Doctoral Thesis

Development of a neutron spin filter based on protons dynamically polarized using photo-excited triplet states

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Development of a Neutron Spin Filter

Based on Protons Dynamically Polarized

Using Photo-Excited Triplet States

A dissertation submitted to

ETH ZURICH

for the degree of

Doctor of Sciences

presented by

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2012
This thesis work was performed in the Sample Environment and Polarised Targets Group of the Paul Scherrer Institute in Switzerland.
Abstract

A successful test of principle experiment of a neutron spin filter based on polarized protons has been carried out. The proton polarization was obtained through dynamic nuclear polarization (DNP) using the short-lived photo-excited triplet state of pentacene molecules in a host crystal of naphthalene. The specific technique of DNP we used to polarize the spin filter is the integrated solid effect (ISE) where a microwave pulse is applied while simultaneously sweeping the external magnetic field, transferring the electron polarization to the protons. In contrast to classical DNP we have been able to operate the spin filter at relaxed conditions. This was possible due to the high electron spin polarization of the triplet state which is independent of magnetic field and temperature. A maximum proton polarization of 13% has been recorded by nuclear magnetic resonance (NMR) at a magnetic field of 0.3 T and a temperature of 100 K. This corresponds to a polarization enhancement of 40000.

For the purpose of this thesis, an X-band DNP polarizer has been set up at the Paul Scherrer Institute (PSI) in Switzerland. A laser system, consisting of a frequency tripled Nd:YAG and an optical parametric oscillator (OPO), has been installed. The system delivers laser pulses of 600 nm, optimized for the zero-phonon absorption line of the pentacene molecule, at a repetition rate of 30 Hz. The preparation of samples required special equipment. We have built a zone refinement apparatus to purify the naphthalene and equipment for crystal growth using the Bridgman method. With these combined tools several spin filter crystals of excellent quality have been produced. Using the X-band DNP polarizer the crystals grown have been thoroughly characterized, and the parameters of the ISE technique have been explored and optimized.

Once positioned on a neutron beam at PSI, the sample with its polarized protons was used to demonstrate spin filtering of the neutrons. For a cubical sample with a volume of 125 mm$^3$ we obtained an analyzing power of 0.17. The polarization of the protons was then measured by the neutron beam, confirming the results of the NMR measurements. In a final experiment, we used the neutron beam to map the polarization distribution throughout the spin filter. Most surprisingly, our experiment showed that the polarization distribution was homogeneous. This was the case even at low laser pulse powers. This result directly contradicts the existing theoretical model, calling for a new description of the photo-excitation process.
Zusammenfassung


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1 Introduction

Neutrons have been used in science for almost 70 years [1], and today neutron scattering is routinely used in many fields of research. It is applied in a wide range of disciplines ranging from fundamental physics to material science and biology. The development of neutron scattering is especially important for condensed matter research where it has become an indispensable tool. Due to the lack of an electrical charge the neutrons penetrate deep into both solids and liquids. There the neutron interacts with the nuclei via the strong force and, with the spins and the magnetic fields of the sample, via the magnetic interaction. Several research fields such as magnetism and superconductivity require means to separate the spin dependent scattering from the non-dependent one. This can be accomplished using polarized neutrons. To polarize a neutron beam one can either use super mirror polarizers [2], polarized gas of Helium-3 [3] or polarized protons [4].

A spin filter of polarized protons shows no limitations in its angular acceptance and can be used for all neutron energies. However, a spin filter obtained through classical DNP [5] has only seen limited use. This is due to the extreme experimental conditions needed for classical DNP to polarize the protons in the spin filter to levels high enough for it to compete with super mirrors and polarized Helium-3 gas. The polarization of the free electrons, which is the source of the polarization transferred to the protons, is given by the Boltzmann distribution. Thus magnetic fields of several Tesla and temperatures around 1 K are needed to substantially polarize the spin filter, requiring a complex cryostat and huge magnet.

This changed with recent published results reporting 10000 fold polarization enhancements at 100 K and 0.3 T [6, 7]. The results were obtained through the use of the integrated solid effect (ISE) [8] technique on the photo-excited triplet states of pentacene, doped into a naphthalene crystal. The short lived triplet state of the pentacene molecule exhibits a high electron polarization independent of magnetic field and temperature [9]. This opens up for spin filtering at relaxed magnetic fields and temperatures, which are factors of great importance in view of applications.

Recent publications' promising high proton polarizations [6, 7] call for a reconsideration of neutron spin filters based on polarized protons. This led to the work presented in this thesis: The implementation of a polarized proton spin filter, based on DNP using photo-excited triplet states [10].

1.1 Structure of the Thesis

In chapter 2 a basic theoretical description of dynamic nuclear polarization and the technique of integrated solid effect in particular are given along with the parameters of the pentacene-naphthalene system. A description of how the crystal is purified, grown and cut is found in chapter 3. The experimental triplet DNP apparatus is introduced in chapter 4 followed by a presentation of the results obtained while optimizing the setup as a preparation for the neutron spin filtering experiment. Chapter 6 deals with the spin filter experiment itself and gives a short introduction to the scattering of thermal neutrons.
followed by a description of the actual experiment and the results obtained. The thesis is summarized, and an outlook is given in chapter 7.
2 DNP on Photo Excited Triplet States

2.1 Introduction

Dynamic nuclear polarization (DNP) [5] is a most powerful tool to obtain high nuclear spin polarization. Originally used to build polarized targets to study the role of spin in nuclear and particle interactions, its potential to achieve strong signal enhancement has now become a driving force in different fields of magnetic resonance [11]. The huge increase in contrast obtained in magnetic resonance imaging (MRI) [12] has recently opened the way to clinical applications [13].

In classical DNP, one introduces ground state paramagnetic centers into the sample, and the electron spin polarization is transferred to the surrounding nuclear spins by means of microwave irradiation. The maximum possible enhancement is limited by the ratio of the gyromagnetic ratios of the electron and nuclear spin, e.g. about 660 in the case of proton spins. Therefore temperatures of 1 K or lower and fields of several Tesla are indispensable to achieve high nuclear polarizations.

This drawback can be relieved using photo-excited triplet states to provide the electron spins. This alternative, also called microwave induced optical nuclear polarization (MIONP) was first reported in [14]. High proton spin polarizations were obtained in a strong magnetic field at liquid helium temperature using long-lived photo-excited triplet states [15]. A breakthrough was achieved using short-lived photo-excited triplet states that are strongly aligned in the optical excitation process. The polarization of the triplet state is transferred to the surrounding protons by irradiating the electrons in the triplet state with a microwave field while adiabatically sweeping through the electron spin resonance (ESR) line. This method, called the integrated solid effect (ISE) requires neither low temperatures nor high fields [16]. Thus the apparatus can be simplified, which is very attractive for applications. A proven system for this method is naphthalene doped with pentacene, in which high proton spin polarizations were obtained [7, 17].

The aim of this chapter is to describe the parameters and properties of the triplet state of the pentacene molecule and to give a summary of the specific theory dealing with dynamic nuclear polarization, using the short lived triplet state of pentacene.

2.2 The Triplet State of Pentacene

The method of DNP using the photo-excited triplet state of pentacene was introduced in [16]. Using a short laser pulse the pentacene molecules are excited from the singlet ground state $S_0$ to the lowest excited singlet state $S_1$. From the excited singlet state the electron either decays back within 20 ns to the ground state, fluorescing at 600 nm, or, through a process called intersystem crossing (ISC), into the lowest triplet state $T_1$, via the $T_3$ state [18]. The sublevels of the triplet state of pentacene are populated in a highly selective way due to the spin-orbit coupling between the excited singlet state and the triplet state [19]. As a result, the triplet state shows a pronounced alignment of its electronic spin [9, 20]. The sublevels of the triplet state are labeled $T_X$, $T_Y$ and $T_Z$, on the basis corresponding to the principal axes ($X$, $Y$, $Z$) of the pentacene molecule (as seen in figure 2.1).
The lifetime of the triplet state is on the order of tens of microseconds, allowing a time window where the technique of DNP can be applied. However, the lifetime of the triplet state is short when compared to the electron spin-lattice relaxation. As a result, the strong initial alignment of the triplet state remains during its lifetime and is thus virtually independent of the magnetic field and temperature. Once the triplet state decays back down to the ground state, it does so through intersystem crossing or through phosphorescence [21]. See figure 2.2 for a schematic drawing of the energy level scheme of the pentacene molecule.

Only a small percentage of the electrons in the excited singlet state actually enters the triplet state [18]. The probability of intersystem crossing (ICS) has been measured in four independent studies and found to be between 0.003 and 0.15 at 2 K [22–25]. The low ISC values are expected to increase with temperature as the energy difference between the third triplet state and the first excited singlet state is bridged by thermal phonons. In other words the probability for a crossing increases when the vibrational levels of the excited singlet state overlaps with the energy level of the triplet state. No measurements of the ISC yield at higher temperatures have been performed so far. We have tried to get an estimate of the ISC yield for pentacene in a naphthalene host at a temperature of around 100 K, see section 5.4 for details.
2.3 The Spin Hamiltonian of the Triplet Spin

2.3.1 The Fine Structure

Two electrons, coupled through dipole-dipole interactions, form either a singlet or a triplet state. While in the singlet state the combined spin of the two electrons is zero, the triplet state has a combined spin of 1. Once excited into the triplet state, a fine splitting of the energy levels of the triplet state is observed. This splitting is normally referred to as the zero field splitting (ZFS). The corresponding Hamiltonian, \( H_D \), is written as [26]:

\[
H_D = D(S_Z^2 - \frac{1}{3}S(S+1)) + E(S_X^2 - S_Y^2)
\]

where \((S_X, S_Y, S_Z)\) are the 3×3 Pauli matrices on the basis of the principal axes of the pentacene molecule. The components of the fine structure tensor, \( D = 2\pi \times 1381 \text{ MHz} \) and \( E = -2\pi \times 42 \text{ MHz} \), have been experimentally determined for pentacene by van Strien [9].

2.3.2 The Zeeman Interaction with a Magnetic Field

With a magnetic field applied, the triplet sublevels mix and become separated by the Zeeman effect. At sufficiently high fields, the Hamiltonian is dominated by the Zeeman term and the triplet sublevels can be written as \( T_+ \), \( T_0 \) and \( T_- \). See figure 2.3 for the full evolution of the triplet sublevels for the special case when the pentacene X axis is parallel with \( B_0 \).

![Figure 2.3: Plot of the energy of the triplet sublevels as a function of the externally applied magnetic field for the specific case of X||B_0. With \( \nu_{0+} \) and \( \nu_{0-} \) the frequencies of the low and high field transitions.]

In the laboratory frame of reference \((x, y, z)\) we chose the magnetic field parallel to \( z \). The splitting of the triplet state depends on the orientation of the pentacene molecule with respect to the magnetic field. The orientation can be defined using two spherical angles, \( \theta \) and \( \phi \), as illustrated in figure 2.4, which describes the orientation of the pentacene molecule with respect to the magnetic field \( B_0 = B_0(\sin \theta \cos \phi, \sin \theta \sin \phi, \cos \theta) \).

With a strong magnetic field applied, the Hamiltonian in the lab frame then writes [27]:

\[
H_Z + H_D = \omega_0 S_z + \frac{1}{2} \left( \frac{D}{3}(3\cos^2 \theta - 1) + E \sin^2 \theta \cos 2\phi \right) (3S_x^2 - S(S + 1)).
\]

Where we set \( \omega_0 = \frac{g}{\hbar} \beta_B B_0 \) while approximating the g-tensor to be isotropic [9].
High Field Approximation

At a high magnetic field the Zeeman term is, as previously stated, the dominant term in the Hamiltonian, and the ZFS term can be treated as a perturbation. The calculation of the eigenstates for equation 2.2 in the high field approximation is given in [27]. For a pentacene molecule arbitrarily oriented with respect to the magnetic field, one obtains the frequencies of the two transitions $T_0 \leftrightarrow T_+$ and $T_0 \leftrightarrow T_-$ to be:

$$\omega_{0\pm} = \omega_{0S} \pm \frac{1}{2} \left( D(3\cos^2\theta - 1) + 3E\sin^2\theta \cos 2\phi \right).$$

(2.3)

As we will see later, it is favorable to orient the $X$-axis of the pentacene molecule along the applied magnetic field. Setting $\theta = 90^\circ$ and $\phi = 0^\circ - X||B_0$—equation 2.3 reduces to:

$$\omega_{0\pm} = \omega_{0S} \pm D'.$$

(2.4)

where the term $-\frac{1}{2}(D - 3E)$ has been replaced with $D'$ for simplicity.

2.3.3 The Contribution of the Nuclear Spins

The hyperfine interaction between the triplet electron spin and the surrounding protons gives rise to a separate contribution to the Hamiltonian. This is the coupling exploited in all DNP schemes to transfer polarization from the electrons to the protons. Furthermore the protons on the pentacene molecule interact with the magnetic field, giving rise to a further Zeeman term. The full term of the Hamiltonian influenced by the proton spins writes:

$$\mathcal{H}_I = \omega_{0I} \sum_{i=1}^{N_I} I_i^z + \sum_{i=1}^{N_I} S \cdot A_i \cdot I_i.$$

(2.5)

The first term is the proton Zeeman effect with the proton Larmor frequency $\omega_{0I}$, and the second term is the hyperfine interaction between the triplet spin $S$ and the $i$’th nuclear spin $I_i$ where the sum counts over all the protons on the pentacene molecule. The components of the hyperfine tensor $A_i$ have most recently been measured in [28]. The full Hamiltonian for the triplet state, with the terms $\mathcal{H}_Z$, $\mathcal{H}_D$ and $\mathcal{H}_I$, writes:

$$\mathcal{H} = \mathcal{H}_Z + \mathcal{H}_D + \mathcal{H}_I = \omega_{0S}S_z + D'(S_z^2 - \frac{1}{3}S(S + 1)) + \omega_{0I} \sum_{i=1}^{N_I} I_i^z + \sum_{i=1}^{N_I} S \cdot A_i \cdot I_i.$$

(2.6)
2.3.4 Pentacene in a Naphthalene Host Crystal

Pentacene molecules, randomly oriented with respect to a magnetic field will give rise to a broad spectrum of frequencies, as seen from equation 2.3. To optimize the DNP yield, it is important to be able to orient all the pentacene molecules in the magnetic field so that the electron polarization is maximized.

Incorporating pentacene in a single crystal of naphthalene fulfills the requirements. The pentacene molecules are all aligned with their X axes pointing in the same direction within the crystal. A further advantage of the naphthalene crystal is that it is transparent to light with a wavelength of 600 nm allowing for the creation of the triplet state of the pentacene molecule.

With the pentacene molecules aligned with \( X \parallel B_0 \), a measured ESR spectrum as shown in figure 2.5 can be used to judge the quality of the crystal. Observing more than one frequency component of the splitting of the lines generally means that the crystal is not monocrystalline.

![ESR spectrum figure](image)

**Figure 2.5:** ESR spectrum of pentacene incorporated in a naphthalene single crystal. The spectrum shows a shift of around ± 750 MHz for the two transitions corresponding for an alignment of the crystal with \( X \parallel B_0 \). The sign of the plot has been determined by a comparison to a ESR signal of the stable radical TEMPO (see figure 5.12).

The well separated peaks of the ESR spectrum do indeed correspond to the transitions between the triplet sublevels, as previously indicated in figure 2.3. As expected from equation 2.3 the frequency shift is close to 753.5 MHz. Furthermore the effect of the hyperfine interaction between the electron and the protons can also be seen in the spectrum.

The naphthalene-pentacene system has a further advantage. A single naphthalene crystal exhibits a very long proton relaxation time. The relaxation time has been measured to 28 hours at 0.094 T and at a temperature slightly below 100 K [29]. As the enhanced polarization remains for such a long period of time the conditions are favorable to attempt to polarize the protons of a naphthalene crystal. The system of naphthalene-pentacene is treated in more detail in chapter 3.
**Triplet Parameters Specific to the Naphthalene-Pentacene System**

The properties of the triplet state as well as their decay times depend on the host material. The case of pentacene in naphthalene has been investigated by van Strien [9]. Another good candidate for orienting the pentacene molecule is a single crystal of p-terphenyl [20]. However, at 100 K a single crystal of p-terphenyl gives rise to a slightly lower electron polarization [20] and a faster proton relaxation time, making the naphthalene-pentacene system the preferred choice. The properties of the naphthalene-pentacene system are given in table 2.1.

<table>
<thead>
<tr>
<th>Population</th>
<th>Lifetime [µs]</th>
<th>Decay Rate s⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>NX = 0.91</td>
<td>τX = 15</td>
<td>kX = 6.7 × 10⁴</td>
</tr>
<tr>
<td>NY = 0.09</td>
<td>τY = 35</td>
<td>kY = 2.9 × 10⁴</td>
</tr>
<tr>
<td>NZ = 0</td>
<td>τZ = 280</td>
<td>kZ = 3.6 × 10³</td>
</tr>
</tbody>
</table>

Table 2.1: Populations, lifetimes and decay rates of the triplet sublevels of pentacene in a naphthalene host crystal [9].

With a magnetic field applied, the populations of the triplet states, \(N\), \(N_0\) and \(N_+\), will be a mixture of the populations at zero field. For \(X || B_0\) (\(\theta : 90^\circ\), \(\phi : 0^\circ\)) the populations mix as follows:

\[
N_- = \frac{1}{2}(N_Y + N_Z),
\]

\[
N_0 = N_X,
\]

\[
N_+ = \frac{1}{2}(N_Y + N_Z).
\]  

(2.7)

The decay rates \(k_-\), \(k_0\) and \(k_+\) are obtained accordingly. The strength of the observed ESR signal is proportional to the difference in population between the triplet sublevels \(T_+\), \(T_0\) and \(T_-\). The ESR signal, denoted by \(\xi\), is also a function of time as the populations of the triplet sublevels decay:

\[
\xi(t) = N_0e^{-k_0t} - N_\pm e^{-k_\pm t}.
\]  

(2.8)

For \(X || B_0\) the high field approximation of the population difference seen in the ESR signal becomes:

\[
\xi(t) = N_Xe^{-k_Xt} - \frac{1}{2}(N_Y + N_Z)e^{-\frac{(k_Y + k_Z)t}{2}}.
\]  

(2.9)

**Decay of the Triplet State**

The populations of the triplet state decay rapidly. This decay is an effect of the intersystem conversion and thus governed by the spin-orbit coupling between the singlet and triplet state. The different lifetimes of the triplet sublevels are a direct result of the same strong spin-orbit coupling which also produces the different populations of the substates in the first place [19]. As a consequence, the strongest populated substate will also decay the fastest leading to a decrease in polarization of the triplet state. Due to the mixing of states, the triplet polarization decays slower than the population (as seen in figure 2.6).

We see that the polarization transfer needs to take place in a short time as the electron population and polarization of the triplet state decay quickly. When optimizing the transfer of the polarization, it is mainly the decay of the ESR signal intensity that limits the process. The transfer needs to be optimized to occur within the lifetime of the \(T_X\) state. This puts a time limit of around 15 µs on the transfer.
The Spin-Lattice Relaxation

At room temperature the spin-lattice relaxation time has been measured to be on the same order of magnitude as the triplet decay times [30]. At low temperatures, around 1 K, albeit for phenazine, van der Waals [21] observed that the spin-lattice relaxation within the triplet state is several orders of magnitude slower than the triplet decay. The same study showed that the triplet state decay times are far less sensitive to changes of temperature compared to the spin-lattice relaxation. This suggests that the lattice-relaxation only plays a small roll for pentacene at 100 K. As a result, the spin-lattice relaxation between the individual substates of the triplet has been neglected in the following theory and in the analyzation of the measurements presented in this thesis.

2.4 DNP using Short-Lived Triplet States

This section shortly summarizes the theory needed to provide a general understanding of the DNP mechanism using short-lived triplet states. Here we will closely follow the theory as presented by Henstra [31, 32].

2.4.1 The Solid Effect

Classically, DNP has been performed using the solid effect (SE), where one irradiates the electron spins with a continuous microwave field. The original theory was developed by Abragam [5] and is well suited for the treatment of a permanent paramagnetic state irradiated by a weak microwave field. However the short lifetime of the electronic spin of the pentacene triplet state used in this work requires a strong microwave field to induce a fast polarization transfer. In a recent theoretical paper by Wenckebach [33] a more general approach was presented.

To transfer the high electronic polarization of the triplet state to the protons, a microwave field inducing flip-flop transitions between the electron and proton spins is applied. Due to the low concentration of pentacene molecules, no dipole-dipole interactions occur between the electrons of the different triplets state. The ESR spectrum can be pictured as an
assembly of individual narrow spin packages that do not interact with one another. Such a line is called inhomogeneously broadened, which has been illustrated in figure 2.7.

![Figure 2.7: Illustration of a single electron-spin package in a measured ESR spectrum.](image)

**The Hamiltonian in the Lab Frame**

We define a lab frame where the static field $B_0$ points along the z-axis and the applied microwave field rotates in the x-y plane with frequency $\omega$ and strength $\omega_1 S$. Choosing the orientation of the pentacene molecules X-axis along the static field, the full Hamiltonian writes [31]:

$$\mathcal{H}_{\text{lab}} = \omega_0 S_z + D'(S_z^2 - \frac{1}{3}S(S + 1)) + 2\omega_1 S_x \cos \omega t + \omega_0 \sum_{i=1}^{N_1} I_z^i + \sum_{i=1}^{N_1} S \cdot A^i \cdot I^i \quad (2.10)$$

**The Rotating Frame of Reference**

It is difficult to solve a Hamiltonian including a time-dependent microwave field. One circumvents this by transferring it to a frame of reference rotating around the z-axis with frequency $\omega$ of the applied microwave field. The electron spins still align along the z-axis, but the applied field now aligns along the new $x'$-axis instead of rotating around z, see figure 2.8.

![Figure 2.8: The rotating frame of reference with the angle $\theta$ between $\Delta$ and $\omega_R$.](image)
The Hamiltonian in the new frame of reference \((x', y', z' = z)\) then writes:

\[
H_{\text{rot}} = \Delta S_z + \omega_1 S x' + \omega_0 I \sum_{i=1}^{N_I} I_z^i + \sum_{i=1}^{N_I} S_z \left( A_{zx}^i I_x^i + A_{zy}^i I_y^i + A_{zz}^i I_z^i \right),
\]

with \(\Delta = (\omega_0 S - \omega \pm D')\) and the terms \(A_{\pm}^i\) the different components of the hyperfine interaction.

**Fictitious Spin \(\frac{1}{2}\) System**

The ESR spectrum in figure 2.5 shows two distinct frequencies of \(\omega_0 S \pm D'\). When conducting DNP, only one of the transitions is irradiated by the microwave field. Thus, choosing one of the transitions the triplet system can be treated as a highly polarized fictitious spin \(\frac{1}{2}\) system. This applies under the condition of \(\gamma_S B_1 \ll D'\) as shown by Sloop [20]. With the 2×2 Pauli matrices denoted as \(\sigma_{x'}, \sigma_{y'}\) and \(\sigma_z\), taking into account the change in rotation of a spin 1 to a spin \(\frac{1}{2}\) system by defining the Rabi frequency as \(\omega_R = \sqrt{2}\omega_1 S\), the Hamiltonian is once again rewritten [32]:

\[
H_{\text{rot}} = \frac{1}{2} \Delta \sigma_z + \frac{1}{2} \omega_R \sigma_{x'} + \omega_0 I \sum_{i=1}^{N_I} I_z^i + \sum_{i=1}^{N_I} S_z \left( A_{zx}^i I_x^i + A_{zy}^i I_y^i + A_{zz}^i I_z^i \right).
\]

Choosing the low field transition leads to \(\Delta = (\omega_0 S - \omega + D')\)

**The Tilted Rotating Frame**

The applied microwave field with strength \(\omega_1 S\) along the \(x'\) axis will tilt the effective field seen by the electron spin away from the \(z\) axis. Only the component of the electron spin aligned along the tilted field will be available for transfer to the protons. It is thus advantageous to transfer the Hamiltonian once again to a new frame of reference, with its new \(z\) axis along the effective field \(\omega_{\text{eff}}\) (drawn in figure 2.8).

The transformation is done by tilting the old frame of reference around \(y'\), giving the new frame \((\bar{x}, y', \bar{z})\). Introducing the step operators \(\sigma_{\pm} = \sigma_x \pm i\sigma_y\), \(I_{\pm} = I_x^i \pm iI_y^i\) and \(A_{\pm}^i = A_{zx}^i \pm iA_{zy}^i\) and truncating the Hamiltonian averaging over a time period of \(2\pi/\omega\) gives the final Hamiltonian (see [31] for a detailed description).

\[
H_{\text{tilt}} = \frac{1}{2} \omega_{\text{eff}} \sigma_{\bar{z}} + \omega_0 I \sum_{i=1}^{N_I} I_z^i
\]

\[
+ \frac{1}{2} \sum_{i=1}^{N_I} (1 + \cos \theta \sigma_{\bar{z}}) A_{zz}^i I_z^i
\]

\[
- \frac{1}{8} \sum_{i=1}^{N_I} (A_{zx}^i \sigma_{+} I_x^i + A_{zy}^i \sigma_{-} I_y^i) \sin \theta
\]

with \(\omega_{\text{eff}} = \sqrt{\Delta^2 + \omega_R^2}\). The first line is the electron Zeeman interaction, with the Larmor frequency \(\omega_{\text{eff}}\) as seen by the electron in the tilted frame, and the Zeeman interaction of the protons. The second line shifts the energy levels of the triplet state, but does not contribute to the polarization transfer. The last term causes the flip-flop transitions between the electron and the proton spins when the microwave field is applied. The solid effect can then be described by a simple vector diagram as shown in figure 2.9.
Polarization Transfer using the Solid Effect

When polarizing using the solid effect, only the projection of the electron polarization $P_S$ along $\omega_{\text{eff}1}$ can be transferred to the nuclear spins. Furthermore, when an ESR line is broad relative to the proton NMR frequency $\omega_{0 I}$, one also irradiate a second electron spin-package ($N^-_i$), that sees the frequency $\omega_{\text{eff}2}$. However the projection of $P_S$ on $\omega_{\text{eff}2}$ is negative, and the population $N^-_i$ will contribute negatively to the overall polarization build-up. This leads to the equation for the polarization transfer of so called differential solid effect (DSE) [16]:

$$\frac{dP_I}{dt} \propto (N^+_i - N^-_i) \cdot P_S \cos \theta_1.$$  \hspace{1cm} (2.14)

By setting the microwave irradiation frequency off center of the ESR one can nevertheless increase the polarization of the protons. This is due to the fact that the number of electrons in the two spin packages are different. A further problem of the solid effect is that the microwave field, $\omega_{1S}$, must be weak, or else the electron polarization available for transfer ($P_S \cos \theta_1$) to the protons will be too small. As seen from the third term in 2.13, the polarization transfer will be proportional to $\sin^2 \theta$. We then have a situation where the two terms can not be optimized individually.

2.4.2 Integrated Solid Effect

All the above mentioned drawbacks of the solid effect have been overcome by an improved technique of polarization transfer developed by Henstra [8], the so called integrated solid effect (ISE). While applying the microwave field, an adiabatic sweep of the external magnetic field is conducted. The adiabatic sweep through the ESR line locks the electron spins to the effective field $\omega_{\text{eff}}$. This leads to an inversion of the electron polarization because the sweep passes through the whole ESR line, letting the electrons contribute twice to the polarization build-up [16]. The adiabatic sweep includes each single electron spin-package in the polarization transfer, no matter where in the ESR spectrum it is situated. The polarization grows at a rate:

$$\frac{dP_I}{dt} \propto \sum_i N_i P_S.$$  \hspace{1cm} (2.15)
The transferred polarization no longer depends on the strength of the applied microwave field which can be increased up to resonant conditions without losing polarization. The effective field seen by the electron spin-package is slightly modulated by the adiabatic sweep, changing $\Delta$ as seen in figure 2.10.

The transfer of polarization takes place when the electron spin of the fictitious spin $\frac{1}{2}$ system and the surrounding proton spins are on speaking terms ($\omega_{\text{eff}} = \omega_{0I}$). This allows for a resonant polarization transfer taking place in about 200 ns [31] for each spin package. Each single spin package can transfer its polarization twice during the sweep when $\omega_{\text{eff}1} = \omega_{\text{eff}2} = \omega_{0I}$.

**Polarization Transfer**

A rigorous mathematical description of the polarization transfer is a demanding task. One has to consider the polarization transfer between the electron of the triplet state to the protons on the pentacene molecule, each having a different hyperfine constant. Furthermore the polarization transfer goes directly to the bulk, i.e. to the protons on the surrounding naphthalene molecules. The full theory of the integrated solid effect, including all protons in the vicinity of the triplet spin, is currently being developed by Wenckebach. A first attempt has been made by Henstra [32]. We give here his explanation of the transfer of polarization in a simple electron-proton spin system:

In figure 2.10 a level diagram describing the evolution of the energy levels of such a simple one electron one proton spin system during an ISE sweep is shown. Sweeping through the ESR spectrum with the applied magnetic field leads to two crossings where polarization transfer can take place. For a given hyperfine coupling strength, $A_{z+}/A_{z-}$, the polarization transfer between an electron and proton is affected by the speed of the ISE sweep, $\dot{\omega}$, and to a lesser extent the strength of the locking microwave field. Those three parameters determine the probability ($W$) of a polarization transfer to occur at the two crossing points in figure 2.10.

A very fast sweep, indicated by the dashed lines, leads to an inversion of the electron spin while the proton spin remains unchanged, corresponding to a diabatic sweep. An example is the transition from $(+\frac{1}{2}, -\frac{1}{2})$ to $(-\frac{1}{2}, -\frac{1}{2})$, as illustrated in figure 2.11. A too
slow sweep speed will not induce any change in the spins of the electron nor the proton, corresponding to a truly adiabatic sweep. In this case \( (+\frac{1}{2}, -\frac{1}{2}) \) will follow the solid lines conserving the spins of both the electron and proton. Polarization transfer only occurs if one ends up in the state \( (−\frac{1}{2}, +\frac{1}{2}) \) and the transferred polarization is equal to \( 2W(1−W) \).

It is easily seen that the maximum amount of polarization that can be transferred is \( \frac{1}{2} \) \( (W = \frac{1}{2}) \) of the maximum. The probability, \( W \), to jump from one curve to the other in the level diagram is deduced by the Landau-Zener theory and given by Henstra [32] to be:

\[
W = \exp \left( -2\pi \frac{|\frac{1}{2} A_z|}{|\dot{\omega}|} \times \frac{\omega_R^2}{\delta^2 \sqrt{\delta^2 + \omega_R^2}} \right), \tag{2.16}
\]

with the term of the hyperfine interaction \( A_z \) (see equations 2.10 to 2.13 for its derivation) responsible for the transfer of the electron polarization to the protons of the pentacene molecule, \( \dot{\omega} \) the ISE sweep speed and \( \delta = \pm \sqrt{\omega_I^2 - \omega_R^2} \).

However, the polarization can also be transferred directly to the 'bulk', i.e. directly to the surrounding naphthalene molecules. Such a process may play a large role in the total polarization transfer. However the two different transfer mechanisms are difficult to distinguish from an experimental point of view. They both contribute to the growth of the polarization.
3 The Naphthalene-Pentacene Crystal

3.1 The System Pentacene-Naphthalene

The monocrystalline naphthalene crystal is well suited as a matrix for the pentacene molecule. Its crystal structure was determined by Abrahams [34], refined by Cruickshank [35] and recently more accurately determined by Brock and Dunitz [36] (see table 3.1 for its properties). The similarity of the pentacene molecule to the naphthalene lets the pentacene replace two of the naphthalene molecules in the crystal without introducing defects in the crystal. An ESR experiment by van Strien [9] has determined the exact orientation of the pentacene molecule in the naphthalene unit cell. It was found that the pentacene molecule replaces two naphthalene molecules at two different positions in the unit cell, see figure 3.1.

<table>
<thead>
<tr>
<th>Naphthalene Crystal Properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular formula</td>
</tr>
<tr>
<td>Crystal structure</td>
</tr>
<tr>
<td>Space group</td>
</tr>
<tr>
<td>a</td>
</tr>
<tr>
<td>b</td>
</tr>
<tr>
<td>c</td>
</tr>
<tr>
<td>β</td>
</tr>
<tr>
<td>Cleavage plane</td>
</tr>
</tbody>
</table>

Table 3.1: Properties of the naphthalene crystal. The unit cell values are given for 92 K [36].

Figure 3.1: The pentacene molecule replaces the naphthalene at two positions, the one drawn to the left in the figure and the one drawn in the middle. To the right the angles of the crystal are marked. The angle between the a and b axes and between the b and c axes are both 90°.
Important to note is that both the X-axes of the two possible positions of the pentacene crystal make an angle with the c-axis of the naphthalene crystal of about $10^\circ$. The pentacene molecules are thus magnetically equivalent when the magnetic field is oriented parallel to X. The Y and Z axes of the two pentacene molecules are rotated with $47 \pm 3^\circ$ to one another [9], and any other orientation than $X||B_0$ will produce four ESR lines: Two from each pentacene molecule, as seen from equation 2.3 in the previous chapter.

3.2 Crystal Preparation

From previous works by Wenckebach [16], Inuma [17, 37] and Takeda [7] it is known that a pentacene concentration, in the order of $10^{-5}$ to $10^{-4}$ mol/mol, leads to good crystal quality. The naphthalene used for growing the crystals is of $>99\%$ purity and is close to the purest one can buy. However unless further purified, the impurities present will outnumber the added pentacene molecules with a factor of 1000:1 for a pentacene concentration of $10^{-5}$ mol/mo. Fortunately, the low melting point of naphthalene allows for a simple purification procedure.

3.2.1 Naphthalene Purification through Zonerefinement

Originally developed to purify the raw material for producing transistors [38], the method of zonerefinement is applicable to any substance that can be melted under experimentally achievable conditions. For naphthalene, the conditions are rather trivial as it enters its liquid state just above 80$^\circ$C.

Zonerefinement works on the principle that impurities tend to diffuse through the boundary layer of a solid into a liquid. Passing a molten zone through a solid will have the effect of lowering the concentration of impurities in the solid part, pulling them along in the liquid zone. Many zone passes are needed for producing a pure sample. Naphthalene sublimes at room temperature and needs to be purified inside a closed glass tube in order not to lose all of the material. The solid impurities will concentrate at the bottom of the closed tube overtime, while the gaseous impurities will slowly rise through the tube with each zone passing and gather at the top.

For our purpose, a simple zonerefinement apparatus has been built. It consists of a 1 meter long outer glass tube with an inner diameter of 16.0 mm and an outer diameter of 19.8 mm. On the outer tube there are 8 groups of heating wire wound around the tube, glued in place with ceramic glue. Inside the outer tube, a with naphthalene filled thinner tube, is pulled up and down, purifying the naphthalene. The inner tube has an inner diameter of 10.0 mm and an outer diameter of 15.0 mm, just fitting through the outer tube. The length of the inner tube depends on how it was sealed. It is normally around 40 cm long. See figure 3.2 for a schematic drawing of the zonerefinement setup.

The apparatus possess the following design features:

- Eight separate windings of resistance wire mounted on the outer glass tube. Each winding is approximately 40 cm long. The heating wire (RW 45 Resistance Wires) has a resistance of $1.2 \Omega$/meter resulting in a total resistance of $3.8 \Omega$.

- Applying 3 Watts of power on each individual winding melts the naphthalene in the inner glass tube. The heating power is kept low enough that the melting results in localized liquid zones.
3.2. Crystal Preparation

Figure 3.2: Zonerefinement of naphthalene. The inner glass tube is pulled upwards by a stepper motor with a speed of 10 mm/h accumulating the impurities at the bottom. After reaching the top the glass tube is quickly lowered to the bottom and the process repeated. The distance between the center of two heating wire windings is 8 cm.

- Tilting the outer glass tube by $45^\circ$ allows for easy rising and lowering of the inner glass tube, filled with naphthalene. The tilting will also allow any sublimated naphthalene to rise to the top of the glass tube, along with any other gaseous impurity.

- A stepper motor is used to slowly pull the inner glass tube upwards, passing 6 of the 8 windings, with a speed of 10 mm/hour. Once the upper position is reached, the inner glass tube is quickly lowered to its starting position and the process is repeated again.

We have found that for a full purification around 180 single zone passes are needed. Once the naphthalene has been purified, the lower solid impurities and the upper gaseous impurities are cut off. This leaves less than half of the naphthalene to be used, the rest is discarded. The remaining material is extremely pure. While not experimentally confirmed, the concentration of impurities in the part not discarded is estimated to be $<10^{-6}$ mol/mol. This estimation is based on a measurement where the amount of zonerefinement passes was compared to the concentrations of the remaining impurities as a function of the position in the zonerefinement tube [39].

3.2.2 Bridgman Growth

A single crystal of naphthalene (doped or undoped) is grown using the Bridgman technique. This technique shows many similarities with the technique of zonerefinement: A single molten zone is passed through the sample at a speed of around 1 mm/hour, allowing a perfect single crystal to be grown. Part of the dopant can not be incorporated in the crystal and is pushed out, gathering at the top of the crystal. Thus, one needs to start with a higher concentration of the dopant than the desired final concentration. It has been found that the final concentration in the crystal will be around a factor 2 less than what was initially added to the growth ampoule. Producing a concentration higher than $10^{-4}$ mol/mol is hardly possible as one is close to the saturation limit of the naphthalene-pentacene mixture.

The growth ampoule containing the naphthalene and pentacene mixture is passed through a steep and stable temperature gradient slowly growing the crystal at the boundary layer of the solid and liquid crystal. The crystal grows at a temperature which is dependent on the concentration of dopant, in our case around $80^\circ$. A steep enough temperature gradient can be created by heating a container filled with two liquids of different density. The upper liquid, in our case silicon oil, is heated to above $90^\circ$ (pure naphthalene melts at $81.3^\circ$) while leaving the lower liquid, in our case glycerol, at room temperature (see figure 3.3).
The grow ampoule is crucial for the successful growth of a high quality crystal. The ampoule used has a double-wall [40], which has several advantages over a single walled ampoule:

- This ampoule allows the outer cavity to act as seed for the inner cavity, giving the technique its full name of the self-seeding vertical Bridgman technique (SSVBT).

- The outer cavity acts as a thermal insulation, reducing the impact of temperature oscillations on the growth.

- The cone angle of the inner wall of approximately 25° reduces any strain induced on the sample by the glass walls.

- The only improvement made to the original design is the introduction of a second horizontal opening in the ampoule. This allows the inserted naphthalene-pentacene mixture to enter the outer cavity much more efficiently as the gas in the outer cavity, otherwise trapped, can escape.

A growth procedure to increase the quality of the grown doped naphthalene crystal has been suggested [41]: During the growth process, different speeds are used when lowering the ampoule down through the temperature gradient. The growth is initiated by positioning the ampoule in such a way that the entire naphthalene inside the ampoule is liquefied. During the first part of the growth, the ampoule is lowered slowly, with a speed of 0.5 mm/h. During this first part of the growth, a few millimeters of crystals with many different growth directions are formed. The growth speed is then increased during the second part of the growth to 3 mm/h in order to suppress all slow growing crystal directions. Once the inner cavity has been seeded with only one crystal growth direction, which is
necessary for the growth of a single crystal, the speed is reduced down to 1–1.5 mm/h in the last stage of the growth. The final growth speed can be fine tuned to optimize the crystal quality and concentration. The faster the growth speed, the higher the final concentration of pentacene will be, but at higher speeds the risk of imperfections in the crystal also increases.

A detailed step-by-step description of the growth process and pictures of both the zone-refinement and the Bridgman growth can be found in appendix 7.

3.3 Growth Results

During the initial setup and fine tuning of the growth procedure, quite a few growth attempts failed. In these cases the crystal always turned yellow and the pentacene, partially or fully, disappeared. If a very high concentration of pentacene was used, a mixture of the pentacene purple and the yellow colour would appear. This led to the conclusion that the pentacene molecule reacts with another chemical and degrades. The chemical must be present in a limited concentration, otherwise no purple colour would remain even at high concentrations of pentacene. A gas chromatography measurement did not give any conclusive results as to what the yellow impurities could be. Either they were in too low concentrations to be measured, or they degraded during the measurement.

As pentacene is the best candidate for organic thin-film transistors, its properties have been well studied. It has been reported that pentacene degraded rapidly, when exposed to humidity, oxygen, and light all at the same time [42]. This leads to a significant oxidation of the pentacene molecule. Some of the phenols created in the degradation process are indeed yellow.

Initially, it was assumed that the leakage of air during the transfer process of the zone-refined naphthalene into the growth ampoule could be the reason for the degrading of the pentacene molecule. Equally plausible was the introduction of oxygen and humidity during the addition of pentacene to the sample as well as an insufficient cleaning of the growth ampoule. Eventually, a much stronger correlation between the degradation of the crystal to the quality of the added pentacene was found: The use of a new pentacene bottle almost always lead to good growth results suggesting that the pentacene decays rapidly and that its quality is of great importance when growing a pentacene doped naphthalene crystal. One must take extreme care to avoid any air and humidity entering the pentacene bottle as the pentacene will degrade over time.

For the successful growths it was observed that a too high pentacene concentration in the crystal would lead to the agglomeration of excess pentacene molecules inside the crystal, visible as small black spots. We found a strong correlation between finding clusters of pentacene in the crystal and a low quality crystal with short proton relaxation times. Among the crystals grown, four stood out from the rest in terms of colour and size (see appendix 7 for pictures of the difference in colour of crystals #2 and #4). Once a polarization enhancement had been made, the proton relaxation time could be measured, which gives a good indication of the quality of the crystal. See table 3.2 for a summary of the measured crystal properties.

Crystal #2, #4 and especially #7 gave very promising initial results. The highest polarization values measured also came form those three crystals. The reason for the short relaxation time of crystal #6 has not been fully determined, but it is assumed that a paramagnetic species of unknown type must have been incorporated into the crystal during the growth process.
<table>
<thead>
<tr>
<th>Crystal #</th>
<th>Concentration [mol/mol]</th>
<th>Relaxation Time [hours]</th>
</tr>
</thead>
<tbody>
<tr>
<td>#2</td>
<td>$1.5 \times 10^{-5}$</td>
<td>15</td>
</tr>
<tr>
<td>#4</td>
<td>$4 \times 10^{-5}$</td>
<td>7</td>
</tr>
<tr>
<td>#6</td>
<td>$1.2 \times 10^{-5}$</td>
<td>0.5</td>
</tr>
<tr>
<td>#7</td>
<td>$2.0 \times 10^{-5}$</td>
<td>29</td>
</tr>
</tbody>
</table>

Table 3.2: Results of crystal growth for four different crystals. The concentrations were measured by comparing the absorption in liquids to a reference sample and the proton relaxation time after a DNP experiment. The concentration value for crystal #6 is an estimate made by comparing the colour of the crystal to the colour of crystal #2.

Concentration Measurement

It was not possible to accurately estimate the pentacene concentration in the crystal from the weight of the added pentacene alone. Part of the pentacene was always pushed out of the crystal when grown, as outlined in the previous chapter. Instead, we measured the concentrations of pentacene in the crystals by absorption of the crystal in its liquid state. The general law describing the attenuation of light as it passes through a sample is the Beer-Lambert law:

$$I = I_0 e^{-\alpha x}$$  \hspace{1cm} (3.1)

where $x$ stands for the path length that the light travels through the medium and $\alpha$ for the attenuation coefficient, which is proportional to the pentacene concentration.

Using a Varian spectrometer of type Cary 500, a spectrum of the liquefied sample could be measured and compared to a reference sample. The reference sample was prepared using a well know concentration of pentacene, which was then liquefied and the absorption of light around 600 nm measured (see figure 3.4 for such a scan).

Figure 3.4: Graph showing a transmission measurement of the pentacene reference sample in liquid form. By measuring the absorption at 585 nm, marked in the figure, one can calculate the absorption coefficient which depends on the concentration of the pentacene molecule.

Thus by comparing the absorption of the known reference sample to the absorption of
the liquefied crystals, a very good approximation of the pentacene concentration of the crystal can be made. All concentration values have an uncertainty of only ± 10%. The largest uncertainty is due to the degrading of pentacene during the measurement. One can not avoid getting air and humidity into the cuvette, and applying light means that the conditions for a fast degrading of the pentacene is created. However, the drop in absorption could always be fitted by an exponential decay curve and the final error stems mainly from the fit itself.

3.4 Cutting and Mounting

When cutting and mounting the crystal in a cryostat, the crystal must be oriented with \( X \parallel B_0 \), as explained in chapter 2. Once the direction of the pentacene \( X \) axis has been determined, the crystal is cut into a cubical shape. The reason why a cubical shape is preferred is that once the crystal is put in a neutron beam the pathway through the crystal seen by the neutrons needs to be equal which ever part of the crystal the neutrons penetrates. Thus, only small errors of a couple of degrees are allowed when cutting the crystal. Furthermore, it becomes impossible to find the \( X \parallel B_0 \) orientation if the crystal is mounted in such a way that the \( X \) axis is turned out of the plane of rotation (a plane of rotation that is determined by the mounting of the sample in the cryostat). See figure 3.5 for a picture of a mounted crystal with the magnetic field, neutron beam and laser light indicated in the figure.

![Figure 3.5](image.png)

The process of cutting and mounting the sample is not trivial: Refer to figure 3.1 for the relation between the crystal axes and the pentacene \( X \) axis. One normally starts with finding the cleavage plane (the a-b plane) of the crystal. Finding and cutting along the cleavage plane on both sides of the crystal piece will allow one to observe the birefringence through the crystal. By watching the birefringence one finds the optical plane of the crystal, which equals finding the a-c plane of the crystal. See the next subsection for a detailed description of how it is found. Finally, by finding the optical axis of the crystal, one can find the orientation of the pentacene \( X \) axis in the crystal.

As seen from figure 3.1, cutting along the a-c plane produces a plane in which the \( X \) axis resides. However, throughout numerous cutting and mounting procedures it has been found that the initial cut along the a-c plane is prone to errors. The errors stems mainly from the difficulty to accurately determine the position of the a-c plane by watching the birefringence of the crystal. If one instead makes a second cut along the X-b plane the impact of the error of the first cut can be reduced. Even if a large error in cutting along the a-c plane did occur, it can be corrected once the crystal has been mounted by rotating the
crystal in the magnetic field. The reason that the second cut can be made more accurately, is that one uses the cleavage plane, a perfectly cut and defined side of the crystal, as a reference when cutting along the X-b plane, minimizing the errors made. This approach includes an extra step in the cutting process while reducing the risk of errors and especially the risk of mounting the crystal with a deviation out of the horizontal plane.

### 3.4.1 Cutting Procedure

A detailed description of how to cut the crystal along the X-b plane is given here:

1. The initial step is to find the cleavage plane of the crystal. This plane is spanned, as seen in figure 3.6a, by the a and b axes of the crystal.
   - By carefully pressing a scalpel against the side of the crystal one can incite the crystal to break along the cleavage plane.

2. After cutting the crystal along the cleavage plane on both sides, the crystal a-c plane is found and cut by observing the birefringence of the crystal.
   - The axes describing the refractive index of a crystal \((x,y,z)\), normally referred to as the indicatrix, is needed to explain how the orientation of the crystal is found by observing the birefringence of the crystal.
   - The y axis of the optical indicatrix of naphthalene coincides with the b axis of the naphthalene crystal, while the x axis lays in the a-c plane, rotated \(23.3°\) above the a axis \([43]\). This puts the z axis around \(10°\) of the c axis, by pure coincidence, almost parallel to the X axis of the pentacene molecule.
   - Viewing a thin line drawn on a paper through a birefringent crystal will produce two parallel lines (see the pictures in appendix 7 for a visualization), unless viewed in the optical plane where the two lines overlap. This plane is spanned by the x and z axes of the optical indicatrix \([43]\) translating to the a-c plane of the naphthalene crystal. Thus rotating the crystal until only one line is seen and cutting the crystal along this line is the same as cutting the a-c plane of the crystal.

3. With the a axis, and thus also the b-axis, found in the cleavage plane, the next step is to find one of the two optical axes of the crystal and thereby the direction of the crystal c axis and the pentacene X axis.
   - An optical axis is the axis where the refractive index seen by a light wave entering the crystal remains constant for any polarization of the light. Thus finding the axis where a single dot drawn on a piece of paper is not duplicated, i.e. no noticeable effect of birefringence, equals finding one of the two optical axes.
   - The optical axes always lay in the x-z plane by definition. For a single naphthalene crystal, the angle the two optical axes make with the z axis is \(±41.5°\). This is easily calculable from the refractive indexes of naphthalene given in \([43]\). This puts one optical axis between the a and c axis as drawn in figure 3.6b and the other between the negative a axis and the c axis. The second optical axis lies close to parallel to the a-b plane. One can thus easily distinguish the two optical axes, making it easy to find the true crystal orientation.

4. Once the direction of the pentacene X-axis is known, the crystal is flipped on its side with the a-c plane facing downwards and cut along the X-axis, using the cleavage plane as a reference point.

5. The final step, shown in figure 3.6c, is to cut the crystal into a cubical shape and mount it in a sample holder so that one can rotate the sample around the normal of the plane spanned by the X and the b axis. Once mounted, the final alignment of the X-axis in the magnetic field is made by observing the ESR signal, maximizing it for a frequency shift of 753.5 MHz as given by equation 2.4 for \(X||B_0\).
Figure 3.6: Alignment and cutting of the crystal is done by first finding and cutting along the cleavage plane, a-b. The optical axis is then found by observing the birefringence of the crystal. The crystal is cut along the a-axis (not shown in the figure) and then flipped on its side to be cut along the X-axis. The angle the pentacene X-axis makes with the a axis is known [9], and the crystal is cut into its cubical shape with one side being the pentacene X-axis.
4 Experimental Apparatus

In this chapter, we give an overview of the apparatus used in the ESR and DNP experiments. It consists of the following main components:

- An optical setup with an optical parametric oscillator generating light at 600 nm, pumped by a frequency tripled Nd:YAG. The light is delivered to the cryostat through an optical fiber that is connected to the bottom of the cryostat.

- A continuous flow Helium cryostat that operates between 4 K and 300 K and is suited for experiments on a neutron beam.

- An electro magnet capable of reaching 0.63 T.

- A unique X-band pulse ESR/DNP spectrometer built to give full freedom in designing the ESR and DNP pulse sequences.

- An insert with an ESR cavity consisting of a dielectric ring resonator structure.

- A pulse NMR spectrometer to measure the nuclear polarization using two different NMR coils.

- A system to generate the field sweep used in the ISE DNP.

Furthermore, we describe how to optimize the ISE sequence to obtain the highest rate of polarization growth possible. Finally, we give the protocol of the experimental procedure that is used during a normal experiment: from mounting and cooling the crystal to obtaining the NMR signal of a polarized sample.

4.1 Laser Setup

The optimum wavelength to excite the pentacene molecules into their excited singlet state is close to 600 nm. Unfortunately, no single laser operating at this wavelength exists, and we use instead a Nd:YAG together with an optical parametric oscillator [44] (OPO). The pulsed Nd:YAG laser (Quanta-Ray PRO 270 from Spectra-Physics) operates at the third harmonic wavelength of 355 nm. The OPO (PremiScan 400 BB from GWU-Lasertechnik) converts the light of 355 nm, producing light at 600 nm. The light output from the OPO is tunable in the range of 520 to 620 nm by angle tuning of a nonlinear BBO crystal. The input beam, normally referred to as pump, is converted into two new frequencies called signal and idler through wave-vector matching. The idler and any remains of the pump beam are filtered out by the optics inside the OPO, and only the signal is guided to the experiment. The frequencies of the signal, idler and pump are governed by a simple relation:

$$\omega_P = \omega_S + \omega_I$$  \hspace{1cm} (4.1)  

It is the geometrical limits of the BBO crystal that determines the effective range of wavelengths one can generate.

The OPO is aligned in such a way that the laser light from the pump laser is reflected directly back into the laser. This arrangement is needed to be able to align the oscillator...
of the OPO for the highest conversion efficiency. As a result, the reflected pump laser beam heats up the harmonic crystals of the Nd:YAG laser. When optimizing the entire setup, the heating of the harmonic crystals in the Nd:YAG laser has to be compensated in an iterative process. Each adjustment of the harmonic crystals of the laser is followed by a slow thermalization. This is due to the fact that the harmonic crystals heats up due the increase in laser power being reflected back at them. When starting up from cold, the system takes about 30 min to stabilize and reach its highest output.

Once thermalized, the output of the OPO is in the range of 10–20 mJ depends on how well the OPO resonator is aligned with the incoming pump light. The repetition rate of the laser is 30 Hz and the energy of the pump laser is typically 230 mJ per pulse, putting the total input power into the OPO at 7 W, and the output power of the signal close to 0.6 W. It could be set far higher, but the sensitive optical parts of the OPO would be at risk of burning. See table 4.1 for a list of the laser and OPO parameters.

<table>
<thead>
<tr>
<th>Nd:YAG pump laser</th>
<th>OPO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Model</td>
<td>Quanta-Ray PRO 270-30 PremiScan 400 BB</td>
</tr>
<tr>
<td>Repetition Rate</td>
<td>30 Hz set by pump</td>
</tr>
<tr>
<td>Wavelength</td>
<td>355 nm 520–620 nm</td>
</tr>
<tr>
<td>Line Width</td>
<td>&lt; 1 cm$^{-1}$ 30 cm$^{-1}$</td>
</tr>
<tr>
<td>Pulse Energy</td>
<td>~230 mJ 10–20 mJ</td>
</tr>
<tr>
<td>Pulse Length</td>
<td>12 ns 12 ns</td>
</tr>
</tbody>
</table>

Table 4.1: Parameters of laser setup used in the DNP experiments presented in this thesis.

To deliver the laser light to the cryostat, positioned 20 meters away, an optical fiber is used. The output from the OPO is originally polarized but loses its polarization as it passes through the multi-mode fiber. However, the polarization of the light can be used in order to add tunability of the laser power as well as to allow a more complex optical setup where more than one experiment can be run in parallel. See figure 4.1 for a schematic drawing of the laser setup.

![Figure 4.1: Basic blockdiagram of laser setup. Marked in the figure is the λ/2 plate (1), the polarizing beam splitter cube (2) and the fiber coupling (3). The fiber delivers the laser pulse to the insert in the cryostat in a different room 20 meters (of fiber) away.](image)

By tuning the λ/2 plate, the amount of light sent down into the fiber can be controlled continuously. In principle, the pump laser could also be controlled by tuning the power sent to the laser flashlamps. However, this is not recommended, as the thermalization of the laser would lead to unwanted drifts in the laser power. Any light sent into the second beam line can be used for other experiments. If no such experiments are performed, the beam is sent into a dump to avoid dangerous scattered light. The entire laser table has been covered in a black aluminum housing as an extra layer of protection.

The laser pulse energies given in table 4.1 are the energies just behind the OPO. The power that reaches the sample will be less: Coupling into the fiber will result in a loss of 20% of the full energy measured at the far end of the fiber. An additional 4% of the laser energy will be lost at each of the four surfaces of the two cryostat windows (see
Finally, perfectly matching the circular beam on a square target will lead to a further loss of a factor $\sqrt{2}$. In total, only roughly 40% of the OPO output will actually reach the sample. This corresponds to laser pulses in the energy range of $5 - 10 \text{ mJ}$.

In our setup, the laser triggers the rest of the experimental setup. It sends out a trigger at the same time as the oscillator flashlamps fire. The time delay between the flank of the oscillator signal and the laser pulse has been measured and is used to time the entire ISE sequence. The delay varies slightly with the fine tuning of the Q-switch delay, a fine tuning done to optimize the laser output, but it normally is in the range of $180-190 \mu s$.

### 4.2 Cryostat and Insert

#### 4.2.1 The Cryostat

The $^4\text{He}$ flow cryostat has been designed and built at PSI by the Polarized Target group and is especially suited for experiments on neutron beams. The part of the cryostat where the neutrons pass is completely made out of aluminum, transmitting more than 90% of the neutrons. The laser light needed to excite the pentacene molecules enters the cryostat from the bottom through two sapphire windows. Cold helium gas is fed through a sinter and cools the sample to any temperature in the range between 4 K and 300 K. The insert consists of a top flange, a baffle system with support structure for the ESR cavity and coaxial lines to the NMR coils and ESR antenna (see subsection 4.2.2 for a detailed description).

A drawing of the cryostat and insert can be seen in figure 4.2. The cryostat has a height of 467 mm and an outer diameter of 65 mm fitting inside the 68 mm wide bore of the electromagnet used (see section 4.3). The amount of aluminum that the neutron beam has to pass through has been minimized in order to keep the attenuation of the neutron beam at a minimum. At the height of the neutron beam, the cryostat has an outer wall thickness of only 1.5 mm. A very thin aluminum radiation screen is positioned inside the outer walls followed by a 0.5 mm thick inner wall with an inner diameter of 49 mm. A neutron beam that passes through the cryostat thus passes through 4 mm of aluminum. The outer wall of the cryostat is one solid piece of aluminum. The inner tube consists out of stainless steel in the upper part to increase the stability of the cryostat, and aluminum in the lower part where the neutrons pass through. This is possible by the use of a stainless steel-aluminum friction weld. A copper piece filled with a sinter heat exchanger is glued to the lower end of the tube.

The two sapphire windows that the laser light is fed through are 2 mm thick, have a diameter of 20 mm and are sealed with indium. A mounting for the optical fiber, centered over the sapphire windows, with a focusing lens pressed against the outer glass window, has been constructed. An index matching gel is used to reduce reflections of the laser light between the lens and window. By moving the fiber back and forth relative to the lens, a fine adjustment of the fiber position can be made. The optimum distance between the end of the fiber and the lens is found by maximizing the ESR signal. This corresponds to optimizing the laser beam spot on the sample.

A 340 Temperature Controller from Lakeshore stabilizes the temperature through a PID control, applying heat over three in parallel coupled strain gauges of 120 $\Omega$ each, glued to the outside of the copper part of the cryostat. The temperature is measured by a temperature sensor attached to the bottom of the inner wall in a position close to where the helium is fed into the inner cavity. The helium gas is pumped into the cryostat through a stainless steel flexible syphon from Oxford Instruments that is inserted into a helium dewar. A needle valve on the syphon regulates the flow of helium gas. The cold
Figure 4.2: The cryostat (left) with a) an aluminum radiation screen, b) the inner stainless steel wall of $\phi 49 \text{ mm}$, c) an electron-beam weld, d) a friction weld, e) aluminum tube f) SMA-mounting for the laser fiber and two sapphire windows, g) a double helium inlet and h) a sinter heat exchanger. The insert (right) with i) sample holder and positioner, j) the SMA throughput sending the ESR pulses down into the ESR antenna, k) connectors for the NMR coils, l) connections for the ISE sweep, m) supports for positioning the insert, n) the NMR coil used for measuring the thermal equilibrium signal, o) the sapphire dielectric ring (DR) resonator, p) the ISE sweep coil and q) the integrated NMR coil mounted on the Teflon piece which holds the DR in place inside the ESR cavity. The coaxial lines between the NMR coils and the ISE sweep to the outside connectors are not shown.
helium gas is fed through a capillary that passes between the radiation screen and the inner wall of the cryostat before it reaches the sinter heat exchanger made out of brass. The helium is passed through the sinter where it assumes the desired temperature before reaching the sample. Around 4 liters of helium gas per minute are needed to keep the temperature stable at 100 K. The liquid helium needed to operate the cryostat is stored in a dewar with a capacity of 100 liters. It last around 10 days in continuous operation, which is ideal for experiments on a neutron beam line where exchanging the dewar can be difficult. Cooling down the sample requires more helium during a short period of time before it stabilizes to a value between 0 and 41/min. The amount of helium used depends on the amount of heat applied through the strain gauges. A higher flow leads to a more efficient cooling of the sample, but also a faster consumption of the helium. It has been found that applying a heating power of 0.3 W for stable operations at 100 K gives a good compromise. This corresponds to a helium flow of around 41/min. The actual cool down takes around 2 to 3 hours as can be seen from figure 4.3.

![Figure 4.3: The cooldown of the cryostat and the corresponding helium consumption.](image)

Due to the distance between the thermometer and the sample, a slightly higher temperature can be assumed for the latter. Measurements done inside the ESR cavity during steady state operations at 100 K (with no laser applied) indicate a temperature difference of around 2 K. Once the laser is turned on, the temperature of the sample can be expected to rise if the cooling is not sufficient. No direct measurement of the temperature inside the sample can be made, but during measurements of thermal ESR signals of the free radical TEMPO (see chapter 5.4), we did not observe any heating at temperatures above 80 K.

### 4.2.2 The Insert

The insert consists of a flange with feedthroughs for the electrical connections leading down to the lower part of the insert where the ESR cavity, ISE sweep coils and NMR coils are mounted. The two parts are joined together by two metal rods stabilized by four brass baffles, as already shown in figure 4.2.

The sample is mounted in a Kel-F (chlorotrifluoroethylene) holder (see figure 3.5) and can be brought in place (moved along and rotated about the vertical axis) by a sample stick of
$\varnothing 7 \text{ mm}$ through a port in the top flange. The ESR cavity, based on the design presented in [45], is mounted at the bottom of the insert and positioned so that the center of the ESR cavity is on the height of the neutron beam. A longitudinal cross-section showing all the parts of the ESR cavity is shown in figure 4.4.

![Diagram of the ESR cavity](image)

**Figure 4.4:** The lower part of the insert with 1) mounting for the crystal holder, 2) the soldering between the coaxial line (3) with the ESR antenna mounted at the bottom and the sliding brass cylinder (4), 5) the integrated NMR coil, 6) the top and bottom brass pieces which form the ESR cavity together with the brass cylinder, 7) a more sensitive NMR coil where thermal equilibrium signals are measured, 8) the Teflon holder of the ISE sweep coil (marked with 9), 10) the sapphire dielectric ring resonator and 11) the outer aluminum cup that holds the entire construction together.

The ESR cavity consists of a dielectric ring (DR) resonator made of sapphire with a dielectric constant of $\epsilon = 10$ and a surrounding brass cylinder. The DR resonator is 13 mm long with an inner diameter of 7 mm and an outer diameter of 11 mm. This allows for a sizable crystal ($5 \times 5 \times 5 \text{ mm}$) to fit inside. A sliding brass cylinder together with two brass end pieces forms the cylindrical TE011 cavity with a diameter of 20 mm and a length of 47 mm. Resonances can be expected to be found anywhere in the range 8.9–9.5 GHz for this structure. The sliding cylinder is soldered to the coaxial line that sends the ESR signal into the cavity via the ESR antenna. The antenna consists of a 1/3 loop extending through a hole in the brass cylinder. The antenna has been arranged to follow the circular electric field in the dielectric ring. The coaxial line can be moved up and down by pulling on the part of the coaxial line extending up through the flange. The ESR cavity resonance is tuned and matched by moving the ESR antenna, and thus also the brass cylinder, up and down. The dielectric ring is positioned and held in place inside the brass cavity by two Teflon holders. A metal spring, positioned at the bottom of the ESR cavity between two brass pieces, fixes the Teflon holders and the dielectric ring in place. The spring compensates for the shrinking of the Teflon used in the cavity as the insert is cooled down. All parts of the cavity are held together by an aluminum cup. See appendix 7 for pictures of the insert and the ESR cavity.

One NMR solenoid coil is mounted on the lower one of the two Teflon holders inside the cavity. It is used to monitor the enhanced proton polarization. The coil degrades the quality factor of the cavity to a value around 300 at a resonance of 9.3 GHz, which is still sufficient for our purposes. Just above the ESR cavity, a second more sensitive NMR solenoid coil is mounted. The coil is used to measure the thermal equilibrium (TE) signal...
of the sample. Both NMR coils are matched and tuned by circuits positioned at the top of the ESR cavity. A ISE saddle coil producing the fast field modulation for the ISE sweep is mounted on a Teflon holder that is positioned around the ESR cavity (see section 4.5).

4.3 Magnet

For the experiments we used a water cooled low impedance electro magnet of type Varian V3706 driven by a E2903 power supply. It is capable to reach 630 mT. The magnetic field is stabilized by a LakeShore 475 DSP Gauss-meter which in turn is controlled by the lab computer where the desired field can be set.

4.4 The ESR/DNP and NMR Apparatus

4.4.1 Effect of an ESR/NMR Pulse on Spin $\frac{1}{2}$-Particles

When performing ESR and NMR measurements on electrons or nuclei, it is always an ensemble of spins that is manipulated and measured. Limiting ourself to protons in the case of NMR or electrons in the case of ESR, the spin $\frac{1}{2}$ particles, once aligned in a magnetic field, occupy one of two energy levels, normally labeled $\alpha$ (up) and $\beta$ (down). A sample in thermal equilibrium will always show a small excess of spins in the lower energy level, leading to a net magnetization $M$ of the sample. This magnetization aligns with the static magnetic field until a pulse is applied. The pulse tilts the magnetization vector away from equilibrium and it begins to precess around the magnetic field with the Larmor frequency (42 MHz/T for protons and 28 GHz/T for electrons). As described in the theory chapter, it is advantageous to transfer to a rotating frame, here indicated by x, y and z, that rotates with the magnetization vector. In this rotating frame, the visualization of each pulse becomes surprisingly simple. Applying a pulse along the x axis will tilt the magnetization towards the -y axis as shown in figure 4.5.

By choosing the strength ($\omega_1 = \gamma B_1$) and length ($t_P$) of the pulse, one can control the tipping angle $\theta$ the magnetization vector rotates with. The angle is given by $\theta = \omega_1 t_P$. Flipping the magnetization vector to align with the -y would require a pulse along the x axis flipping the magnetization vector $90^\circ$, written $90^\circ_x$ in short form. One can, by changing the phase of the excitation pulse, flip the magnetization down anywhere in the x-y plane. The phase is not an absolute phase, but given relative to a reference frequency. Shifting the pulse frequency with $90^\circ$ to align with the y axis would
flip the magnetization vector down towards the x axis. In our case, it is only important to be able to shift the frequency in jumps of $90^\circ$. For NMR measurements, it is normally sufficient to apply a $90^\circ$ pulse and measure the free induction decay (FID) to record a signal. The spin-spin relaxation of the protons in naphthalene is on the order of tenths of microseconds, as can be seen from figure 4.6 where a typical (enhanced) FID signal can be seen.

The free induction decay (FID) for the electrons of the triplet state of pentacene on the other hand is too fast for the ESR signal to be measured by a simple $90^\circ$ pulse. In our case, it will be buried by the ringing of the ESR cavity. Instead, one of the most simple multi-pulse sequences available is applied: an electron spin echo (ESE) sequence. The ESE sequence consist of one $90^\circ_x$ pulse followed a time $\tau$ later by a refocusing pulse $180^\circ_y$. The first pulse flips all of the electrons down along the -y axis. Due to inhomogeneous effects in the sample different electron spins will have slightly different Larmor frequencies, and the magnetization vector will spread out in the x-y plane. The second pulse inverts the magnetization vectors, letting them refocus after a further time delay of $\tau$.

**4.4.2 ESR/DNP Pulse Shaping**

When applying an ESR or DNP pulse sequence, the setup is set to wait for the trigger sent from the laser before initiating the pulse sequence. The simple electron spin echo (ESE) pulse sequence will serve as an illustration of how the pulsing is sequenced: For the ESE pulse sequence, one needs to set the pulse lengths of the two pulses ($t_1$ and $t_2$), the time delay ($\tau$) in between the pulses and the microwave pulse strength $\omega_{1S}$. The actual pulse shaping and acquisition sequence is shown in figure 4.7.

Once initiated, the pulse sequence runs one full loop until it arrives back waiting for the next trigger. This continues until a predetermined amount of measurements have been acquired.
4.4. The ESR/DNP and NMR Apparatus

4.4.3 Detection of an ESR Signal

To detect a FID or echo signal a technique called quadrature detection is used. This allows to distinguish between negative and positive frequencies relative to the pulse frequency. By measuring on two channels, phase shifted by 90°, one records both the real and the imaginary part of the signal. The phase shifting and demodulation of the signal is done by the ESR spectrometer. The real and imaginary signals are then acquired and digitized. Transferring the recorded signal to the frequency domain through a fast fourier transform (FFT) gives two signals: the real (absorptive) and the imaginary (dispersive) signal. Generally, the two signals are mixtures of real and imaginary components, and a phase shift needs to be added after the FFT to extract the real and an imaginary signal as shown in figure 4.8.

4.4.4 ESR System

The ESR spectrometer has previously been explained in full detail in the thesis of Jannin [46] and only the information needed to understand its functions will be given here. A blockdiagram of the electronics inside the spectrometer is given in figure 4.9. The PCI board, a spincore PulseBlasterESR-PRO card, controls most of the parameters used in an ESR/DNP sequence directly. Only the ISE sweep settings and the microwave strength are set separately. The card communicates with the spectrometer via a 25-pin D-sub cable. The microwave frequency, generated by a synthesizer (QuickSyn FSW-0010), is fed into the spectrometer where the actual pulse shaping is done. The continuous-wave (CW) microwave frequency is sent through a power divider, one part used in the later demodulation, and the other part sent to a quadrature phase-shift modulator which shifts the frequency in steps of 90°, controlled by two TTL signals. The phase shifted microwave frequency is then sent through a mixer where the frequency is mixed with a DC voltage...
Figure 4.8: Real and imaginary signal recorded using an ESE sequence on pentacene in a naphthalene sample.

Figure 4.9: Blockdiagram of the ESR spectrometer which allows for nanosecond pulse forming (Switches), 4 different phases (QPSK Modulator) and a variable attenuation of the pulses (Mixer). The layout of the blockdiagram mimics the physical layout of the components as seen in figure 4.10. The ESR spectrometer was originally described in the thesis of Jannin [46] and has been designed by J. J. van der Klink.
from channel 2 on the DAC unit, attenuating the microwave power if a low voltage has been set on the DAC. The CW microwave is sent through two switches, shaping the pulses that are finally fed out from the spectrometer. The length of the shortest obtainable pulses is 12 ns with a resolution of 2.5 ns given by the 400 MHz clock frequency of the card. The output of the ESR spectrometer is amplified by two X-band amplifiers coupled in parallel (Aethercomm SSPA 8.5-9.6-30). Their maximum power has been measured to be close to 50 W. The echo signal is pre-amplified (MITEQ AFS3-08501160-09-S-4) before it is sent back to the spectrometer where the frequency is demodulated and separated into a real and an imaginary part. A high speed 8-bit digitizer (Agilent U1071A) acquires and digitizes the signal which is stored on the computer. Figure 4.10 shows a picture of the front and back side of the spectrometer as well as the electronics inside.

On the front side of the ESR spectrometer, the input and output connections for the microwave frequency and the connection for the signal from the ESR cavity can be found. On the back side of the spectrometer, the connections for the 25-pin D-sub cable and the usb cable to the DAC unit are found. Note that there are several further BNC connectors which provide TTL signals to control different parts of the hardware, triggering the ISE sweep, the power amplifiers and the signal pre-amplifier.

### 4.4.5 The NMR System

NMR is performed with a system based around a Spincore RadioProcessor card. The card both shapes the NMR pulses and records the NMR signal of the sample. The generated pulses are amplified by a pulse amplifier (250 W TOMOCO RF). The proton
signal is amplified by two Miteq preamplifiers (AU-1327 and AU-1466) before being sent back to the NMR card and recorded. In order to increase the signal to noise ratio, a bandpass filter (SIF-21.4+) and a low pass filter (SLP-30+) (both from Mini-Circuits) are used. In the event that the amplified proton signal would saturate the NMR card or the preamplifiers, a set of variable attenuators positioned just before the preamplifiers are used. Two separately tuned and matched coils measure the proton NMR signal of the sample. The upper coil with 25 windings and a diameter of 7 mm, situated just outside the ESR cavity, is tuned to 24.2 MHz. It is used due to its high sensitivity for measuring the thermal equilibrium signal of the sample. The sample can easily be moved between the ESR cavity and the NMR coil by sliding on the sample stick. The lower coil with 6 windings and a diameter of 15 mm has been tuned to 22.8 MHz and is positioned inside the ESR cavity, as shown in figure 4.4. The coil is employed to be able to monitor the enhanced polarization during the experiment.

In order to get the highest signal to noise ratio, the monitor coil should conserve the polarization and much weaker NMR pulses with a tipping angle of 3–4° are used. The weaker pulses still produce extremely strong signals as one is measuring proton signals enhanced thousand fold over the TE signal. The weak TE signals are measure with a full 90° pulse on the upper coil. See figure 4.11 for a comparison between the thermal signal of crystal # 7 and a scaled enhanced signal.

Both coils show a pulse to pulse error of ±2%. They are carefully cross-calibrated at the end of each experimental run. A typical calibration factor between a 1.5 µs (90°) pulse on the upper coil and a 500 ns (4°) pulse on the lower coil has been measured to 280 ± 35.

4.5 The ISE System

The fast field sweep required for the ISE is produced by a saddle coil of 18 turns, positioned just outside the ESR cavity. It is directly connected to an analog amplifier (Servowatt DCP390/30 AX) and driven by an arbitrary waveform generator (Aglient 33250A). The waveform generator is preprogrammed with a waveform, approximately drawn in fig-
4.5. The ISE System

Figure 4.12, and triggered by a TTL pulse from the ESR card. The ISE sweep can be manually altered by two parameters, set on the waveform generator. The sampling frequency sets the speed with which the waveform is read, thus shortening or lengthening the sweep. The peak to peak voltage (Vpp) changes the amplitude of the waveform. Setting a high voltage gives a large sweep range, and as a result a fast sweep speed. The analog amplifier is capable of producing a maximum of ±15 A, giving a field modulation of ±6 mT. The sweep trigger (figure 4.12) is generated by the ESR card a set time after the initial trigger from the laser, starting the pre-programmed ISE sweep. The sweep is timed so that the laser pulse arrives just as the magnetic field starts to sweep. Immediately after the laser pulse has created the triplet states a microwave locking pulse is applied. The locking pulse is kept high until the magnetic field sweep has finished sweeping through the ESR line. The entire sequence shown in the figure is repeated with a rate of 30 Hz and typically, after 54000 pulses (corresponding to half an hour of ISE), the ISE build-up is stopped, the magnetic field shifted to the NMR frequency and a NMR signal recorded before the ISE sequence is continued.

4.5.1 Optimization of the ISE Sweep

To characterize and optimize the parameters of the ISE sweep, several different experiments are performed on the sample. One needs to optimize the timing of the sweep, the sweep speed and the microwave locking power. Here, a standard protocol developed for the optimization of the ISE yield is given. Important to note is that a prerequisite for the optimization is a naphthalene-pentacene crystal of good quality well aligned in the magnetic field, and a measured ESR spectrum.

- First, the shape of the ISE sweep is determined the following way: The trigger for the sweep relative to the arrival of the laser pulse is shifted stepwise. For each value of the start of the trigger pulse, the value of the static magnetic field that gives the largest ESR signal is found. If, e.g., the static field needs to be increased by 3 mT to maximize the ESR signal, the ISE sweep is generating a field of -3 mT. The center of a typical generated sweep can be seen in figure 4.13.

- Once the structure of the ISE sweep is know, the timing of the ISE sweep relative to the laser pulse can be optimized. The sweep is timed so that it passes through the ESR line directly after the triplet states have been created in order not to allow the
electron polarization to decay. A calculation of the optimum timing was performed taking into account the shape of the ESR spectrum, the measured decay of the triplet state and the structure of the ISE sweep. The measured ESR spectrum is divided up into narrow bins and the estimated time for the ISE sweep to reach each bin is obtained from a measurement of the ISE sweep timing such as the one shown in figure 4.13. The reduced population and alignment of the triplet state that remains once the ISE sweep reaches a specific bin is calculated from the measured decay (see figure 5.9 for such a measurement). The result of the calculations is a weighted ESR spectrum and integrating over it produces the lines for four different ISE sweep speeds seen in figure 4.14 (the lines have been scaled to an actual measurement). One sees that the simulation is in good agreement with the experimental results as long as the ISE sweep starts outside the ESR line. As the starting point of the ISE sweep is moved through the ESR line, less electrons will be locked by the adiabatic sweep, and a mixture of the solid effect and the integrated solid effect will occur.

- Once the sweep timing is optimized, measurements of the enhanced polarization as a function of the ISE parameters, controlled by the waveform generator, can be performed. Figure 4.15 shows a measurement where the achieved enhancement has been compared to the ISE sweep speed. The sweep becomes non-adiabatic when a sweep speed of above 0.4 mT/µs is used. A too slow and narrow sweep excludes the edges of the ESR signal and lets the polarization of the triplet state decay before the polarization can be transferred. It was found that a sweep speed of around 0.3 mT/µs gives the best polarization enhancements.

- Finally, the optimum microwave power needs to be found. The optimum power should be close to, but not above, the power that equals to the Hahn-Hartman condition. Otherwise no polarization can be transferred. As seen from figure 2.10 in chapter 2.4.2, a too weak microwave pulse power will lead to a shorter interaction time between the electron and proton spins, leading to a less efficient polarization transfer. For a too large microwave field amplitude $B_1$, the Hahn-Hartman condition...
4.5. The ISE System

Figure 4.14: Simulation of the ISE efficiency for different ISE sweep speeds; 1: 0.53, 2: 0.27, 3: 0.13 and 4: 0.074 mT/µs. The red dashed curve represents the ESR spectrum of crystal #2 with $X||B_0$. The circles have been measured for a sweep speed of around 0.27 mT/µs.

Figure 4.15: Effect of the sweep width on the obtained polarization. The optimum speed is typically close to 0.3 mT/µs. All sweeps lasted 15 µs.
Experimental Apparatus

(\omega_{\text{eff}} = \omega_I$, see section 2.4.1) is never fulfilled during the sweep. By shortly polarizing the sample with different microwave powers and measuring the NMR signal enhancement the optimum conditions for the polarization transfer are found experimentally. For each microwave power setting, $B_1$ is found by measuring the 90° pulse length:

$$\sqrt{2}\gamma_S B_1 t_{90°} = \frac{\pi}{2}$$

Here the factor $\sqrt{2}$ comes from the spin 1 system as described in the theory chapter, and $\gamma_S$ is the electron gyromagnetic ratio. Figure 4.16 shows the NMR signal enhancement as a function of the microwave power.

![Graph showing the NMR signal enhancement as a function of $B_1$](image)

Figure 4.16: Optimization of the ISE locking power. The Hartman-Hahn condition is achieved at a $B_1$ of 0.33 mT, as can be seen in the sharp drop in polarization transfer happening around this value. The ISE sweep speed is 0.32 mT/\(\mu\)s.

### 4.5.2 Standard ESR and DNP Settings

The standard experimental settings used in the ESR and DNP experiments reported in this thesis are given in table 4.2 for later reference. If not otherwise stated, these settings are used to measure the reported ESR and DNP values.
### Table 4.2: List of typical experimental parameters used in the ESR and ISE measurements reported in this thesis.

<table>
<thead>
<tr>
<th>Experimental Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>ESR Magnetic Field</td>
<td>310 mT</td>
</tr>
<tr>
<td>Microwave Frequency</td>
<td>9.3 GHz</td>
</tr>
<tr>
<td>Microwave Power</td>
<td>~0.2 mT</td>
</tr>
<tr>
<td>NMR Magnetic Field</td>
<td>~550 mT</td>
</tr>
<tr>
<td>NMR Frequency</td>
<td>~23 MHz</td>
</tr>
<tr>
<td>NMR Pulse Length</td>
<td>0.5–1.5 µs</td>
</tr>
<tr>
<td>ISE Sweep Rate</td>
<td>0.3 mT/µs</td>
</tr>
<tr>
<td>Sample Temperature</td>
<td>100 K</td>
</tr>
</tbody>
</table>

#### 4.6 The Experimental Control Program

In order to perform ESR and DNP experiments on a pentacene doped naphthalene crystal, several experimental components working in unison are needed. The task of controlling and coordinating is done by an instrument control software written in LabVIEW. The LabVIEW program is split into several subprograms, each dealing with different tasks. A diagram of the data flow between the program and the individual components is shown in figure 4.17.

As indicated in the figure, the magnet and cryostat are part of the sample environment and are continuously monitored and controlled by the LabVIEW program keeping the sample at a fixed temperature and magnetic field. The ESR and DNP hardware are controlled by...
triggers sent out by the LabVIEW program via the ESR card. The entire setup can be automated, allowing experiments to run for a few seconds up to several hours, or even days.

4.7 The Standard Experimental Procedure

Performing a DNP experiment can be a daunting task. Below follows the sequence of steps one goes through during a full experiment:

1. The (cut) sample is put in its Kel-F holder, mounted on the insert and installed in the cryostat.

2. The cryostat with insert is then cooled down. As the temperature of the cryostat starts to drop, the heating of the cryostat is turned on.

3. Once a temperature of 100 K is reached, the two NMR coil resonances are checked, using a network analyzer. The resonant frequencies are noted down for later use.

4. The ESR and DNP apparatus are turned on along with the laser.

5. After the laser has reached its full operational power, the shutter is opened and the ESR program is started. The resonance of the ESR cavity is found by viewing the cavity ringing. The ringing should not show any signs of a frequency modulation.

6. While performing an ESE pulse sequence, the sample position relative to the static magnetic field is optimized. This is done by turning the crystal slowly in the magnetic field in order to find the position where the crystal is aligned as close as possible to $X \parallel |B_0|$.

7. The optimization of the ISE sweep is then done as described in section 4.5.1.

8. After the settings have been optimized the ISE sequence is started.

9. NMR signals are recorded using small tipping angles at set intervals while the ISE sequence is running. Depending on the ISE polarization growth rate, the experiment may last from a couple of minutes to several hours. When the ISE sequences is finished, the laser and DNP apparatus are turned off.

10. Once the maximum polarization has been reached, the NMR signal is measured with a small tipping angle on the lower coil and with a $90^\circ$ pulse on the upper coil to get a calibration factor between the two coils.

11. If needed, the sample is then left to relax long enough to record a thermal equilibrium signal which is done with the help of the upper NMR coil. The sample should rest at least five times its relaxation time to let the sample fully relax.

12. Lastly, the PID control of the cryostat is turned off, and the needlevalve of the syphon are closed simultaneously. The cryostat is then left to warm up. One can speed up the heating process by blowing Helium gas of room temperature through the cryostat. Around 12 hours are required to reach room temperature if the cryostat is left to heat up on its own.
5 Experimental Results

In this chapter we give a summary of the ESR and DNP results obtained in the lab. The experiments presented have been performed using the experimental configuration given in the previous chapter. These experiments can be seen as a characterization of the setup in preparation for the neutron spin filter experiment, which will be presented in chapter 6. The first section describes how the crystal is oriented in the magnetic field by observing the ESR line shift. In the following sections the excitation of the triplet state is treated, and an experiment to determine the triplet yield is presented in detail. In the final sections of this chapter the results of the DNP experiments on the different crystals are presented.

5.1 Optimization of Sample Orientation

As described in chapter 2, the orientation of the sample has a great influence on the triplet state polarization. A precise alignment of the crystal in the cutting and mounting phase makes orienting the sample in the magnetic field a simple process. Figure 5.1 presents a schematic drawing of the mounted sample. Refer to figure 3.1 in chapter 3 for the relationship between the crystal axes and the principal axes of pentacene.

- The first step is to find the cavity resonance, which is close to 9.3 GHz, with the integrated NMR coil mounted in the cavity. Coupling the resonance is done by moving the ESR antenna up and down while observing the cavity ringing. A strong ringing normally corresponds to a good cavity coupling. Removing the NMR coil shifts the resonance to lower frequencies.

- A resonance at 9.30 GHz puts the resonant magnetic field of a single electron at 0.332 T (the gyromagnetic ratio of the electron is 28.025 GHz/T).

- Assuming the alignment X||B₀, the low field transition is observed at a frequency of (ω - ω₀S)/2π = 753.5 MHz with respect to ω₀S the electron Larmor frequency at 9.3 GHz. Thus the low field transition can be expected to be found at 0.305 T. Rotating the sample in a magnetic field of 0.305 T while optimizing the ESR signal integral will orient the pentacene molecule as close as possible to X||B₀. Any other orientation of the sample will also give a detectable ESR signal, albeit at a different frequency. The frequency shifts of the ESR transition with respect to the electron Larmor frequency are given by equation 2.3 and repeated here for convenience:

$$\omega_{0\pm} - \omega_{0S} = \pm \frac{1}{2} (D (3 \cos^2 \theta - 1) + 3E \sin^2 \theta \cos 2\phi)$$  \hspace{1cm} (5.1)

The frequency shifts for a pentacene molecule, aligned with one of its molecular axes along the magnetic field, are given in table 5.1. The full ESR spectrum is measured by keeping the frequency fixed while varying the magnetic field and recording the ESR signal for several orientations of the sample. Such a measurement is presented in figure 5.2. The measurement was carried out on crystal #2 using an electron spin echo (ESE) sequence with a π/2 time of 18 ns, which corresponds to a B₁ of 0.35 mT. As seen by the frequency
Figure 5.1: Scheme of a perfectly oriented crystal mounted in a magnetic field. The laser hits the sample perpendicular to the magnetic field and to the crystal b axis.

Table 5.1: The frequencies shift continuously as the molecule is rotated in the magnetic field. The table gives the values for the three directions of a single pentacene molecule when one of its molecular axis is parallel to the magnetic field.

<table>
<thead>
<tr>
<th>Position of molecule</th>
<th>$(\theta, \phi)$</th>
<th>$(\omega - \omega_{0S})/2\pi$ [MHz]</th>
</tr>
</thead>
<tbody>
<tr>
<td>X</td>
<td></td>
<td>B$_0$</td>
</tr>
<tr>
<td>Y</td>
<td></td>
<td>B$_0$</td>
</tr>
<tr>
<td>Z</td>
<td></td>
<td>B$_0$</td>
</tr>
</tbody>
</table>

Figure 5.2: The frequencies observed in the ESR spectrum give a hint of the orientation of the pentacene-naphthalene crystal.
shift, the $0^\circ$ position of the crystal corresponds to a pentacene X axis aligned parallel to the magnetic field $B_0$. The frequency shift observed for $90^\circ$ corresponds to an orientation of the two molecules where their Z axes are almost parallel to the external magnetic field.

### 5.1.1 ESR Spectra for $X||B_0$

A detailed scan of the low field transition is performed once a crystal is aligned close to $X||B_0$, using the method described in the previous section. For an almost perfectly oriented sample (a maximum error of a few degrees or less), the hyperfine structure of the triplet state becomes visible. This can be seen in figure 5.3. The figure combines three different crystal measurements. The clear hyperfine structure is a good indication that the crystals are all oriented with $X||B_0$. This confirms that the procedure of cutting and mounting the crystal we developed produces excellent results.

However the measurements show a small discrepancy with the theory. The expected frequency shift for a perfect alignment of the X axis parallel with $B_0$ is $+753.5$ MHz (or $-753.5$ MHz for the high field transition). The spectra are all shifted around $6.5$ MHz less than what the theory predicts. This corresponds to a small misalignment of $\approx 3^\circ$, which can be seen in equation 5.1. While an error of only $3^\circ$ is small, it appears unlikely that the mounting procedure would cause the same error each time. A small systematic error in the experimental setup or a slight error in the two constant $D$ and $E$ describing the level splitting of the triplet state are more likely to be the cause of the discrepancy between the measured and the calculated frequency shift. For the actual DNP experiment however, such a small misalignment is negligible.

![Figure 5.3: The ESR spectra for three separately cut and grown crystals show all close to perfect alignment of the X-axis to the magnetic field.](image)

### Crystal Misalignments

A mounting of the crystal in a perfect orientation could not always be achieved. However, by measuring the ESR signal while rotating the crystal, one can still align the pentacene molecule as close as physically possible to $X||B_0$. Note that it is always be possible to orient the crystal with $X||B_0$ if the sample can be rotated around an additional axis, which is perpendicular to the mounting axis. Unfortunately, due to the geometrical constraints
of the magnet and cryostat, this is not possible. One can estimate the ‘misorientation’ of the crystal for each position by measuring the ESR spectra for several different orientations of the crystal. Figure 5.4 shows three spectra of crystal #2, each with a different orientation of the crystal relative to the magnetic field. The first measurement at $0^\circ$ shows two distinct peaks in the ESR spectrum. The two peaks stem from the two possible orientations of the pentacene molecule in the naphthalene crystal. As the sample is rotated by $10^\circ$, the two peaks merge and a single, however broadened, ESR line can be observed. In this orientation, the frequency shifts of the two pentacene orientations in the crystal coincide. However the center frequency of the peak has shifted away from $X\parallel B_0$. A further $10^\circ$ rotation separates the two peaks once again. The peaks’ shifts make it clear that the crystal is now even further away from $X\parallel B_0$.

**Calculation of the Frequency Shifts**

To find the misalignment of the pentacene X-axis relative to the magnetic field, we calculate the frequency shift of all possible orientations, using equation 2.3. The frequencies of $\phi$ and $\theta$ correspond to the observed frequencies in the case for the $0^\circ$ orientation, e.g. 742 MHz and 627 MHz, which is plotted in figure 5.5. The black lines correspond to the frequencies close to 742 MHz, and the gray lines to frequencies around 627 MHz. Around the black lines, the gray line is split up into two thin lines (for each of the two pentacene orientations). The lines intersect at four different points, corresponding to $\phi = 0^\circ \pm 8^\circ$ and $\theta = 90^\circ \pm 16^\circ$. Similar plots can be drawn for the orientations of $10^\circ$ and $20^\circ$. When analyzing the spectra, it is advantageous to temporarily ignore frequency shifts with $\phi < 0$ and $\theta > 90^\circ$. One finds the following orientations of the crystal for the three spectra in figure 5.4:

- The spherical angles matching the frequencies of the $0^\circ$ orientation (solid back line) corresponds to $(\phi, \theta) = (8^\circ, 74^\circ)$.
- The second curve (long red dashed) corresponds to $(8^\circ, 86^\circ)$
- The third curve (short green dashed) to $(11^\circ, 98^\circ)$.
5.2 Laser Excitation

In this thesis a tunable laser source with a pulse length of 10 ns has been used. It allows for exploring and optimizing many of the parameters that influence the triplet yield of pentacene. The optimum wavelength to excite the pentacene molecule into its triplet state is easily found by measuring the ESR signal integral as a function of the laser wavelength (figure 5.6).

From the figure one sees that the ESR signal drops sharply above 600 nm. Photons with a wavelength longer than 600 nm lack the necessary energy to excite the pentacene molecule into its first excited state [47]. The figure shows a pronounced structure with clear maxima and minima for photons with a wavelength shorter than 600 nm. This is due to the change in absorption probabilities for the different vibronic states of the pentacene molecules singlet state [48]. From the measurement one concludes that not only a laser wavelength of around 600 nm has the potential to be used, but wavelengths around 550 nm also create a high number of triplet states.

Finding the angles closest to (0°, 90°), in our case the second ESR spectrum (10°), equals finding the position where the mounting error can be corrected by tilting the crystal upwards or downwards when remounting it in its Kel-F holder. In our case, it seems we should tilt the crystal 8° upwards. However, as the figure is symmetric, the φ rotation for the crystal could be negative, i.e. the fitted angles invert in the point (0°,90°). Only by trial and error can one find out which way to turn the crystal, as neither the crystal nor the magnetic field can be turned out of the horizontal plane. Only the amount one needs to turn the crystal can be determined. All estimates of the orientations have an error of ±2°, which stems from the visual fit of the overlapping frequency bands in the contour plot. Such a fit can be seen as a way to correct the misalignment of the mounted crystal but it also to quantifies the absolute error made when cutting the crystal. Thus the calculation provides a tool to qualitatively evaluate the cutting process.

Figure 5.5: Frequencies in the ESR spectrum as a function of the alignment of the two pentacene molecules in the magnetic field. The black colour in the middle represents the frequency shift of 742 MHz. The gray colour represents 627 MHz. All other frequencies have been removed from the graph for clarity.
The three wavelengths that give the strongest ESR signal were studied in more detail. The ESR signals were recorded as a function of the light energy at the wavelengths 554 nm, 598.5 nm and the zero phonon excitation at 600 nm. The laser energy is varied by inserting neutral density filters with varying attenuation factors into the beam. The result of the measurement can be seen in figure 5.7. Taking into account all losses in the path to the sample, the number of photons exciting the sample can be estimated from the measured laser beam power entering the cryostat.

The light at 600 nm is exciting the pentacene into its lowest excited state (zero phonon transition), while the excitation at 598.5 nm and 554 nm excites the molecule into vibronic states above the singlet state. The increase in ESR signal for wavelengths below 600 nm is likely due to a slight population inversion between the singlet ground state
5.2 Laser Excitation

and the excited singlet state. When shining light with the wavelength of 600 nm onto a pentacene molecule, no population inversion can occur. This is due to the fact that stimulated emission and stimulated absorption limits the excited pentacene molecules to half of the total available. Exciting the pentacene molecule at a wavelength below 600 nm is equal to the three level pumping schemes used to create population inversions in laser mediums. Via a fast radiationless transition one pumps the molecule into a level which quickly decays to a slower relaxing level, thus creating a population inversion.

The conclusion from the experiment is that when using a laser with a slightly lower photon to pentacene ratio, it is advantageous to excite at 600 nm. This is especially true for larger crystal samples. With a high enough laser power it could still be advantageous to excite at a shorter laser wavelength.

5.2.1 Laser Light Penetration

To understand how well the ESR signal strength corresponds to the concentration of pentacene in the crystal, the measurement in figure 5.7 was repeated for each crystal. A comparison of crystals #2, #4, #6 and #7 can be seen in figure 5.8. The laser energies given in the figure are the output of the OPO just before being coupled into the fiber. All crystals had the same approximate size, which were almost cubical with sides measuring 5 mm.

As seen from table 3.2, crystal #4 has a concentration around 2 times higher than the other three crystals. For lower laser energies the ESR signal is proportional to the pulse energy, and linear fits can be made up to the point where the curves start to show signs of saturation. Comparing the values at the end points of the linear regimes for the three crystals shows a factor 1.5 more ESR signal for crystal #4. The growth rate for crystal #4 is roughly a factor 1.4 higher than the other three. We would have expected a difference close to 2 times more ESR signal and growth rate due to the difference in pentacene concentration. The derivation from the expected factor of 2, albeit small, could possibly be attributed to a too low number of photons (compared to the amount of pentacene molecules) reaching the sample: Each laser pulse exiting the fiber has an energy close to

Figure 5.8: Relation between the ESR signal strength and the concentration of pentacene of the sample. Laser light with a wavelength of 600 nm was used to excite the pentacene into its triplet state. The values of crystal #7 were recorded during the neutron experiments and have been scaled to an arbitrary value. Important is only the point where the saturation of the signal become apparent.
10 mJ. This corresponds to around $3 \times 10^{16}$ photons (at 600 nm). A crystal sample of size $5 \times 5 \times 5$ mm$^3$ and a pentacene concentration of $4 \times 10^{-5}$ mol/mol contains $2.6 \times 10^{16}$ pentacene molecules. Taking into account the losses associated with entering the cryostat through two sapphire glass windows and a circular beam hitting a square surface (see section 4.1), the amount of photons reaching the sample drops below the amount of pentacene molecules in the sample. For crystal #2, #6 and #7 the photon to pentacene ratio is a factor 2 better. This suggest that the ratio of photons to pentacene molecules does play a role when larger crystals are used. Unless more photons are available crystals of lower concentrations ($\sim 2 \times 10^{-5}$ mol/mol) and longer relaxation times are preferred.

The observation that the initial growth rate of the ESR versus light energy depends on the pentacene concentration of the crystal contradicts the model of laser penetration as suggested by Takeda [49]. This model predicts that using lower energies than are needed to excite all of the pentacene molecules will result in a non-uniform distribution of triplet yield, which is highest at the surface where the laser light enters the crystal. This is not observed in our measurements (see also section 6.7.1).

To get an idea of how much light is lost due to scattering, we measured the attenuation of the laser light as it passes through the crystal. To avoid the influence of light absorption by the pentacene molecules, a diode laser operating at 670 nm, far above the absorption of the pentacene molecule, was used. The results of the transmission measurement for different crystal samples are given in table 5.2.

<table>
<thead>
<tr>
<th>Crystal type</th>
<th>Surface properties</th>
<th>Thickness</th>
<th>Penetrating light</th>
</tr>
</thead>
<tbody>
<tr>
<td>#4</td>
<td>cleavage plane</td>
<td>3.4 mm</td>
<td>40 %</td>
</tr>
<tr>
<td>#4 mounted</td>
<td>very rough surface</td>
<td>4.5 mm</td>
<td>$\approx 1 %$</td>
</tr>
<tr>
<td>#2 mounted</td>
<td>well cut surface</td>
<td>4.8 mm</td>
<td>50 %</td>
</tr>
<tr>
<td>#2 mounted</td>
<td>rough surface</td>
<td>5.3 mm</td>
<td>20 %</td>
</tr>
</tbody>
</table>

Table 5.2: Measurement of laser penetration through various crystals. The measurement was done with laser light at 670 nm which is not absorbed by the pentacene molecules.

One directly notices the lack of a clear difference between crystal #2 and #4. This suggests that only the quality of the surface and to a much lesser extent the thickness.

### 5.2.2 Influence of the Laser Polarization

Due to the dipole moment of the pentacene molecule, one would expect the excitation of the molecule, and thus also the ESR signal, to be dependent on the direction of the polarization vector of the light that reaches a monocristalline sample. Equation 5.2 relates the transition probability ($W_{ij}$) between the two vibrational states $i$ and $j$ to the energy of the light and the polarization vector.

$$W_{ij} = \frac{\pi}{2} \frac{\mu_0}{\varepsilon_0} \frac{1}{\hbar^2} I \langle i | eX | j \rangle^2 \delta(\omega - \omega_{ij})$$ (5.2)

Here $I$ is the energy of the light, $\langle i | eX | j \rangle$ the transition matrix elements on the basis of the pentacene principal axes (written as $eX$, $eY$ and $eZ$) and $\omega_{ij}$ the frequency units of the transition. The allowed transitions are given by group theory and can be summarized to [50]:

$$\langle S_0 | eX | S_1 \rangle = 0$$
$$\langle S_0 | eY | S_1 \rangle \neq 0$$
$$\langle S_0 | eZ | S_1 \rangle = 0$$ (5.3)
Only light polarized along the Y axis excites the pentacene molecule into its $S_1$-state. Thus, no ESR signal should be seen when the polarization vector of the light is parallel to the X or Z axis of the pentacene molecule.

A measurement exploring the influence of the polarization vector on the ESR signal was performed with an earlier version of the setup where the light enters the cryostat from the side, coupled in by mirrors which maintain the polarization of the light. The polarization vector of the light was turned continuously by rotating a $\lambda/2$ plate. The crystal was mounted such a way that it could be rotated around the b-axis. By positioning the crystal once with its X axis and once with its Z axis parallel to the magnetic field one could explore all possible directions of the polarization vector of the light in respect to the axes of the pentacene crystal. The results of the polarization dependence measurements are presented in table 5.3.

| $X||B_0$ | $Z||B_0$ |
|----------|----------|
| $\uparrow||X$ | $\uparrow||Y$ |
| $\uparrow||Z$ | $\uparrow||Y$ |
| 172.3 | 174.4 |
| 30.2 | 31.3 |

Table 5.3: ESR signal strength observed for different orientations of the pentacene molecule with respect to the light polarization direction (indicated by $\uparrow$). The sample was put in two different orientations and the polarization of the light was rotated continuously. No effect of polarization could be seen.

The experimental data suggests that the direction of the polarization vector has no influence on the ESR signal obtained. The reason for this is not fully understood. An explanation could be that the polarization of the light is lost due to scattering inside the naphthalene-pentacene crystal.

However, the result of this experiment has an important practical implication. Instead of mirrors, a multi-mode fiber can be used. Such a fiber does not maintain the polarization of the light. Because we were able to transport the light over long distances we could now separate the laser from the rest of the apparatus.

### 5.3 Triplet Decay

A measurement of the triplet decay of pentacene is of importance when optimizing the ISE sweep (see section 4.5.1). Furthermore, such a measurement allows us to compare our results to that of previous measurements by van Strien [9] and Inuma [51]. By stepwise increasing the delay between the electron spin echo sequence and the laser pulse and recording the ESR integral for the orientation of $X||B_0$, one measures a decay curve as seen in figure 5.9.

The decay of the ESR signal follows equation 2.9, repeated here for convenience:

$$\xi(t) = N_X e^{-k_X t} - \frac{1}{2}(N_Y + N_Z)e^{-\frac{(k_Y t + k_Z t)}{2}}$$

(5.4)

The triplet state $T_Y$ and $T_Z$ mix and one can only determine the decay time of $T_X$. However by setting $N_Z$ to zero, as measured by van Strien, one can fit the populations of $T_X$ and $T_Y$. Fitting the measured decay to equation 5.4 one finds:

- The triplet decay time of $T_X$ to be $\tau_X = 33\, \mu s$.
- The triplet populations to be $N_X = 0.87$ and $N_Y = 0.13$.
- The decay time $\tau_2 = \frac{\tau_Y + \tau_Z}{2} = 69\, \mu s$
The decay times measured by van Strien were 15, 35 and 280 µs for \( \tau_X \), \( \tau_Y \) and \( \tau_Z \). The value of \( \tau_X \) measured in this thesis is a factor 2 higher. However, Iinuma measured \( \tau_X \) and \( \tau_Y \) to 26 and 83 µs [51] closer to our results. We have not been able to explain the discrepancy between our and the original measurements. It is possible that the quality of the crystal, i.e. the concentration of impurities, could shorten the triplet lifetime. This has been observed for the triplet lifetime for naphthalene in a single crystal [39].

The triplet decay measurement was repeated for \( Y \parallel B_0 \), see figure 5.10. The two \( Y \) axes of the two different pentacene orientations in the crystal make an angle of \( \pm 23.5^\circ \) with the magnetic field. Thus equation 5.4 is rewritten as:

\[
\xi(t) = (\cos^2(\theta)N_Y + \sin^2(\theta)N_Z)e^{-k_1t} - \frac{1}{2} (\sin^2(\theta)N_Y + \cos^2(\theta)N_Z + N_X)e^{-k_2t})
\] (5.5)

Once again setting \( N_Z \) to zero and \( \theta \) to 23.5°, the fit gives two decay times of 45 and 161 µs. Due to the mixing of states, no information can be extracted from these decay times. However, we could still fit the triplet population. We found values fitting exactly to the ones given by van Strien:

- \( N_X = 0.91 \) and \( N_Y = 0.09 \)

The measurements for both orientations give triplet level populations in agreement with van Strien. The decay time could only be fitted for \( T_X \) and appears to be a factor 2 longer, which is actually beneficial for us as the alignment of the triplet state remains longer and thus the electron polarization decays slower.
5.4 Determination of the Triplet Yield

As stated in the theory chapter, the triplet yield of pentacene has only been measured at around 2 K [22–25] while no values have been found for higher temperatures. The references give varying numbers for the ISC yield, from 0.003 to 0.15.

A first estimate for the triplet yield at 100 K can be obtained by measuring the ESR signal at different temperatures between 150 K and 4 K and extrapolating the data down to 2 K. The results of the measurement can be seen in figure 5.11.

The temperature was measured at the bottom of the ESR cavity with a second temperature sensor. The ESR cavity resonance had to be reoptimized continuously as the temperature changed. This led to the sudden jumps seen in the graph. The ESR signal increased...
almost linearly from 3 K up to 100 K. Above 120 K the increase stops. This is assumed to
be due to the loss of resonance of the ESR cavity as the coupling got considerably worse
when the temperature rose above 120 K. If one assumes a linear decrease down form the
lowest measured point at 3.1 K to 2 K (disregarding the measurements done above 100 K)
one can, by comparing to the reported triplet yield of 0.03 at 2 K [22], estimate the triplet
yield to be between 0.16 and 0.19 at 100 K.

5.4.1 Measurements using a Composite Sample

A more accurate knowledge of the triplet yield was needed. It would allow a comparison
of our DNP results with proton polarization enhancements obtained using laser sources
with different pulse parameters. The idea was to compare the thermalized ESR signal of
a known amount of the free radical TEMPO ((2,2,6,6-Tetramethylpiperidin-1-yl)oxyl) to
the ESR signal from a small piece of naphthalene crystal with a known concentration of
pentacene molecules.

5.4.2 Sample Preparation

A small piece of crystal #2 was immersed in a TEMPO-butanol mixture in a standard
ESR glass tube. Inside the glass tube, the crystal was oriented with the crystal b-axis
parallel to the mounting axis and perpendicular to the magnetic field. One could thus
easily find $X|B_0$ by rotating the glass tube. The composite sample was mounted and
frozen in the cryostat as it cooled down.

We prepared the sample to yield comparable signal strength from the triplet state of
pentacene and from the thermally polarized TEMPO. We accounted for the fact that the
electron spin polarization of the triplet state of the pentacene molecule does not depend
don temperature or field and is close to 0.9, we further assumed that the polarization
of the TEMPO molecule follows the Boltzmann law and is inverse proportional to the
temperature in the sample. The weight of the #2 naphthalene-pentacene crystal was
measured to be 11.0($\pm0.5$) mg which corresponds to $7.8 \times 10^{14}$ pentacene molecules in
the sample. The number of TEMPO molecules was calculated to $1.9 \times 10^{17}$ for the full
sample.

5.4.3 Triplet Yield Measurements

The ESR signals from pentacene and TEMPO was compared at temperatures of 20, 50
and 80 K. It was found that the ESR signal of TEMPO at 100 K is too weak. Therefore, no
comparison with the pentacene signal could be made at that temperature (see figure 5.12
for a measurement at 30 K). In order to avoid the signal being hidden in the noise of
the cavity ringdown, we measured the signals with a large delay time, on the order of
$\tau = 1 \mu s$. The dephasing of the spins in TEMPO and pentacene have very different time
constants. In order to be able to extrapolate back to the initial ESR signal at time $\tau = 0$,
the time constants of both TEMPO and pentacene had to be measured. The measurement
of TEMPO (figure 5.13) shows a simple exponential decay behavior of the ESR signal as
a function of $2 \times \tau$. The factor 2 stems from the double time delay in the ESE pulse
sequence before the signal is measured.

The pentacene molecule on the other hand shows a strong electron spin echo envelope
modulation (ESEEM) [52] (figure 5.14), making an estimation of its initial value difficult.
For the measurements at 80 K, the ESR cavity resonance was detuned on purpose in order
to decrease the cavity ringdown time, thus allowing for more data points to be made of
the ESEEM effect of pentacene.
Figure 5.12: Plot of the relative ESR signals of TEMPO and pentacene at 30 K. The inserted graph shows the true sign convention of the low field transition.

Figure 5.13: The measurement of the decay time of TEMPO at 20 K show an exponential decay behavior with a time constant of 450 ± 4 ns.
Figure 5.14: The measurement of the decay time of pentacene at 80 K is also a measurement of the ESEEM effect. The modulation of the proton frequency is seen in the figure.

The method used to estimate the initial ESR signal of pentacene is based on a paper by Sloop [20] which treats the ESEEM effect of pentacene in p-terphenyl crystals. Experimental data (see figure 3 of the paper) suggest that the ESR signal of pentacene does not start to decay until after more than 1 µs. One sees that the maximum of the ESR signal integral can be found at a delay of around $\tau = 1 \mu s$. Thus the correction of the pentacene ESR signal integral is small. All signal integrals were measured with a delay of exactly $\tau = 1 \mu s$.

5.4.4 Sample Heating

When measuring the TEMPO ESR signal at 20 K it was found that the signal decreased when laser light irradiated the sample (see figure 5.15). This heating effect actually provides an additional data point at 30 K. The 20 K value for pentacene is taken just after the laser has been turned on (see figure 5.16), whereas the data point at 30 K was measured after thermal stabilization. The corresponding TEMPO signals at 30 K were measured the same way. This laser heating effect could not be observed at the higher temperatures of 50 and 80 K.

By applying Boltzmann’s law, one can estimate the temperature to have increased from around 20 to 30 K as shown in the figure. We then end up with four different temperatures at which the triplet yield can be estimated: 20, 30, 50 and 80 K. The decay time of the pentacene signal at 20 K could not be measured because the laser heating made it impossible. It has been assumed that the correction factor obtained for 30 K can be used for the measurement at 20 K.

5.4.5 Evaluation and Results

To estimate the triplet yield, the measured ESR signals of pentacene and TEMPO are compared at the different temperatures. To get a correct value, several different factors need to be accounted for:

- Correction for the decay of both the TEMPO and the pentacene signals.
5.4. Determination of the Triplet Yield

Figure 5.15: The measurement of the influence of laser irradiation of TEMPO at an initial temperature of 20 K shows a decrease of the ESR signal as the sample heats up from the laser beam.

Figure 5.16: The measurement of the influence of laser irradiation on pentacene at 20 K shows a clear rise of the ESR signal.
For TEMPO the correction factor is obtained using the fit of the decay time and extrapolating back the value of the ESR signal to $\tau = 0 \, \mu s$. The pentacene signal is corrected with respect to $\tau = 1 \, \mu s$ \cite{20}.

- One then compares the ESR signal of TEMPO to the ESR signal of pentacene in order to extract the concentration of triplet states in the sample.

- When comparing a spin 1 (pentacene) system to a spin $\frac{1}{2}$ (TEMPO) a decrease with a factor $\sqrt{2}$ needs to be taken into account. The effective rotation of the spin 1 system is a factor $\sqrt{2}$ faster than the spin $\frac{1}{2}$ system. See section 2.4.1 for details.

- One needs to take the decay of the triplet state into account. After $2 \, \mu s$ of decay (approximate time from the laser flash to the measurement of the signal) the ESR signal has decreased to 0.95, as extracted from figure 5.9.

- Furthermore, one needs to take into account the polarization of the fictitious spin $\frac{1}{2}$ system of pentacene. It is given by equation $(N_0 - N_-)/(N_0 + N_- + N_+)$, using the values of $N_0$ and $N_-$ given by van Strien \cite{9} and confirmed in section 5.3. This is 0.865 at $\tau = 0 \, \mu s$.

- Finally, we assume that our laser pulse fully saturates the transition and thus only half of the pentacene molecules have been excited into their excited singlet state, increasing the final number of the triplet yield with a factor 2. This leads to the triplet yield presented in table 5.4.

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Sample Type</th>
<th>ESR Integral [nVs/mT]</th>
<th>Correction factor</th>
<th>Triplet Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>20 K</td>
<td>Pentacene</td>
<td>~300</td>
<td>1.10</td>
<td>13% ± 3%</td>
</tr>
<tr>
<td></td>
<td>TEMPO</td>
<td>198</td>
<td>62</td>
<td></td>
</tr>
<tr>
<td>30 K</td>
<td>Pentacene</td>
<td>418</td>
<td>1.10</td>
<td>16% ± 4%</td>
</tr>
<tr>
<td></td>
<td>TEMPO</td>
<td>121</td>
<td>87</td>
<td></td>
</tr>
<tr>
<td>50 K</td>
<td>Pentacene</td>
<td>629</td>
<td>1.08</td>
<td>30% ± 8%</td>
</tr>
<tr>
<td></td>
<td>TEMPO</td>
<td>59</td>
<td>72</td>
<td></td>
</tr>
<tr>
<td>80 K</td>
<td>Pentacene</td>
<td>889</td>
<td>1.11</td>
<td>31% ± 8%</td>
</tr>
<tr>
<td></td>
<td>TEMPO</td>
<td>52</td>
<td>75</td>
<td></td>
</tr>
</tbody>
</table>

Table 5.4: The measured integrals of the field scans are multiplied with the $T_2$ correction factor to get the signal strength at $\tau = 0$. The triplet yields are found by comparing the ESR signal strength for the known concentration of TEMPO to the ESR signal of the pentacene for the different temperatures. The estimated triplet yield errors used for calculating the triplet yields can be found in table 5.5.

Important to note is that if the fit of the $T_2$ decay of pentacene (currently done accordingly to \cite{20}) should be exponential, the triplet yield would potentially be a factor 1.3±0.1 higher than given here.

The errors used in the triplet yield calculations can be found in table 5.5.

5.4.6 Conclusions of the Triplet Yield Measurement

Our absolute value for the triplet yield allows us to scale the data presented in figure 5.11 (see figure 5.17). Extrapolating a curve fitted to the data, one finds a triplet yield of 0.06 at 2 K within the range given by \cite{22–25}. Calculating the triplet yield from the
### Table 5.5: List of the estimated errors used in the calculation of triplet yields as seen in table 5.4.

<table>
<thead>
<tr>
<th>Type of Error</th>
<th>Estimated Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>Weighting of TEMPO-Butanol mixture</td>
<td>20%</td>
</tr>
<tr>
<td>Weighting of TEMPO</td>
<td>10%</td>
</tr>
<tr>
<td>Weighting of pentacene-naphthalene crystal</td>
<td>5%</td>
</tr>
<tr>
<td>Measurement of pentacene field scans</td>
<td>5%</td>
</tr>
<tr>
<td>Estimation of initial pentacene ESR signal from $T_2$ measurements</td>
<td>5%</td>
</tr>
<tr>
<td>Measurement of TEMPO field scans</td>
<td>5%</td>
</tr>
<tr>
<td>Estimation of initial TEMPO ESR signal from $T_2$ measurements</td>
<td>5%</td>
</tr>
</tbody>
</table>

Total error \(\approx 25\%\)

Table 5.5: List of the estimated errors used in the calculation of triplet yields as seen in table 5.4. It is much harder to measure the weight of a small amount of liquid compared to a solid, as seen in the difference of error in the weighting of the TEMPO-butanol mixture and the crystal. The error in the estimation of the initial pentacene ESR signal includes the large uncertainty of the extrapolation to time 0.

![Figure 5.17: The figure shows the ESR signal converted to triplet yield and compares it to the calculated triplet yield.](image)

Figure 5.17: The figure shows the ESR signal converted to triplet yield and compares it to the calculated triplet yield.

TEMPO-pentacene comparison includes several steps and several correction factors. Thus, obtaining a value in the middle of the range given by the references is reassuring. One can conclude that the triplet yield appears to be a few tens of percent at 100 K. A long pulse laser could potentially increase the triplet yield, and thus the DNP growth rate up to a factor of 3. This factor will be used when analyzing our DNP results in the following sections.

### 5.5 Dynamic Nuclear Polarization Measurements and Results

As already stated in chapter 3, the ESR measurements on crystals #2, #4, #6 and #7 showed that all four were potential candidates for reaching high proton polarization values in a DNP experiment. To determine which crystal to use in the neutron spin filter experiment detailed DNP measurements on the different crystals were performed. The crystals were polarized long enough to be able to reliably fit an exponential build-up curve where crystal #4 showed the strongest initial growth. This is not surprising considering its
high concentration of pentacene, noticeable already in the darker colour. The polarization of crystals #2 and #7 grew well, eventually reaching a higher end polarization than crystal #4, while crystal #6 barely managed to get polarized at all. It became clear that crystal #6 suffered severely from impurities and had a relaxation time of 26 min at 100 K while the other crystals had much longer relaxation times. Therefore, only crystals #2, #4 and #7 were thoroughly investigated by DNP build-up and proton relaxation time measurements.

5.5.1 DNP Build-up

A higher concentration of pentacene leads to a higher polarization growth rate $A$, but also to a decrease in the proton relaxation time $T_1$. Furthermore, a too high pentacene concentration can eventually degrade the crystal quality. To optimize the polarization build-up, a balance needs to be found between the relaxation and the increase in polarization rate. The polarization build-up process can be described as follows:

$$\frac{dP_p}{dt} = A(P_e - P_p) - \frac{1}{T_1}(P_p - P_{th}) = \frac{1}{\tau}(P_p - P_{max}) \quad (5.6)$$

Here $P_p$ is the achieved proton polarization, $P_e$ the average electron polarization during the 15 $\mu$s ISE sweep, $T_1$ the relaxation time of the protons, $P_{th}$ the thermal polarization of the protons and $\tau$ the build-up time. The thermal polarization $P_{th}$ can be set to zero as the enhanced polarization achieved in a successful DNP experiment will be 10000-fold higher. The following three equations can be derived from equation 5.6:

$$A = \frac{1}{\tau} \frac{P_p}{P_e} \quad (5.7)$$

$$T_1 = \frac{P_p}{A(P_e - P_p)} \quad (5.8)$$

$$\frac{1}{\tau} = A + \frac{1}{T_1} \quad (5.9)$$

These equations will be used to analyze the experimental results in this section. Every crystal exhibits a specific growth rate and relaxation rate depending on its crystal quality and pentacene concentration. The polarization build-up of the three crystals that gave the best DNP results is shown in figure 5.18.

The initial polarization build-up of all crystals appears to be equal. However crystal #4 is slightly faster. Due to its short relaxation time of only a few hours (see table 5.6) it quickly reaches its maximum with a growth time of only $\tau = 1.8$ hours. Compared to crystal #4, crystal #2 and #7 have a concentration of pentacene a factor 2-3 less. At the same time both crystal show relaxation times of at least a factor 3 longer than crystal #4, thus achieving higher polarization values.

5.5.2 Proton Relaxation Time

While measuring the DNP build-up, it was confirmed that the proton relaxation times play a very important role as a limiting factor in the polarization build-up. Thus, the relaxation time of each crystal was measured by using non-destructive NMR pulses taking one measurement point every 30 min over several hours. The proton signal is normally set to relax at 100 K and 0.31 T. This is done with and without laser irradiation applied to the sample. The field is changed quickly for the actual NMR measurement of around 0.6 T. A typical relaxation graph for crystal #7, with and without laser irradiation, can
5.5. Dynamic Nuclear Polarization Measurements and Results

Figure 5.18: Three different DNP growth experiments with crystals #7 (black circles), #2 (blue squares) and #4 (red triangles) are shown. The growth time of the respective crystals are 4.9, 4.0 and 1.8 hours while the maximum polarizations obtained through fitting is 0.115, 0.082 and 0.050.

Figure 5.19: The longest relaxation time at 100 K and 0.3 T ever recorded during this work came from crystal #7 and was over 27 h long without laser irradiation, and 13 h with laser irradiation. The red circles represent the relaxation time when the crystal is irradiated by 5 mJ of laser energy.
be seen in figure 5.19.
During the measurements of the relaxation time of crystal #2, an interesting phenomenon was observed: The relaxation time of crystal #2 depended on its orientation in the magnetic field (see figure 5.20).

![Figure 5.20: Proton relaxation times at 100 K and 0.3 T as a function of the crystal orientation. The crystal has been mounted with its b-axis parallel to the axis of rotation. 0° corresponds to X∥B0. The laser light polarization is parallel to the mounting axis.](image)

This finding is in opposition to theoretical calculations [50] which predict that there could be orders of magnitudes difference between the relaxation time of the 0° and 90° orientation. According to the theory, the excitation of the pentacene molecule to the triplet state and the subsequent decay to the singlet ground state result in an increase in the nuclear spin-lattice relaxation. This depends on the hyperfine interaction and should therefore differ for different orientations of the pentacene molecule. One expects the fastest relaxation for a crystal orientation of 90°. However, our measurements show results opposite to what is predicted by the theory. Further measurements should be made in order to gain more insight into the relaxation process.

### 5.5.3 Effect of Laser Pulse Energy

From equation 5.9 and the results presented in the two previous sections, it is clear that growth rate and proton relaxation have to be optimized together. It was found that, using a laser pulse of full energy, crystal #7 gave the highest polarization. However, as shown in the previous section, irradiating the sample with laser light decreases the relaxation time. If the heating of the sample gets too severe, it might be beneficial to polarize at a lower laser energy. The relaxation time will become longer, possibly balancing the slower growth rate.

We see from figure 5.21 that a laser pulse of 9.6 mJ hitting the sample has more than enough photons to saturate the pentacene molecules in the crystal. Only as the laser power drops to ~4 mJ does the ESR signal begin to decrease linearly with the laser power. At 4 mJ, the laser pulse contains around $1.2 \times 10^{16}$ photons, while the crystal contains approximately $1.4 \times 10^{16}$ pentacene molecules. We decided to use the laser pulse with full power and compare it to a laser pulse of 2.4 mJ. The results of the DNP experiments using the two laser pulses intensities, indicated in figure 5.21 by two circles, can be found in figure 5.22.
Figure 5.21: The two circles mark the used laser powers for a subsequent series of DNP experiments on crystal #7. The laser energy is lowered by a factor 4 while the ESR signal only drops by a factor of 1.9.

Figure 5.22: DNP growth with two different laser powers for crystal #7. The faster growing curve increases with a time constant of 5.0 hours, and has a maximum polarization of 0.112. For the slower growing curve the values are 9.7 hours and 0.105.

At 9.6 mJ the polarization grows with a rate of \( A = 0.027 \text{ h}^{-1} \) whereas at 2.4 mJ the rate is about a factor 2 lower and amounts to \( A = 0.013 \text{ h}^{-1} \). This fits well to the corresponding ESR signals seen in figure 5.21. The end polarization value of the lower energy is surprisingly high, but it still is advantageous to use the full power of the laser.

5.5.4 Analysis of Results and Conclusion

The growth rate \( A \) for the different crystals can be obtained by fitting the growth curve of the DNP experiment and calculating the growth rate using equation 5.7. Once the
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growth rate is found, a ‘true’ relaxation time $T_1$ can be calculated through equation 5.8. The fitted growth time $\tau$ is 4.9 hours leading to a calculated relaxation time of 5.6 hours, using equation 5.8. This is far less than the measured 13 hours relaxation time with full laser irradiation applied (plotted in figure 5.19). For all crystal samples the calculated relaxation time is found to be shorter than the measured one. The large discrepancy could not be explained so far. Even with everything running, including the ISE sweep and microwave locking power (with the magnetic field set to a value where no polarization build-up could occur), no noticeably decrease in the relaxation time below the previously measured 13 hours where measured.

A theoretical growth rate $A^{\text{theo}}$ can be calculated by

$$A^{\text{theo}} = K_{\text{yield}} \times \frac{N_S}{N_I} \times S \times R \times K_{\text{ISE}}$$  \hspace{1cm} (5.10)

where $K_{\text{yield}}$ is the triplet yield estimated to 0.3 in section 5.4.6 (for a long pulsed laser it is assumed to be 1), $N_S$ the amount of pentacene molecules, $N_I$ the number of protons in the sample, $S = 0.54$ the product of the average numbers of spin and the average triplet polarization available during the 15 $\mu$s ISE sweep, $R = 30$ Hz the repetition rate of the ISE cycle and $K_{\text{ISE}}$ the efficiency of the ISE transfer. The efficiency of the transfer is not fully known, but from section 2.4.2 we know that it can be a maximum of 0.5. Thus, for a crystal with a pentacene concentration of $2 \times 10^{-5}$, the theoretical growth rate becomes: $A^{\text{theo}} = 0.3 \times 2 \times 10^{-5} / 8 \times 0.54 \times 30 \times 0.5 = 6 \times 10^{-6} \text{s}^{-1} = 0.022 \text{h}^{-1}$

Table 5.6 shows a comparison of the calculated and theoretical growth rates, and the measured relaxation times (under laser irradiation) $T_1^{\text{laser}}$ for the experiment carried out in this thesis with that of earlier works.

<table>
<thead>
<tr>
<th>Crystal</th>
<th>$P_{\text{max}}$</th>
<th>$\tau$</th>
<th>$R$</th>
<th>$A^{\text{calc}}$</th>
<th>$A^{\text{theo}}$</th>
<th>$T_1^{\text{laser}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>#2</td>
<td>0.082</td>
<td>4.0</td>
<td>30</td>
<td>0.023</td>
<td>0.016</td>
<td>10.1</td>
</tr>
<tr>
<td>#4</td>
<td>0.050</td>
<td>1.8</td>
<td>30</td>
<td>0.032</td>
<td>0.044</td>
<td>3.1</td>
</tr>
<tr>
<td>#7, 9.6 mJ</td>
<td>0.115</td>
<td>4.9</td>
<td>30</td>
<td>0.027</td>
<td>0.022</td>
<td>13.3</td>
</tr>
<tr>
<td>#7, 2.4 mJ</td>
<td>0.104</td>
<td>9.6</td>
<td>30</td>
<td>0.013</td>
<td>0.022</td>
<td>18</td>
</tr>
<tr>
<td>Iinuma [37]</td>
<td>0.17</td>
<td>12.5</td>
<td>70</td>
<td>0.015</td>
<td>0.26</td>
<td>16.7</td>
</tr>
<tr>
<td>Iinuma [17]</td>
<td>0.35</td>
<td>5.7</td>
<td>50</td>
<td>0.068</td>
<td>0.061</td>
<td>15.2</td>
</tr>
<tr>
<td>Takeda [7]</td>
<td>0.70</td>
<td>2.2</td>
<td>50</td>
<td>$\sim 0.4$</td>
<td>1.1</td>
<td>$&lt; 8$</td>
</tr>
</tbody>
</table>

Table 5.6: The growth rate, $A$, has been calculated from the measurements of figures 5.18 and 5.22 or from the references given. The theoretical rates have been calculated from the amount of pentacene in the crystal. The relaxation time of Takeda is only know for a crystal without laser irradiation.

The calculated growth rates fit very well with the theoretical ones. This is especially case for the results where the laser pulse had enough photons to fully excite the pentacene molecules in the crystal. Figure 5.7 clearly shows that the full concentration of pentacene in crystal #4 can not be excited by the laser pulse. Thus, a lower growth rate can be expected. For crystal #7 (irradiated with 2.4 mJ) a correction of a factor 1.9 (obtained from figure 5.21) gives a growth rate of 0.011, which is very close to the rate obtained from the build-up measurement. Finally, the theoretical growth rate of the measurements of Iinuma using a laser with 70 Hz also needs to be corrected. The amount of photons in each pulse could maximally excite a crystal with a factor 10 less pentacene molecules, thus reducing the corrected growth rate to 0.026, if not lower. The results of the two last entries in the table were obtained with long laser pulses and should thus have a factor $\sim 3$ higher
growth rate from the increase in triplet yield alone. Still, the much higher growth rate by Takeda is possibly a result of a reported pentacene concentration an order of magnitude higher than that of any other crystal used. However, assuming that the factor 3 higher growth rate is correct and multiplying the growth rate of crystal #4 with a factor 5/3 to account for the difference in laser repetition rate, we could potentially get a growth rate of $0.16 \text{h}^{-1}$ for crystal #4 if irradiated by the same laser used by the last two entries in the table.

Furthermore, there is reason to doubt the high polarization value given by Takeda. If one calculates the $T_1$ relaxation time (using equation 5.8) one arrives at 10 hours, longer than the reported $T_1$ (no laser applied) of 8 hours [7]. The same calculation for all the other experiments and crystals listed in table 5.6 gives a calculated $T_1^{\text{laser}}$ that is far shorter than what is given in the table. It is possible that the polarization values and thus also the growth factor $A$ given by Takeda has been overestimated.

The conclusion of the analysis done is that the crystals grown, especially crystal #7, are of comparable quality, if not better, than the ones of Inuma and possibly Takeda. Crystal #7 is also the crystal that was selected to be used in the spin filter experiment. The polarization values obtained for all crystals did never reach as high as the reported values by Inuma and Takeda, but the comparison to other laser sources suggest that higher polarizations can be obtained by a suitable light source. With a laser with a higher repetition rate and to a lesser extent more pulse power and longer pulse lengths, the growth rate $A$ can be increased orders of magnitude. However, increasing the growth rate also leads to a higher number of triplet states per unit time, which in turn leads to a stronger heating of the sample. To reach high polarization values, not only the growth rate $A$, but also the ‘true’ relaxation time $T_1$ need to increase. The only way to increase the relaxation time is through better crystal quality, which arguably is hard to achieve, or through a more efficient cooling of the sample.

### 5.6 Detailed ISE Measurement

A series of DNP measurements were performed on crystal #7 aimed at optimizing the DNP by fine tuning the ISE timing and length of the microwave pulse as well as supplying data needed for the further development of the ISE theory. For all measurements, the ISE sweep range is set to cover the entire ESR spectrum of around 6 mT. The start of the microwave pulse relative to the laser pulse is kept fixed and the crystal is mounted with its X-axis close to parallel to the magnetic field.

#### ISE Sweep Timing

The first experiment is aimed at finding the optimum start and direction of the ISE sweep. For the ‘up-sweep’ the magnetic field is swept from low to high, corresponding to a sweep from high to low frequencies. The trigger for the magnetic field sweep is changed stepwise relative to the laser trigger, thus changing the start of the microwave pulse within the magnetic field sweep. This corresponds to changing the start of the ISE sweep relative to the ESR spectrum. See figure 5.23 for a descriptonal drawing.

The enhanced NMR signal is recorded after a 1 min ISE sequence. The power of the microwave pulse corresponds to a $\pi/2$ of 35 ns, equaling a $B_1$ of 0.2 mT while the length of the pulse is set long enough to cover the entire ESR line. The results of the measurement is presented in figure 5.24.

The optimum start of the ISE sweep is confirmed to be just at the edge of the ESR line, as calculated in figure 4.14 in section 4.5.1. We also see that both sweeping up or down
Experimental Results

Figure 5.23: The laser pulse and the microwave pulse arrive at a fixed time after the laser trigger. The sweep trigger can be varied so that the ISE sweep can be started at different positions in the ESR spectrum. The microwave pulse is kept intentionally long to include as much of the sweep in the polarization transfer as possible. To illustrate the sweep with a measured ESR spectrum has been positioned over the sweep, showing that the sweep just covers the entire spectrum.

Figure 5.24: Initial polarization of crystal #7 at the low field transition as a function of the starting point of the ISE sweep. The black circles indicate the starting points for the up-sweep, and the white circles the starting points for the down-sweep.
give similar enhancement values. The only difference is that the polarization created is of opposite sign. The later one starts the sweep, the lower the polarization enhancement created. In fact, the resulting polarization even changes sign when only the second part of the ESR line is covered with the sweep. It appears as if the electron polarization is not caught in the adiabatic sweep and the polarization enhancements instead corresponds to what could be expected for the solid effect.

**Comparison between the integrated solid effect (ISE) and the solid effect (SE)**

To compare the polarization efficiency of the ISE and the SE, the polarization build-up has been measured with both polarization techniques. The length of the microwave pulse is set to a fixed value of 30 µs. The results of this measurement are plotted in figure 5.25.

![Figure 5.25: Comparison of the initial polarization growth rate between ISE and DSE. The settings are the same as in the previous figure.](image-url)

To evaluate the results of the polarization enhancement, we use equations for the polarization growth rate of the differential solid effect (DSE) 2.14 and the ISE 2.15. We have to account for the effect of DSE, because the ESR spectrum is much wider than then nuclear Larmor frequency. We first estimate the term \( \cos \theta_1 \) in the equation for the DSE. The measurements took place in a magnetic field of around 0.31 T putting the frequency for the Hartmann-Hahn condition at \( \omega_R/2\pi \approx 42.6 \times 0.31 = 13.2 \) MHz. We used a microwave field strength of \( \omega_1/2\pi = 7.1 \pm 1.0 \) MHz which gives a \( \theta_1 \) angle (refer back to figure 2.9 for its definition) of \( \theta_1 = 90^\circ - \arccos(7.1/13.2) = 33^\circ \pm 6^\circ \). This gives a factor \( 1/\cos 33^\circ = 1.2 \pm 0.1 \) in favor for the ISE technique.

More important is to estimate the amount of electron spins that take part in the polarization transfer for both the ISE and the SE technique. For the ISE technique, a weighted ESR spectrum is calculated, following the same procedure as explained in section 4.5.1. With the start of the 15µs sweep set at 770 MHz and the end at 670 MHz, we arrive at a value of 31.9 for the area under the weighted ESR spectrum. The number of spins taking part in the DSE can be found by estimating the factor \( (N_i^+ - N_i^-) \) in equation 2.14.

When irradiating microwaves at a frequency \( \omega \) in the ESR line, we assume that the two spin packets \( N^- \) at \( (\omega - 13.2) \) MHz and \( N^+ \) at \( (\omega + 13.2) \) MHz will contribute to the differential solid effect. We represent these spin packets as gaussians and fit their height to the ESR line (see figure 5.26).

We repeat this for each point of the ESR line and evaluate the factor \( (N_i^+ - N_i^-) \) by
Experimental Results

Figure 5.26: As an example of how the \((N_i^+ - N_i^-)\) factor is calculated, two gaussians, multiplied with the ESR spectrum, have been plotted. The red plot is centered around \((750 - 13.2)\) MHz and the blue plot around \((750 + 13.2)\) MHz, both with a FWHM of 10 MHz. The original ESR spectrum has been plotted with a black line.

Subtracting the area of the two gaussians. Assuming a width of 10 MHz for a spin packet is not unreasonable considering the strong hyperfine interaction between triplet spin and the protons on the pentacene molecule [28]. In order to illustrate the effect of the packet width, we scaled the values for the factor \((N_i^+ - N_i^-)\), determined with 10 MHz, to the experimentally observed values for the DSE polarization growth rate and plotted the curves for different spin packet widths in figure 5.27.

Figure 5.27: The six calculated DSE enhancements can be seen in the graph. The 10 MHz line has been fitted to the measured values. The measured SE polarization enhancement values are plotted with open circles.

The shapes of the theoretical curves nicely reproduce the experimental values. The slight shift with respect to the experimental curve is due to a shift of the magnetic field between the ESR and DNP measurements. Table 5.7 gives the maximum factor \((N_i^+ - N_i^-)\) in units of the ESR line for different packet widths.

For a packet width of 10 MHz, the ISE is thus expected to be a factor of \((31.9/6) \times 1.2 = 6.4\)
better than the DSE. Surprisingly, this value is exactly the same as observed in the experiment \((0.027/0.004 = 6.4\), evaluated from figure 5.25). This is probably just a coincidence, as equations 2.14 and 2.15 give only proportionality and say nothing about the efficiency of the polarization transfer itself. Further, the assumption about the packet width has also influence on the final result.

### Comparison between High and Low Field

So far, we have only performed ISE on the low field transition. However, the high field transition could equally well be used for DNP. The question is which transition would be more efficient in polarizing the sample. ESEEM measurements of Sloop et al [20] indicate that the electron proton coupling is weaker for the high field transition. On the other hand, we know that a stronger ESR signal is obtained for the high field transition (see figure 5.2).

The result of the polarization enhancement for the low field transitions is presented in figure 5.28, and the high field transition in figure 5.29. The start of the ISE sweep, indicated in the figures, is set at the position that gives the highest polarization enhancement. The optimum length of the microwave pulse is found by stepwise increasing the length of the pulse. The circles in the figure represent the ending points of the ISE sweep. We see that extending the pulse for more than 10 µs does not increase the polarization further.

<table>
<thead>
<tr>
<th>FWHM [MHz]</th>
<th>5</th>
<th>10</th>
<th>15</th>
<th>20</th>
<th>25</th>
<th>30</th>
</tr>
</thead>
<tbody>
<tr>
<td>Weighted ESR value [nVs]</td>
<td>3</td>
<td>6</td>
<td>8.5</td>
<td>10.5</td>
<td>12</td>
<td>13</td>
</tr>
</tbody>
</table>

Table 5.7: Values calculated for the factor \((N^+_i - N^-_i)\) of the ESR spectrum plotted in figure 5.27, see text for details.

![Figure 5.28](image-url)

Figure 5.28: Optimizing the ISE locking length for the low field transition. The starting point of the ISE sweep is chosen from the maximum as seen in figure 5.24, and the length of the ISE locking pulse varied. The numbers below the circles correspond to the length (in microseconds) of the microwave pulse.

Only a sweep over the first two thirds of the ESR line seems to contribute to the polarization growth. Considering that the decay of the triplet state is on the same order of
magnitude as the time it takes to sweep through the ESR line, it is not surprising that the last third of the ESR line does not contribute as much to the build-up. The graph shows that the ISE sweep does indeed manage to invert the electron spin. Otherwise, the polarization would start to decrease as the sweep passes the center of the ESR line.

The ESR signal of the high field transition is a factor 1.4 larger than that of the low field transition. At the same time, the polarization growth of the low field transition is a factor 1.5 times better than the one of the high field. We therefore used the low field transition for our DNP experiments throughout.

The experimental results presented in this section are important input for the theory describing the polarization transfer during an ISE pulse sequence, which is currently being developed by W. Th. Wenckebach.
6 Spin Filtering Neutrons with a Polarized Proton Target

Neutrons are uncharged subatomic particles with spin \( \frac{1}{2} \) and a mass slightly larger than that of the proton. Due to the lack of an electrical charge, the neutrons only weakly interact with matter via magnetic interaction and the strong force. Slow neutrons are well suited for investigating the structure and magnetic properties of new materials. This is because the typical de Broglie wavelength of slow neutrons (in the range of Ångströms) matches the typical length scale found in solids.

The neutron was discovered in 1932 by James Chadwick [1], a discovery for which he was awarded the noble price in 1935. Thirteen years later, Ernest O. Wollan carried out the first neutron diffraction experiments in Oak Ridge, USA. He was later joined by Clifford Shull, and together they pioneered and developed the basic principles of the neutron scattering technique, a work for which Shull was awarded the noble prize in 1994. Neutrons used in science are either produced in a nuclear research reactor, as was originally done at Oak Ridge, or by a spallation source, as is done at PSI.

A wide range of scientific phenomena, such as magnetism, superconductivity, cosmology, and particle physics, are spin-dependent and can only be studied by spin-polarized neutrons. The techniques normally used to polarize neutrons are based either on super mirror polarizers, or more recently also on optically polarized Helium-3 [3]. However, both techniques have their limitations. A filter of polarized protons is a very attractive alternative which relieves some of the drawbacks of the other two techniques.

A proof of principle experiment needed to be carried out on a neutron beam to show that a polarized proton target, based on dynamic nuclear polarization (DNP) using photo-excited triplet states, is feasible as a neutron spin filter. This chapter presents the experiment which was performed on a neutron beam [10] using the triplet DNP system developed during this thesis, and described in the previous chapters. The first section gives an overview of the Helium-3 different polarization techniques, their drawbacks and advantages. A short introduction to the theory of neutron scattering following the thorough introduction of the Saclay school [53, 54], is given in the second section. This is followed by a layout of the experiment that has been setup up at the BOA beam line at PSI. In the final section of this chapter, the results of the experiment are given.

6.1 Neutron Polarization Devices

Super mirror polarizers are the standard device for neutron beam polarization. They have several advantages: They rely on spin-dependent neutron optical reflection, are easy to set up and use, have a high polarizing efficiency for cold and thermal neutrons, are stable in time and need no maintenance [2]. However, the mirrors only work at grazing angles and are thus systematically limited in their angular acceptances. Furthermore, the functional range of the coating, and thus the mirrors, are limited to energies below 20 meV (wavelengths longer than 2 Ångström).

Neutron spin filters, based on polarized protons [4] or polarized Helium-3 [3], do not have
these limitations. A filter made of polarized protons relies on spin-dependent nuclear scattering to filter the neutron beam, while the Helium-3 filter relies on spin-dependent absorption. The analyzing power and transmission of such filters are practically independent on the beam divergence. This leads to a principle advantage for high precision neutron polarimetry [55, 56]. More importantly, spin filters are ideal to use at pulsed sources as they allow time-of-flight methods to be employed to analyze all wavelengths in a single experiment [57].

Helium-3 filters are already available at several neutron research centers and present efforts to further optimize this technique [57]. However, the energy-dependent neutron absorption cross-section of Helium-3 makes it difficult to optimize the filter thickness for higher neutron energies. Most importantly, the technical requirements of the Helium-3 spin filter are far higher compared to that of the super mirrors. It should be operated in a very homogeneous magnetic field \((dB/B < 5 \times 10^{-4} \text{ cm}^{-1})\), something that is difficult to maintain in the vicinity of the strong magnets normally found in a neutron research facility.

In contrast, a target of polarized protons [4], which relies on spin-dependent nuclear scattering, overcomes the limitations of the polarizing super mirrors and the technical requirements of the Helium-3 spin filter. The acceptance angle of the spin filter is only limited by the size of the target, which is effective over all neutron energies. However, high magnetic fields of up to 5 T and temperatures of 1 K and below are still required, if the protons are polarized using the scheme of classical dynamic nuclear polarization [5]. Up till recently, the super mirrors and Helium-3 filter combined covered most experimental conditions and requirements. So far an actual implementation of a proton spin filter has been restricted to a few special cases, e.g., for a precise beam polarization determination [58] or to polarize neutrons of thermal [59] and epithermal energy [60]. For the latter implementation, the proton spin filter is the only method currently available. The Helium-3 filter is limited at higher energies and with the advent of megawatt-class pulsed spallation sources (SNS, JSNS, ESS) alternatives for the well established neutron polarization techniques have to be found.

Considering that a spin filter based on polarized protons can polarize the whole range of cold, thermal and hot neutrons, coupled with the much relaxed technical requirements of a filter polarized through triplet DNP (operating at temperatures of around 100 K or higher and magnetic fields below 1 T) the use of polarized protons in neutron spin filters is recalled. The promising result recently published [6, 7] has lead to the implementation of a polarized proton spin filter based on DNP using photo-excited triplet states at PSI [10].

### 6.2 Scattering of Thermal Neutrons by Polarized Nuclei

An incident neutron wave, that is traveling along the z axis with the wave vector \(k\), and scatters elastically on a stationary nuclei at position \(r = 0\) is described by equation 6.1.

As the wavelength of the cold neutron (on the order of a few Å) is far longer than the length scale on which the strong force interacts, the scattered wave can be approximated with scattering on a point source.

\[
\psi(r) \approx \exp(i k \cdot r) + f(\theta) \frac{\exp(i k' r)}{r}
\]

(6.1)

Here, \(f(\theta)\) is the scattering amplitude, with \(\theta\) being the angle between the incoming and outgoing neutron, and \(k'\) the wave vector of the scattered neutron (as shown in figure 6.1). There is no \(\phi\) dependence of the scattering amplitude because one chooses the incident
wave to travel along the z axis.

![Elastic scattering of a neutron beam incident on a point source when traveling as a plane wave in the z direction. The scattered neutron beam spreads out in spherical waveforms. The neutron has an initial wave vector $k$ that changes to $k'$ after scattering with an angle $\theta$ on the point source.](image)

Figure 6.1: Elastic scattering of a neutron beam incident on a point source when traveling as a plane wave in the z direction. The scattered neutron beam spreads out in spherical waveforms. The neutron has an initial wave vector $k$ that changes to $k'$ after scattering with an angle $\theta$ on the point source.

To find the scattering strength we need to solve the Schrödinger equation of the system, which is given by:

$$\left(-\frac{\hbar^2}{2m} \Delta + V(r)\right) \psi(r) = E \psi(r).$$

(6.2)

The solution to the Schrödinger equation is equation 6.1 with $f(\theta)$ given by Green’s function:

$$f(\theta) = -\frac{m}{2\pi\hbar^2} \int d^3r' V(r') \psi(r') \exp(-k' \cdot r').$$

(6.3)

Because the interaction potential of the Schrödinger equation ($V(r)$) can be approximated to a point source the term $\exp(-k' \cdot r')$ can be set to unity. With this approximation, the dependence on the angle $\theta$ disappears from the equation, and the scattering can be described as a s-wave scattering with no orbital momentum. The equation thus reduces to:

$$f = -\frac{m}{2\pi\hbar^2} \int d^3r' V(r') \psi(r').$$

(6.4)

The scattering length is found by approximating the potential $V_F(r)$ with the Fermi potential:

$$V_F(r) = \frac{2\pi\hbar^2}{m} \delta(r).$$

(6.5)

Inserting the Fermi potential into equation 6.4, one arrives as the scattering length:

$$-f = a.$$  

(6.6)

The factor $a$ is called the free scattering length. In general the scattering length may be complex ($a = a' - ia''$). The imaginary part describes the absorption of a neutron. The optical theorem relates the effective scattering cross section $\sigma_{tot}$ to the scattering cross section $\sigma_S$ and the absorptive cross section $\sigma_A$:

$$\sigma_{tot} = \sigma_S + \sigma_A = \frac{4\pi}{\hbar k} Im(f).$$

(6.7)

For most nuclei, the absorptive part of the cross section is several orders of magnitude lower than the scattering part of the cross section. This leads to the final equation for the total cross section:

$$\sigma_{tot} = 4\pi|a|^2 + \frac{4\pi}{\hbar} a''.$$  

(6.8)

For scattering on a bound nucleus, one needs to introduce the bound scattering length $b = \left(\frac{A+1}{A}\right)a$, where $A$ is the mass of the nucleus.
Scattering on a Macroscopic Sample

The scattering amplitude of a collection of scattering centers (each described by the Fermi potential) at position \( r \) with scattering length \( b_i \) is given by

\[
f(q) = \sum_{j=1}^{N} b_j \exp(iq \cdot r_j), \tag{6.9}
\]

with \( q = k - k' \). The differential cross section for scattering on a macroscopic sample of two different isotopes is obtained by taking \( |f|^2 \) over all possible configurations:

\[
d\sigma/d\Omega(q) = \left\langle \sum_{k,j} b_k^* b_j \exp(iq(r_l - r_k)) \right\rangle. \tag{6.10}
\]

6.2.1 Spin Dependence of the Scattering

The strong interaction is spin dependent and needs to be taken into account in the scattering length. The total momentum of the neutron and interacting nuclei is \( J = s + I + l \), with \( l = 0, s \) the spin of the neutron and \( I \) that of the nuclei.

As the neutron is a spin \( \frac{1}{2} \) particle, there exist two scattering channels for the total spin \( j = I \pm \frac{1}{2} \) with different scattering lengths (\( b_+ \) and \( b_- \)) as the eigenvalues of the spin dependent operator. We write the scattering length operator as:

\[
b = b_0 + b_N s \cdot I, \tag{6.11}
\]

with \( b_0 \) the coherent, spin-independent scattering length and \( b_N \) the incoherent, spin-dependent scattering length. Using \( J^2 = (s + I)^2 = \frac{3}{4} + I(I+1) + 2s \cdot I = J(J+1) \) one arrives at the following two equations for the eigenvalues:

\[
b_+ = b_0 + \frac{b_N I}{2}, \tag{6.12}
\]

and

\[
b_- = b_0 - \frac{b_N(I+1)}{2}. \tag{6.13}
\]

The inversion of these two equation yields:

\[
b_0 = \frac{(I+1)b_+ + Ib_-}{2I+1}, \tag{6.14}
\]

and

\[
b_N = \frac{2(b_+ - b_-)}{2I+1}, \tag{6.15}
\]

where \( b_0 \) and \( b_N \) have to be measured experimentally. For hydrogen the values are:

\[
b_0 = -0.37426 \times 10^{-12} \text{ cm} \tag{6.16}
\]

and

\[
b_N = 5.8236 \times 10^{-12} \text{ cm}. \tag{6.17}
\]
Spin Incoherence

Different isotopes in the sample may have different scattering length, and their position in the sample is not exactly known. This is referred to as isotopic incoherence. However, the word 'incoherence' only make sense when describing neutron scattering on the spins, which are not fixed in space but statistically distributed throughout the sample.

When analyzing the efficiency of a spin filter, one is mainly interested in the spin dependent scattering. According to equation 6.11, and knowing that \( \mathbf{s} \cdot \mathbf{I} = s_z I_z + \frac{1}{2} (s_+ I_- + s_- I_+) \), the scattering length can be written as:

\[
\begin{align*}
 b &= b_0 + b_N s_z I_z \quad \text{coherent with spin flip} \\
 &+ \quad 1/2 \cdot b_N (s_+ I_- + s_- I_+) \quad \text{coherent without spin flip}
\end{align*}
\]  

Here the equation has been arranged into two parts:

1. A scattering process without an induced spin flip, including both a coherent and an incoherent part. The incoherent part is due to the disorder in a not completely polarized sample.

2. An entirely incoherent scattering process resulting in a spin flip of both the neutron and the scattering nucleus. There is no interference between different nuclear spins, as their final states are not the same.

While using the commutation relations for spin operators and assuming that there is no correlation between the moments of spin and their position, that the neutron and the nuclei are polarized along the same axis \( e_z \) and that the polarization \( P \) and \( p \) of the nuclei and neutrons are defined as \( \langle I_k e_z \rangle = P I \) and \( \langle s e_z \rangle = \frac{1}{2} p \), one can write the scattering cross section as [53]:

\[
\begin{align*}
 \frac{d\sigma}{d\Omega}(q) &= \sum_{k,l} \left[ (b^2_k - \langle b^2_k b_l \rangle) \delta_{k,l} + \langle b_k^* b_l \rangle \right] \sum_{k,l} \exp(iq(r_l - r_k)) \quad \text{(6.19)}
\end{align*}
\]

Here the first term on the right hand side corresponds to incoherent scattering, and the second term corresponds to Bragg scattering. Finally, one defines the coherent and incoherent scattering cross section:

\[
\begin{align*}
 \frac{d\sigma}{d\Omega}(q) &= N \left( \frac{d\sigma}{d\Omega} \right)_{\text{incoh}} + N \left( \frac{d\sigma}{d\Omega} \right)_{\text{coh}} \times \frac{1}{N} \sum_{k,j} \exp(iq(r_l - r_k)), \\
 \quad \text{(6.20)}
\end{align*}
\]

with

\[
\frac{d\sigma}{d\Omega}(q)_{\text{incoh}} = b_0^2 + b_N p^2 (P^2 I^2 - 1 - P I - P^2 I^2) \quad \text{(6.21)}
\]

and

\[
\frac{d\sigma}{d\Omega}(q)_{\text{coh}} = b_0^2 + b_0 b_N p P I + \frac{b_N^2 P^2 I^2}{4} . \quad \text{(6.22)}
\]

When the spins are anti parallel \( (pP = -1) \), the incoherent scattering is at its largest value, while for parallel spins \( (pP = 1) \) there is no incoherent scattering, and a spin flip can not take place as there is no spin disorder. Therefore, there is a higher probability for neutrons passing through a highly polarized target with opposite polarization to scatter than for neutrons with the same polarization. This is due to the spin flip scattering process. Figure 6.2 shows the coherent and incoherent scattering as a function of the proton polarization for the interaction between a neutron and a single proton.
6.3 Neutron Spin Filtering with Polarized Protons

Polarization by a Transmission Spin Filter

To polarize a neutron beam, one can, as seen from equations 6.21 and 6.22, send the beam through a polarized proton target. As the target can never be fully polarized, the neutron undergoes lots of spin flip processes when traversing the target. The neutron beam becomes more polarized as it passes through the target and at the same time it also loses intensity. The spin dependent attenuation of the neutron beam traversing a spin filter is described by an effective cross section $\sigma_{\text{eff}}$:

$$\sigma_{\text{eff}} = \sigma_0 \pm \sigma_P(P, \lambda),$$  \hspace{1cm} (6.23)

where $+$ represents the case when the neutron spin is aligned parallel to the polarization of the spin filter (and $-$ for opposite alignment), $\sigma_0$ the neutron spin independent part, and $\sigma_P$ the neutron spin dependent part (the so called polarization cross section) which depends on the polarization of the sample $P$ and the wavelength of the neutron $\lambda$.

To find the neutron polarization after the target, one divides the beam in two partial beams with opposite polarization and measures the transmission through the target for both beams. For an incoming unpolarized neutron beam with the initial intensity $I_0$ one obtains the intensities of the two partial beams behind the spin filter to be:

$$n^+ = \frac{I_0}{2} \exp(-\sigma_0 + \sigma_P)Nd,$$  \hspace{1cm} (6.24)

and

$$n^- = \frac{I_0}{2} \exp(-\sigma_0 - \sigma_P)Nd.$$  \hspace{1cm} (6.25)

Here, $N$ is the number density of the polarized nuclei and $d$ the thickness of the spin filter. The polarization of the transmitted neutron beam $p$ (also referred to as the analyzing power $A$ or the polarizing efficiency $P_F$ of the filter) is thus given by:

$$p = \frac{n^+ - n^-}{n^+ + n^-} = -\tanh(\sigma_P Nd) = A = P_F.$$  \hspace{1cm} (6.26)
The transmission $T$ of the neutron beam is given in a similar way:

$$T = \frac{n_\uparrow + n_\downarrow}{I_0} = \exp(-\sigma_0 N d) \cosh(\sigma_P N d). \quad (6.27)$$

As already mentioned and plotted in figure 6.2, the polarizing effect of a polarized proton target is due to the spin dependent scattering of neutrons by protons. The proportionality of the polarization dependent cross section $\sigma_P$ to the proton polarization $P$ defines the normalized cross section $\sigma_{-1,P}$ (normalized to $P = -1$):

$$\sigma_{P}(P,\lambda) = -\sigma_{-1,P}(\lambda) \cdot P. \quad (6.28)$$

The general trend of the polarization cross section for protons is given by figure 6.3. For long wavelengths, above 5 Å, the cross section is determined by the incoherent scattering and absorption on bound nuclei. Between 2 and 5 Å, the neutron resolves the chemical structure of the target, and the coherent scattering dominates. As the neutron energy increases further, the cross section approaches the one given by the scattering on isolated protons [61].

![Plot of the general trend for the normalized polarization cross section $\sigma_P$ as a function of the neutron wavelength and energy. The data points are a compilation of literature values [4, 59, 60, 62].](image)

**Incoherent Scattering at Long Wavelength**

Above a certain wavelength, the so called Bragg cutoff, the coherent scattering of the neutrons disappears. No matching crystal planes exist, and only the incoherent scattering remains. For amorphous samples, the transition to purely incoherent scattering is smooth, and no coherent scattering remains above 9 Å for hydrogen. The incoherent part of the polarization dependent cross section is derived from 6.21:

$$\sigma_{P}^{inc} = -\frac{\pi}{2} b_N^2 P = -53.3 \cdot P \times 10^{-24} \text{ cm}^2, \quad (6.29)$$
and according to equation 6.22, we obtain cross section $\sigma_0$, independent of the neutron polarization, to be:

$$\sigma_{0}^{inc} = -\frac{\pi}{4} b_N^2 (3 - P^2) = 79.9 \times 10^{-24} \text{ cm}^2 \cdot (1 - \frac{1}{3} P^2). \quad (6.30)$$

In our spin filter the only other nuclei present is carbon. Carbon-12 (with a natural abundance of 98.9%) has no spin and does not contribute to the polarization dependent cross section.

For long wavelengths the transmission of the spin filter is rewritten as:

$$T = \frac{n_\uparrow + n_\downarrow}{I_0} = \exp(-\sigma_0^{inc} N d) \cosh(\sigma_P^{inc} N d). \quad (6.31)$$

Remark that the total transmission of the spin filter increases with the proton polarization, even for an unpolarized neutron beam.

**Absorption of the Neutron by Polarized Protons**

The absorption cross section of the polarized protons has to be accounted for to complete the picture of the different ways a neutron can interact with a sample at long wavelengths. In a simple model, the absorption of a neutron by the proton in the triplet state is not accounted for, and we obtain the absorption of the polarized protons $\sigma_{abs}$ to be [63]:

$$\sigma_{abs} = -0.185 \times 10^{-24} \text{ cm}^2 \cdot \lambda(\text{Å}) \cdot P. \quad (6.32)$$

At long wavelengths, combining the the incoherent scattering and the absorption, one gets the total polarization cross section of a polarized proton target to be:

$$\sigma_P = \sigma_P^{inc} + \sigma_{abs} = -\sigma_{-1,P} \cdot P = -(53.3 + 0.185 \cdot \lambda(\text{Å})) \cdot P \times 10^{-24} \text{ cm}^2. \quad (6.33)$$

### 6.4 Expected Efficiency of a Proton Spin Filter

With the equations given in the previous sections, we can estimate the efficiency of the spin filter at long wavelengths by evaluating the analyzing power $A$ and the transmitted intensity $T$ as functions of the sample polarization $P$ and thickness $d$. Figure 6.4 illustrates the analyzing power that can be expected from naphthalene-pentacene crystals of typical thickness. Figure 6.5 gives the corresponding transmission of the filter. At low polarization values, the analyzing power scales almost linearly with the thickness. A thicker sample also leads to a stronger non-spin dependent scattering, lowering the transmission of the neutron beam, an effect visible in graph 6.5. At the same time, the total transmission of the spin filter increases with the filter polarization (refer back to equation 6.31). The so called figure of merit $Q = A^2 \times T$ is customarily used to characterize the performance of the filter. In figure 6.6, the analyzing power, transmission and the figure of merit have been plotted for a sample of 5.6 mm thickness. This corresponds to the actual thickness of the sample later used on the neutron beam.

One can estimate the optimum thickness of a target as a function of the polarization, which has been done in figure 6.7.

The figure shows that a sample thickness between 5 mm and 6 mm is ideal for target polarization values up to 0.5. The optimum thickness of the sample increases rapidly as the target polarization approaches unity.
6.4. Expected Efficiency of a Proton Spin Filter

Figure 6.4: Analyzing power as a function of the proton polarization for three crystal thicknesses. To calculate the graph the following constants have been used: $N = 4.285 \times 10^{22} \text{ cm}^{-3}$ and $\sigma_P = 53.3 \times 10^{-24} \text{ cm}^2$.

Figure 6.5: Transmission for different polarization values as function of the filter thickness according to 6.31.
Figure 6.6: Plot of the figure of merit $Q$, the analyzing power $A$ and the transmission $T$ for a 5.6 mm thick sample.

Figure 6.7: A calculation of the optimum thickness of the target as a function of the polarization.
Experimental Polarization Analysis

A simplistic drawing of the main parts of the actual experiment is shown in figure 6.8. Using the adiabatic spin flipper, the polarization direction of the incoming neutron beam can be selected. Four different count rates can be determined together with the possible polarization directions of the protons in the filter using a super mirror polarizer instead of the spin filter to obtain two more count rates. These count rates are directly tied to the parameters of the main parts of the experimental setup: the adiabatic spin flipper efficiency \( f \), the neutron beam polarization \( p \), the analyzing power of the target \( A \) and the super mirror polarizer of known polarizing efficiency \( P_{SM} \).

From the four different count rates measured with the spin filter, two sets of flipping ratios, \( R_+ \) and \( R_- \), can be defined:

\[
R_+ = \frac{N_{0+}}{N_{0-}} = \frac{1 + pA_+}{1 - fpA_+} \tag{6.34}
\]

and

\[
R_- = \frac{N_{1+}}{N_{1-}} = \frac{1 + pA_-}{1 - fpA_-}. \tag{6.35}
\]

The flipping ratio \( R_+ \) describes the situation where the polarization direction of the spin filter is parallel to the neutron polarization, while \( R_- \) describes the situation for the opposite polarization direction. Worth to note is that the flipping ratio \( R_- \) is less sensitive to the spin flipper efficiency \( f \) when the factor \( pA \) is close to unity: It is therefore better to use a negatively polarized sample when measuring the flipping ratio, something that was also done in the experiment. Replacing the spin filter by the super mirror polarizer yields the additional flipping ratio:

\[
R_{SM} = \frac{N_{0+}}{N_{0-}} = \frac{1 + pP_{SM}}{1 - fpP_{SM}}. \tag{6.36}
\]

Determination of the Normalized Polarization Cross Section

In a real sample, several scattering processes between the neutron and the sample protons take place. Thus, the polarization dependent cross section \( \sigma_P \) is an experimental parameter that has to be determined in an actual neutron experiment. In our case, \( \sigma_P \) is determined through the measurement of the two flipping ratios, \( R_{SM}(\lambda) \) and \( R_F(\lambda) \) respectively:

\[
R_{SM}(\lambda) = \frac{1 + p(\lambda)P_{SM}(\lambda)}{1 - fp(\lambda)P_{SM}(\lambda)}. \tag{6.37}
\]
and
\[ R_F(\lambda) = \frac{1 + p(\lambda)A(\lambda)}{1 - fp(\lambda)A(\lambda)}. \]  
(6.38)

Knowing the efficiency of the super mirror \( P_{SM}(\lambda) \), the beam polarization \( p(\lambda) \) can be calculated from flipping ratio 6.37. The beam polarization is then used to obtain the analyzing power of the sample \( A(\lambda) \) through the flipping ratio 6.38. With the analyzing power known, one arrives at the polarization cross section \( \sigma_P \) by rewriting equation 6.26:
\[ \sigma_P(\lambda) \cdot P = -\frac{1}{Nd} \text{artanh}(A(\lambda)). \]  
(6.39)

To this data we fit the theoretical polarization cross section at long wavelengths (using equation 6.33) to obtain the proton polarization:
\[ \sigma_P(\lambda) \cdot P = -(53.3 + 0.185 \cdot \lambda(\text{Å})) \cdot P \times 10^{-24} \text{cm}^2 = -\frac{1}{Nd} \text{artanh}(A(\lambda)). \]  
(6.40)

Finally, dividing the polarization cross section with the proton polarization over the whole range of measured wavelengths, one arrives at the normalized cross section \( \sigma_{-1,P}(\lambda) \).
\[ \sigma_{-1,P}(\lambda) = -\frac{\sigma_P(\lambda)}{P}. \]  
(6.41)

### 6.5 Experimental Setup

Using the experimental setup described in chapter 4, the neutron spin filter experiment was performed at the new BOA beam line at the continuous spallation neutron source SINQ at the Paul Scherrer Institute in Switzerland. The BOA beam line is a recent upgrade to the previous beam line FUNSPIN [64]. A schematic drawing of the setup is given in figure 6.9. The incoming neutron beam with a spectral distribution determined by the liquid deuterium moderator is polarized by the original bender. The polarization of the beam is maintained by a holding field, consisting of metal plates and small permanent magnets. In it, several small apertures had been placed, reducing the divergence of the neutron beam to around 2.5 mrad at the target. The neutron polarization was reversed by turning on the adiabatic spin flipper. The cryostat was positioned on a stainless steel table in the middle of the beam area, approximately 5.5 m away from where the neutrons enter through the wall. Positioned behind the cryostat were the neutron detectors, a CCD camera with a scintillating material in front, used for neutron imaging, and a Helium-3 counter.

![Figure 6.9: Schematics of neutron setup. 1: chopper wheel, 2: apertures, 3:adiabatic spin flipper, 4: magnetic field, 5: polarized target, inside magnet, and/or polarizing super mirror, 6: scintillating material, 7: CCD camera and 8: Helium-3 neutron counter. The arrows represent the possible polarization directions of the neutron beam as it passes through the experiment.](image)

The rest of the lab equipment was positioned throughout the experimental area (see figure 6.10 for a picture of the setup). The laser and OPO were setup and aligned to deliver
laser pulses of 16 mJ via an optical fiber to the cryostat.
The naphthalene-pentacene crystal used on the neutron beam was of the size $4.65 \times 5.35 \times 5.60 \text{mm}^3$ with the neutrons passing through the longest axis of the crystal. A $3 \times 4 \text{mm}^2$ aperture (sample aperture), made out of lithium doped plastic, ensured that no neutrons could pass around the sample. The sample aperture was mounted just 15 mm away from the crystal sample on the Teflon ISE sweep holder itself, which was positioned around the ESR cavity. In order to block the beam around the sample aperture completely, a $5 \times 5 \text{mm}^2$ aperture was positioned about 1 meter before the cryostat. A final aperture in front of the Helium-3 counter was optimized to get as much signal as possible without flooding the detector, which had a dead time of $10 \mu\text{s}$.

To position the target on the neutron beam, the stainless steel table on which the cryostat was mounted was equipped with adjustable legs which allowed a rough adjustment of the vertical position of the magnet. The center of the ESR cavity could then be fine-adjusted by the X-Z-translation stage mounted on the magnet, positioning the center of the ESR cavity on the height of the neutron beam.

A small cadmium piece with the dimensions of $1 \times 2 \times 10 \text{mm}$ had been mounted on the back side of the ESR cavity in order to be able to reliably check whether the rotation of the insert, and thus also the sample, was correct. Figure 6.11 illustrates the alignment process of the insert and the sample in the horizontal plane.

The optimum vertical position of the sample was found taking images with the CCD camera (see figure 6.12) while slowly lowering the sample towards the center of the ESR cavity. The orientation of the naphthalene-pentacene crystal in the ESR cavity was initially found to be not consistent with $X||B_0$. The alignment error was calculated using the procedure outlined in section 5.1.1. However, we could only determine the angle between the X axis of the pentacene molecule and the external magnetic field. Not in which direction to rotate the crystal to compensate for the misalignment. To try and correct the observed mounting error the crystal was remounted slightly tilted around its axis parallel to the neutron beam. The direction in which to tilt the crystal was determined by observing the crystal with the naked eye and through the birefringence of the crystal. The ESR signals before and after the correction can be seen in figure 6.13. As seen from the figure, a perfect orientation of the crystal could not be found. However, a slight improvement over the first mounting was confirmed by the ESR spectrum.
Figure 6.11: Illustration of the alignment process of the insert with (1) the vague outlines of the Teflon holder, (2) the silhouette of the crystal, (3) the diaphragm and (4) the cadmium piece where the gray colours represent a misalignment of the insert.

Figure 6.12: Image taken by the CCD camera. The diaphragm on the ESR cavity and the naphthalene-pentacene crystal positioned above are visible. One also sees the vague outline of the Teflon ISE sweep holder.

Figure 6.13: The ESR spectrum of the initial orientation of the naphthalene-crystal (black) clearly shows a misalignment of the pentacene X axis with respect to the external magnetic field. The ESR spectrum recorded after the realignment of the crystal (red) still shows a misalignment of the crystal. However the spectrum shows a pronounced peak and is slightly narrower compared to the earlier one, which is advantageous when performing an ISE sweep over the ESR line.
Time of Flight Measurement

A measurement of the time of flight (TOF) was necessary as the polarization cross section is wavelength dependent. Several TOF spectra were measured throughout the experiment. As each TOF measurement took several hours per flipper state, the proton polarization was continuously monitored by NMR. Any recorded change in proton polarization between the two measured count rates was corrected in order to find the accurate flipping ratio. The fast neutrons from the source were not fully blocked by the chopper wheel, and a constant background was present in all time of flight measurements. The background was removed by subtracting the average neutron count for wavelengths above the actual spectrum from the entire time of flight spectrum. The velocity of the neutron measured by its time of flight spectrum is related to its wavelength via de Broglie’s formula:

\[
v[m/s] = \frac{h}{m\lambda} = \frac{3956}{\lambda[\text{Å}]}.
\]

To extract the velocity distribution (and thus the wavelength distribution) from the TOF measurement, the distance between the chopper wheel and the neutron detector was measured to be 637 cm. The delay between the trigger pulse from the chopper wheel to the actual neutron pulse was calibrated by shining laser light through the chopper wheel, detecting the laser pulse with a light sensitive diode and comparing it to the trigger signal. A small time delay of 50 µs was observed and has been corrected in all the measurements (see figure 6.14 for an image of the chopper wheel and spin flipper used in the TOF measurements).

Figure 6.14: To the left side of the picture, the neutron shutter can be seen. The yellow chopper wheel is positioned just after the neutron shutter. The chopper had to be replaced during the measurements as it was revealed that the iron in the chopper wheel destroyed the holding field and thus the polarization of the neutron beam. To the right in the picture the blue adiabatic spin flipper can be seen. At the far right is the holding field consisting of iron sheets magnetized with small permanent magnets.
6.6 Results and Discussion

The experimental data acquisition followed the procedure laid out in section 6.3, albeit at times in a different order. Here, the data will be presented in the order the post-experimental data analysis and evaluation were performed.

6.6.1 Determination of the Analyzing Power

Measurement of the Flipping Ratio $R_{SM}(\lambda)$ and Determination of the Beam Polarization $p(\lambda)$

The first step in the experiment was to measure the wavelength dependent beam polarization $p(\lambda)$ using a calibrated super mirror polarizer. For this measurement, the spin filter sample was lifted out of the beam path and the super mirror polarizer was placed after the triplet apparatus. Figure 6.15 shows the TOF spectra obtained for the two states of the spin flipper from which the flipping ratio $R_{SM}(\lambda)$ is obtained.

![Figure 6.15: The TOF measurement was conducted during two days as the measurement with the spin flipper ON (red line) had an extremely low count rate.](image)

The background of the TOF measurements has been subtracted by fitting the baseline to wavelengths above 16 Å. We know that the polarization efficiency $P_{SM}$ should be around 0.97 and is wavelength dependent [65]:

$$P_{SM}(\lambda) = 0.966 \times (1 - (\lambda - 2) \times 0.008833) \pm 0.005 \quad (6.43)$$

With the given value of $P_{SM}$ and the spin flipper efficiency of $f = 0.98 \pm 0.005$ [58], the neutron beam polarization as a function of wavelength can be extracted from:

$$p(\lambda) = \frac{1}{P_{SM}(\lambda)} \cdot \frac{R_{SM}(\lambda) - 1}{R_{SM}(\lambda) \cdot f + 1}. \quad (6.44)$$

The result is plotted in figure 6.16, where for better data handling 8 raw data points have been binned into a single point. The mean beam polarization averaged over the wavelength spectrum in the range of 2 to 12 Å was found to be $\bar{p} = 0.966 \pm 0.010$. This fitted well to the neutron beam polarization of 0.97 measured in a previous experiment [58].
Figure 6.16: The calculated neutron beam polarization as a function of wavelength. The sources of error are the counting statistics of the TOF measurement, background correction, flipper efficiency and analyzer efficiency.

**Measurement of the Flipping Ratio** $R_F(\lambda)$ **and Determination of the Analyzing Power** $A(\lambda)$

To obtain the analyzing power of the sample $A$ the two TOF measurements, seen in figure 6.17, were recorded.

Due to the protons of the spin filter being negatively polarized the count rate was higher with the spin flipper on. The background has been corrected by fitting the baseline to the counts for wavelengths above 11.5 Å. From the TOF measurement the flipping ratio $R_{SM}$ was calculated (see figure 6.18).

The errors in the graph are greater to the sides, especially for wavelengths above 8 Å. This is...
due to the counting statistics as very few neutrons were recorded with a wavelength greater than 8 Å (refer back to figure 6.17). The analyzing power $A$ can finally be calculated by combining equation 6.38 with 6.37:

$$A(\lambda) = \frac{R_F(\lambda) - 1}{R_F(\lambda) \cdot f + 1} \cdot \frac{1}{p(\lambda)} = \frac{R_F(\lambda) - 1}{R_F(\lambda) \cdot f + 1} \cdot \frac{R_{SM}(\lambda) \cdot f + 1}{R_{SM}(\lambda) - 1} \cdot P_{SM}(\lambda). \quad (6.45)$$

A plot of the calculated wavelength dependent analyzing power can be seen in figure 6.19.
6.6.2 Determination of the Polarization Cross Section

Calculation of the Polarization Cross Section $\sigma_P(\lambda)$ and Determination of the Normalized Polarization Cross $\sigma_{-1,P}(\lambda)$

With the analyzing power $A(\lambda)$ known, we could now extract the proton spin polarization $P$ of the spin filter via the product $\sigma_P(\lambda) \cdot P$. The product was found by inserting the measured analyzing power $A(\lambda)$, the thickness $d = 0.56 \pm 0.01 \text{ cm}$, and the proton density $N = 4.285 \times 10^{22} \text{ cm}^{-3}$ of the spin filter into equation 6.39:

$$\sigma_P \cdot P = -\frac{1}{Nd} \text{artanh}(A(\lambda)). \quad (6.46)$$

The result is plotted in figure 6.20.

![Figure 6.20: Product of the polarization cross section $\sigma_P(\lambda)$ and the filter polarization $P$. Fitting of equation 6.40 to the data points in the range 3.3 to 9.5 Å (indicated by the open circles) allows us to determine the average proton polarization (see text for details).](image)

In order to extract the proton polarization dependence, leaving only the polarization cross section $\sigma_P(\lambda)$, equation 6.40 was fitted to the product $\sigma_P(\lambda) \cdot P$ at long wavelengths (as already indicated by the drawn line in figure 6.20). As explained in section 6.3, the polarization cross section for longer neutron wavelength approaches the one given by the scattering on isolated protons [61]. Simulations performed with the software package FullProf [66] showed that coherent scattering can be safely excluded above 3 Å. This was done taking into account the beam collimation and detector opening of our setup and even assuming a considerable disorientation of the crystal. The fit of the product of the polarization cross section and the proton polarization in the wavelength range of 3.3 to 9.5 Å determined the sample polarization to $P = -0.126 \pm 0.002$. This corresponded well to the polarization of around -13% obtained from NMR measurements recorded during the TOF measurements.

The normalized polarization cross section $\sigma_{-1,P}(\lambda)$ could now be obtained via the proton polarization $P$. However, this was only done for wavelengths below 3.3 Å. For wavelengths above 3.3 Å, equation 6.40 replaced the measured values (see figure 6.21).

Finally, the averaged polarization cross section $\bar{\sigma}_{-1,P}$ is determined from the values
plotted in figure 6.21 and was found to be \( \bar{\sigma}_{-1,P} = (50.71 \pm 1.2) \times 10^{-24}\text{cm}^2 \).

**Neutrons as a Polarization Probe**

With the average polarization cross section \( \bar{\sigma}_{-1,P} \) and the average neutron polarization \( \bar{p} \) known, we now had the ability to determined the proton polarization \( P \) of the spin filter directly from the flipping ratio \( R_F \), eliminating the need to measure a TOF spectrum:

\[
P = \frac{1}{\bar{\sigma}_{-1,P}} \frac{1}{Nd} \text{artanh}\left( \frac{R_F - 1}{R_F \cdot f + 1} \cdot \frac{1}{\bar{p}} \right)
\]

(6.47)

This opened up the ability to use the neutron beam as a polarization probe. The polarization of the sample had been continuously measured with NMR during the entire experiment. Through equation 6.47, the proton polarization calculated from the flipping ratio could easily be compared to the polarization data measured with the NMR apparatus (see figure 6.22 for the comparison).

The NMR measurements corresponded well to the proton polarizations calculated from the flipping ratio, validating the results of the neutron experiment. Using the neutron beam as a polarization probe has one major advantage over conventional NMR: We could, by narrowing the neutron beam down to a size smaller than the spin filter, map the polarization distribution of the filter (see section 6.7.2 for details). This would have been impossible using NMR measurements alone.
6.7 Further Experiments on the Neutron Beam

6.7.1 DNP Build-up Time and Proton Relaxation Rates

During the course of the experiment the sample was polarized and depolarized several times. As a result, the effect of different laser pulse powers on the polarization build-up were measured, see figure 6.23, and the proton relaxation under said laser irradiation obtained, see figure 6.24.

The data shown in the figures have already been included in the discussion in chapter 5 (table 5.6).
Proton Relaxation at Low Magnetic Fields

It was found that the polarization of the neutrons was maintained by the remanent field of the magnet alone, which was on the order of 50 G. This allowed us to measure the relaxation rate of the protons at very low magnetic fields, something not possible with NMR. In figure 6.25, the result of the measurements are presented.

The fitted relaxation times are on the order of 2 to 3 hours and dependent on the temperature of the cryostat. The measured relaxation times are sufficiently long for the spin filter to be useful even at very low magnetic fields. One could potentially polarize the sample at a higher magnetic field before ramping it down to the level desired for the specific spin filter experiment, knowing that the filtering effect will remain for several hours.
6.7.2 Probing the Optical Excitation Process

Reducing the laser power decreases the amount of pentacene molecules excited into their triplet states and decreases the proton polarization growth rate (see figure 6.23). A model presented by Takeda [49] suggests a strong gradient of excited triplet states along the axis parallel with the incoming laser light. This is especially true for a laser pulse containing considerably less photons than the amount of pentacene molecules present in the sample. When polarizing the sample, the number of excited triplet states is directly tied to the proton polarization obtained. The ability to use the neutrons as a polarization probe (as described in section 6.6.2) allowed us to perform a direct measurement of the proton polarization distribution in the spin filter. By measuring the flipping ratio for tiny slices of crystal along the z-axis, the proton polarization as a function of the position in the sample could be fitted through equation 6.47. The beam was collimated vertically with a 1 mm thin slit, made out of cadmium, that was positioned on the cryostat wall itself, 32 mm from the target. This together with the $3 \times 4$ mm aperture on the insert resulted in a neutron beam with the dimensions of $3 \times 1.3$ mm hitting the target. The orientation of the sample in the neutron beam can be seen in figure 6.26.

![Diagram of neutron beam and laser setup](image)

Figure 6.26: Using a thin neutron beam, the polarization distribution of the crystal can be measured by moving the crystal up and down along the z-axis. This in turn gives information about the penetration depth of the laser light. The sample is positioned so that the magnetic field is parallel to the pentacene X-axis. The laser light enters from the bottom of the cryostat, and the thin neutron beam hits the sample perpendicular to the laser beam and the magnetic field. The sample has two axes of freedom, rotation around the mounting axis, to find $X||B_0$, and a movement up and down.

The crystal was polarized using three different laser pulse energies of 9.6, 2.1 and 1.0 mJ, respectively (see figure 6.23). The position of the sample was changed with the caliper in steps of 0.5 mm and the flipping ratio measured. The calculated polarization distribution is plotted in figure 6.27. At full laser power (9.6 mJ), there is roughly two times more photons present in the laser pulse than there is pentacene molecules in the sample. For the 1.0 mJ laser pulse, there is a pronounced lack of photons hitting the sample: There is approximately five times more pentacene molecules than photons. Yet, the measurements show that the triplet states have been created homogeneously over the sample for all three laser powers. The spin diffusion of the protons in the sample is too slow to homogenize the polarization, and we concluded that the predicted strong gradients were not observed in our sample.
6.7.3 Conclusions of the Spin Filter Experiment

The results presented in this chapter show that we have been able to develop a working neutron spin filter based on polarized protons. The analyzing power $A$ obtained thus far was rather modest, around 0.17, but the experiments also showed that there is room for improvement. We precisely determined the polarization cross section $\sigma_P(\lambda)$ of the spin filter, which allowed us to measure the proton polarization of the filter with the neutron beam alone. The independent measurement of the proton spin polarization was in good agreement with the value determined with NMR. This opened up the possibility for measuring the relaxation time of the proton polarization at low magnetic fields and for measuring the proton spin polarization as a function of position in the naphthalene sample. Most surprisingly, the result of the polarization distribution measurements shows that the polarization is homogeneous throughout the sample, even for low laser power. This is in direct contradiction with the existing model describing the photo-excitation process [49]. While further study is needed to explain the results, the measurement is very important for the further development of the spin filter. Different types of laser sources can now be considered. Emphasize should be shifted from optimizing the pulse power of the laser to lasers with longer pulse lengths and very high repetition rates.

Figure 6.27: Using a 1.3 mm thin neutron beam allowed us to measure the polarization homogeneity of the spin filter. The full laser power gave a polarization of 0.1 with the lower intensities giving 0.08 and 0.04 respectively. The slopes of the polarization on the the sides of the graph are a result of the neutron beam only partially hitting the target.
7 Conclusion and Outlook

A working neutron spin filter could be developed consisting of a single crystal of naphthalene doped with pentacene. We polarized the spin filter using dynamic nuclear polarization (DNP) to transfer the electron polarization of the pentacene molecule’s photo-excited triplet state to the surrounding protons. A direct comparison of our proton polarization results with earlier reported values [6, 7] is difficult. On one hand, different laser excitation techniques were used due to their availability, on the other hand, there is reason to believe that the reported pentacene concentrations as well as the obtained proton polarizations might have been overestimated. Based on the long proton relaxation alone, we can conclude that our crystals are of an excellent quality: Relaxation rates exceeding our measured 27 hours were not earlier reported elsewhere.

We built a zone refinement apparatus for the purification of naphthalene and a Bridgman growth apparatus that were used to produce a large number of crystals with different pentacene concentrations. The concentration of pentacene in the crystals was close to the maximum limit (a too high concentration will degrade the quality of the crystal) and was on the order of $10^{-5}$ mol/mol. The laser system was improved by adding an optical fiber, connected to the bottom of the cryostat, delivering the laser pulses to the pentacene-naphthalene crystal with a minimal loss of power. The X-band electron spin resonance (ESR) apparatus was upgraded, adding a stronger and faster integrated solid effect (ISE) sweep. This allowed us to reach proton polarizations of around 13% at a magnetic field of 0.3 T and a temperature of 100 K. This corresponds to a substantial enhancement of the polarization on the order of 40000 compared to the thermal equilibrium value as described by the Boltzman equation. The triplet yield of the pentacene molecule was explored and was found to be close to 0.3 at 100 K. Additionally, the parameters of the DNP build-up process were studied experimentally. We showed that the experimental setup operates reliably over periods of several weeks, both in the lab and on the BOA neutron beam line at the Paul Scherrer Institut. This is of great importance in view of future applications as a spin filter.

Using the neutron beam as a polarization probe, we found that the polarization distribution over the spin filter sample was homogeneous. This lead to the conclusion that a new laser with low pulse power and a higher repetition rate, resulting in a higher average power, could be used to considerably increase the polarization of the spin filter. With the increase in average power of such a laser the efficiency of the cooling of the spin filter will have to be improved. We conclude that the interesting aspects of the physics of the special DNP process and the challenges to develop this into a neutron polarizer for routine operation deserve further study.
Appendix A

Crystal Growth and Results

What follows is a step by step procedure on how to successfully grow a single crystal of naphthalene doped with small amounts of pentacene. The procedure is based on the self-seeding vertical Bridgman technique. The two main papers of inspiration are Arulchakkaravarthi [40] and Selvakumar [41]. The growth technique has been further refined and adapted to the specific conditions used in this work through trial and error.

Chemicals, tools and apparatus needed:

- double walled growth ampoule
- zonerefined naphthalene
- PID controlled temperature gradient
- triple sublimed pentacene
- spatula for adding the pentacene
- scale for weighting the pentacene
- home made connection between zonerefinement tube and growth ampoule
- vacuum pump and connection tubes
- Argon/Nitrogen gas bottle
- cleaning liquids (Acetone and Propanol)
- oven
- heat gun
- glovebox (optional)
- plastic gloves

The step-by-step process:

1. Clean the growth ampoule and tools.
   - Clean for 15 min in an ultrasonics bath.
   - Flush with Acetone/Propanol.
   - Flush out/away the liquid with Argon/Nitrogen gas.
   - Bake out in oven at over 150°C (especially recommended for the growth ampoule).
   - Use plastic gloves at all times and especially after cleaning the tools.

2. Open the zonerefinement glass tube by cutting the glass.
   - Cut the bottom 1/3 or more depending on the amount of impurities visible.
   - Cut the top 1/4–1/5 of the naphthalene.

3. For 1 g of naphthalene, one needs to add 0.217 mg pentacene to get a 0.01% mol mixture.
   - To get the highest possible concentration one should add far more pentacene than what can be dissolved in the crystal.
If a specific concentration is desired, it is recommended to add twice as much pentacene than is actually calculated.

4. Transfer the purified naphthalene from the opened glass tube. If working without glovebox, make sure to keep air out at all times by applying vacuum.

5. Heat the glass tube and ampoule with the heat gun in order to melt and transfer the naphthalene into the ampoule and let it cool down.

6. Be careful when adding the pentacene as it easily gets stuck on the ampoule walls.

7. Seal off the growth ampoule with argon/nitrogen added at a slight underpressure.

8. Wrap the growth ampoule in aluminum foil in order to avoid getting light on the mixture.

9. Heat up the ampoule in the oven at 100–150 °C and keep it heated until the pentacene has dissolved into the naphthalene.

10. Mount the ampoule on the stepper motor and lower it down into the liquid bath, preheated to 90 °C.

11. Start the crystal growth.
   - Initially, a very slow growth speed of 0.5 mm/hour is used to initiate a limited number of growth directions in the outer tube.
   - After a few millimeters, the speed is changed to 3 mm/hour in order to suppress all slow growing crystal directions.
   - After the crystal has entered the inner cavity, the speed is lowered to 1 mm/hour and the crystal is left to grow to its full size.

**Figures of the Zonerefinement Setup, Bridgman Growth Apparatus and Grown Crystals**

![The zonerefinement setup.](image1)

![Close-up of the zonerefinement tube.](image2)

Figure 1: The entire zonerefinement setup is shown in picture (a) and consists of the outer zonerefinement tube mounted at 45°, the control computer, a stepper motor, a voltage supply and (shown in detail in picture (b)) a sealed glass tube with naphthalene inside.
Figure 2: Picture of the Bridgman growth apparatus. The growth ampoule (filled with naphthalene for testing purposes) hangs from a stepping motor and can be moved up or down. Two liquids with different densities are used to create a boundary in the middle of the container. The upper liquid is silicon oil and the lower is glycerol. A voltage of 50 V is applied over the top heating pad (red), heating the liquid in the container to 90°C. The bottom liquid is left at room temperature.

Figure 3: A drawing with the dimensions of the double walled ampoule is shown in figure (a). Picture (b) shows the actual ampoule used in the Bridgman growth.
Figure 4: Picture (a) shows the cut double walled ampoule with the grown crystal still inside the second wall. Picture (b) shows the large crystal piece that we were able to remove from the ampoule.

Figure 5: In order to find the crystal a-axis in the cleavage plane, one tries to arrange the crystal so that only one line (as seen in picture (a)) is visible when viewed from above. Cutting along the single line equals cutting along the a-axis. Picture (b) shows two lines visible, an effect of rotating the crystal 90°.

Figure 6: Picture clearly showing the difference in concentration between crystal #2 (weaker colour) and #4 (stronger colour). The difference in concentration is close to a factor 3.
Appendix B

Pictures of the Cryostat and Insert

Figure 7: Picture (a) shows the cryostat without the outer aluminum wall to show more details. At the bottom of the cryostat one sees the heating pads, glued to the sinted heat exchanger. The capillary that feeds the helium into the cryostat is seen running along the right side of the cryostat. Picture (b) shows the parts of the insert consisting of (from top to bottom) a caliper for positioning the spin filter, connectors for the NMR coils, ISE sweep and ESR signal, four brass supports stabilizing the insert, and the ESR cavity at the bottom (shown in more detail in figure 8).
Figure 8: Exploded view of the ESR cavity. The parts (from left to right) are, 1) the aluminum cup keeping all the parts together, 2) the ISE saddle coil, mounted on a Teflon holder with an aperture made of lithium doped plastic in the center of the Teflon piece, 3) the sapphire dielectric ring mounted on a small Teflon holder with a NMR coil wound around it (barely visible beneath the Teflon tape that is used to hold the coil in place) and 4) the ESR cavity, mounted at the bottom of the insert with the two circuits used for tuning the two NMR coils, visible at the top of the figure.
Bibliography


