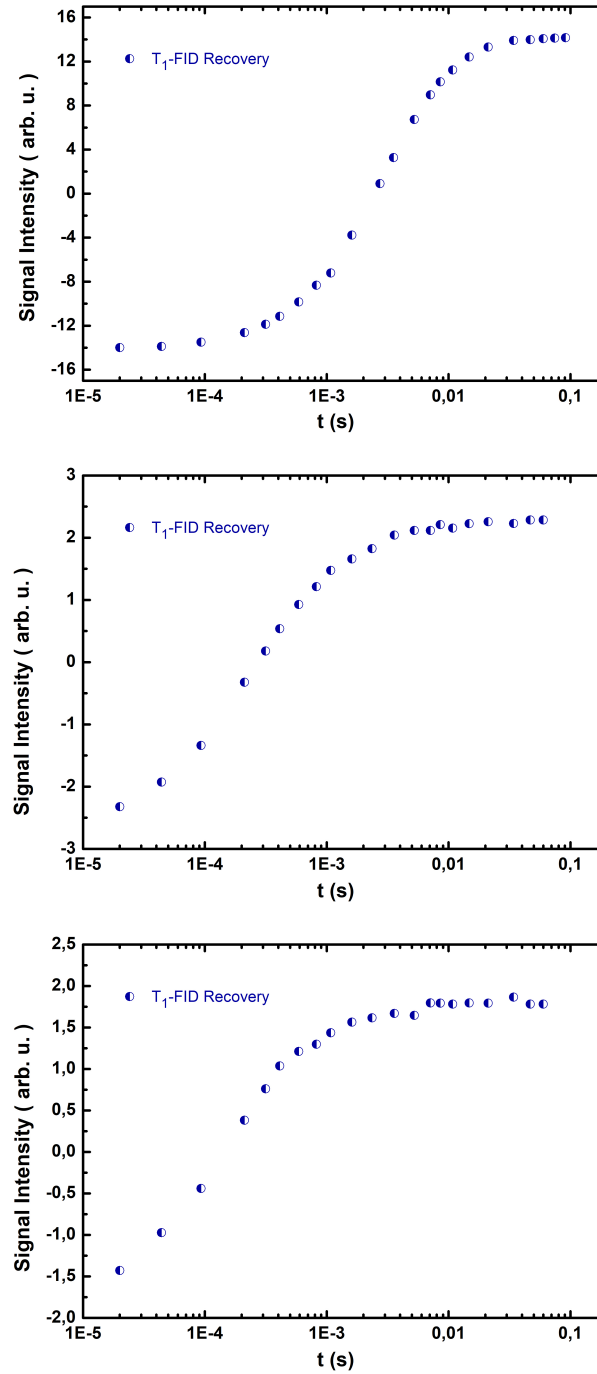


Figure 4.9: T_1 relaxation regimes at different temperature values (from top to bottom: 305-121-105 K).

To resolve this, a more robust excitation protocol was adopted during the temperature descent by adding a comb of $\pi/2$ pulses, namely a saturation pulse train, before the standard sequence, as discussed in Section 2.4.6. This comb of pulses ensures that the initial longitudinal magnetization is consistently nullified across the entire broadened spectral width before the actual inversion and subsequent echo-reading pulses. This preparation sequence proved essential for stabilizing the signal and achieving reproducible T_1 measurements in the high-field, low-temperature regime.

For each temperature point where a relaxation measurement was performed, the longitudinal relaxation time (T_1) was estimated using the fitting protocols established in Chapter 2. Preliminary analysis revealed that the experimental recovery curves could not be accurately described by a standard mono-exponential model. This is physically justified by the molecular structure of the Dy-SQ complex: the ^1H nuclei are located in chemically and magnetically non-equivalent positions within the ligands and the radical units. Different hydrogen atoms experience distinct local magnetic environments and varying proximities to the paramagnetic Dysprosium center, leading to a distribution of relaxation rates.

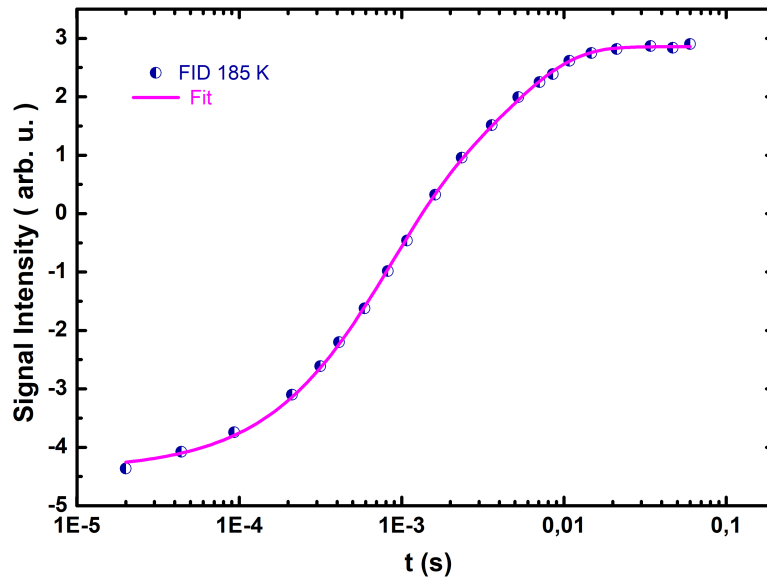


Figure 4.10: *Experimental longitudinal magnetization recovery acquired at 185 K.*

To account for this multi-component behavior, a two-component model was adopted. This approach allows for the identification of two distinct characteristic relaxation times, T_{1a} and T_{1b} [37, 57]. The experimental data were fitted using the following expression:

$$I(\tau) = y_0 + A_1 \left[1 - \exp\left(-\frac{\tau}{T_{1a}}\right)^{\beta_1} \right] + A_2 \left[1 - \exp\left(-\frac{\tau}{T_{1b}}\right)^{\beta_2} \right] \quad (4.5)$$

The physical significance of each parameter in the equation is defined as follows:

- $I(\tau)$: The measured NMR signal intensity as a function of the delay time τ .
- y_0 : The vertical offset of the recovery curve, introduced because in an inversion-recovery sequence the initial magnetization is inverted and the measured signal starts from a negative value before relaxing back toward equilibrium.
- A_1 and A_2 : The amplitudes (or weights) of the two relaxation components. These values are proportional to the relative populations of protons contributing to each specific relaxation path.

- T_{1a} and T_{1b} : The characteristic longitudinal relaxation times for the two distinct groups of protons.
- β_1 and β_2 : The stretching exponents (typically ranging between 0.5 and 1). These parameters account for a potential distribution of relaxation times within each component, often resulting from structural disorder or slight local variations in the magnetic environment.

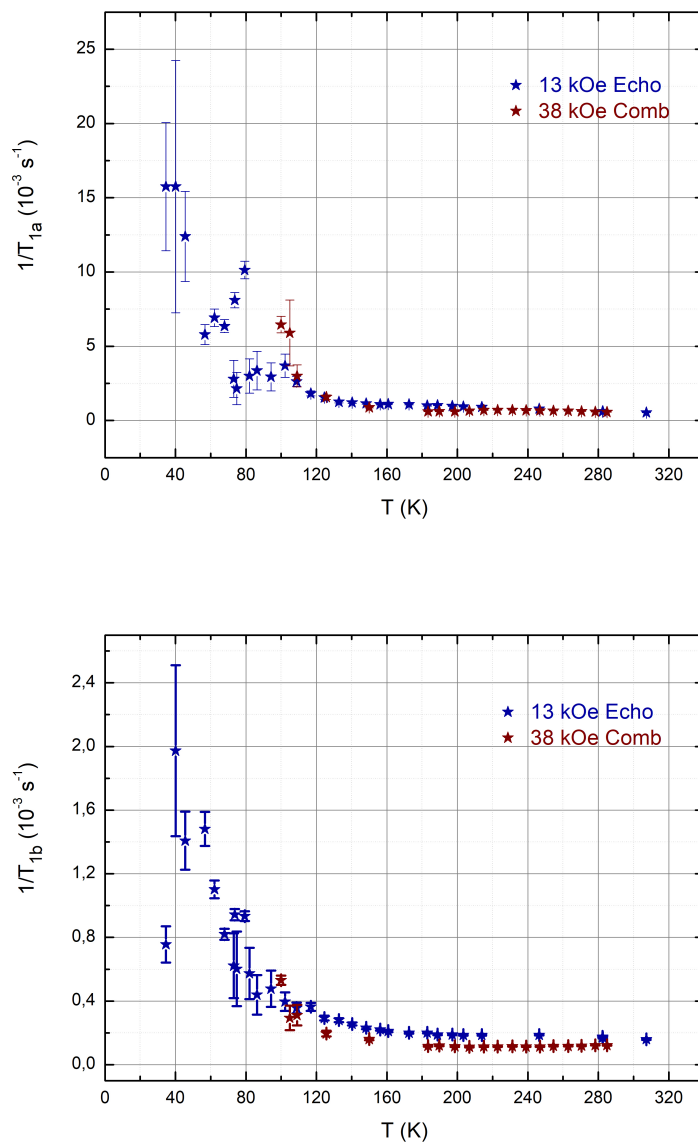


Figure 4.11: Temperature dependence of both the longitudinal relaxation rates ($1/T_{1a}$ and $1/T_{1b}$) at 13 kOe and 38 kOe.

The robustness of the aforementioned fitting model is evidenced by the high quality of the numerical agreement with the experimental datasets. To illustrate this, a representative recovery curve acquired at 185 K is reported in Figure 4.10.

The temperature dependence of the longitudinal relaxation rates, $1/T_{1a}$ and $1/T_{1b}$, is presented in Figures 4.11 for both applied magnetic fields (13 kOe and 38 kOe). It is immediately evident that the high-field dataset (38 kOe) is limited to temperatures above approximately 100 K. As previously discussed, below this threshold, the signal-to-noise ratio and the extreme broadening of the resonance line made the data unreliable, preventing a meaningful extension of the high-field study into the low-temperature regime of interest. Despite this limitation, a clear physical trend emerges from both plots: as the temperature decreases, the relaxation rates exhibit a consistent upward trajectory. This behavior strongly suggests the approach toward a relaxation peak at lower temperatures, a classic signature in molecular magnetism [36, 37]. A comparison between the two plots reveals several key insights:

Scale of Relaxation: The relaxation rate of the fast component ($1/T_{1a}$) is approximately one order of magnitude larger than that of the slow component ($1/T_{1b}$), reaching values up to $20 \times 10^{-3} \text{ s}^{-1}$ compared to $2.5 \times 10^{-3} \text{ s}^{-1}$ at 40 K. This confirms that the two proton populations are located at significantly different distances from the paramagnetic Dysprosium centers.

Field Independence at High Temperature: In the high-temperature regime ($T > 150 \text{ K}$), the data for both 13 kOe and 38 kOe are nearly superimposed. This indicates that, in this range, the relaxation is dominated by fast, field-independent fluctuations, likely related to the paramagnetic lattice dynamics.

Low-Temperature Divergence: Below 100 K, the 13 kOe data show a much more pronounced increase and a higher degree of scatter (larger error bars). This increase in uncertainty is a direct consequence of the experimental challenges mentioned in the previous sections, where the rapid shortening of T_1 and the degradation of the FID signal required the transition to echo-based protocols and the use of a saturation comb og pulses.

4.2.3 T_2 Measurements

The measurements of the transverse relaxation time, T_2 , yielded more satisfactory and robust results across the entire investigated thermal range, including the lowest temperatures achieved. The persistence of a well defined spin-echo signal allowed for a consistent monitoring of the T_2 dynamics down to 30-20 K in both high and low field regime. This indicates that while the energy exchange with the lattice (T_1) was heavily perturbed by the fluctuating electronic environment of the single-ion magnet, the dephasing mechanisms governing the spin-spin interactions remained experimentally accessible and provided a reliable probe for the local magnetic fluctuations of the Semiquinonate-Dysprosium system in all thermal regimes.

As illustrated in Figure 4.12, the functional form of the decay profiles undergoes a significant evolution as the temperature is lowered. When plotted on a semi-logarithmic scale, the high-temperature data (e.g., 293 K) exhibits a pronounced

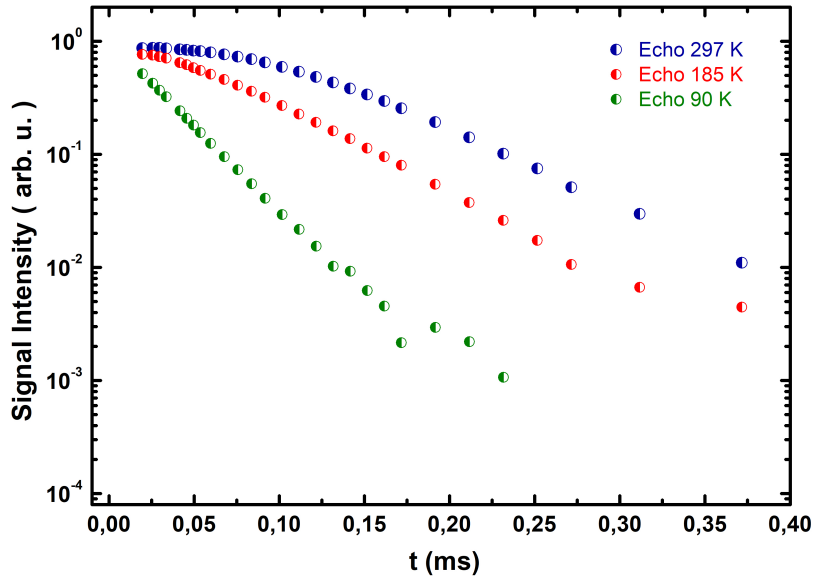


Figure 4.12: Representative decay of the spin-echo amplitude (T_2) acquired at different temperatures using a Hahn echo sequence. The data has been at $t = 0$ to better highlight the form comparison.

downward curvature. This deviation from linearity indicates a dominant Gaussian dephasing regime, likely linked to the static dipolar interactions within the ^1H nuclear bath that are probed while the electronic fluctuations are in a specific frequency regime. In contrast, as the temperature decreases, the data regains linearity. This shift toward a purely exponential decay indicates that in the low-temperature regime the transverse relaxation is governed by a single characteristic rate (or a distribution of rates described by the stretched exponential), where the Lorentzian contribution from the electronic-nuclear coupling becomes the prevailing mechanism.

To extract the characteristic relaxation parameters, the decay curves were analyzed using the fitting model described in Chapter 2, which is specifically designed to account for the complex interactions in solid-state paramagnetic systems. The experimental data were fitted according to the following expression:

$$I(t) = A \cdot \exp[-(tR_1)^\beta] \cdot \exp\left[-\frac{1}{2}(tR_2)^2\right] \quad (4.6)$$

The physical significance of the parameters is defined as follows:

- $I(t)$: The measured echo intensity as a function of the evolution time t (where $t = 2\tau$).
- A : The initial amplitude of the signal, representing the maximum detectable magnetization immediately following the pulse sequence.
- R_1 : The transverse relaxation rate associated with the stretched exponential component. This term accounts for the Lorentzian contribution to the line

shape, often dominated by the electronic-nuclear dipolar interactions and fluctuations of the paramagnetic centers.

- β : The stretching exponent ($0.5 < \beta \leq 1$), which reflects the degree of distribution of the relaxation rates within the sample.
- R_2 : The Gaussian relaxation rate. This quadratic term accounts for the dipolar coupling between the ^1H nuclei within the rigid lattice of the molecular complex.

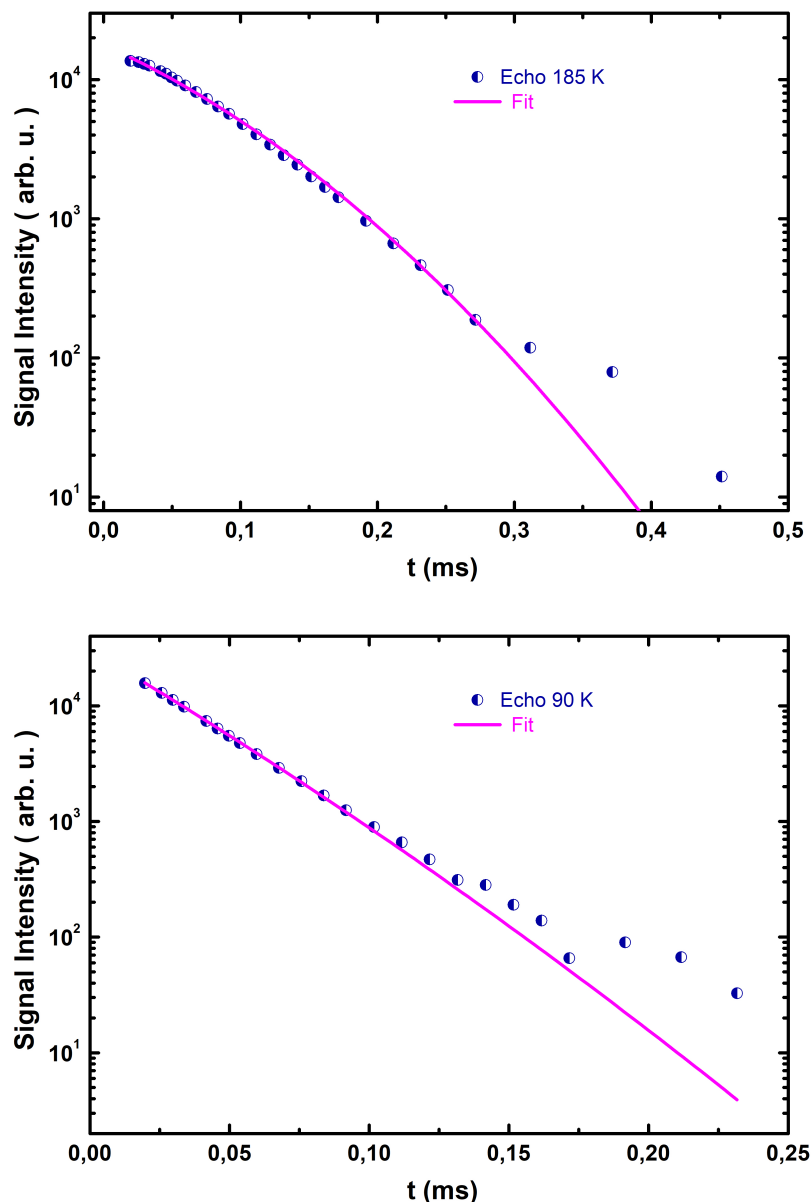


Figure 4.13: Representative transverse magnetization decay (T_2) profiles and relative fits acquired at 185 K and 90 K.

To ensure the highest accuracy in determining the relaxation parameters, the analysis of the experimental data was conducted following two sequential fitting proto-

cols, differentiated by thermal regime and parameter sensitivity. Initially, in the high-temperature regime, where the Gaussian contribution is predominant and clearly visible as a downward curvature in the semi-logarithmic plot, the fitting was performed by leaving all optimization parameters free. This exploratory analysis revealed that the Gaussian relaxation rate, R_2 , tended to stabilize around a specific value, remaining approximately constant at each applied magnetic field.

Based on this experimental evidence, a second, more robust protocol was adopted: the R_2 value was fixed to the average obtained from the high-temperature measurements. The entire dataset, from high to low temperatures, was then re-fitted by leaving only the exponential term R_1 as a free parameter. This procedure allowed for a more precise isolation of the electronic relaxation dynamics, minimizing parameter correlation in the regions where the two contributions overlap.

As shown in Figures 4.13, the theoretical model perfectly matches the experimental data across the entire investigated thermal range. The quality of the fit confirms the effectiveness of the adopted strategy, demonstrating that the hybrid expression is capable of accurately describing both the phase dominated by static nuclear fluctuations and the phase where the electronic relaxation of the Dysprosium-Semiquinone system takes over.

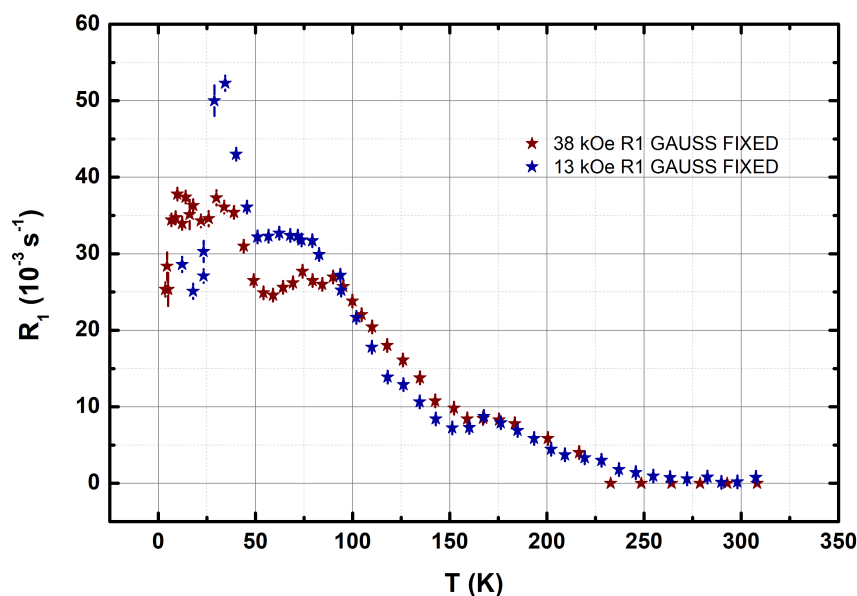


Figure 4.14: Temperature dependence of the inverse of the transverse relaxation rate R_1 measured at 13 kOe and 38 kOe, showing the emergence of distinct relaxation peaks in the low-temperature regime.

The temperature dependence of the transverse relaxation rate, derived from the stretched exponential component of the T_2 decay (R_1 in the fitting model), is illustrated in Figure 4.14. Unlike the T_1 measurements, the T_2 protocol allowed for a continuous and reliable characterization across the entire temperature range, from 300 K down to 2 K, for both applied fields (13 kOe and 38 kOe). The most striking feature of the T_2 data is the presence of a multi-peak structure below 100 K,

which points to the existence of different relaxation regimes or distinct magnetic dynamics within the Dy-SQ complex:

- **High-Temperature Regime ($T > 100$ K):** Similar to what was observed for T_1 , the relaxation rates measured at 13 kOe and 38 kOe are essentially superimposed over most of the high-temperature range. In this region, R_1 generally increases as the temperature decreases, suggesting that the relaxation is mainly driven by fast electronic fluctuations that are not yet strongly sensitive to the strength of the external magnetic field.
- **Weak anomaly (150–180 K):** A small feature is visible in the intermediate-temperature region, approximately between 150 K and 180 K. Interestingly, this is the same temperature range where the low-field SQUID measurements at 0.1 kOe show the opening of a separation between the ZFC and FC curves. This correspondence suggests that the weak anomaly observed in R_1 may not originate from an intrinsic relaxation channel of the Dy–SQ molecular system, but rather from the same spurious magnetic contribution inferred from the magnetometry data.
- **The 70 K Feature:** Around 70 K, a broad shoulder or local maximum is visible, particularly in the 13 kOe dataset.
- **The Low-Temperature Peak (30–40 K):** A prominent and much sharper peak emerges at lower temperatures. Interestingly, this peak exhibits a clear field dependence: at 13 kOe, the peak is centered around 35 K and reaches a maximum value of approximately $50 \times 10^{-3} \text{ s}^{-1}$. At 38 kOe, the feature appears broader and shifted toward slightly higher temperatures, with a reduced maximum intensity.

This shift and damping of the peak with increasing field are characteristic of a relaxation process where the matching condition between the nuclear Larmor frequency and the electronic fluctuation rate ($\omega_L \tau_c \approx 1$) is satisfied. Since ω_L is proportional to the applied field, the observation of this shift confirms that we are probing the intrinsic slow dynamics of the Dysprosium magnetic moments [36, 37, 44].

4.2.4 Frequency-Swept NMR Spectroscopy

During both the low-field ($H_0 = 13$ kOe) and high-field ($H_0 = 38$ kOe) experimental campaigns, part of the measurement time was devoted to the reconstruction of frequency-swept NMR spectra. The measurements were performed following the procedure discussed in Chapter 2.5, where the spectrum is obtained by probing the nuclear response at different excitation frequencies rather than by relying on a single broadband pulse. This approach is particularly important in molecular nanomagnets at low temperature, where the inhomogeneous broadening of the resonance line can become larger than the excitation bandwidth of an individual radio-frequency pulse [41, 42].

The operating frequency of the spectrometer, ω_{RF} , was varied in discrete steps

around the expected Larmor frequency, ω_L . At each frequency, the intensity of the nuclear signal was extracted by integrating either the FID or the spin-echo, depending on the relaxation regime and on the experimental conditions. The resulting spectra were then obtained by plotting the normalized signal intensity as a function of frequency. Since this reconstruction is intrinsically point-by-point, the choice of the frequency step is crucial: when the resonance line is not sampled with sufficient resolution, the resulting profile can distort the apparent width, position, or shape of the peak. For this reason, spectra acquired with an inadequate frequency step were not retained in the final analysis. This selection criterion explains why fewer temperature-dependent spectra are reported for the high-field campaign.

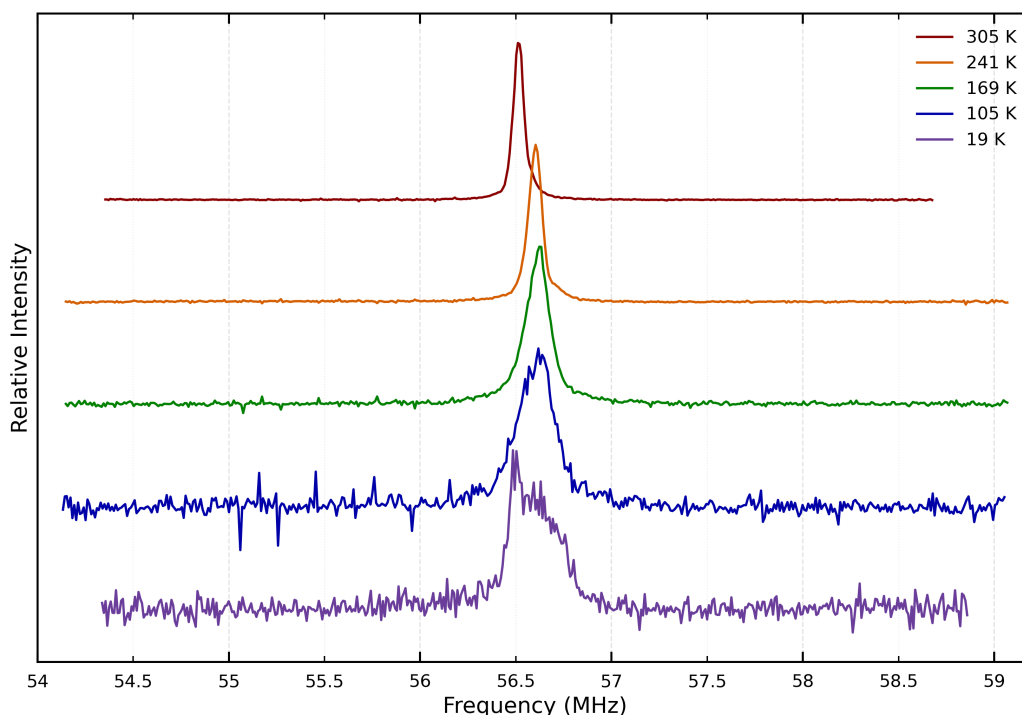


Figure 4.15: Frequency-swept NMR spectra measured at $H_0 = 13$ kOe at selected temperatures. The spectra are normalized and vertically offset for clarity. The vertical offsets have no physical meaning and are introduced only to highlight the temperature evolution of the resonance line.

The retained spectra are shown in Figures 4.15 and 4.16. The curves are normalized and vertically offset for clarity, so that the vertical displacement has no direct physical meaning. At $H_0 = 13$ kOe, spectra were collected over a broader temperature range, allowing the temperature evolution of the resonance line to be followed from room temperature down to the low-temperature regime. A progressive broadening of the line is observed upon cooling. In the high-temperature spectra, a small apparent shift of the resonance position is also visible. This shift should not be interpreted as an intrinsic effect of the Dy–SQ magnetic response. Rather, it is most likely related to small changes in the magnetic field generated by the resistive electromagnet after switching the apparatus off and on during the first weeks of measurements. Since the NMR resonance frequency is directly proportional to the

applied field, even a slight change in the actual value of H_0 produces a corresponding displacement of the measured resonance frequency.

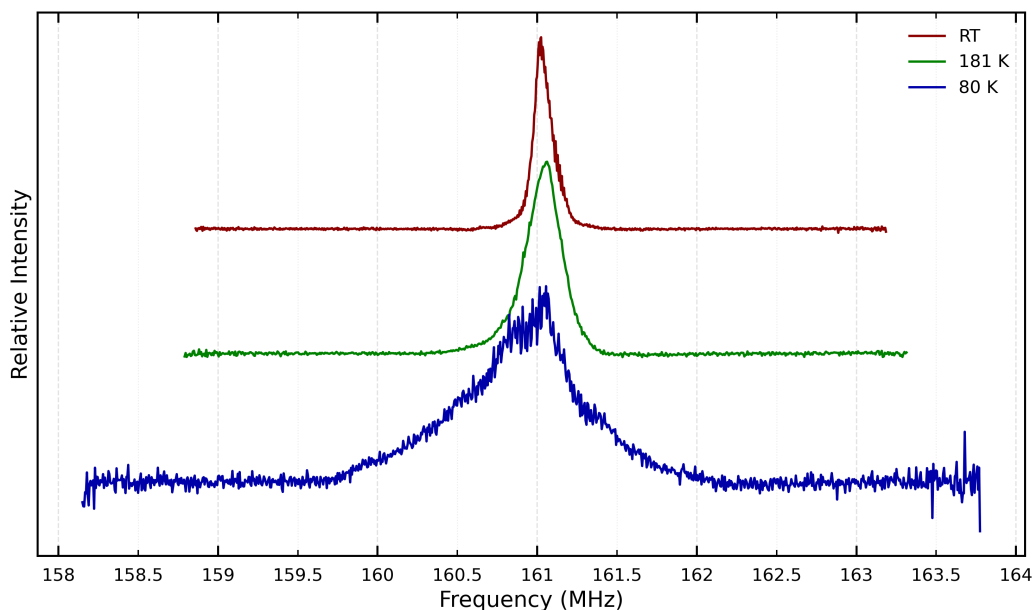


Figure 4.16: Frequency-swept NMR spectra measured at $H_0 = 38$ kOe. Only spectra acquired with a sufficiently fine frequency sampling are shown. The spectra are normalized and vertically offset for clarity.

At $H_0 = 38$ kOe, only the spectra acquired with a sufficiently fine frequency sampling are displayed. Although the available temperature set is more limited, the same qualitative broadening trend is visible, with a much broader low-temperature spectrum. These spectral changes provide a direct indication that the local magnetic-field distribution sensed by the nuclei becomes increasingly broad as the Dy magnetic moments enter the slow-fluctuation regime.

4.3 Muon Spin Spectroscopy

Following the detailed description of the Paul Scherrer Institute (PSI) facility and the various magnetic field configurations presented in chapter 3, this section delineates the specific experimental protocols adopted during the μ SR measurement campaign. After loading the sample into the GPS spectrometer, the initial phase of the experiment focused on the precise calibration of the instrumental asymmetry. This procedure is fundamental to account for the intrinsic differences in the solid angle and detection efficiency between the forward (F) and backward (B) positron counters. To determine the calibration constant, denoted as α , a weak transverse field of 50 Oe was applied while the sample was maintained in its high-temperature (300 K) paramagnetic state (see Figure 4.17).

Under these conditions, the muon spin ensemble undergoes a coherent Larmor precession, allowing for the direct comparison of the oscillation amplitudes recorded

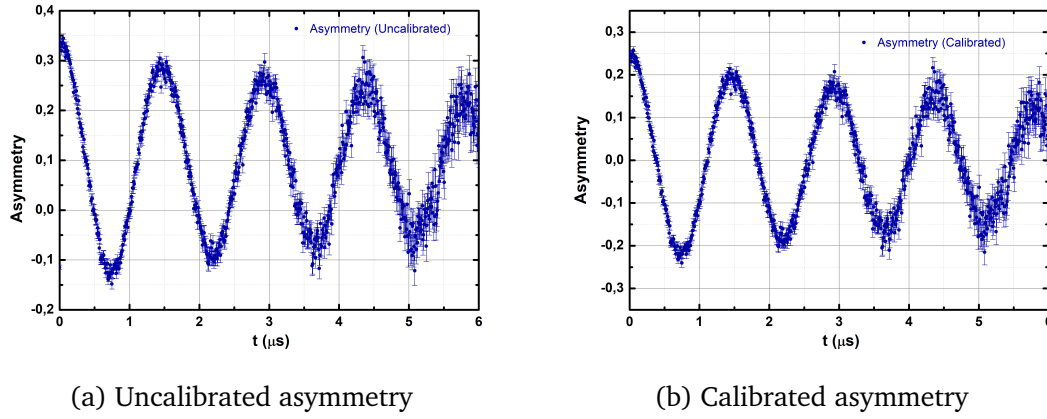


Figure 4.17: Asymmetry calibration procedure performed at 300 K under a 50 Oe transverse field. (a) Precession signal obtained with an uncorrected α value, showing a clear vertical offset and baseline shift due to detector imbalance. (b) Optimized calibration where the oscillation is perfectly centered around the zero-asymmetry axis (α correction), ensuring that the forward and backward detector efficiencies are properly balanced.

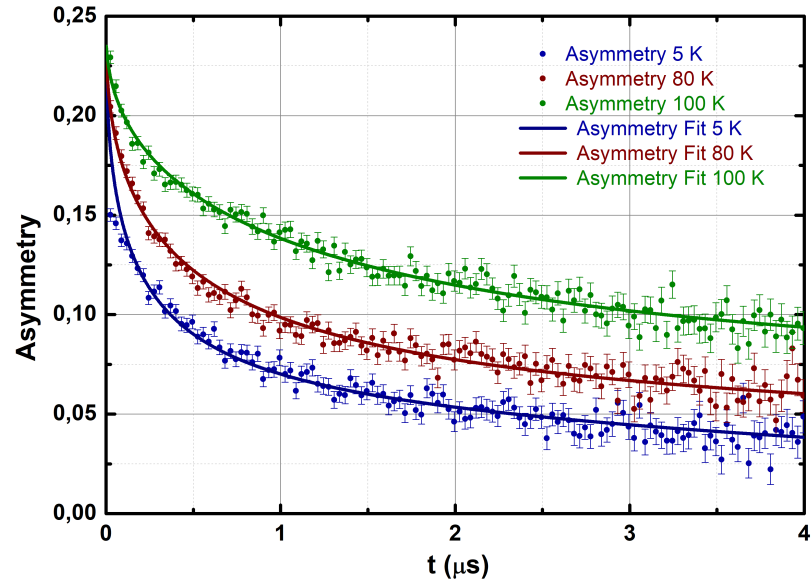
by the opposing detectors. By adjusting the α parameter until the oscillating signal is perfectly centered around the zero-asymmetry axis, the geometrical and electronic imbalances of the apparatus are effectively neutralized. This calibration ensures that any subsequent relaxation or shift observed in the asymmetry function $A(t)$ originates strictly from the internal magnetic properties of the sample rather than instrumental artifacts [38, 39, 52].

The impact of this calibration is visually summarized in Figure 4.17, which compares the raw precession signal before and after the numerical optimization of the α parameter. Once the optimal α value was locked, the spectrometer was deemed ready for the systematic temperature-dependent investigation in zero-field (ZF) and longitudinal-field (LF) geometries.

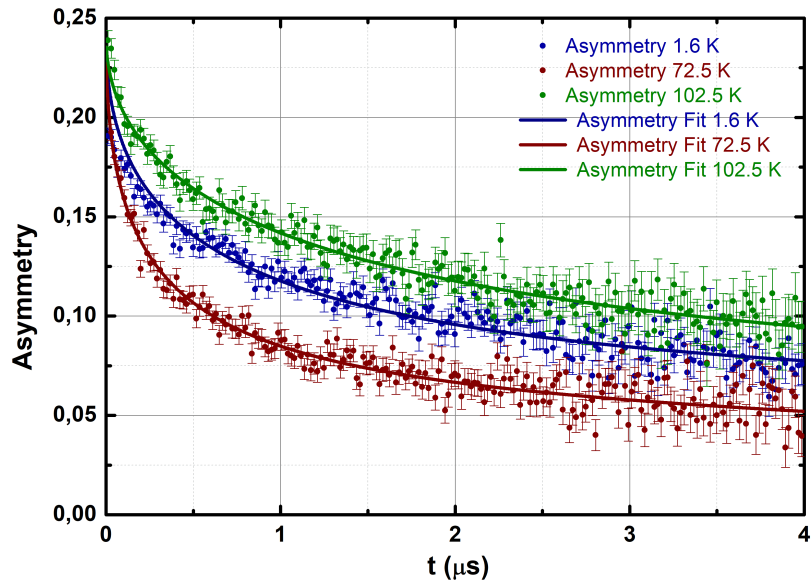
Following the initial instrumental setup, the experimental campaign proceeded with a series of LF measurements under an applied magnetic field of 1.5 kOe. To ensure the integrity of the data and preclude any influence from the sample's thermal history, the thermal protocols and cooling procedures described in the preceding sections were rigorously maintained. These measurements focused on the temperature region below 110 K, utilizing the GPS spectrometer's cryogenic system to reach a base temperature of 1.6 K.

To further scrutinize the spin dynamics and the decoupling behavior of the muon ensemble, an additional comprehensive temperature sweep was performed in a longitudinal field of 3 kOe. This higher-field dataset was systematically acquired over the exact same temperature range utilized for the preceding 1.5 kOe measurements. This matched-range protocol was explicitly implemented to facilitate a comparative analysis between the two field regimes. By directly comparing the temperature-dependent relaxation parameters at 1.5 kOe and 3 kOe, a precise eval-

uation of how the applied field intensity modulates the magnetic dynamics of the Dysprosium-Semiquinonate complex could be achieved.



(a) $H = 1.5$ kOe



(b) $H = 3.0$ kOe

Figure 4.18: Decays of the muon asymmetry $A(t)$ for the Dy-SQ system at different longitudinal fields representative temperature values. The dots represent the experimental data, while the solid lines show the fit obtained with the two-component function reported in Eq. 4.7.

As shown in Figures 4.18, the relaxation behavior exhibits a significant evolution across the investigated thermal range. At high temperatures, the signal remains relatively flat, indicating slow relaxation; however, as the temperature decreases, a pronounced fast initial drop emerges, followed by a slower recovery tail. This visual

divergence in the decay rates strongly suggests the presence of multiple relaxation channels. Specifically, the emergence of a fast component at low temperatures reflects the coupling of the muon spin to the slowing electronic fluctuations of the Dy^{3+} centers. To capture the multi-component nature of the relaxation, the experimental data were fitted using a hybrid model consisting of a fast and a slow relaxation component [37, 57]:

$$A(t) = a_f \cdot \exp[-(\lambda_f t)^{0.5}] + a_s \cdot \exp(-\lambda_s t) \quad (4.7)$$

In this expression, the first term, a stretched exponential, accounts for the fast relaxation (λ_f) typically associated with the dense and fluctuating electronic environment near the muon implantation sites. The second term represents a slower, purely exponential relaxation (λ_s). The analysis was performed through a global fit of the LF- μ SR spectra measured at both applied fields and at all temperatures. To reduce the number of free parameters and ensure a stable convergence of the fitting algorithm, the amplitudes of the fast and slow components were treated as global parameters. In other words, the same values of a_f and a_s were imposed for all temperatures and for both magnetic fields, with the additional constraint

$$a_f + a_s = 0.24 \quad (4.8)$$

This value corresponds to the maximum experimental asymmetry observed across the entire dataset and is consistent with the standard instrumental maximum for the GPS spectrometer [52]. With this constraint, changes in the measured spectra are described mainly through the temperature- and field-dependence of the relaxation rates, rather than through artificial variations of the component amplitudes.

After extracting the phenomenological parameters from the muon asymmetry decay fits, the temperature dependence of both relaxation components was analysed. The two rates, λ_f and λ_s , correspond respectively to the fast and slow components introduced in the fitting model. In the following discussion, these quantities are treated as phenomenological relaxation rates describing different contributions to the depolarization of the muon ensemble.

The comparison between the two components is useful because they probe the same magnetic system over different relaxation scales. The fast component describes the rapidly relaxing part of the asymmetry, while the slow component accounts for a more weakly relaxing contribution that remains visible over longer times. Their temperature and field dependences therefore provide complementary information on the distribution and dynamics of the local magnetic fields sensed by the implanted muons.

Figure 4.19 shows the temperature dependence of the fast relaxation rate. The data display a strongly non-monotonic behaviour for both applied fields. At $H = 1.5$ kOe, λ_f reaches large values at low and intermediate temperatures, with a broad high-relaxation region below approximately 30 K and an additional enhancement around 55–60 K, before decreasing progressively at higher temperatures. At $H = 3$ kOe, the relaxation rate is generally smaller in the low-temperature region, in-

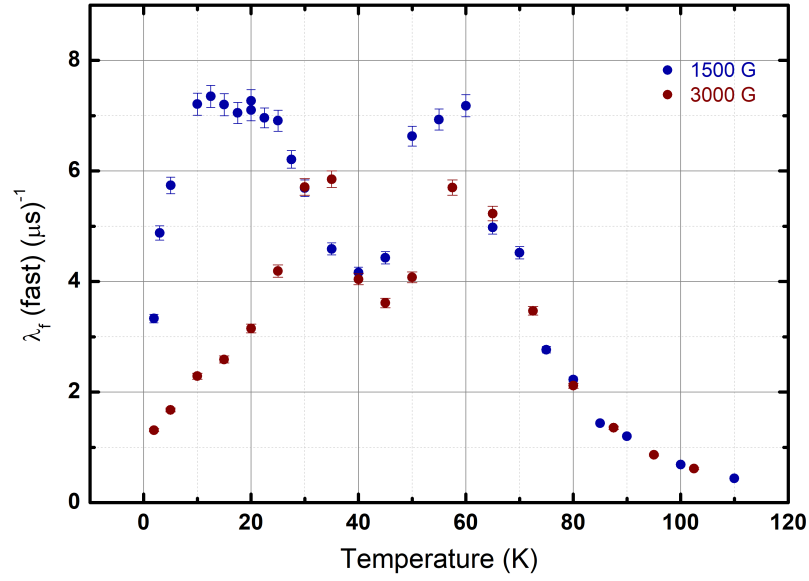


Figure 4.19: Temperature dependence of the fast relaxation rate λ_f obtained from the phenomenological fit of the μSR asymmetry spectra for applied longitudinal fields of $H = 1.5 \text{ kOe}$ and $H = 3 \text{ kOe}$.

creases towards a maximum at intermediate temperatures, and then decreases at higher temperatures. The comparison between the two fields indicates that the fast relaxation channel is field dependent, both in magnitude and in the temperature range where the largest relaxation rates are observed.

It is worth noting that this temperature dependence closely resembles the behaviour observed in the NMR relaxation measurements, especially in the temperature dependence of R_1 previously discussed. In both cases, the relaxation rate displays a non-monotonic evolution, with enhanced relaxation in the low- and intermediate-temperature regions. This qualitative similarity suggests that the fast μSR component and the NMR relaxation anomaly are sensitive to related magnetic fluctuations of the Dy moments. The correspondence should not be interpreted as a strict quantitative equivalence, since NMR and μSR probe different local environments and different time windows, but it supports the idea that both techniques detect the slowing down of the same underlying spin dynamics.

The slow relaxation rate, shown in Figure 4.20, is approximately one order of magnitude smaller than λ_f , confirming that the two fitted components describe relaxation processes occurring on clearly distinct timescales. Nevertheless, λ_s also exhibits a pronounced temperature dependence. For both applied fields, the slow relaxation rate increases from low temperature towards a broad maximum in the intermediate-temperature region and then decreases at higher temperatures. The maximum is more pronounced for the $H = 3 \text{ kOe}$ data, while the $H = 1.5 \text{ kOe}$ data show a smaller and broader enhancement.

Taken together, the two relaxation rates reveal that the muon depolarization is gov-

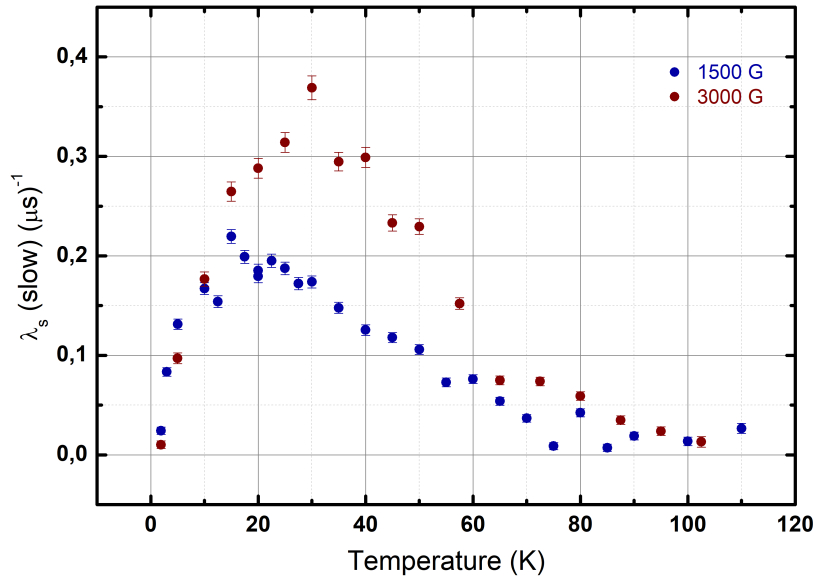


Figure 4.20: *Temperature dependence of the slow relaxation rate λ_s obtained from the phenomenological fit of the μSR asymmetry spectra for applied longitudinal fields of $H = 1.5 \text{ kOe}$ and $H = 3 \text{ kOe}$.*

erned by more than one characteristic relaxation scale. The non-monotonic temperature dependence observed in both components suggests that the local magnetic-field fluctuations sensed by the muons evolve significantly with temperature and applied longitudinal field. At this stage, however, λ_f and λ_s should be regarded as phenomenological parameters extracted from the fitting procedure. A microscopic interpretation in terms of specific relaxation mechanisms, such as phonon-assisted processes, slowing down of electronic fluctuations, or tunnelling-related dynamics, requires comparison with the behaviour of both components and with the complementary magnetic and spectroscopic measurements discussed in the following chapter.

Concluding Remarks

This chapter established the experimental basis of the work. The Dy-SQ sample was introduced together with the SQUID, NMR, and μSR protocols used to investigate its magnetic response. Particular attention was devoted to the practical aspects that affect the reliability of the measurements, such as the preparation of the powder sample, the comparison between loose powder and resin-embedded powder, the correction for the epoxy contribution, and the experimental strategies adopted to acquire broad NMR spectra and field-dependent μSR relaxation data.

These procedures define the framework within which the experimental results can be interpreted. The combination of macroscopic magnetometry and local-probe techniques provides complementary information on the magnetic behaviour of Dy-SQ, but a microscopic understanding of the observed relaxation and anisotropy also

requires a description of the electronic structure of the Dy^{3+} ion in its molecular environment. The following chapter therefore turns to the crystal-field analysis of the Dy–SQ complex, with the aim of connecting the experimental observations to the energy-level structure and magnetic anisotropy expected for the dysprosium centre.

Chapter 5

Interpretation and Discussion

The previous chapter described the experimental results of the investigation of Dy–SQ sample through SQUID magnetometry, nuclear magnetic resonance, and muon spin spectroscopy. The present chapter moves from the acquisition of the data to their physical interpretation. The aim is to connect the macroscopic magnetic response and the local-probe relaxation measurements to the microscopic magnetic properties of the Dy–SQ molecular system. In particular, the discussion focuses on three closely related aspects: the crystal-field anisotropy of the Dy^{3+} ion, the magnetic coupling between the lanthanide centre and the semiquinonate radical, and the thermally-activated spin dynamics probed by NMR and μSR .

Since no complete *ab-initio* description of Dy–SQ is available yet, the analysis starts from a simplified microscopic reference and then progressively incorporates the experimental information. Section 5.1 presents a point-charge estimate of the Dy^{3+} crystal-field level scheme using the Python-based software PYCRYSTALFIELD, with the purpose of identifying the dominant Stevens contributions and the expected energy levels in turn. Section 5.2 discusses the effective modelling of the SQUID data with the software PHI. The analysis focuses first on DyTrp, a molecular analogue of Dy–SQ which lacks the radicalic spin and can be used to study the crystal field in the absence of magnetic couplings. We then extend the discussion to Dy–SQ by including the exchange interaction with the radical. The comparison between Dy–Trp and Dy–SQ is used to test whether the crystal field of a related dysprosium compound can be transferred to Dy–SQ, while the final model provides an estimate of the leading axial crystal-field parameter and of the Dy–radical exchange interaction. The last part of the chapter is devoted to the spin dynamics. Section 5.3 connects the features observed in the NMR relaxation data with the longitudinal-field μSR results and analyses the slow μSR relaxation component within a BPP-like framework. The same section also discusses the quantification of an effective correlation time and the corresponding activated energy scale. Finally, the high-temperature NMR relaxation data in the fast-fluctuation regime are revisited, providing an independent estimate of the Orbach activation energy and comparing it with the value inferred from the μSR analysis. Overall, the chapter combines modelling and local-probe relaxation data to identify the dominant physical ingredients governing the magnetic behaviour of Dy–SQ.

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5.1 Crystal-Field from Point-Charge Modelling

5.1.1 PyCrystalField and Stevens Hamiltonian

The expected crystal-field levels of the Dy^{3+} ion were first estimated using the Python package `PYCRYSTALFIELD`, developed by A. Scheie for the calculation, analysis, and fitting of single-ion crystal electric-field Hamiltonians [59]. The software can construct a crystal-field Hamiltonian from a point-charge representation of the coordination environment using a crystallographic information file (.cif) as input. Subsequently it can determine the symmetry-allowed crystal-field parameters, and calculate the corresponding eigenvalues and eigenstates.

As discussed in Section 1.4.2, the ground multiplet of Dy^{3+} is described by the term ${}^6H_{15/2}$, corresponding to a total angular momentum $J = 15/2$. Within the Stevens-operator formalism, the crystal-field Hamiltonian can therefore be written as

$$H_{\text{CF}} = \sum_{k=2,4,6} \sum_{q=-k}^k B_k^q O_k^q(J) \quad (5.1)$$

where $O_k^q(J)$ are the Stevens operator equivalents and B_k^q are the corresponding crystal-field parameters. For $J = 15/2$, the Hamiltonian acts on a 16-dimensional basis formed by the states $|J, m_J\rangle$. Since Dy^{3+} is a Kramers ion, diagonalization of the zero-field Hamiltonian produces eight doubly degenerate crystal-field levels in the absence of external magnetic fields.

The calculation was based on the crystallographic structure of the isomorphous yttrium derivative, for which structural data were available. The Y site was replaced by Dy while all atomic coordinates were kept unchanged. This procedure assumes that the local coordination geometry of the dysprosium derivative is sufficiently close to that of the yttrium analogue.

The local coordination environment was defined by the eight atoms directly bonded to the metal centre. These comprise six nitrogen atoms belonging to two tridentate hydrotris(pyrazolyl)borate ligands and two oxygen atoms belonging to the bidentate semiquinonato ligand. The resulting local coordination sphere is therefore described as DyN_6O_2 , consistently with the slightly distorted square-antiprismatic geometry introduced in Section 1.5.

The electrostatic potential acting on the Dy^{3+} ion was approximated through a point-charge model of the form

$$V(\mathbf{r}) = \sum_i \frac{q_i}{|\mathbf{r} - \mathbf{R}_i|} \quad (5.2)$$

where $\mathbf{R}_i$ is the position of the i -th coordinating atom relative to the dysprosium centre and q_i is the effective point charge assigned to that site. The geometrical part of the model is therefore fixed by the crystallographic coordinates, whereas the calculated crystal-field parameters and energy separations depend on the adopted charge parametrization.

5.1.2 Point-Charge Parametrization

The crystallographic file (.cif) provides the atomic positions of the molecular complex but does not contain experimentally or theoretically determined atomic partial charges. A more rigorous electrostatic description would require the molecular charge distribution to be obtained from an electronic-structure calculation specifically performed on Dy-SQ. In particular, density functional theory could provide atom-resolved partial charges through electrostatic-potential fitting or population-analysis schemes, allowing the potential experienced by the Dy³⁺ centre to be represented more realistically. Such a calculation is not available yet for the present compound and could not be performed within the scope of this work. Consequently, a simplified local point-charge model was adopted, in which effective charges were assigned only to the eight atoms directly coordinating the Dy³⁺ ion.

Two alternative parametrizations were considered for the nitrogen donor atoms. In the first model, a point charge of $-2e$ was assigned to each coordinating nitrogen, taking numerical inspiration from the formal oxidation-number analysis of the pyrazolyl framework. In the second model, a more negative value of $-3e$ was assigned to each nitrogen as a sensitivity test of the calculated crystal-field spectrum. In both cases, a charge of $-2e$ was assigned to each coordinating oxygen atom. The two parametrizations are therefore defined as

$$q_{\text{O}} = -2e \quad q_{\text{N}} = -2e \quad (5.3)$$

and

$$q_{\text{O}} = -2e \quad q_{\text{N}} = -3e \quad (5.4)$$

The second parametrization should not be interpreted as a distinct oxidation state produced by formation of the Dy–N coordination bond. More generally, neither model should be regarded as a quantitative determination of the atomic charge distribution, since oxidation numbers do not coincide with molecular partial charges and the remaining atoms of the ligands were not explicitly included. The two local donor-only parametrizations were instead employed as limiting electrostatic models through which the sensitivity of the calculated level scheme to the assumed nitrogen charge could be assessed.

5.1.3 Estimated Crystal-Field Levels

For each parametrization, PYCRYSTALFIELD calculated the complete set of crystal-field coefficients B_k^q with $k = 2, 4, 6$. All terms allowed by the low symmetry of the coordination environment were retained, including the non-axial contributions with $q \neq 0$. The resulting 16×16 Hamiltonian was then diagonalized, yielding eight Kramers doublets whose energies were referred to the ground-state doublet. Since the aim of this calculation is not to obtain a refined crystal-field parametrization, but rather to identify the dominant energy scales and anisotropy terms, only the second-order Stevens coefficients are reported explicitly in Table 5.1.

Stevens parameter	$q_N = -2$	$q_N = -3$
B_2^{-2}	0.185	0.195
B_2^{-1}	-0.309	0.208
B_2^0	0.562	0.721
B_2^1	-0.212	-0.023
B_2^2	-0.220	0.233

Table 5.1: *Second-order Stevens parameters obtained from the PYCRYSTALFIELD point-charge calculation for the two charge assignments considered for the coordinating nitrogen atoms, namely $q_N = -2$ and $q_N = -3$. The values are reported in the internal energy units used by PYCRYSTALFIELD. In both cases, the axial parameter B_2^0 is the largest contribution in absolute value.*

The comparison shows that the calculated crystal-field parameters are sensitive to the adopted nitrogen charge, as expected for a point-charge model. Nevertheless, the same qualitative feature emerges from both parametrizations: among the second-order terms, the axial coefficient B_2^0 gives the dominant contribution. This observation does not imply that the non-axial terms are negligible in an exact microscopic description, but it provides a useful indication that the leading anisotropy of the Dy^{3+} centre can be discussed, at first approximation, in terms of an axial component.

The corresponding Kramers-doublet energy schemes are shown in Figure 5.1. Both charge assignments produce a sizeable splitting of the Dy^{3+} ground multiplet. Changing the nitrogen charge from $q_N = -2$ to $q_N = -3$ modifies the detailed spacing of the doublets and increases the overall energy span of the calculated spectrum. This confirms that the point-charge calculation is sensitive to the assumed electrostatic parametrization and should therefore be interpreted as a qualitative microscopic estimate rather than as a refined determination of the crystal-field Hamiltonian.

Overall, the PYCRYSTALFIELD analysis provides two important pieces of information for the following modelling. First, it gives an approximate energy scale for the crystal-field splitting of the Dy^{3+} ion in the Dy-SQ coordination environment.

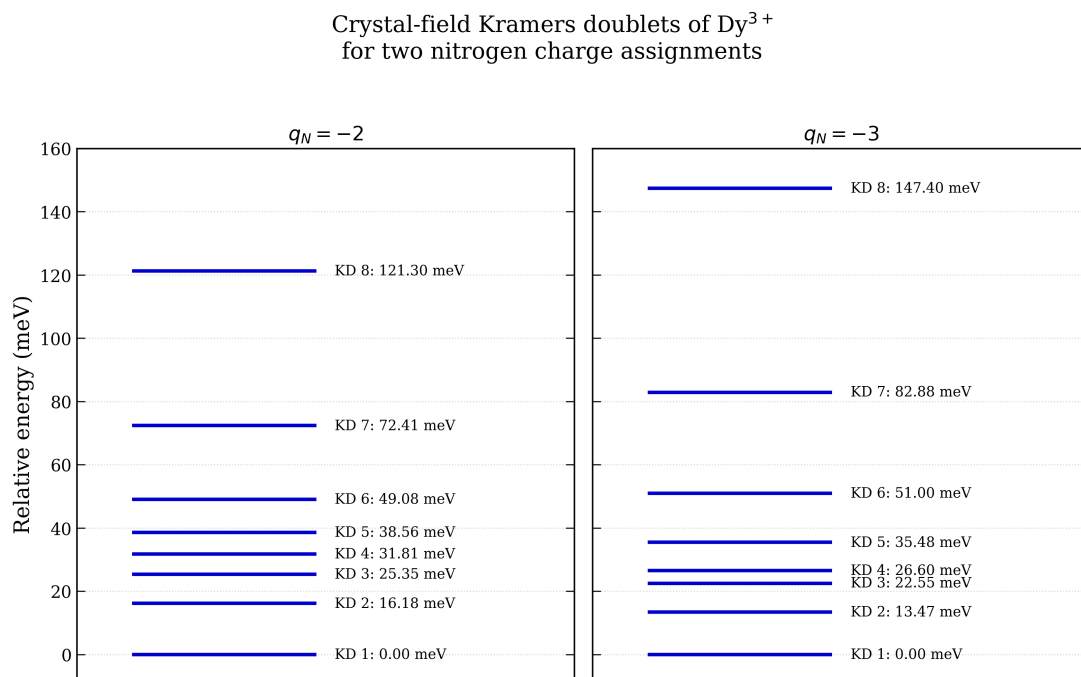


Figure 5.1: Crystal-field splitting of the Dy^{3+} ground multiplet calculated with PYCRYSTALFIELD for the two nitrogen charge assignments considered in the point-charge model. The energies of the Kramers doublets are referred to the ground-state doublet.

Second, it indicates that the axial second-order term is a robust and dominant contribution within the adopted point-charge parametrizations. At the same time, the dependence of the calculated parameters and level spacings on the assumed donor charges shows that the point-charge model cannot be used to extract quantitative Stevens parameters. For this reason, the PYCRYSTALFIELD results are used only as a guide for constructing a reduced model, while a more quantitative comparison with the experimental magnetic data is carried out in the following section using PHI.

5.2 Modelling of Dy-Trp and Dy-SQ with PHI

The crystal-field analysis presented in the previous section provides a first microscopic estimate of the energy-level structure of the Dy^{3+} ion in Dy-SQ. However, the point-charge approach implemented in PYCRYSTALFIELD should be regarded as a qualitative or semi-quantitative description of the local crystal field. The calculated Stevens parameters depend on the chosen charge parametrization and cannot be directly interpreted as refined experimental values. For this reason, in order to obtain a more quantitative estimate of the relevant crystal-field anisotropy and of the magnetic exchange interaction between the Dy^{3+} ion and the semiquinonato radical, the analysis was extended using the software PHI [60].

PHI was developed for the analysis of anisotropic monomeric and exchange-coupled polynuclear d - and f -block complexes, and allows the magnetic response of a

molecular spin system to be calculated by diagonalizing a model spin Hamiltonian. It also enables direct comparison with experimental observables through simultaneous fits of different magnetic datasets. In the present work, the fits were performed simultaneously on the temperature dependence of χT and on the field dependence of the magnetization M . This point is important, since the two quantities probe complementary aspects of the magnetic response: χT is particularly sensitive to the low-temperature evolution of the magnetic susceptibility, whereas the magnetization curves provide information on the field-dependent population of the magnetic levels.

The aim of the PHI analysis is not to construct a fully general crystal-field Hamiltonian including all allowed Stevens operators. Such a procedure would introduce a large number of free parameters and would be poorly constrained by the available magnetic data. Instead, the PYCRYSTALFIELD results are used as a guide to build a reduced and physically motivated model. In particular, the axial second-order Stevens parameter B_2^0 is found to provide the dominant contribution to the crystal-field anisotropy, while higher-order terms are comparatively smaller. The modelling was therefore progressively restricted towards a minimal axial description of the Dy^{3+} crystal field, in which the main single-ion anisotropy is described by B_2^0 , and the interaction with the radical is introduced through an exchange coupling constant.

5.2.1 Model Hamiltonian used in PHI

The following discussion is based on the theoretical background and notation reported in the PHI manual and in the original PHI reference [60, 61]. In the present analysis, the magnetic response is calculated from a model Hamiltonian including crystal-field, exchange and Zeeman contributions:

$$H = H_{\text{CF}} + H_{\text{ex}} + H_{\text{Z}} \quad (5.5)$$

The crystal-field term acts on the ground multiplet of the Dy^{3+} ion, here described in the $\text{Dy}(J)$ representation. Since the aim of the PHI modelling is not to determine a complete crystal-field parameter set, but rather to obtain an effective description of the magnetic response, only the dominant axial Stevens terms were considered in the main fits (see the forthcoming discussion for DyTrp):

$$H_{\text{CF}}^{\text{ax}} = B_2^0 O_2^0(J) + B_4^0 O_4^0(J) \quad (5.6)$$

where B_k^q denote the effective crystal-field parameters. In particular, the two axial Stevens operators entering the model are

$$O_2^0(J) = 3J_z^2 - J(J+1) \quad (5.7)$$

and

$$O_4^0(J) = 35J_z^4 - [30J(J+1) - 25]J_z^2 + 3J^2(J+1)^2 - 6J(J+1) \quad (5.8)$$

For Dy-SQ , the semiquinonate radical was included explicitly as an additional spin centre. The interaction between the Dy^{3+} ion and the radical was described through

the isotropic exchange term

$$H_{\text{ex}} = -2J_{\text{ex}} \mathbf{J}_{\text{Dy}} \cdot \mathbf{S}_{\text{rad}} \quad (5.9)$$

With this convention, negative values of J_{ex} correspond to antiferromagnetic coupling, while positive values correspond to ferromagnetic coupling. This sign convention is important for the interpretation of the fitted exchange constant.

For each set of parameters, PHI constructs the Hamiltonian matrix in the angular-momentum product basis and diagonalizes it. The resulting field-dependent eigenvalues $E_i(H)$ are then used to calculate the thermodynamic response of the system. The partition function is given by

$$Z = \sum_i e^{-E_i(H)/k_B T} \quad (5.10)$$

and the magnetization along a given field direction α is obtained from the field derivative of the free energy:

$$M_\alpha = k_B T \frac{\partial \ln Z}{\partial H_\alpha} \quad (5.11)$$

In the finite-field calculations used here, the magnetic susceptibility is evaluated as the field-normalized magnetization,

$$\chi_\alpha \simeq \frac{M_\alpha}{H_\alpha} \quad (5.12)$$

so that the calculated χT curves are directly comparable with the experimental SQUID data acquired at finite applied fields.

Since the measurements were performed on powder samples, the calculated response must also be averaged over all possible orientations of the molecular anisotropy axes with respect to the applied magnetic field. For a generic magnetic observable X , this corresponds to

$$\langle X \rangle_{\text{powder}} = \frac{1}{4\pi} \int X(\theta, \phi) d\Omega \quad (5.13)$$

In practice, PHI performs this orientational average numerically through the Field Powder option. The calculated powder-averaged $\chi T(T)$ and $M(H)$ curves are then compared with the experimental data, and the fit parameters are obtained by minimizing the residual between calculated and measured magnetic observables.

Within this framework, the different PHI fits presented below correspond to different choices of which terms in H_{CF} are retained and which parameters are allowed to vary. The simplest models retain only B_2^0 , while more flexible descriptions also include B_4^0 and the Dy-radical exchange constant. This stepwise procedure makes it possible to distinguish parameters that are robustly required by the data from parameters that merely improve the numerical residual without leading to a physically stable fit.

5.2.2 Dy–Trp Reference: Axial Crystal-Field Fit

The first step of the PHI analysis was performed on the diamagnetic analogue Dy–Trp. This compound represents a useful reference system because it preserves the same Dy³⁺ coordination environment of Dy–SQ, but it does not contain the semiquinonato radical. As a consequence, the magnetic response of Dy–Trp is expected to be dominated by the single-ion crystal-field anisotropy of the Dy³⁺ centre, without the additional complication of an exchange interaction with a ligand-based spin. The comparison between Dy–Trp and Dy–SQ therefore provides a way to separate, at least phenomenologically, the crystal-field contribution from the Dy–radical exchange contribution.

The experimental magnetic data for Dy–Trp were taken from the work reported in Dalton Transactions in 2004 [35]. The fitting procedure was designed as a progressive refinement of the crystal-field description. In the first and simplest model, only the axial second-order Stevens parameter B_2^0 was left free. All other crystal-field parameters were neglected. This first fit was not intended to provide a complete description of the Dy³⁺ crystal field, but rather to test how much of the magnetic response could already be reproduced by the leading axial anisotropy term suggested by the PYCRYSTALFIELD analysis.

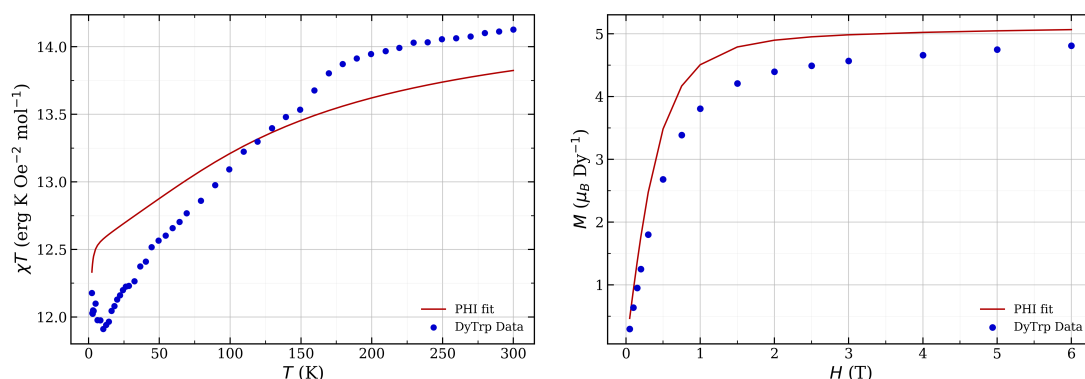


Figure 5.2: Simultaneous PHI fit of the Dy–Trp magnetic data using only the axial second-order Stevens parameter B_2^0 as a free parameter. Left: temperature dependence of χT . Right: field dependence of the magnetization.

The result of this minimal fit is shown in Figure 5.2. The calculated χT curve captures the overall scale of the experimental data and reproduces part of the temperature evolution, especially in the intermediate-temperature range. However, clear discrepancies remain both at low temperature and at high temperature. In particular, the experimental χT shows a more structured low-temperature behaviour than the one obtained from the purely axial B_2^0 model. This indicates that the leading axial term alone is not sufficient to describe the full crystal-field splitting relevant to the susceptibility.

The limitation of the model becomes even more evident in the magnetization curve. Although the calculated M vs H curve reproduces the qualitative tendency to-

wards saturation, it systematically overestimates the experimental magnetization and reaches the high-field regime too rapidly. This means that the field dependence of the magnetic levels is not properly captured by a model containing only B_2^0 . The simultaneous fit of χT and M vs H is therefore particularly useful: while the susceptibility alone could suggest that the minimal axial description is reasonably adequate, the magnetization curve reveals that additional crystal-field terms are required.

This first result shows that the dominant axial anisotropy is an essential ingredient of the Dy^{3+} magnetic response, but it cannot be the only one. A more flexible description of the crystal field is needed in order to improve the agreement with the magnetization data while preserving the correct temperature dependence of χT .

As a second attempt, the model was made more flexible by allowing all five second-rank Stevens parameters B_2^q to vary simultaneously. This choice was intentionally ambitious, since it introduces several free crystal-field parameters while the fit is still constrained only by bulk magnetic observables. The fit was again performed simultaneously on χT and M vs H . Although the calculated χT curve remained reasonably close to the experimental trend, the agreement with the magnetization curve did not improve in a significant way. Moreover, the optimization did not provide a stable and physically meaningful set of parameters, indicating that the available data are not sufficient to constrain such a general second-order crystal-field description.

For this reason, this fit is not shown and was not considered further in the discussion. Nevertheless, it provides an important indication for the modelling strategy: simply increasing the number of free parameters does not necessarily lead to a better or more reliable description of the magnetic response. A more controlled refinement of the minimal axial model is therefore required.

Starting from the limitations of the previous attempts, the final model considered for Dy-Trp was built by returning to an axial description, but with one additional degree of freedom. Together with the second-order axial parameter B_2^0 , the fourth-order axial parameter B_4^0 was introduced as a second free crystal-field parameter. The fit was again performed simultaneously on the χT and M vs H datasets.

The result is shown in Figure 5.3. With respect to the model based on B_2^0 only, the inclusion of B_4^0 leads to a clear improvement in the description of the magnetization curve. The calculated M vs H curve now follows the experimental data over the whole field range, reproducing both the initial increase at low field and the gradual approach to saturation. This indicates that the fourth-order axial term plays an important role in determining the field-dependent population of the Dy^{3+} magnetic levels.

The agreement with the χT curve is less satisfactory at low temperature. In particular, the calculated curve underestimates the experimental values in the low-temperature region, where the susceptibility is most sensitive to the detailed struc-

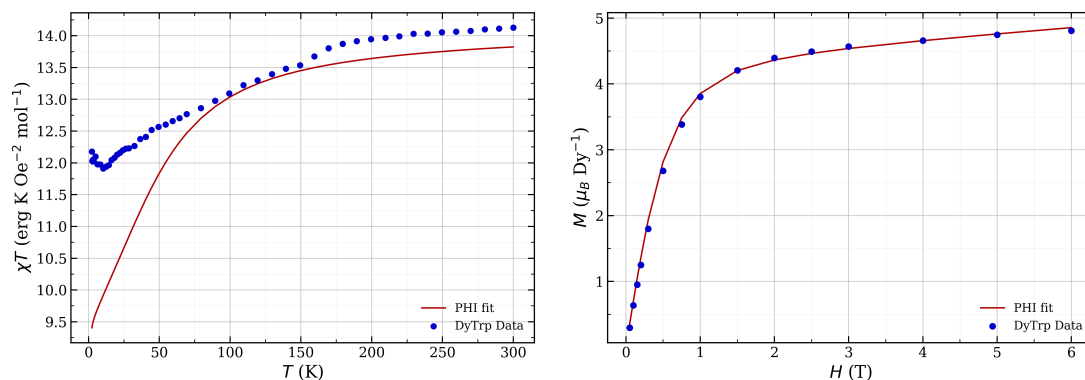


Figure 5.3: Simultaneous PHI fit of the Dy–Trp magnetic data using the axial crystal-field parameters B_2^0 and B_4^0 as free parameters. Left: temperature dependence of χT . Right: field dependence of the magnetization. The inclusion of B_4^0 improves the description of the magnetization curve while preserving a reasonable overall description of the susceptibility.

ture of the lowest crystal-field states. Nevertheless, the model reproduces the overall temperature evolution of χT at intermediate and high temperatures and provides a much better simultaneous description of the two magnetic observables than the previous one-parameter fit. This result suggests that the combination of B_2^0 and B_4^0 can be regarded as an effective axial description of the Dy^{3+} crystal field in Dy–Trp. It should not be interpreted as a complete crystal-field determination, since non-axial terms and higher-order contributions are still neglected. However, it provides a physically meaningful compromise between the oversimplified B_2^0 model and the overparametrized fit including all second-rank Stevens parameters. For this reason, the parameters obtained from this fit were used as a reference for the subsequent analysis of Dy–SQ.

5.2.3 Transfer of the Dy–Trp Crystal Field to Dy–SQ

After establishing an effective axial crystal-field description for Dy–Trp, the same parameters were used as a starting point for the analysis of Dy–SQ. The underlying assumption was that the Dy^{3+} ion experiences approximately the same local crystal field in the two compounds, since the molecular structures are closely related and differ mainly by the presence of the semiquinonato radical. Within this approximation, the parameters B_2^0 and B_4^0 obtained from the Dy–Trp fit were kept fixed, and only the exchange interaction between the Dy^{3+} ion and the radical spin was introduced as a free parameter.

This represents the most direct way to test whether the magnetic response of Dy–SQ can be described as the sum of two ingredients: the Dy^{3+} crystal-field anisotropy already determined from the diamagnetic analogue, and an additional Dy–radical exchange coupling. The fit was performed simultaneously on the two χT curves measured at 0.1 and 1 T and on the three magnetization isotherms measured at 2, 3, and 5 K.

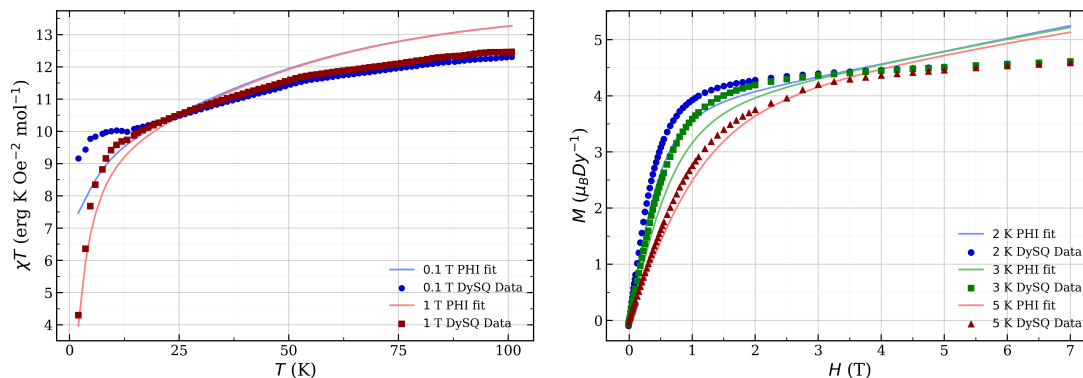


Figure 5.4: Simultaneous PHI fit of the Dy-SQ magnetic data using the Dy-Trp crystal-field parameters fixed from the previous analysis and leaving only the Dy-radical exchange coupling as a free parameter. Left: temperature dependence of χT measured at 0.1 and 1 T. Right: magnetization isotherms measured at 2, 3, and 5 K.

The result is shown in Figure 5.4. The agreement is not satisfactory. In the χT curves, the calculated response strongly deviates from the experimental data at low temperature, especially for the curve measured at 1 T. At higher temperatures, the calculated curves recover the general increasing trend, but they remain systematically displaced with respect to the experimental datasets. This indicates that the low-energy magnetic structure generated by the fixed Dy-Trp crystal field is not appropriate for Dy-SQ.

The same conclusion is reinforced by the magnetization isotherms. The experimental curves show a rapid increase at low field followed by a tendency towards saturation. The calculated curves, instead, rise more slowly at low field and continue increasing almost linearly at higher fields. As a result, the model underestimates the magnetization in the low-field region and overestimates it at high field. This behaviour cannot be corrected by changing only the exchange coupling constant, because the discrepancy affects the field dependence of the Dy³⁺ levels themselves.

The failure of this fit shows that the crystal-field parameters obtained for Dy-Trp cannot be transferred directly to Dy-SQ. Although the two compounds are structurally related, the presence of the semiquinonato radical is not a passive perturbation. It likely modifies the charge distribution on the ligand environment and therefore changes the effective crystal field experienced by the Dy³⁺ ion. Consequently, the Dy-SQ magnetic response cannot be described by fixing the Dy³⁺ anisotropy to the Dy-Trp values and fitting only the Dy-radical exchange interaction.

The failure of the previous fit indicates that the Dy³⁺ crystal field cannot be kept fixed to the values obtained for Dy-Trp. As a natural next step, a less constrained model was therefore tested by allowing both axial crystal-field parameters, B_2^0 and B_4^0 , to vary together with the Dy-radical exchange coupling J . This fit was again performed simultaneously on the two χT curves measured at 0.1 and 1 T and on the three magnetization isotherms measured at 2, 3, and 5 K. Although the resulting curves gave a visually reasonable description of the experimental data, the

optimization did not reach a stable convergence and the fitted parameters were not associated with reliable numerical uncertainties. For this reason, the result was not considered sufficiently robust to be discussed as a quantitative model.

This outcome shows that, even after restricting the crystal field to axial terms only, three free parameters are still too many for the available set of bulk magnetic data.

5.2.4 Final Effective Model for Dy–SQ

The final model for Dy–SQ was obtained by combining the information gathered from the previous fits. The comparison with Dy–Trp showed that the crystal field cannot be transferred unchanged from the diamagnetic analogue to Dy–SQ, while the unconstrained fit including both B_2^0 , B_4^0 , and J introduced too many free parameters to obtain a stable optimization. Moreover, the Dy–Trp analysis indicated that the fourth-order axial contribution is small compared with the leading second-order axial term within the effective Stevens parametrization adopted here.

The adopted Hamiltonian therefore retains only two free parameters: the axial second-order crystal-field parameter B_2^0 and the exchange coupling constant J between the Dy^{3+} ion and the semiquinonato radical. This represents the simplest model able to account simultaneously for the modification of the Dy^{3+} crystal field induced by the radical and for the magnetic interaction between the two spin centres. The fit was performed simultaneously on the two χT curves measured at 0.1 and 1 T and on the three magnetization isotherms measured at 2, 3, and 5 K.

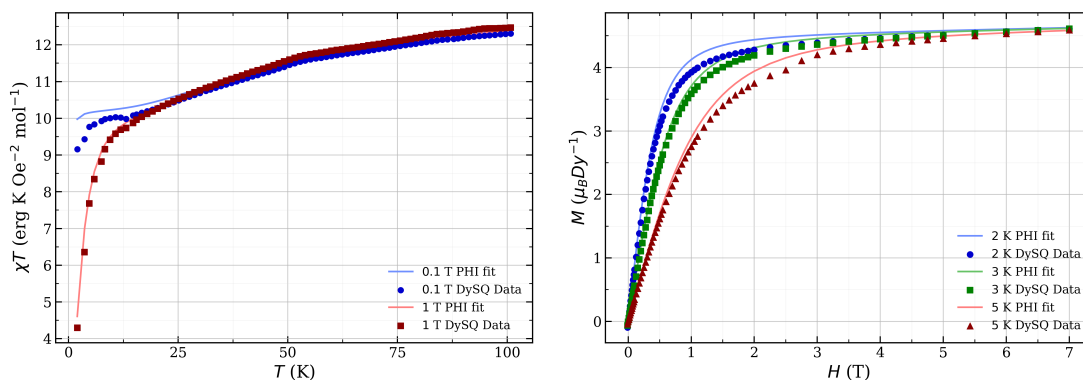


Figure 5.5: Final simultaneous PHI fit of the Dy–SQ magnetic data using B_2^0 and the Dy–radical exchange coupling J as free parameters. Left: temperature dependence of χT measured at 0.1 and 1 T. Right: magnetization isotherms measured at 2, 3, and 5 K.

The result is shown in Figure 5.5. The agreement with the χT data is very satisfactory over most of the investigated temperature range. Both experimental curves are reproduced well at intermediate and high temperatures, where the model captures the overall evolution of the susceptibility. Some deviations remain at the lowest temperatures, especially in the low-field dataset, where the experimental curve shows a more pronounced structure than the calculated one. This discrepancy is

not unexpected, since the low-temperature susceptibility is particularly sensitive to small details of the lowest crystal-field levels and to possible non-axial terms that are neglected in the present effective model.

The magnetization isotherms are also reproduced with good overall accuracy. The calculated curves follow the experimental evolution from the initial low-field increase to the high-field saturation region. The agreement is particularly good in the intermediate and high-field range, while small deviations remain in the low-field curvature of the curves. These discrepancies indicate that the model should not be regarded as a complete microscopic description of the Dy^{3+} crystal field. Nevertheless, the simultaneous reproduction of two χT datasets and three M vs H isotherms using only two free parameters is a strong indication that the dominant physics is correctly captured.

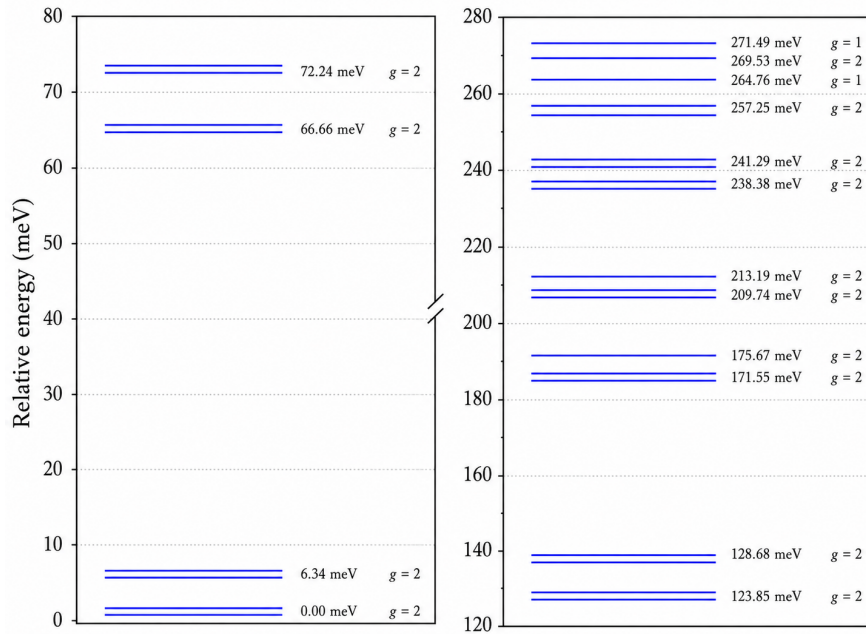


Figure 5.6: Relative energy spectrum calculated with PHI for the $\text{Dy}(J)\text{-radical}(S = 1/2)$ exchange Hamiltonian. The left-hand panel shows the low-energy part of the spectrum, while the right-hand panel displays the higher-energy manifold, with the intermediate energy region omitted for clarity. Blue horizontal lines indicate the calculated levels: double lines represent doubly degenerate states, whereas single lines correspond to non-degenerate states. All energies are reported relative to the ground state in meV.

The final fitted parameters provide a quantitative estimate of the two dominant contributions retained in the model. The exchange coupling was found to be

$$J = (-10.16 \pm 0.13) \text{ cm}^{-1} \quad (5.14)$$

while the corresponding effective axial Stevens parameter was found to be

$$B_2^0 = (-12.73 \pm 0.69) \text{ cm}^{-1} \quad (5.15)$$

The fitted value of B_2^0 differs from the one obtained for Dy–Trp, confirming that the presence of the semiquinonato radical modifies the effective crystal field experienced by the Dy^{3+} ion. This supports the conclusion already suggested by the failure of the previous fit with fixed Dy–Trp crystal-field parameters: the radical cannot be treated only as an additional spin coupled to an otherwise unchanged Dy^{3+} centre. Instead, it also affects the local electrostatic environment of the lanthanide ion. At the same time, the fitted exchange constant is negative, as expected for an antiferromagnetic interaction between the Dy^{3+} magnetic moment and the radical spin. The final model therefore provides an effective but physically consistent description of Dy–SQ, in which the magnetic response is governed by a modified axial crystal field and by an antiferromagnetic Dy–radical exchange coupling.

On the basis of the final fitted parameters, the corresponding energy-level scheme of the effective model can also be calculated. Although this level structure should not be regarded as a complete microscopic determination of the Dy–SQ electronic spectrum, it provides a useful visualization of the low-energy states associated with the final PHI Hamiltonian. The resulting level scheme is shown in Figure 5.6.

5.3 Spin Dynamics from Local-Probe Relaxation

5.3.1 From NMR Relaxation Features to μSR

After the analysis of the magnetization data discussed in the previous sections, a possible crystal-field level scheme and an effective description of the magnetic response of Dy–SQ were obtained. A natural next step is to test whether this picture is also consistent with the spin dynamics probed by local relaxation measurements. In this respect, NMR and μSR provide a complementary perspective, since both techniques are sensitive to the time dependence of the local magnetic fields generated by the electronic moments.

The most direct NMR quantity to compare with the longitudinal-field μSR relaxation rate would be the spin-lattice relaxation rate $1/T_1$. Indeed, both $1/T_1$ and the longitudinal muon relaxation rate are governed, within a Redfield-like description, by fluctuating transverse local fields sampled at the corresponding Larmor frequency. However, in the present case the experimental determination of T_1 becomes problematic in the temperature region where the relevant anomaly is expected. The relaxation is too fast to be followed reliably over a sufficiently broad time window, making the extraction of quantitative and reproducible $1/T_1$ values difficult. For this reason, the NMR $1/T_1$ data cannot be used as the main quantitative reference for the dynamical analysis.

A more robust indication is provided by the transverse NMR relaxation. In particular, the echo-decay signal used to extract T_2 can be followed more reliably down to low temperature, even in the region where the direct T_1 analysis becomes unstable. As discussed in Section 2.4.5, the transverse relaxation rate is not completely independent of the longitudinal relaxation channel, since within the Redfield framework

one can write

$$\frac{1}{T_2} = \frac{1}{2T_1} + \frac{1}{T'_2} \quad (5.16)$$

where T'_2 represents the pure dephasing contribution. Therefore, although T_2 and T_1 are not equivalent quantities, the temperature dependence of $1/T_2$ can still carry information on the same fluctuating local fields responsible for spin-lattice relaxation.

Experimentally, the NMR transverse relaxation rate displays a non-monotonic temperature dependence. In particular, it shows a clear anomaly around 60–70 K and additional low-temperature structures, possibly corresponding to one or more further maxima. These features indicate that the local magnetic dynamics changes significantly in the same temperature range where the crystal-field modelling suggests the relevance of low-lying magnetic states. However, the NMR data remain difficult to analyse quantitatively: the transverse relaxation is experimentally more accessible than T_1 , but the presence of broad spectra, reduced signal intensity, and multiple relaxation contributions prevents a fully reliable microscopic fit.

For this reason, the analysis was extended to the longitudinal-field μ SR data. The aim is to move away from the NMR-specific limitations associated with excessively fast relaxation and to use a local probe whose time window is well suited to follow the slowing down of the magnetic fluctuations. The comparison between the NMR anomalies and the temperature dependence of the slow μ SR relaxation component then provides an independent test of whether the dynamical behaviour is compatible with the level scheme inferred from the magnetic analysis.

5.3.2 Slow μ SR Relaxation Component

The μ SR longitudinal-field spectra were fitted using two relaxation components, as described in Chapter 4. Both components contain useful information on the local spin dynamics, but they emphasize different aspects of the relaxation process. The fast component displays a richer temperature dependence, with two anomalies occurring in the same temperature regions where the NMR transverse relaxation rate also shows maxima. This correspondence supports the idea that NMR and μ SR are sensitive to the same underlying magnetic processes, although they probe them through different local interactions and within different time windows.

The slow component, denoted hereafter as $\lambda_2 \equiv \lambda_s$, shows a simpler and more systematic behaviour. In particular, it displays a broad maximum at low temperature, in the same region where one of the anomalies is observed both in the NMR data and in the fast μ SR component. For this reason, the slow component was selected for the quantitative modelling discussed below. This choice allows us to focus on the relaxation feature that is common to both μ SR components and that can be followed in a more stable way as a function of temperature. The fast component therefore provides an important qualitative confirmation of the connection with the NMR dynamics, while the slow component is used as the most suitable

quantity for the BPP-type analysis.

The temperature dependence of λ_2 was then modelled using a BPP-type approach. The same physical framework was introduced in Chapter 2 for magnetic relaxation and is based on the idea that the relaxation rate is governed by the spectral density of the fluctuating local magnetic fields evaluated at the Larmor angular frequency of the probe. In this picture, a maximum in the relaxation rate appears when the characteristic fluctuation time enters the experimental time window, namely when the condition $\omega_L \tau_c \simeq 1$ is approximately satisfied. Therefore, fitting the temperature dependence of λ_2 provides a way to test whether the low-temperature anomaly can be interpreted as the result of a progressive slowing down of the local magnetic fluctuations.

To make this interpretation quantitative, the fluctuating transverse components of the local field were described through an exponentially decaying autocorrelation function. This assumption corresponds to a single characteristic correlation time τ_c and leads, after Fourier transformation, to a Lorentzian spectral density. Evaluated at the muon Larmor angular frequency, this gives

$$J(\omega_L) = \frac{\tau_c}{1 + \omega_L^2 \tau_c^2} \quad (5.17)$$

where the Larmor angular frequency depends on the applied longitudinal field according to Equation 3.5, and τ_c is the correlation time of the fluctuating local field. A closely related approach was adopted by Prando and co-workers [62], where the spin-lattice relaxation rate was modelled using a Kubo–Tomita expression based on a Lorentzian spectral density and on a thermally activated correlation time. In that case, the full expression contains two contributions, evaluated at ω_L and $2\omega_L$, as expected for nuclear dipole-dipole relaxation.

In the present μ SR analysis, however, the aim is not to reproduce the complete Kubo–Tomita expression for a nuclear spin system, but to construct an effective Redfield-like description of the slow longitudinal-field muon relaxation component. For this reason, only the spectral density sampled at the muon Larmor frequency was retained. This choice is consistent with the longitudinal-field μ SR formalism introduced in Chapter 3, where the relaxation rate is governed by the transverse spectral density of the fluctuating local field evaluated at ω_L . Including an additional contribution at $2\omega_L$ would introduce a further microscopic assumption that is not required by the present analysis.

Once the relevant spectral contribution has been identified, the remaining ingredient needed to describe the temperature dependence of λ_2 is the behaviour of the correlation time τ_c . Following the activated form used by Prando and co-workers [62], τ_c was assumed to increase upon cooling according to the exponential law

$$\tau_c(T) = \tau_0 \exp\left(\frac{\theta}{T}\right) \quad (5.18)$$

where τ_0 represents the limiting value of the correlation time in the high-temperature regime, while θ is an effective activation temperature associated with the energy scale of the fluctuating process. Equivalently, the corresponding activation energy can be written as $E_a = k_B \theta$. Within this phenomenological description, decreasing the temperature progressively slows down the magnetic fluctuations, producing an exponential increase of τ_c . The relaxation rate is then expected to reach a maximum when the fluctuation time becomes comparable with the inverse of the Larmor angular frequency, namely when $\omega_L \tau_c \simeq 1$. For this reason, the position of the maximum in $\lambda_2(T)$ provides an estimate of the temperature range in which the local magnetic fluctuations enter the μ SR time window.

Within this effective description, the slow relaxation component is written as proportional to the spectral density sampled at the muon Larmor frequency,

$$\lambda_2(T, H) = C J(\omega_L) \quad (5.19)$$

where the prefactor C contains the coupling between the muon spin and the fluctuating transverse components of the local magnetic field. Up to a numerical factor depending on the precise definition of the transverse field variance, it can be written as

$$C \simeq \gamma_\mu^2 \langle \delta H_x^2 + \delta H_y^2 \rangle \quad (5.20)$$

where δH_x and δH_y are the fluctuating components of the local field perpendicular to the longitudinal quantization axis. Equivalently, for isotropic transverse fluctuations one may write $C \simeq 2\gamma_\mu^2 \langle \delta H_\perp^2 \rangle$.

Substituting the Lorentzian spectral density and the activated expression for $\tau_c(T)$ gives the fitting function

$$\lambda_2(T, H) = C \frac{\tau_0 \exp\left(\frac{\theta}{T}\right)}{1 + \omega_L^2 \tau_0^2 \exp\left(\frac{2\theta}{T}\right)} \quad (5.21)$$

The previous expression assumes a single well-defined activation temperature θ . However, in a molecular system such as Dy-SQ, different local environments may lead to a distribution of characteristic activation energies. Following the approach adopted by in [62], this effect was included by assuming a flat distribution of activation temperatures centred around θ and extending over the interval

$$[\theta - \delta\theta, \theta + \delta\theta] \quad (5.22)$$

The same distribution procedure was then applied to the single BPP contribution retained in the present μ SR model.

After introducing this distribution and performing the corresponding integration over the activation temperature [62], the fitting function becomes

$$\lambda_2(T, H) = \frac{CT}{4\omega_L \delta\theta} \left\{ \arctan \left[\sinh \left(\frac{\theta + \delta\theta}{T} + \ln(\omega_L \tau_0) \right) \right] - \arctan \left[\sinh \left(\frac{\theta - \delta\theta}{T} + \ln(\omega_L \tau_0) \right) \right] \right\} \quad (5.23)$$

where, as previously stated, θ is the central activation temperature, and $\delta\theta$ describes the width of the activation-temperature distribution.

The datasets measured at 1500 and 3000 G were analysed within the same BPP-based framework, using the corresponding value of ω_L for each applied field. However, the most stable and physically meaningful fit was obtained for the data measured at 3000 G. For this reason, the quantitative discussion was focused on this dataset, while the lower-field data were mainly used as a qualitative reference for the field dependence of the relaxation maximum.

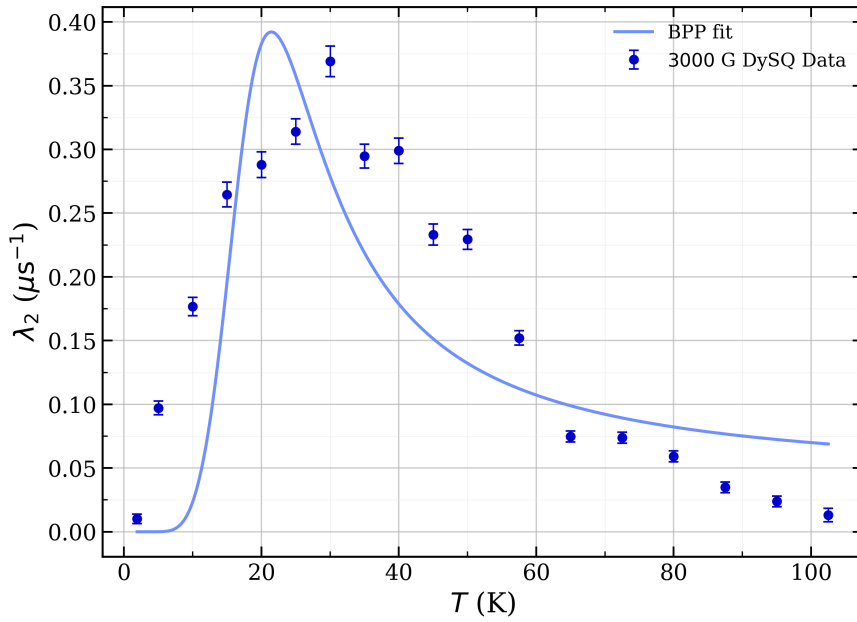


Figure 5.7: *Temperature dependence of the slow μ SR relaxation component λ_2 measured under a longitudinal field of 3000 G. The solid line represents the BPP-type fit obtained by assuming a single activation temperature, corresponding to the case $\delta\theta = 0$.*

As a first step, the slow μ SR relaxation component measured at 3000 G was analysed by assuming a single activation temperature, corresponding to the limiting case $\delta\theta = 0$. The result of this fit is shown in Figure 5.7. Although this simplified model reproduces the presence of a broad maximum in $\lambda_2(T)$, it does not provide a fully satisfactory description of the experimental data over the whole temperature range. In particular, the shape of the peak and the asymmetry of the temperature dependence are not captured adequately within a single-activation-energy picture.

This indicates that the dynamical process responsible for the relaxation anomaly cannot be described satisfactorily by a unique characteristic activation scale.

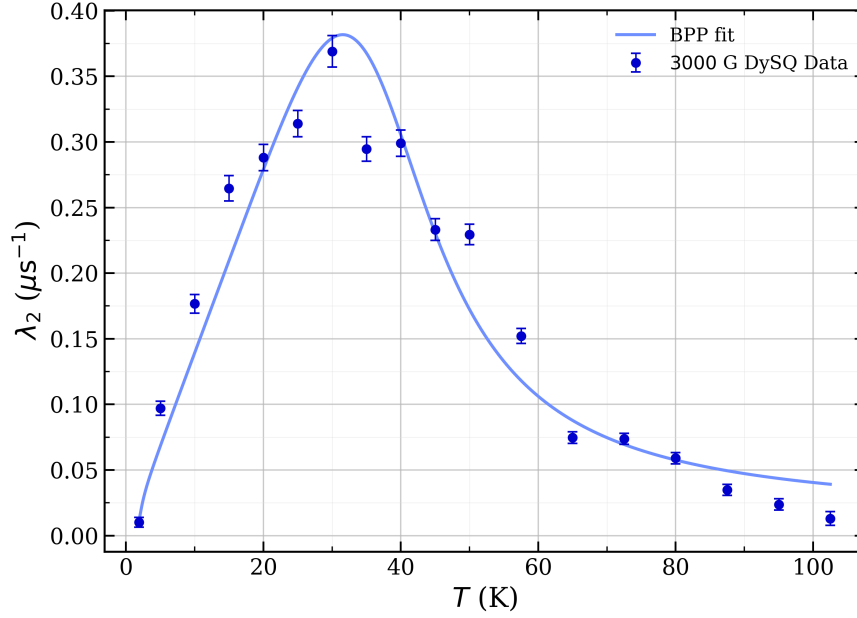


Figure 5.8: Temperature dependence of the slow μSR relaxation component λ_2 measured under a longitudinal field of 3000 G. The solid line represents the BPP-type fit obtained by including a flat distribution of activation temperatures.

For this reason, the analysis was extended by introducing a flat distribution of activation temperatures centred around θ and spanning the interval $[\theta - \delta\theta, \theta + \delta\theta]$. The corresponding fit is shown in Figure 5.8. The improved agreement obtained with the distributed model indicates that a single activation scale is not sufficient to reproduce the broad and asymmetric relaxation maximum. Within this phenomenological description, the introduction of a distribution of activation temperatures accounts effectively for the broadening observed in $\lambda_2(T)$. This result is consistent with the idea that, in a molecular system such as Dy-SQ, the slowing down of the local magnetic fluctuations is characterized by a distribution of effective activation scales rather than by a single sharply defined one.

The best-fit parameters obtained within this distributed-BPP model are reported in Table 5.2. Although the distributed-BPP model provides a satisfactory description of the experimental data, the fitted distribution is remarkably broad. In particular, the value $\delta\theta = (98 \pm 3)$ K is comparable to the central activation temperature $\theta = (108 \pm 3)$ K, corresponding to an activation-temperature interval extending from 10 to 206 K. Such a wide range cannot be associated reliably with a well-defined distribution of microscopic energy barriers and suggests that $\delta\theta$ mainly acts as an effective parameter accounting for the complexity and broadening of the relaxation anomaly. The fit supports the general picture of a thermally activated slowing down of the local magnetic fluctuations, but it does not provide a sufficiently constrained quantitative determination of the underlying activation scales.

Parameter	Value	Unit
C	$(4.50 \pm 0.10) \times 10^2$	μs^{-2}
τ_0	$(2.62 \pm 0.2) \times 10^{-5}$	μs
θ	108 ± 3	K
$\delta\theta$	98 ± 3	K
ω_L	255.485 fixed	μs^{-1}

Table 5.2: *Best-fit parameters obtained from the BPP-type analysis of the slow μ SR relaxation component measured at 3000 G. The Larmor angular frequency ω_L was fixed according to the applied longitudinal field.*

This limitation motivates the complementary analysis presented in the following section, in which an effective correlation time τ_c is extracted from the experimental relaxation rates. This approach makes it possible to investigate the temperature evolution of the fluctuation timescale without imposing a broad distribution of activation temperatures from the outset.

5.3.3 Extraction of an Effective Correlation Time

The BPP-type fit discussed above provides a direct way to model the temperature dependence of the slow μ SR relaxation component by assuming a functional form for the correlation time $\tau_c(T)$. A complementary approach consists instead in reversing the argument: rather than imposing a specific temperature dependence for τ_c from the beginning, the experimental relaxation rate can be used to extract an effective correlation time at each measured temperature. This procedure provides a more model-independent way to visualize the slowing down of the local magnetic fluctuations and to test whether the resulting $\tau_c(T)$ is compatible with an activated behaviour or with a combination of different spin-relaxation processes. The possibility of extracting an effective correlation time from local-probe relaxation rates follows the approach used in Ref. [63], where the temperature dependence of τ_c was derived from the μ SR relaxation rate by inverting a Redfield-like expression based on a Lorentzian spectral density.

The starting point is again the Redfield-BPP expression for the longitudinal relaxation rate, in which the slow μ SR component is assumed to be proportional to the spectral density of the transverse fluctuating local fields evaluated at the muon Larmor angular frequency,

$$R(T, H) \equiv \lambda_2(T, H) = A \frac{\tau_c}{1 + \omega_L^2 \tau_c^2} \quad (5.24)$$

where A contains the coupling of the muon spin to the fluctuating transverse components of the local magnetic field, while $\omega_L = \gamma_\mu H$ is fixed by the applied longitudinal field. This expression has a maximum when the fluctuation time matches the inverse Larmor angular frequency,

$$\omega_L \tau_c = 1 \quad (5.25)$$

At this point the relaxation process is most efficient, because the spectral weight of the magnetic fluctuations is centred in the frequency window probed by the muon. The corresponding maximum relaxation rate is

$$R_{\max} = \frac{A}{2\omega_L} \quad (5.26)$$

so that the unknown prefactor is

$$A = 2\omega_L R_{\max} \quad (5.27)$$

Substituting this relation into the BPP expression gives

$$R = 2\omega_L R_{\max} \frac{\tau_c}{1 + \omega_L^2 \tau_c^2} \quad (5.28)$$

This equation can then be inverted to determine τ_c directly from the experimental value of R . After rearranging the terms, one obtains a quadratic equation for the correlation time,

$$\tau_c^2 - \frac{2}{\omega_L} \frac{R_{\max}}{R} \tau_c + \frac{1}{\omega_L^2} = 0 \quad (5.29)$$

whose two solutions are

$$\tau_c^{\pm}(T) = \frac{R_{\max}}{R(T)} \frac{1}{\omega_L} \left[1 \pm \sqrt{1 - \left(\frac{R(T)}{R_{\max}} \right)^2} \right] \quad (5.30)$$

The presence of two branches reflects the fact that the same relaxation rate can be produced either by fast fluctuations, with $\omega_L \tau_c < 1$, or by slow fluctuations, with $\omega_L \tau_c > 1$. This ambiguity is illustrated in Figure 5.9, where the two solutions $\tau_c^+(T)$ and $\tau_c^-(T)$ obtained from the experimental $\lambda_2(T)$ data are reported. The two branches merge at the temperature corresponding to the maximum of the relaxation rate, where $R(T) = R_{\max}$ and therefore $\tau_c = 1/\omega_L$. Away from this point, the inversion of the BPP expression yields two mathematically allowed values of the correlation time, corresponding to the fast- and slow-fluctuation regimes.

In order to construct a physically meaningful temperature dependence of the correlation time, the effective $\tau_c(T)$ was obtained by selecting, at each temperature, the branch that increases upon cooling. This criterion is consistent with the expected slowing down of the electronic spin dynamics as the temperature is lowered. In practice, this corresponds to following the τ_c^- branch on the high-temperature side of the relaxation maximum and the τ_c^+ branch on the low-temperature side, thus obtaining a continuous trend characterized by progressively longer correlation times in the low-temperature regime. The opposite choice would instead imply a decrease of τ_c upon cooling, which would be difficult to reconcile with the physical interpretation of the relaxation peak in terms of thermally slowed magnetic fluctuations.

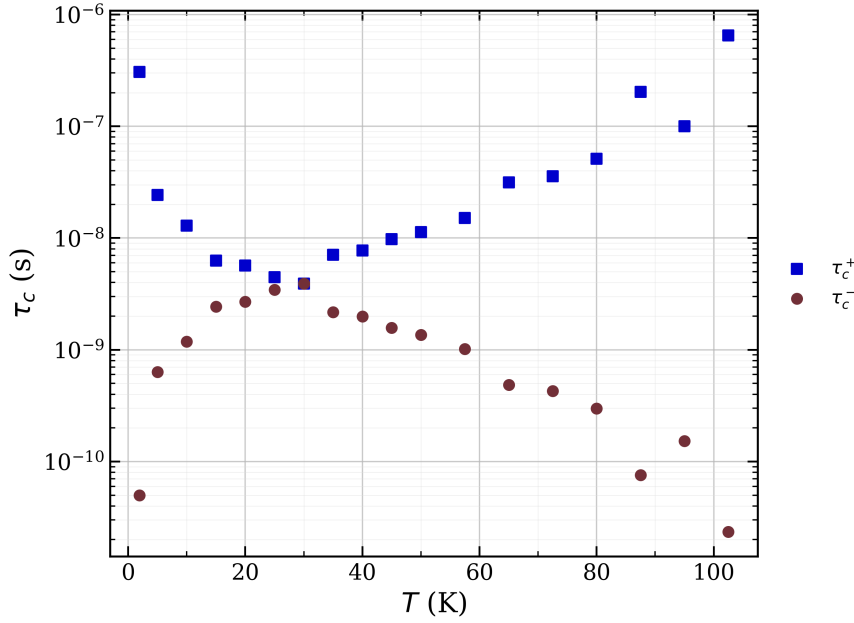


Figure 5.9: Temperature dependence of the two correlation-time branches τ_c^+ and τ_c^- obtained by inverting the BPP expression for the 3000 G μ SR dataset. The two solutions correspond to the slow- and fast-fluctuation regimes, respectively, and merge at the maximum of the relaxation rate, where $\omega_L \tau_c = 1$.

Once the effective correlation times had been extracted, their temperature dependence was analysed in terms of the inverse correlation time, since different relaxation channels are naturally expected to add at the level of the rates. Following the phenomenological approach commonly adopted for lanthanide-based molecular magnets (see Equation 1.31), $\tau_c^{-1}(T)$ was fitted by retaining an Orbach contribution together with a linear term accounting for the direct process, while the Raman contribution was neglected in the present analysis in order to avoid overparameterization. At fixed longitudinal field, this yields

$$\tau_c^{-1}(T) = BT + \tau_0^{-1} \exp\left(-\frac{\Delta}{T}\right) \quad (5.31)$$

where B is the effective coefficient of the direct process, including the field dependence, τ_0 is the characteristic attempt time, and Δ is the activation temperature associated with the Orbach mechanism. In this way, the μ SR data are not only described through the BPP-like temperature dependence of $\lambda_2(T)$, but are also recast into an effective microscopic timescale whose thermal evolution can be directly compared with standard spin-lattice relaxation mechanisms.

The result of this analysis is shown in Figure 5.10, where the inverse correlation times extracted from the two longitudinal-field datasets are fitted simultaneously. The fit was performed using a global model in which the Orbach contribution is shared by the two fields, while the coefficient of the linear direct term is allowed to be field dependent,

$$\tau_c^{-1}(T, H) = B_H T + \tau_0^{-1} \exp\left(-\frac{\Delta}{T}\right) \quad (5.32)$$

Here, the same values of τ_0 and Δ are imposed for the 1500 G and 3000 G datasets, whereas two independent coefficients, B_{1500} and B_{3000} , are used to account for the field dependence of the direct process. This choice reflects the idea that the activated Orbach channel is associated with an intrinsic energy scale of the molecular spin system, while the direct contribution is expected to depend more explicitly on the applied longitudinal field.

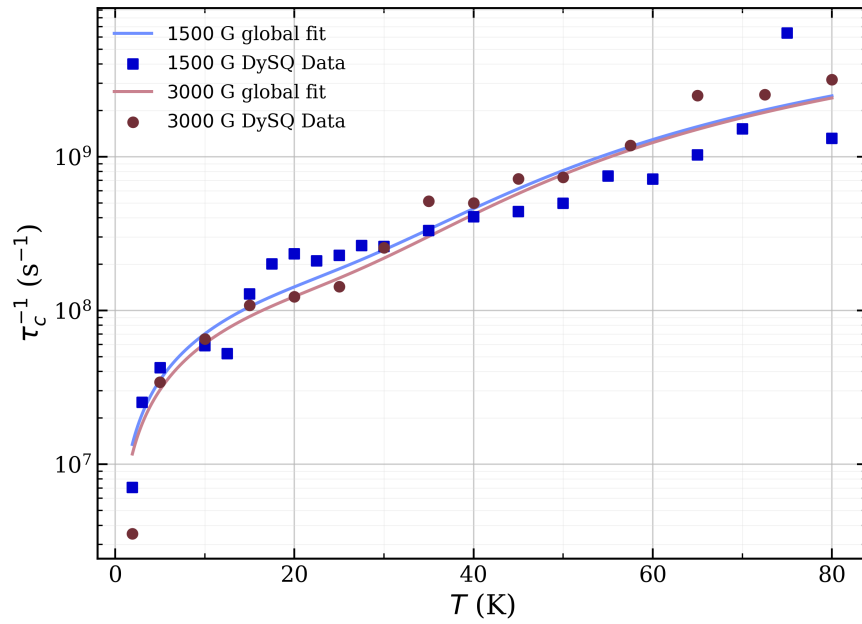


Figure 5.10: Global fit of the inverse correlation times extracted from the 1500 G and 3000 G μ SR relaxation data. The fit was performed using a phenomenological direct-plus-Orbach model, with a field-dependent linear coefficient and shared values of τ_0 and Δ for the two datasets.

Despite the scatter of the reconstructed τ_c^{-1} values, the global fit reproduces the overall increase of the inverse correlation time with temperature over the investigated range. At low temperature, the linear term gives the dominant contribution to the relaxation rate, whereas the activated term progressively becomes more relevant at higher temperature. The analysis therefore supports the interpretation that the temperature evolution of the μ SR relaxation peak can be recast in terms of a slowing down of the local magnetic fluctuations upon cooling, with an effective relaxation rate compatible with the coexistence of a direct-like process and an activated Orbach-like contribution. It should be stressed, however, that this procedure is phenomenological: the extracted $\tau_c(T)$ values depend on the branch selection in the BPP inversion, and the limited number of available fields prevents a more stringent determination of the field dependence of the direct process.

Parameter	Value	Unit
B_{1500}	$(7.03 \pm 0.81) \times 10^6$	$s^{-1} K^{-1}$
B_{3000}	$(6.07 \pm 0.98) \times 10^6$	$s^{-1} K^{-1}$
τ_0^{-1}	$(2.1 \pm 1.6) \times 10^{10}$	s^{-1}
τ_0	$(4.8 \pm 3.7) \times 10^{-11}$	s
Δ	190 ± 50	K

Table 5.3: *Best-fit parameters obtained from the global fit of the inverse correlation times extracted from the 1500 G and 3000 G μ SR datasets. The coefficients B_{1500} and B_{3000} describe the field-dependent linear contribution, while τ_0 and Δ are shared parameters associated with the activated Orbach-like term.*

5.3.4 Estimate of the Orbach activation energy from NMR relaxation data

The previous analysis showed that the slow μ SR relaxation component can be interpreted within a BPP-like framework, in which the relaxation rate is governed by the spectral density of the fluctuating local fields evaluated at the probe Larmor frequency. Although the NMR longitudinal relaxation data were not used as the main quantitative reference in the previous dynamical analysis, due to the experimental difficulties discussed above, their high-temperature behaviour can still provide a useful independent estimate of the activated energy scale.

The starting point is the same Redfield-BPP argument used in Equations 5.17 and 5.24. On the high-temperature side of the relaxation anomaly, the spin fluctuations are expected to be in the fast-fluctuation regime, namely

$$\omega_L \tau_c \ll 1 \quad (5.33)$$

This condition corresponds to the regime opposite to the matching condition reported in Equation 5.25. In this limit, the Lorentzian spectral density reduces to a quantity proportional to the correlation time itself. Therefore, for the NMR longitudinal relaxation rate one obtains

$$\frac{1}{T_1} \propto \tau_c \quad (5.34)$$

or, equivalently,

$$T_1 \propto \tau_c^{-1} \quad (5.35)$$

This relation makes it possible to connect the high-temperature behaviour of T_1 to the relaxation mechanisms discussed in the previous section. In particular, if the direct contribution in Equation 5.32 is neglected in the selected fitting range, the inverse correlation time is controlled by the activated Orbach term. As a consequence, the NMR relaxation time is expected to follow an activated law,

$$T_1(T) = A \exp\left(-\frac{\Delta}{T}\right) \quad (5.36)$$

The same reasoning can be used, with the necessary caution, to analyse the relaxation information extracted from the transverse NMR data. As discussed in Chapter 2, T_2 cannot be directly identified with T_1 , since it also contains dephasing contributions which are not associated with longitudinal relaxation. However, the temperature dependence of T_2 can still contain information on the same electronic spin fluctuations that determine the longitudinal relaxation channel. For this reason, the quantity considered in the following is not T_2 itself, but the inverse of the R_1 -like contribution extracted from the transverse relaxation analysis. This quantity, written as R_1^{-1} , represents the effective longitudinal time scale inferred from the analysis of the T_2 relaxation process.

The activated law of Equation 5.36 was therefore applied in two complementary ways. First, it was used to fit the effective R_1^{-1} contribution obtained from the transverse relaxation analysis at 13 kOe and 38 kOe. Second, it was applied directly to the longitudinal relaxation times T_{1a} and T_{1b} measured at the same two magnetic fields. In both cases, a global fit was performed by using independent prefactors for the different datasets and a common activation energy.

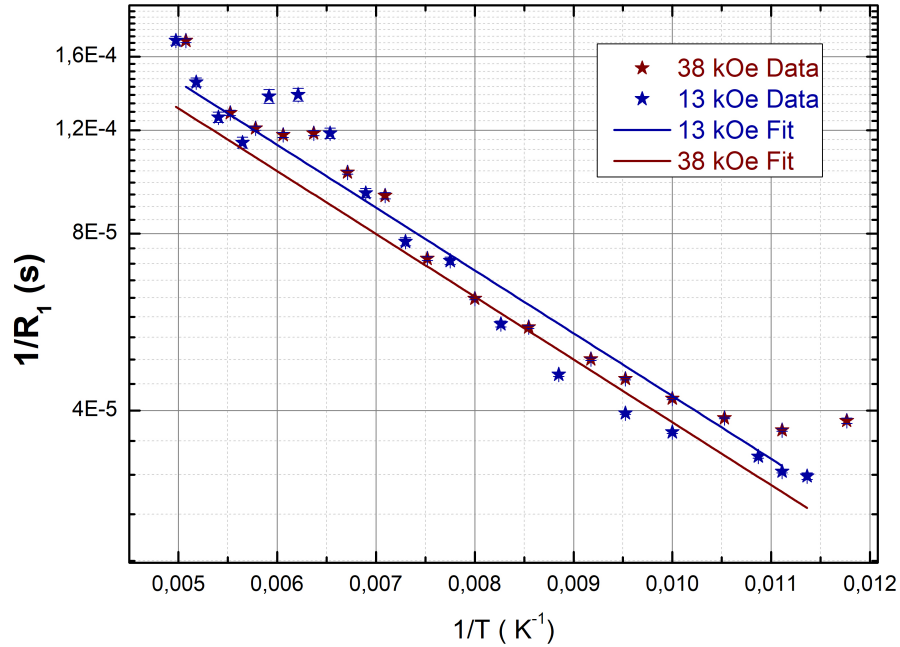


Figure 5.11: Activated fit of the effective R_1^{-1} contribution extracted from the transverse relaxation analysis at 13 kOe and 38 kOe. The two datasets were fitted using independent prefactors and a common activation energy.

The fits were restricted to the high-temperature region, defined here as $T > 70$ K.

This choice is motivated by the fact that, in this range, the spin dynamics is expected to be sufficiently fast for the condition $\omega_L \tau_c \ll 1$ to represent a reasonable approximation. In terms of the variable used in the plots, this corresponds approximately to $1/T < 1.43 \times 10^{-2} \text{ K}^{-1}$.

This temperature window also includes the region around 160–170 K, where an apparent anomaly had been observed in the NMR relaxation data. Including this region in the activated analysis allows one to test whether this feature follows the same high-temperature trend or whether it appears as a deviation from the thermally activated behaviour. In this sense, the fit is not only used to extract an effective activation energy, but also to check the consistency of the suspected spurious anomaly with the overall relaxation dynamics.

The result obtained from the global fit of the R_1^{-1} contribution extracted from the transverse relaxation data is shown in Figure 5.11. The two datasets measured at 13 kOe and 38 kOe were fitted using independent prefactors and a common activation energy. The fit gives

$$\Delta_{R_1^{-1}} = (246.0 \pm 10.1) \text{ K} \quad (5.37)$$

A fully independent estimate was then obtained from the direct analysis of the longitudinal relaxation data.

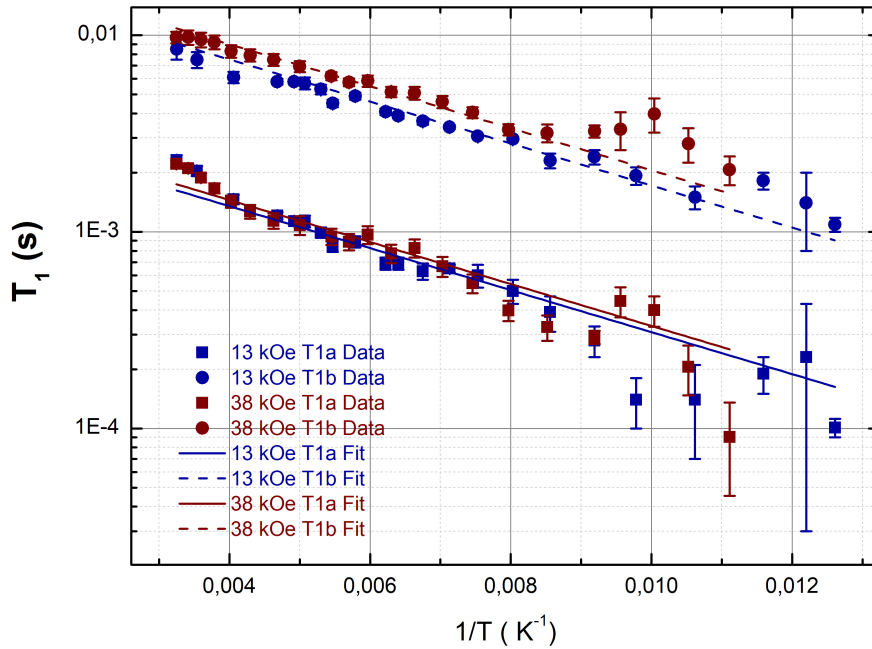


Figure 5.12: Activated fit of the longitudinal relaxation times T_{1a} and T_{1b} measured at 13 kOe and 38 kOe. The four datasets were fitted using independent prefactors and a common activation energy.

In this case, the global fit included both magnetic fields and both relaxation components, T_{1a} and T_{1b} , as shown in Figure 5.12. The four datasets were described using four independent prefactors and a single activation energy, yielding

$$\Delta_{T_1} = (245.9 \pm 7.8) \text{ K} \quad (5.38)$$

The two NMR estimates are essentially identical within the experimental uncertainty. This agreement indicates that the effective R_1^{-1} contribution extracted from the transverse relaxation analysis and the directly measured longitudinal relaxation times are sensitive to the same thermally activated spin dynamics. The result is particularly relevant because the two quantities are obtained from different relaxation channels: the former is inferred from the analysis of T_2 , while the latter is measured directly from the recovery of the nuclear magnetization.

The activation energies obtained from NMR are slightly larger than the value extracted from the μ SR correlation-time analysis, $\Delta = (190 \pm 50) \text{ K}$, but they remain compatible within the uncertainty of the latter. The difference between the central values should not be overinterpreted, since the two approaches rely on different probes and different approximations. The μ SR value was obtained from an effective reconstruction of the correlation time, whereas the NMR estimates are based on the high-temperature fast-fluctuation limit of the BPP expression.

Overall, the three estimates point to the same order of magnitude for the activated energy scale, namely $\Delta \sim 200\text{--}250 \text{ K}$, corresponding to approximately 17–22 meV. This agreement supports the interpretation that the high-temperature spin dynamics of Dy–SQ is governed by a thermally activated process involving low-lying excited electronic states.

Concluding Remarks

This chapter presented the analysis of the experimental results obtained on Dy–SQ by combining microscopic modelling and local-probe relaxation data. The discussion started from a crystal-field estimate based on a point-charge description, used as a first qualitative reference for the electronic structure of the Dy^{3+} ion. This was followed by an effective modelling of the SQUID magnetometry data, aimed at identifying the minimal magnetic ingredients needed to describe the response of the system.

The second part of the chapter focused on the spin dynamics. The NMR and μ SR relaxation measurements were analysed as complementary probes of the local magnetic fluctuations. In particular, the relaxation data were used to discuss the slowing down of the spin dynamics and to obtain effective estimates of the activated energy scale involved in the relaxation process.

The characteristic energy scales inferred independently from the μ SR, NMR T_1 , and NMR T_2 measurements are in substantial agreement, indicating that the different local probes are sensitive to the same underlying spin dynamics. However,

these estimates are not consistent with the low-lying level separation obtained from the effective PHI modelling. This discrepancy suggests that, although the simplified Hamiltonian reproduces the main features of the bulk magnetic response, it does not provide a sufficiently accurate description of the electronic level scheme relevant to the relaxation dynamics. A more elaborate computational treatment of the crystal-field and exchange interactions is therefore required to obtain a reliable microscopic description of the low-energy states of Dy-SQ.

Overall, the chapter showed how the combination of magnetometry, NMR, μ SR, and modelling can provide a coherent, although still effective, description of Dy-SQ. The following chapter summarizes the main conclusions of the thesis, discusses the limitations of the present approach, and outlines possible directions for a more complete microscopic description of the system.

Conclusions

The aim of this thesis was to investigate the magnetic properties of the dysprosium-based single-ion magnet Dy–SQ and to use them as indirect probes of the microscopic electronic structure of the system. The compound is particularly interesting because the magnetic response is not determined by the Dy^{3+} ion alone, but also by the presence of a semiquinonato radical, which introduces an additional spin degree of freedom and modifies the local magnetic environment of the lanthanide centre.

The work combined bulk magnetometry, local-probe relaxation measurements, and computational modelling. SQUID magnetometry provided the macroscopic magnetic response through the temperature dependence of χT and the field dependence of the magnetization. NMR measurements gave access to the local magnetic environment sensed by the nuclei, showing a progressive broadening of the resonance spectra upon cooling and clear anomalies in the transverse relaxation rate. Finally, longitudinal-field μSR measurements provided a complementary local probe of the spin dynamics, allowing the slowing down of the Dy magnetic fluctuations to be followed on a different time scale.

A first microscopic reference was obtained through crystal-field calculations based on a point-charge model. These calculations provided an approximate level scheme for the Dy^{3+} ground multiplet and indicated that the leading axial second-order Stevens term plays a dominant role in the local anisotropy. However, the calculated level spacings and Stevens parameters were found to depend significantly on the assumed donor charges. This shows that the point-charge calculation is useful as a qualitative guide, but it cannot be regarded as a quantitative determination of the Dy–SQ crystal-field Hamiltonian.

The magnetic data were then analysed using the software PHI through a sequence of progressively refined effective models. The comparison with the diamagnetic-ligand reference Dy–Trp showed that the crystal field obtained for the reference compound cannot be transferred directly to Dy–SQ. In particular, fitting only the Dy–radical exchange interaction while keeping the Dy–Trp crystal-field parameters fixed did not reproduce satisfactorily either the χT curves or the magnetization isotherms. This result is important because it shows that the semiquinonato radical cannot be treated simply as an additional spin coupled to an otherwise unchanged Dy^{3+} centre. Instead, its presence also affects the effective crystal field experienced by the dysprosium ion.

The final effective PHI model retained only the leading axial crystal-field parameter and the Dy–radical exchange coupling as free parameters. Despite its simplicity, this model reproduced the main features of the two χT curves and of the three magnetization isotherms. The fitted exchange constant was found to be negative, indicating an antiferromagnetic interaction between the Dy³⁺ moment and the radical spin, while the effective axial parameter differed from the value obtained for Dy–Trp. The model therefore gives a physically consistent picture in which the magnetic response of Dy–SQ is governed by a modified axial crystal field and by an antiferromagnetic Dy–radical exchange interaction. At the same time, the remaining discrepancies, especially at low temperature and low field, indicate that the model should not be interpreted as a complete microscopic description of the electronic structure.

The relaxation measurements support this interpretation from a complementary point of view. The NMR transverse relaxation rate displays anomalies in the same temperature region where the local magnetic dynamics becomes slow, while the frequency-swept spectra show a broadening of the resonance line upon cooling. The μ SR data confirm the presence of a non-trivial slowing down of the local magnetic fluctuations. In particular, the slow relaxation component can be described within a BPP-like framework, where the relaxation maximum arises when the fluctuation time enters the experimental time window. The introduction of a distribution of activation temperatures produces an apparently improved description of the broad relaxation peak. However, the fitted distribution width $\delta\theta$ is comparable to the central value θ , making the resulting distribution too broad to retain a meaningful quantitative interpretation. The improved fit quality should therefore not be regarded as evidence for an intrinsic distribution of well-defined activation barriers. Rather, the large value of $\delta\theta$ likely compensates phenomenologically for the limitations of a model in which the temperature dependence of the correlation time is described solely by an activated Orbach-like process.

This limitation becomes clearer from the analysis of the effective correlation time τ_c extracted from the μ SR relaxation rates. The temperature dependence of τ_c^{-1} shows that an activated Orbach-like contribution alone is not sufficient to describe the full temperature range, since a direct-like relaxation channel cannot be neglected at low temperatures. A phenomenological model combining direct-like and Orbach-like contributions provides a more consistent description of the spin dynamics and yields an effective activation energy of approximately $\Delta = (190 \pm 50)$ K. This value represents an experimental estimate of the energy scale involved in the thermally activated relaxation process.

The high-temperature NMR relaxation data provided an independent check of this energy scale. In the fast-fluctuation regime, the BPP expression implies that the longitudinal relaxation time is proportional to the correlation time. This makes it possible to fit the high-temperature behaviour of both the directly measured T_1 components and the effective R_1^{-1} contribution inferred from the transverse relaxation analysis using an activated Orbach-like law. The two NMR analyses gave essentially the same activation energy, around $\Delta \simeq 246$ K, corresponding to about

21 meV. This value is slightly larger than the central value obtained from the μ SR correlation-time analysis, but remains compatible within the uncertainty of the latter.

Taken together, the μ SR and NMR relaxation analyses point to a common activated energy scale of the order of 200–250 K. This agreement is significant because the two techniques probe the spin dynamics on different time scales and through different microscopic couplings. At the same time, the comparison should remain phenomenological: the extracted activation energies characterize the dynamics of the local magnetic fluctuations and cannot be assigned unambiguously to a single electronic excitation without a more complete microscopic model.

Overall, the results identify the dominant ingredients governing the magnetic response of Dy–SQ: a strongly anisotropic Dy³⁺ centre, a crystal field modified by the radical-containing ligand environment, and an antiferromagnetic interaction between the dysprosium ion and the semiquinone radical. Nevertheless, the comparison between the different approaches also reveals the limitations of the present microscopic modelling. The effective activation energies independently inferred from the NMR and μ SR relaxation data are in substantial agreement with each other, suggesting that the two local probes detect the same underlying spin-relaxation process. However, the corresponding energy scale cannot be associated, even qualitatively, with any of the relevant level separations predicted by the effective PHI Hamiltonian. This discrepancy indicates that, although the simplified model reproduces the main features of the bulk magnetic response, it does not provide a sufficiently accurate description of the low-energy electronic structure governing the spin dynamics. The point-charge calculation remains strongly dependent on the assumed charge distribution, while the PHI Hamiltonian is deliberately reduced in order to remain constrained by the available magnetic data. A natural continuation of this work would therefore be a more refined electronic-structure calculation of Dy–SQ. In particular, a density-functional-theory-based description of the molecular charge distribution would allow more realistic partial charges, ligand-field parameters, and radical spin density to be obtained. These quantities could then be used as input for improved crystal-field calculations and for a more constrained magnetic model. Such an approach would make it possible to test whether the energy separations inferred from magnetometry and local-probe relaxation can be reconciled within a single microscopic description of the Dy–SQ electronic structure.

In this sense, the present thesis should be viewed as a first step toward a complete microscopic understanding of Dy–SQ. The experimental results establish clear constraints on the magnetic anisotropy, the Dy–radical coupling, and the spin dynamics of the system. The computational analysis identifies the dominant physical ingredients, but also shows where the simplified models fail. This tension between experiment and modelling is not merely a limitation: it provides the central indication for future work, namely that a realistic description of the electronic structure of Dy–SQ requires going beyond formal point charges and effective axial Hamiltonians toward a more complete calculation of the molecular electronic environment.

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