USE OF ATOMIC AND MOLECULAR PROBES IN NMR STUDIES OF MATERIALS AND CONSTRUCTION OF A XENON-129 HYPERPOLARIZER

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XENON-129 HYPERPOLARIZER

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Abstract

Xenon atoms and sulfur hexafluoride (SF₆) molecules can be dissolved in liquids and liquid crystals or adsorbed in porous materials. Nuclear magnetic resonance (NMR) spectra of ¹²⁹Xe or ¹⁹F nuclei reveal information about their surroundings. This means that xenon atoms and SF₆ molecules can be used as probes to indirectly study materials by NMR spectroscopy. The change in the spectra arises from a NMR interaction called shielding. Especially in the case of xenon, shielding reveals even the slightest changes, for example, in the density of a liquid it is dissolved in. Because a change in temperature leads to a change in the density of the liquid as well, temperature change is observed as a shift of the resonance line in the ¹²⁹Xe NMR spectrum. This property can be utilized in the accurate determination of the sample temperature. Self-diffusion measurements of the gases provide additional information on a larger scale rather than just the immediate surroundings of atoms or molecules. Various liquid crystals were studied using xenon and SF₆ as probes proving their applicability.

It is often considered that the signal observed in NMR experiments is very weak and limits the full potential of the method. This is true especially with the samples in gaseous form. The Spin-Exchange Optical Pumping (SEOP) hyperpolarization method solves this problem in the case of xenon. A ¹²⁹Xe NMR signal can be enhanced by a factor of $10^4 - 10^5$ by SEOP and this opens access to techniques that are not otherwise possible. The remote detection technique, which separates the encoding and detection steps of the typical NMR experiment both temporally and spatially, is one of these techniques. The potential of the combination of SEOP and remote detection techniques was shown in studies of thermally modified Pinus Sylvestris.

Keywords: nuclear magnetic resonance spectroscopy, shielding, diffusion, liquid crystal, xenon, sulfur hexafluoride, hyperpolarization, remote detection
I have been privileged to belong to the NMR research group of the Department of Physical Sciences at the University of Oulu for the last nine years. I am grateful to Professor Jukka Jokisaari, group leader and supervisor of my thesis, for giving me a chance to become a part of this group and for all the guidance and support that I have received during the years. Besides professor Jokisaari, I also thank Docent Juhani Lounila for a thorough introduction to the theory of nuclear magnetic resonance. Laboratory managers Anu Kantola and Petri Ingman are mainly responsible for my skills with NMR spectrometers. During their periods as laboratory managers Susanna Ahola, Harri Koskela and Sampo Mattila were also there whenever I needed their help.

Jyrki Ruohonen was the first person to get involved in the construction of the xenon hyperpolarizer. His experience and instructions have been a great benefit for me. The personnel of the workshop of the Department of Physical Sciences have been able to fulfill my need for components that often existed only in my mind. I want to thank Mario Cifelli for introducing me to the field of liquid crystals and Henri Tervonen for collaboration and spending the late hours in the NMR lab carrying out numerous measurements in our study of liquid crystals. I am very grateful to Ville Telkki, because without his efficiency during our collaboration this work would still be in progress. And thank you to all the members of the research group for all the fruitful discussions and the pleasant time we have spent together. I appreciate you not only as great colleagues, but true friends as well.

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Finally, I want to thank my parents, brother, sister, relatives and all my friends for their support.

Turku, May 2009
Jani Saunavaara
List of original publications

The present thesis consists of an introductory part and the following articles, which are referred to in the text by Roman numerals I – IV. Copies of articles are found as appendices at the end of the thesis.


The author of this thesis has participated in the writing of each manuscript. His contribution to article II was emphasized in experimental work and analyzing the data. In article III his main contribution is in diffusion measurements, but he was also tutoring the first author of the article during the work. Article IV is a proof of principle study where two novel methods, Spin-Exchange Optical Pumping hyperpolarizing method and remote detection technique, were combined into a new kind of technique used to study the structure of thermally modified wood. The author of this thesis was responsible for planning and constructing the SEOP hyperpolarizer for xenon gas.

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1 Introduction

Nuclear magnetic resonance (NMR) spectroscopy is nowadays a very important tool for chemists, biochemists and physicists studying the structure of matter beyond the scale of optical microscopes. Information may be derived even from the sub-atom scale and the method can be applied to gaseous, liquid and solid samples. Magnetic Resonance Imaging (MRI) is based on the same phenomenon and it offers a great potential for the safe and non-invasive studies of human interiors. Although the history of NMR already began more than 60 years ago and includes Noble prizes in physics (Bloch and Purcell, 1952), in chemistry (Ernst, 1991 and Wüthrich, 2002) and in medicine (Lauterbur and Mansfield, 2003), the field is still progressing rapidly.

The goal of this work is to apply NMR spectroscopy to materials research. This thesis is divided in such a way that the research topics are briefly introduced in the following chapters so that anyone with a basic knowledge of physics should be able to get at least an idea of what has been done. Some supporting information about experimental concepts is given as well, but the actual results of the work are found as attachments in articles I – IV. Chapter 2 is supposed to offer necessary information to understand the principles of the nuclear magnetic resonance phenomenon. The concept of relaxation is unavoidable when dealing with NMR, so it is introduced as well. NMR interactions, particularly shielding, are the basis of xenon thermometer and LC studies applying xenon and SF6 gases. These interactions are described in chapter 2.4. A somewhat simplified description of the experimental aspects of NMR spectroscopy is presented in chapter 2.5, but it should give a sufficient description of the method in order to understand the details of the work introduced in the following chapters.

Chapter 3 is focused on sample temperature and its determination. Methods for determining the actual sample temperature accurately are introduced as well as the basis of xenon thermometer developed in this work. Published results are introduced in article I.

Liquid crystals (LCs), peculiar substances possessing a state of matter that can only be described to be something between liquid and crystal, are introduced in chapter 4. The study of LCs is one of the applications of NMR spectroscopy in materials research. Especially the rapid expansion of LC displays in monitors and televisions has increased LC-related research significantly, but their optical properties are utilized in different kind of polarizers, filters and lenses as well [1]. However, the applications of LCs are not only related to the field of optics, but...
they are used in thermography and gas chromatography. In NMR spectroscopy, they can be applied to orient other molecules so that their anisotropic interactions become detectable. Liquid crystals themselves can be studied by NMR using xenon as a probe atom [2, 3]. Xenon dissolves in LC where its properties are observed from changes in a 129Xe NMR spectrum. Besides the NMR spectrum the diffusion of xenon atoms in the LC were studied as well to derive information about the 10B1M7 (1-methylheptyl 4'-(4-n-decylxybenzoxyloxy)-bi phenyl-4-carboxylate) LC. The results of these studies are presented in article II. SF6 molecules lack some qualities of xenon atoms when considering the sensitivity to its surroundings, but the strong 19F NMR signal arising from six fluorine atoms in the molecule has its benefits. Exploiting the SF6 molecules in diffusion studies turned out to be very efficient. The results of SF6 studies are presented in article III.

Article IV covers a new method, where the structure of wood is studied by time-of-flight (TOF) remote detection MRI of hyperpolarized xenon gas. There are often problems with xenon NMR studies arising from the very low NMR signal. Hyperpolarization methods offer a solution to this problem. In addition, hyperpolarized noble gases can be used together with an advanced method for signal acquisition called remote detection. Especially the studies of porous materials may benefit greatly from the combination of these two techniques. Although not often considered so, dry wood is actually a porous material. Its inner structure consists of large cavities where water and "minerals" are transported in living wood. When wood is used as construction material, water becomes a harmful substance. However, there are numerous ways to protect wood from becoming wet and moldy. Thermal treatment is one of these methods and as hazardous chemicals are not involved, it is considered to be an efficient and environmentally friendly method. Hyperpolarized xenon combined with remote detection offers a new way to study changes that occurred inside the wood during the treatment as is shown in article IV. The author’s main contribution to the article was planning and constructing the continuous flow xenon hyperpolarizer system. The topic is covered in a more detailed way in chapter 5. Both the theory of hyperpolarization and the technical implementation of the hyperpolarizer are introduced.

At a first glance, the topics of the chapters in this thesis may seem to be quite divergent, but there are common denominators. It will be shown that the accurate knowledge of the sample temperature is significant in LC studies, where dynamic NMR spectroscopy with varying temperature is a very common method. 129Xe they are used in thermography and gas chromatography. In NMR spectroscopy they can be applied to orient other molecules so that their anisotropic interactions become detectable. Liquid crystals themselves can be studied by NMR using xenon as a probe atom [2, 3]. Xenon dissolves in LC where its properties are observed from changes in a 129Xe NMR spectrum. Besides the NMR spectrum the diffusion of xenon atoms in the LC were studied as well to derive information about the 10B1M7 (1-methylheptyl 4'-(4-n-decylxybenzoxyloxy)-biphenyl-4-carboxylate) LC. The results of these studies are presented in article II. SF6 molecules lack some qualities of xenon atoms when considering the sensitivity to its surroundings, but the strong 19F NMR signal arising from six fluorine atoms in the molecule has its benefits. Exploiting the SF6 molecules in diffusion studies turned out to be very efficient. The results of SF6 studies are presented in article III.

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NMR is an efficient tool for LC and materials research in general, but a low signal is always an issue. SF₆ gas may substitute xenon gas in some studies and with hyperpolarization methods it is possible to overcome the signal intensity issues.
2 Fundamentals of NMR spectroscopy

Nuclear Magnetic Resonance can be described as a phenomenon taking place when atomic nuclei in a static magnetic field absorb energy from a radio-frequency (RF) field of certain frequency characteristic to the nuclei. Spectroscopy is the study of the interaction of electromagnetic radiation with matter. A more detailed introduction to NMR spectroscopy is found in numerous books [4-6], but in order to understand concepts present in this thesis some fundamentals are covered in this chapter.

2.1 Essential nuclear properties

Every nucleus has a property called spin. It is an intrinsic property of the particle itself, just as mass or charge of the particle. Spin can be considered as a form of angular momentum, although it is not produced by the rotation of the particle. The quantity of spin is expressed as a spin quantum number $I$. Values for the spin angular momentum of particles with spin are quantized and can be expressed as

$$ J = \sqrt{I(I+1)} \hbar. $$

(2-1)

Spin and magnetism are very closely linked. In addition to spin, nuclei with nonzero spin ($I > 0$) also possess intrinsic nuclear magnetism called magnetic moment. The spin angular momentum and the magnetic moment are proportional to each other [7]

$$ \mu = \gamma J, $$

(2-2)

where $\gamma$ is called gyromagnetic ratio and is specific to each nucleus. Particles with negative $\gamma$ have a magnetic moment with an opposite direction to a spin angular momentum, whereas $\mu$ and $J$ are parallel for particles with positive $\gamma$.

When external magnetic field $B_0$ is applied, an interaction called the Zeeman interaction exists between the magnetic moment of a nucleus and $B_0$. The interaction energy is

$$ E = -\mu \cdot B_0. $$

(2-3)

As a result energy levels of the nucleus are quantized as well and particles with spin $I$ have $2I + 1$ sublevels with different energies. These sublevels are specified
by a magnetic quantum number $m_f$ for which possible values are $-I, -I+1, \ldots, I-1, I$. If the amount of both neutrons and protons in a nucleus is even, $I = 0$, and there are no energy levels to be separated by the applied field. These nuclei are NMR inactive. Nuclei with $I > 0$ are NMR active, but in most cases nuclei with $I = \frac{1}{2}$ are considered to be favorable. A spin-$\frac{1}{2}$ nucleus can take only two spin states that can be described as a nucleus having the magnetic moment parallel or opposite to the $B_0$. For a spin-$\frac{1}{2}$ nucleus with positive $\gamma$, the energy level with the spin angular momentum parallel to the external field is slightly lower than the one with the opposite orientation. According to Boltzmann statistics, the low energy level will have a higher population than the high energy level, so that thermal equilibrium is reached. At realistic field strengths the anisotropy of this polarization distribution, referred to as the nuclear spin polarization $\phi$, is directly proportional to the ratio of the magnetic and thermal energies

$$\phi \approx \frac{|\gamma| h B_0}{2kT}. \quad (2-4)$$

$k$ is the Boltzmann constant and $T$ temperature. The equation is valid in typical experimental conditions where $|\gamma| h B_0 \ll kT$.

### 2.2 Macroscopic magnetization and relaxation

In order to understand what happens during the NMR experiment, a more detailed description of the origin of nuclear spin polarization is required. For an in-depth description the textbook by Malcolm H. Levitt [5] is recommended, but a simplified introduction based on that book is given here.

When referring to the direction of spin angular momentum in relation to the $B_0$ field, it is often just referred to as the orientation of the spin or as the spin state. Describing the spin polarization as being parallel or opposite to $B_0$ is actually misleading. Without $B_0$ the distribution of spin orientations is completely isotropic, i.e. all orientations are equally probable. As the $B_0$ is applied, the spins begin a kind of rotational motion called precession around the direction of $B_0$. Angular frequency of this motion is field dependent and known as the Larmor frequency. Precession is a consequence of the nucleus possessing both magnetic moment and spin angular momentum. Despite the precession, the angle between $J$ and $B_0$ remains constant and the distribution of spin polarizations isotropic, at least in the beginning. Small magnetic fields arising from electrons and nuclei

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fluctuate rapidly, because of the thermal motion in the system. These fields slightly alter both direction and magnitude of the total magnetic field experienced by each nucleus, so the angle between the magnetic moment and the external field varies slightly. Over a long period of time (in the order of seconds) this means that spins wander between all the possible orientations. Thermal equilibrium is reached after some time and since the spins slightly prefer lower energy level orientations, the entire sample acquires a small net magnetic moment parallel to $B_0$. Net magnetization is called macroscopic magnetic moment.

This mechanism responsible for growing macroscopic magnetization is called longitudinal relaxation. The buildup curve is exponential and as the direction of $B_0$ is usually considered to be along the $z$-axis, macroscopic magnetization $M_z$ at time $t$ after applying the field is

$$M_z = M_0 \left[ 1 - \exp \left( -\frac{t}{T_1} \right) \right]. \quad (2-5)$$

$M_0$ is the macroscopic magnetization in thermal equilibrium and $T_1$ is known as the longitudinal or spin-lattice relaxation time constant. It describes the time it takes for magnetization to reach 63% of $M_0$. Longitudinal relaxation is actually often referred to as $T_1$ relaxation.

The nuclear spin polarization in the $xy$-plane is cylindrically symmetrical, so there is no transversal nuclear magnetization in thermal equilibrium. The macroscopic magnetization is about four orders of magnitude less than the typical diamagnetism of the sample arising from the orbital motion of the electrons. As $M_0$ is practically not detectable in the direction of $B_0$, the macroscopic magnetization arising from nuclei is rotated into the $xy$-plane to be detected. Macroscopic magnetization is rotating in the $xy$-plane with a precession frequency equal to the individual spins, i.e. the Larmor frequency. However, phase coherence of spins starts to disappear due to so-called transverse relaxation. There is a time constant $T_2$ that is referred to as transverse relaxation, coherence decay or spin-spin relaxation time constant. $T_2$ relaxation time describes the time that it takes for spins precessing in the exact same phase to lose this phase coherence and it can be examined in the transversal $xy$-plane. Magnetization in the $xy$-plane can be described as a function of time

$$M_{xy} = M_0 \exp \left( -\frac{t}{T_2} \right). \quad (2-6)$$
The mechanism of both $T_1$ and $T_2$ relaxation is the small fluctuating fields surrounding the nucleus of interest, but in order to understand the importance of these relaxation mechanisms, it is necessary to know the basic concept of the experiment.

### 2.3 Measuring NMR signal

Longitudinal macroscopic magnetization is rotated to the transversal plane using an oscillating magnetic field $B_1$ that is referred to as an RF-pulse. This field is weak compared to $B_0$, but oscillations are resonant with the precession of the spin and can give rise to a large change in the direction of the spin polarization. Depending on the pulse duration the magnetization can be rotated to the transversal plane (referred to as 90° or $\pi/2$ pulse), in the opposite direction (180°) or in any other direction. When describing the RF-pulse, the term pulse angle or flip angle is used to describe the duration of the pulse.

The precessing transverse magnetization after an RF-pulse is small, but detectable. Magnetic moments rotating with an exact frequency generate an oscillating magnetic field. If there is a coil placed against this oscillating field, an oscillating electric current called Free Induction Decay (FID) is induced to the coil. This FID is the signal observed in NMR experiments and using a mathematical algorithm called the Fourier Transform this time domain data is transformed to the frequency domain, to a NMR spectrum [8]. If the signal is very low, it is possible to use signal averaging. This means that the excitation/detection cycle is repeated several times and FID signals are summed before Fourier Transformation. By accumulating four FID signals it is possible to improve the signal to noise ratio (SNR) by a factor of two.

### 2.4 NMR interactions

Each nucleus has a specific Larmor frequency $\omega_i$ that depends on the product of the gyromagnetic ratio $\gamma$ of the nucleus and the flux density of the magnetic field $B_0$. Though, as it has been described, there are always small fluctuating magnetic fields caused by other nuclei and electrons in the sample. The electrons orbiting a nucleus create a secondary induced magnetic field that opposes the applied field. The nucleus is therefore said to be shielded and its Larmor frequency is changed. Usually NMR spectroscopy is applied to study molecules and this effect is called chemical shift, because the induced field is generated by the valence and bonding.
electrons, which are also responsible for the chemical properties of the molecule. The chemical shift $\delta$ is always measured from a suitable reference frequency $\omega_{\text{ref}}$ and presented on the ppm (parts per million) scale

$$\delta = \left( \frac{\omega_i - \omega_{\text{ref}}}{\omega_{\text{ref}}} \right) \text{ ppm.} \quad (2-7)$$

For example, in the case of $^1$H NMR spectroscopy tetramethylsilane Si(CH$_3$)$_4$ (TMS) is commonly used as a reference. The molecule is highly symmetric and $^1$H nuclei are magnetically equivalent meaning that they all experience similar shielding from the electrons and give a single resonance line in the $^1$H NMR spectrum. Its chemical shift is considered to be 0 ppm and Larmor frequencies of all the other $^1$H nuclei are referenced to it. As the molecules tumble in the liquid, the direction and magnitude of the fields induced by electrons change. This is called chemical shift anisotropy and it is one of those mechanisms mentioned in the previous chapter that lead to relaxation.

The Larmor frequency is also dependent on the presence of other magnetic nuclear spins in the same molecule and the directions of their magnetic moments. The effect called nuclear spin-spin coupling or $J$-coupling is often referred to as indirect coupling, because it works through the electrons in bonds between the nuclei. The magnetic moment of a nucleus $i$ affects the field experienced by a bonding electron and that in turn has an effect on the shielding experienced by the nucleus $j$. In the NMR spectrum this is observed as a multiplet, because the resonance peak of the nucleus $i$ is split into $(2I_i + 1)$ lines depending on the spin of the nucleus $j$. The frequency difference of these resonance peaks has a fixed value, called the spin-spin coupling constant, that is independent of $B_0$. As a nucleus may be bonded to several other nuclei, there sometimes exist complex spin-spin coupling patterns in the NMR spectra.

Each nucleus possessing magnetic moment generates a small magnetic field around itself. Direct dipole-dipole coupling arises from the direct influence of this field on neighbor nucleus $j$ and respectively nucleus $i$ experiences the field generated by nucleus $j$. However, this interaction is efficiently eliminated by the rapid molecular tumbling in gaseous and liquid samples. Dipole-dipole coupling between two nuclei leads to faster relaxation as well, as the magnitude and direction of the magnetic field exerted by one nucleus on the other changes.

Nuclei with $I > 1/2$ are called quadrupolar nuclei and their electric charge distribution is not spherically symmetrical. Because of this, quadrupolar nuclei
interact strongly with the electric field gradients generated by surrounding electron clouds. Like in the case of dipole-dipole interaction, quadrupolar couplings are unseen in the NMR spectra of liquid samples. However, if the molecules are oriented, such as in a solid state, they dominate the spectrum. Quadrupolar interaction is the most efficient relaxation mechanism and this often leads to very broad spectral lines in molecules containing quadrupolar nuclei.

Molecules consist of positive and negative electric charges, nuclei and electrons. If the molecules rotate, then the charges circulate, which corresponds to an electric current. The spin-rotation interaction takes into account the direct interaction between the magnetic fields generated by rapid molecular rotation and the nuclear spins. Although dipole-dipole and CSA mechanisms are usually the most important relaxation mechanisms for spin-$\frac{1}{2}$ nuclei, the spin-rotation mechanism often dominates in gases. As the spin-rotation is clearly weak compared to the other two mechanisms, this means that relaxation times are often exceptionally long in the gas phase.

There is also a sixth NMR interaction called the paramagnetic interaction that is observed in molecules with unpaired electrons like transition metals or radicals. The relaxation time of molecules with unpaired electrons is very short. The chemical shifts of this kind of molecule vary a lot and in addition they are very sensitive to temperature.

### 2.5 Experimental details of NMR spectroscopy

A typical NMR magnet consists of a barrel containing dewars for liquid nitrogen and helium. Inside the helium dewar is wound a superconducting solenoid inducing the strong $B_0$-field (typically 4.7 – 21 T). Nowadays magnets are shielded so that the stray field around the barrel is minimal. Running through the center of the barrel and superconducting solenoid is the bore of the magnet. The magnet is also equipped with two sets of additional coils, called shims, for adjusting the homogeneity of the magnetic field. Superconducting shims are immersed in the liquid helium and as the magnet is installed the currents in these coils are adjusted to provide primary correction for inhomogeneity of the $B_0$-field. Room-temperature shims are located inside the bore and they are adjusted when ever the sample is changed in order to optimize the $B_0$-field homogeneity. This process is called shimming and it is still often carried out manually. The sample is mounted in a cylindrical probe, which is inserted into the bore, so that the sample is positioned in the middle of the superconducting solenoid. Around the sample in
the probe is the coil used for both transmitting the RF pulse and receiving the FID signal. The probe may also contain additional coils for creating magnetic fields with a controlled spatial inhomogeneity. These coils are called gradients and are used for example in diffusion and imaging experiments. Most of the electronics required for transmitting, receiving or controlling gradients are assembled into separate cabinets close to the actual magnet. NMR spectrometers are often classified by the Larmor frequency of the $^1\text{H}$ nucleus in the spectrometer. For example, the 500 MHz NMR spectrometer is a system with an 11.7 T magnet. Modern instruments allow a wide variety of sophisticated NMR techniques to be used. It is impossible to introduce all of them here, but more information is available in numerous textbooks and review articles. However, a closer look at two methods is taken, since they have been the cornerstones of this work.

The technique called dynamic NMR spectroscopy is based on observing physical and chemical changes as a function of time or temperature. Time intervals vary from picoseconds to months, so a wide variety of applications exist. Nowadays it is even possible to study synthetic polymers and biomolecules that are often considered to be too complex to examine by means of conventional NMR spectroscopy. There is a lot of inner movement in these molecules and an exact definition of their structure is not possible without dynamic NMR [9, 10].

Diffusion measurements are the other method exploited heavily in this work. Self-diffusion can be described as a random translational motion of molecules driven by internal kinetic energy. Studies of self-diffusion are a valuable source of information on molecular organization and phase structure. The most widely used NMR techniques for studying self-diffusion are based upon the Pulsed Gradient Spin-Echo (PGSE) method [11, 12]. As seen in figure 1 the basic sequence is rather simple. A 90° RF pulse excites the nuclei and a 180° RF pulse refocuses the spins so that an echo signal is observed at time $2\tau$. Gradients create linear alteration in the $B_0$ field experienced by spins. Due to the effect of the gradient, dephasing of spins occurs. As the second gradient after the 180° pulse is equal to the first one, there is a complete rephasing effect for static spins. However, if the spins have moved in the direction of the gradient during the time $\Delta$, refocusing is not complete and the observed signal is weaker. The higher the self-diffusion is, the more the echo signal is attenuated.

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The technique called dynamic NMR spectroscopy is based on observing physical and chemical changes as a function of time or temperature. Time intervals vary from picoseconds to months, so a wide variety of applications exist. Nowadays it is even possible to study synthetic polymers and biomolecules that are often considered to be too complex to examine by means of conventional NMR spectroscopy. There is a lot of inner movement in these molecules and an exact definition of their structure is not possible without dynamic NMR [9, 10].

Diffusion measurements are the other method exploited heavily in this work. Self-diffusion can be described as a random translational motion of molecules driven by internal kinetic energy. Studies of self-diffusion are a valuable source of information on molecular organization and phase structure. The most widely used NMR techniques for studying self-diffusion are based upon the Pulsed Gradient Spin-Echo (PGSE) method [11, 12]. As seen in figure 1 the basic sequence is rather simple. A 90° RF pulse excites the nuclei and a 180° RF pulse refocuses the spins so that an echo signal is observed at time $2\tau$. Gradients create linear alteration in the $B_0$ field experienced by spins. Due to the effect of the gradient, dephasing of spins occurs. As the second gradient after the 180° pulse is equal to the first one, there is a complete rephasing effect for static spins. However, if the spins have moved in the direction of the gradient during the time $\Delta$, refocusing is not complete and the observed signal is weaker. The higher the self-diffusion is, the more the echo signal is attenuated.
Figure 1. PGSE sequence a) 90° RF pulse is used for spin excitation and 180° RF pulse leads to the formation of a measurable echo signal at time $2\tau$. b) Pulsed gradients are applied to encode information from the diffusion. The diffusion coefficient $D$ can be calculated from the extent of signal attenuation as the strength of the applied gradient $G$, the duration of the gradient pulses $\delta$ or the temporal separation $\Delta$ between them are varied, while keeping the echo time $2\tau$ constant [12]:

$$\frac{A(2\tau)}{A'(2\tau)} = \exp\left[ -\gamma^2 G^2 D \delta^2 \left( \frac{\Delta - \delta}{3} \right) \right]$$ (2-8)

Equation (2-8) is then regressed onto the experimental data and $D$ is determined. Very accurate determination of the gradient field strength is required in order to get reliable values for $D$, so calibration measurements are usually carried out prior to the PGSE experiments.
3 Determination of the sample temperature

As the spectral resolution is becoming ever better due to technical progress, more attention is paid in all the possible factors that may have a negative effect on the quality of a NMR spectrum. Changes in room temperature may have an influence on the spectrometer itself [13], but particularly significant is the temperature stability inside the sample [14-16]. Good temperature stability is essential for studies applying diffusion measurements or dynamic NMR spectroscopy. Accurate NMR thermometers are therefore required to find out the capabilities of the NMR spectrometer.

The basic setup in a modern NMR spectrometer allows measurements in the temperature region 150 – 450 K, though there may be additional limitations if a gradient probe is used. The temperature inside the spectrometer should always be stable during measurements, but dynamic NMR techniques require that it should be carefully adjustable as well. Because of this spectrometers are usually equipped with a variable temperature (VT) unit that gives a reading for the temperature inside the spectrometer. Temperature is actually controlled by adjusting a heater that warms the gas flowing past the sample. Incorrect settings of the VT unit may cause the sample temperature to wander around the target temperature or miss it by several degrees. Exact temperature is derived from a thermocouple located just below the sample tube in the flow of the gas. If this sensor is not positioned correctly there will be false reading for the temperature in the VT unit. Even if sensor is positioned correctly there is some error in the reading, but in the worst cases it can be mistuned by several degrees. When operating below room temperature, liquid nitrogen is vaporized and temperature is controlled by the heater just as in the case of air flow during measurements above room temperature. At lower temperatures the vaporizing rate has to be increased leading to a faster flow rate of N₂. The change of gas from air to nitrogen causes error itself and changes in flow rate further increase the error. It is possible, especially in very high or low temperatures, that flowing gas does not heat or cool a whole sample evenly in the direction of the flow. This leads to temperature gradients within the sample, which causes additional problems [14].

The most severe problem is a possibility of a convective flow that is easily possible in the case of samples with low viscosity [17]. In NMR spectroscopy the sample tube is often rotated in the probe in order to get narrow linewidths, because spinning averages the $B_0$ field inhomogeneities. Normally the spin rate is around 10 – 30 Hz leading to a temperature change of up to 0.2 K. So-called
MAS (Magic Angle Spinning) experiments performed for solid state samples are based on very rapid rotation (>10 kHz) of the sample and this may lead to a temperature rise of several tens of degrees [18]. One more issue related to NMR spectroscopy which may lead to unwanted warming of the sample is the heteronuclear decoupling method, in which non-observed nuclei is constantly pulsed with high RF power [16]. In summary, there is a need to have means to accurately measure and control the sample temperature.

3.1 NMR thermometers

In order to measure actual sample temperature a thermometer should be placed inside the sample volume. Positioning electronic thermometer inside the sample is not possible, but a platinum resistor has been successfully tested [19]. However, the most common way to obtain accurate measurements is the use of a “NMR thermometer sample”. The sample under study is removed for a while to measure the actual temperature using a thermometer sample. Usually determination in these NMR thermometers is based on the temperature dependence of the chemical shift. The most well-known examples are probably methanol and glycol NMR thermometers, where chemical shift between $^1$H resonances in CH$_3$ (methanol) or CH$_2$ (glycol) and OH groups is observed. $^1$H resonance in the OH group is strongly temperature dependent and one degree change in temperature leads to a shift of 0.009 ppm in the spectrum [20]. In the case of the 500 MHz NMR spectrometer (11.7 T) this equals a 4.5 Hz shift. Since linewidth in the $^1$H NMR spectrum is typically in the order of 1 – 2 Hz, change in temperature is easily observed from the spectrum. Several variations of these thermometers exist and usually a substance is dissolved in some deuterated solvent in order to lock the spectrometer frequency and to ease the shimming procedure.

While carrying out measurements it is convenient if there is no need to change observed nuclei during temperature measurements, otherwise retuning of the probe would be necessary. Even sample changes may be avoided by preparing the NMR thermometer in the capillary tube and inserting it in the sample tube itself. In principle, thermometer solvent could be a part of the sample so that sample changes are not required: this would be the most accurate method. There are published results for several substances based on different nuclei ($^1$H [19-22], $^{13}$C [23], $^{19}$F [24], $^{31}$P [25]) that are applicable to be used as NMR thermometers. The most sensitive has been considered to be the one based on $^{59}$Co [26]. Temperature dependence of $^{59}$Co chemical shift in the K$_3$Co(CN)$_6$ compound in
D₂O solvent is 1.5 ppm/K. This is a very accurate measurement tool as a 2 Hz linewidth is achievable. In the case of ¹⁹⁷Co this means that the linewidth in ¹⁹⁷Co NMR spectrum is less than 0.02 ppm in modern NMR spectrometers and even 0.01 K changes in temperature are observable.

3.2 Xenon thermometer

The ¹²⁹Xe nucleus has a spin-½, giving rise to a single resonance peak in the spectrum. It has a relatively high natural abundance (26.4 %) and gyromagnetic ratio, so it is well-suited for NMR spectroscopy. However, the most important property is its large, polarizable electron cloud, which makes ¹²⁹Xe NMR shielding very sensitive to the local environment [2]. Because of this xenon is often used as a probe atom to derive information, for example from the structures of porous materials or liquid crystals [2, 3, 27]. The solubility of Xe is particularly high for organic solvents [28]. This means that in a solvent the xenon spin-density exceeds that in gas. This is an advantage as the low spin density correlates with poor SNR.

Like most other NMR thermometers, the xenon thermometer is based on chemical shift as well. Noble gases are chemically inert, so xenon does not form stable chemical bonds with other atoms, but it is still common to use the chemical shift term. But to be exact, the only interaction having an effect on the ¹²⁹Xe NMR spectrum is the shielding that arises exclusively from environmental effects [3]. In a more detailed way the ¹²⁹Xe NMR shielding of xenon dissolved in a solvent can be expressed as [2]

\[
\sigma_x = \sigma - \sigma_0 = \sigma_s + \sigma_m + \sigma_{\text{aniso}},
\]  

(3-1)

where \(\sigma_0\) is the shielding in the free atom, \(\sigma_s\) arises from the bulk susceptibility, \(\sigma_m\) from the magnetic anisotropy of the neighboring solvent molecules and \(\sigma_{\text{aniso}}\) from the van der Waals interactions. \(\sigma_{\text{aniso}}\) is due to the anisotropy of the nuclear shielding tensor, which averages to zero in isotropic solvents. The solvent affects xenon NMR shielding by altering the total magnetic field at the nuclear site and by interfering with the electron cloud of the molecule. In the case of the xenon thermometer, ¹²⁹Xe atoms are dissolved in an isotropic liquid, so that only terms \(\sigma_s\) and \(\sigma_m\) are relevant. Both terms are strongly dependent on solvent density, and by that, dependent on temperature; this is the basis of the xenon thermometer. It is shown in article 1 that very accurate determination of temperature is possible by

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applying the $^{129}$Xe NMR spectroscopy of xenon gas dissolved in a suitable solvent. A Xenon ethylbromide thermometer has been successfully applied in a study by Telkki et al. [29]. The Xenon thermometer was prepared into a 2.7 mm sample tube and inserted into an actual sample. In ref. [29] the aim was to study the behavior of acetonitrile confined to mesoporous silica gels via $^{129}$Xe NMR spectroscopy, so the temperature was measured simultaneously with actual measurements.

The limitation of the xenon thermometer is usually the same problem that always appears with $^{129}$Xe NMR spectroscopy, i.e. weak NMR signal. Low spin-density in the gas phase may lead to a need of signal averaging. $T_1$ relaxation time of $^{129}$Xe dissolved in liquids is typically measured in minutes [2]. This means that averaging makes measurements using thermally polarized xenon extremely time consuming. $T_1$ relaxation time of xenon has been shortened by adding oxygen to the sample [30]. However, this would reduce $T_2$ relaxation time as well and it broadens the observed resonance line.

With careful shimming the FWHM of the $^{129}$Xe dissolved in solution may be 0.1 – 0.3 Hz in a NMR spectrum. Since the temperature dependency of $^{129}$Xe NMR shielding may be almost 0.4 ppm/K, even the temperature changes in the order of 1 mK can be observed. This means that the xenon thermometer can be even more accurate than the one based on the $^{59}$Co chemical shift in the K$_2$Co(CN)$_6$ compound.
4 Liquid crystal studies

Usually it is considered that there are three states of matter: solid, liquid and gas. In low temperatures matter is solid meaning that atoms and molecules are well organized in matter having both positional and orientational order. As temperature rises, substances become liquid, because bonds between neighboring atoms or molecules are broken due to additional vibration from thermal energy. If temperature is further increased matter turns into gaseous state. In both liquid and gaseous state atoms and molecules tumble and move freely in relation to each other. Liquid crystals have states that possess properties of both crystals and liquids. LC molecules may be diffusive as in liquids, but they still maintain some degree of orientational or even positional order.

Probably the biggest interest in LCs arises from their optical properties, so a wide variety of optical methods are applied in studying LCs [31]. Different kinds of calorimetric methods exist to study energies related to phase transitions [32] and the structural information of the mesophases may be derived from studies with x-ray or neutron diffraction techniques [33, 34]. Methods based on NMR became more popular in the field during the 90’s as they made it possible to study many different properties of LCs. Using NMR spectroscopy it is possible to study structure, phase transitions and viscoelastic properties as well as orientation, conformations, dynamics and self-diffusion of molecules [35]. When the structure of the LC molecule is studied applying NMR spectroscopy, it is usually required that the molecule is labeled with either $^2\text{H}$ or $^{13}\text{C}$ nuclei, because $^1\text{H}$ NMR spectra are too complex to be resolved. This is due to anisotropic interactions that are not averaged to zero in LC mesophase. However, it is possible to study LCs by NMR spectroscopy indirectly by applying probe atoms or molecules which are dissolved in LCs [2].

4.1 Properties of Liquid Crystals

LCs may be divided into thermotropic and lyotropic liquid crystals. Lyotropic LCs consist of two or more components, which possess LC properties only with certain concentrations [10]. The LC phase forms due to the amphiphilic properties of one of the components. These molecules have hydrophobic and hydrophilic parts that cause molecules to become oriented in suitable solvents, so the formation of lyotropic liquid crystals always requires a proper mixture of substances. In this work attention is paid only to thermotropic LCs, where
formation of mesophases is only dependent on temperature. There are numerous mesophases and their properties vary from liquid-like to almost crystalline. The following will introduce the properties of some phases essential to this work.

All LCs are formed by anisotropic molecules. Thermotropic LCs usually consist of several benzene or cyclohexane rings, in which alkaline chains are connected at both ends. This kind of LC molecule is often described as a rod-like molecule. As an example the 10B1M7 (1-methylheptyl 4’-(4-n-decylxoybenzoyloxy)-biphenyl-4-carboxylate) LC is shown in the figure below.

Figure 2. Structure of 10B1M7 liquid crystal

LC may have more than one mesophase and in the case of 10B1M7 as many as five different mesophases exist, if temperature is slowly decreased from an isotropic liquid to the crystalline solid state. In the isotropic liquid positions and orientations of rod-like LC, molecules are randomly distributed due to thermal energy (figure 3 a). In the nematic mesophase a long axis of LC molecules mainly have a parallel orientation, but they do not have any kind of orientational ordering (figure 3 b)). In nematic, as well as in other mesophases, molecules rotate rapidly around their long axis. Mean orientation of the long axis is referred to as a director of the LC. Orientational order parameter \( S \) is used to describe how accurately long axes of the molecules are parallel to the director.[36]

\[
S = \langle P_2(\cos \theta) \rangle = \left\langle \frac{3}{2} \cos^2 \theta - \frac{1}{2} \right\rangle
\]  
(4-1)

The variable \( \theta \) in the equation is the angle between the long axis of each individual molecule and the director. The angle brackets imply that an average over a large number of molecules is taken. For an isotropic liquid \( S = 0 \), whereas for a fully oriented crystal \( S = 1 \). In the nematic mesophase \( S \) gets values 0.4 – 0.7, so molecules may be considered as weakly oriented [36].
In smectic mesophases molecules have some level of positional ordering in addition to orientational ordering. In a small scale (1.5 – 2.5 nm) molecules form layers, although layers are very diffuse and unobservable at a larger scale. In Smectic A (SmA) mesophase the director is orthogonal to the layers, while in SmC phase the long axes of molecules are slightly tilted towards the layers. SmC mesophase forms from SmA mesophase as a result of cooling and the tilt angle of the director in temperature $T$ may be described using the equation

$$\theta(T) = \theta(0)(T_{A-C} - T)^\alpha.$$  \hspace{1cm} (4-2)

Variables $\theta(0)$ and $\alpha$ are constants specific to LC and $T_{A-C}$ is the transition temperature from SmA to SmC mesophase.

Some LC molecules are chiral, meaning that the molecule is not superimposable on its mirror image. 10B1M7 is a chiral molecule and its chiral group is marked with an asterisk (*) in figure 2. When chiral molecules form SmC* mesophase, the direction of the tilt changes slightly from layer to layer. The actual tilt angle remains constant, but the direction gradually rotates from layer to layer eventually forming a helix. Due to chiral molecules symmetry is reduced and as a result inequivalence in the dipole moment along a symmetry axis is created. This in turn generates a spontaneous polarization that is reduced to zero on larger scale due to helical rotation of layers. Ferro- and antiferroelectric SmC* mesophases have a structure similar to ferroelectric mesophase, but the tilt angle varies from layer to layer as shown in figure 4 b) and c). Particularly ferro- and antiferroelectric mesophases have raised a lot of interest, because they could be applied in very fast LC displays.[31]
Structures of the liquid crystal phases described above are very weak and they exist only on a small local scale. However, LC mesophase can be almost crystalline as it is in the case of smectic J (SmJ) mesophase. Molecules are arranged in layers and their long axes tilted. In addition, inside the layers, hexagonal packing may be observed. This mesophase is different from the crystalline phase though, because molecules are still freely rotating around their long axis.

4.2 Studies applying xenon gas

The first $^{129}$Xe NMR studies on xenon dissolved in a thermotropic LC were performed in 1988 [37]. The method is based on the same property of the xenon atom as in the case of the xenon thermometer, namely the sensitive NMR shielding. Changes in the surroundings of the atom are observed in the $^{129}$Xe NMR spectrum. This means that it is possible to derive information from the orientation of the LC director and phase transitions. Typically LC study includes a dynamic NMR spectroscopy experiment, where temperature is decreased with constant steps and the $^{129}$Xe NMR spectrum is measured in each temperature. When $^{129}$Xe shielding is plotted as a function of temperature, phase transitions are easily observed. It is very important that the temperature can be controlled accurately during these studies. Depending on the VT unit and its settings...
temperature may wander around the target temperature during the change. While investigating the phase transition from isotropic to chiral nematic phase in a LC codenamed as DM 8/6, temperature was reduced by 0.1 K steps and the mesophase of interest existed only in the 0.9 K temperature interval. A stackplot of $^{129}$Xe NMR spectra from the temperature range 329.8 – 328.5 K is shown in figure 5.

Figure 5 Stackplot of $^{129}$Xe NMR spectra from xenon dissolved in DM 8/6 LC.

Experiments were performed on a Bruker Avance 500 MHz spectrometer equipped with a BVT2000 unit. Performance of this particular VT unit was studied in a detailed manner during the xenon thermometer study. It was confirmed that the accuracy of the VT unit allows small (0.1 K) changes in temperature and it was possible to repeat the experiments so that exactly the same temperatures were achieved each time. These experiments are a good example of the sensitivity of LC studies applying $^{129}$Xe NMR. The resonance at 188 ppm arises from the xenon in isotropic phase and the one at 191 ppm from the chiral nematic phase. The strongly temperature-dependent resonance at 192.5 – 193 ppm was an unexpected finding. It is still unclear what is causing the effect, but
its appearance was confirmed by repeating the measurements several times. It only appears when the temperature is lowered from the isotropic phase.

LCs very close to 10B1M7 in structure were earlier studied using optical and calorimetric methods [38] and 10B1M7 itself was studied applying $^3$H NMR spectroscopy [39, 40]. While using a probe atom like xenon the labeling of LC molecules becomes unnecessary. This is a great advantage as the labeling process is often difficult and expensive. Solubility of xenon gas in most LCs is very good, but in order to attain a useful NMR signal from $^{129}$Xe nuclei it is often necessary to use isotopically enriched gas or at least high gas pressure in a sealed sample tube. Typical pressures (2 – 6 atm) used in samples lead to a problem, because phase transition temperatures may change by a few degrees. However, the structure of the phase seems to remain unaltered. In the 10B1M7 study the common method of observing $^{129}$Xe NMR shielding as a function of descending temperature was applied [3]. Measurements started from the isotropic phase and continued until the crystal phase formed and xenon gas was squeezed out from the structure. Experimental results and their analyses are presented in article II.

Weak $^{129}$Xe NMR signal intensity complicates the use of xenon in diffusion studies. However, diffusion studies were successfully applied in a study of ferroelectric liquid crystal earlier [41], but structures of ferri- and antiferroelectric mesophases have not been studied earlier by the method. Since notable temperature gradients were observed during the xenon thermometer study, the possibility of thermal convection had to be taken into consideration. Convective flow leads to a physical movement during the experiment and PGSE diffusion measurements would give false values for diffusion constant $D$ [14, 17]. However, there are special pulse sequences to eliminate most of the convection artifacts [41, 42]. DSE sequence was applied in the 10B1M7 study and a detailed description of its principle is found in ref. [41].

After determined xenon self-diffusion coefficients were found to match between PGSE and DSE experiments even at the highest temperatures, the PGSE method was preferred in order to attain better SNR. There is no doubt that a temperature gradient existed within the sample, because significant broadening of the linewidth in the $^{129}$Xe NMR spectrum was observed at high temperatures. Anyway 10B1M7 LC is such a viscous substance, even in the isotropic phase, that convection does not occur.

Since the 5 mm BBI probe used for this study had only gradient coils in the z-direction, diffusion measurements in the transversal direction were carried out by applying the CTPG (Constant Time Pulse Gradient) method [43]. A linear
magnetic field gradient is generated by shim coils and maintained during the experiment.

Figure 6. CTPG pulse sequence. In addition to RF pulses, a constant linear magnetic field gradient is maintained during the sequence.

Determination of diffusion coefficient with the CTPG method is based on a series of measurements where $\tau_1$ and $\tau_2$ times are changed, but total time $(2\tau_1 + 2\tau_2)$ is kept constant. The amplitude of the observed signal is given by

$$A(t) = A(0)\exp\left[\frac{-2(\tau_1 + \tau_2)}{T_2} - \frac{2}{3}\gamma^2G^2D(\tau_1^3 + \tau_2^3)\right],$$

where $A(0)$ is the minimum amplitude, when $\tau_1 = \tau_2$. When $\ln[A(t)/A(0)]$ is presented as a function of $($$\tau_1^3 + \tau_2^3$$)$ the result is a straight line and the diffusion coefficient is simple to calculate from the slope $-2/3\gamma^2G^2D$, as $\gamma$ and $G$ are known constants.

Results in article II show that diffusion studies of $^{129}$Xe give valuable information about the mesophases. However, they are often extremely time-consuming. Measurements of xenon in SmC* antiferroelectric mesophase took up to eight hours, because the signal had to be accumulated to get a decent SNR.

4.3 Studies applying SF$_6$ gas

The $^{19}$F nucleus is very convenient for NMR spectroscopy due to its high gyromagnetic ratio (close to that of $^1$H) and 100 % natural abundance. The sulphur hexafluoride (SF$_6$) molecule is relatively small (5.3 Å), but it contains six magnetically equivalent $^{19}$F atoms, so in terms of NMR it has a rather high spin density even in gas phase. This combined with the short $T_1$ relaxation time of $^{19}$F nuclei in SF$_6$ makes it possible to rapidly accumulate high signal intensity for $^{19}$F NMR spectroscopy. It is actually possible to attain signal intensity from SF$_6$ gas that is 20 % of the intensity in liquid water in the same period of time [44]. This is an exceptionally strong signal from a gas phase and on a totally different scale

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compared to that measured from xenon; the accumulated signal can be four orders of magnitude higher. SF₆ is non-toxic, incombustible, chemically stable and unreactive, so just like the xenon atom it is an excellent NMR probe. It has been applied in the studies of porous materials [45], ethylene-propylene rubbers [44] and even in the MRI of rat lungs [46]. As a part of this work, SF₆ was applied in LC studies. In practice the SF₆ molecule has a single ¹⁹F NMR resonance, and rapid longitudinal relaxation from the spin–rotation interaction [47]. As seen in figure 11 of article III, there is actually more than one peak observed in the spectrum. This is due to different isotopes of sulphur that can be located in the middle of the SF₆ molecule and they have their individual resonances. However, the resonance from the molecules with ³²S isotope is dominant in the spectrum as its natural abundance is almost 95%.

According to a study by Jackowski et al the ¹⁹F gas-to-solution shifts of SF₆ are primarily due to dispersive and repulsive van der Waals interactions with solvent molecules. The ¹⁹F chemical shift range due to solvent effects is about 8 ppm compared to 250 ppm on the ¹²⁹Xe chemical shift. [48, 49] The ¹⁹F NMR shielding of fluorine nuclei in SF₆ molecules dissolved in LC can be described with the same model used for ¹²⁹Xe. However, the contribution of the different terms to shielding is very different from that in ¹²⁹Xe. The fundamental difference between the ¹⁹F and ¹²⁹Xe shielding of SF₆ and xenon, respectively, in liquid crystal solutions, is the bulk susceptibility contribution to ¹⁹F shielding that is as high as over 65% in Phase 4, ZLI 2806, and ZLI 3125 LC and ca. 30% in HAB, while for ¹²⁹Xe this contribution is on the order of 1% in various LCs.

As is shown in article III, there is a spin-spin coupling seen in the ¹⁹F NMR spectrum arising from the ³²SF₆ molecules. The 2D HMOC (Heteronuclear Multiple Quantum Coherence) spectrum presented in figure 12 of article III is a method for studying the chemical shift correlations between ¹⁹F and ³²S nuclei. The 2D spectrum is presented as a contour plot and in this case 1D NMR spectra of the ¹⁹F and ³²S nuclei are presented above and on the right to ease the interpretation of the spectrum. Usually the 2D HMOC experiment is carried out to reveal which resonances in ¹H and ¹³C NMR spectra arise from bonded nuclei, so it is a useful experiment when solving molecular structure. In this case the structure was clear from the beginning, but it was proved that ¹⁹F-³²S correlations are clearly observable with the 2D HMOC experiment and this could be useful with larger molecules. Additional coherence in the middle of the 2D HMOC spectrum (figure 12) is an artifact arising from the strong signal of ³²SF₆ molecules.

compared to that measured from xenon; the accumulated signal can be four orders of magnitude higher. SF₆ is non-toxic, incombustible, chemically stable and unreactive, so just like the xenon atom it is an excellent NMR probe. It has been applied in the studies of porous materials [45], ethylene-propylene rubbers [44] and even in the MRI of rat lungs [46]. As a part of this work, SF₆ was applied in LC studies. In practice the SF₆ molecule has a single ¹⁹F NMR resonance, and rapid longitudinal relaxation from the spin–rotation interaction [47]. As seen in figure 11 of article III, there is actually more than one peak observed in the spectrum. This is due to different isotopes of sulphur that can be located in the middle of the SF₆ molecule and they have their individual resonances. However, the resonance from the molecules with ³²S isotope is dominant in the spectrum as its natural abundance is almost 95%.

According to a study by Jackowski et al the ¹⁹F gas-to-solution shifts of SF₆ are primarily due to dispersive and repulsive van der Waals interactions with solvent molecules. The ¹⁹F chemical shift range due to solvent effects is about 8 ppm compared to 250 ppm on the ¹²⁹Xe chemical shift. [48, 49] The ¹⁹F NMR shielding of fluorine nuclei in SF₆ molecules dissolved in LC can be described with the same model used for ¹²⁹Xe. However, the contribution of the different terms to shielding is very different from that in ¹²⁹Xe. The fundamental difference between the ¹⁹F and ¹²⁹Xe shielding of SF₆ and xenon, respectively, in liquid crystal solutions, is the bulk susceptibility contribution to ¹⁹F shielding that is as high as over 65% in Phase 4, ZLI 2806, and ZLI 3125 LC and ca. 30% in HAB, while for ¹²⁹Xe this contribution is on the order of 1% in various LCs.

As is shown in article III, there is a spin-spin coupling seen in the ¹⁹F NMR spectrum arising from the ³²SF₆ molecules. The 2D HMOC (Heteronuclear Multiple Quantum Coherence) spectrum presented in figure 12 of article III is a method for studying the chemical shift correlations between ¹⁹F and ³²S nuclei. The 2D spectrum is presented as a contour plot and in this case 1D NMR spectra of the ¹⁹F and ³²S nuclei are presented above and on the right to ease the interpretation of the spectrum. Usually the 2D HMOC experiment is carried out to reveal which resonances in ¹H and ¹³C NMR spectra arise from bonded nuclei, so it is a useful experiment when solving molecular structure. In this case the structure was clear from the beginning, but it was proved that ¹⁹F-³²S correlations are clearly observable with the 2D HMOC experiment and this could be useful with larger molecules. Additional coherence in the middle of the 2D HMOC spectrum (figure 12) is an artifact arising from the strong signal of ³²SF₆ molecules.
When comparing properties of the xenon atom and the SF₆ molecule as probes in LC studies, it turns out that both have their advantages. ¹²⁹Xe NMR shielding is more sensitive to the local environment and as this property has been exploited for 20 years, thus there is a lot of useful information available. However, the strong NMR signal from ¹⁹F nuclei makes possible fast and accurate diffusion measurements with SF₆. In addition, quantitative integral measurements and relaxation time measurements could provide an extra benefit when using SF₆ [49].
5 Hyperpolarization of xenon gas

Hyperpolarization of noble gases has recently drawn a lot of interest due to potential applications in medical MRI. Lung ventilation images with an unseen level of detail and applicability of diffusion studies to observe structures even on the alveolar scale have given rise to high expectations for the method [50]. As stated in chapter 2, the basic requirement of NMR is the high homogeneous magnetic field required to create sufficient spin polarization. Nuclear spin polarization follows the Boltzmann distribution as presented in equation (2-4) and is dependent on the gyromagnetic ratio $\gamma$ of the nucleus, magnetic field $B_0$ and temperature $T$. In the case of clinical MRI the only way to increase polarization is the stronger magnetic field. Unfortunately, even in high magnetic fields of modern MRI scanners (typically 1.5 – 3 T) and NMR spectrometers (4.7 – 21 T), the spin polarization of $^1H$ nuclei is only on the order of 0.001 – 0.01 % and even less in the case of other nuclei.

Nuclear spin polarization of noble gas nuclei can be increased by meta-stable exchange (MEOP) or spin-exchange optical pumping (SEOP) techniques. In the MEOP technique electrons of $^3$He atoms are first excited to the meta-stable state and then optically pumped. Nuclear spin polarization is built up through the collisions of the meta-stable $^3$He atoms in the low pressure optical pumping cell. Nuclear spin polarizations close to 80 % can be attained with the MEOP technique. In this chapter, however, the SEOP method is reviewed. It is applicable for $^3$He nuclei as well, but it is particularly suitable for $^{129}$Xe and it can be described as a two-step process. First the electron spins of an alkali metal are polarized by optical pumping and in the second step spin-exchange collisions between the alkali metal and noble gas atoms lead to enhancement of nuclear spin polarization. There are several review articles and a Ph.D. thesis by Iulian Ruset that can be recommended as a source of more information about the SEOP method [51-54].

5.1 Optical pumping

Alfred Kastler won the Noble Prize for Physics in 1966 for his discovery and development of methods for observing Hertzian resonances within atoms. His method of stimulating atoms so that they attain higher energy states was called "optical pumping." In the SEOP method alkali-metal valence electrons are optically pumped applying circular polarized laser light matching their $D_1$-
transition wavelength. $D_1$-transition is the transition from the ground state to the first excited state. Rubidium (Rb) is often used because its low melting point leads to a high vapor pressure already at sufficiently low 80 – 200°C temperatures. In addition, affordable diode laser systems with a wavelength matching the Rb $D_1$-transition wavelength are available. Technical details of the optical pumping setup are quite simple. A circularly polarized laser beam is directed through a cylindrical polarization cell, placed inside a homogenous magnetic field, so that the inner volume of the cell is completely illuminated. A small amount of Rb is placed inside the cell and it vaporizes as the cell is heated. So called continuous flow systems are normally used when hyperpolarizing xenon gas. In this kind of design Rb can be placed inside a separate cell, where it is vaporized. As gas mixture flows through the cell it becomes saturated by Rb and then flows into the polarization cell. Partial pressure of the xenon gas is often rather small (1 – 5 %) and most of the mixture consists of helium, although a portion of nitrogen (1 – 10 %) is included as well.

There are two stable rubidium isotopes present in nature: $^{85}$Rb (72.2 %) and $^{87}$Rb (27.8 %). As with other alkali-metal, there is only one electron on the outer electron shell of the Rb atom. The ground state of this so-called valence electron is $^5S_\frac{3}{2}$. The total angular momentum $j$ of the electron is the sum of its spin ($s = \frac{1}{2}$) and the orbital angular momentum of the electron $l$. The interaction between the spin and the orbital angular momentum is called spin-orbit interaction. The first excited state of the electron is the $^3P_{\frac{3}{2}}$ state, where the spin and the orbital angular momentum are opposite ($j = l - s = \frac{1}{2}$). In the second excited state $^3P_{\frac{1}{2}}$, their direction is parallel ($j = l + s = 3/2$). Hyperfine interaction between the magnetic dipole moments of electron and nuclear spins splits energy levels of ground state and excited states according to the total angular momentum ($F = m_e + I$, where $m_e$ and $I$ are electron and nuclear spin quantum numbers, respectively) [55]. During optical pumping a small magnetic field is applied and the Zeeman interaction divides energy levels even further to $2F + 1$ sublevels. Fortunately, the schematic of Rb atomic levels can be simplified to the form shown in figure 7, if we consider optical pumping related to the hyperpolarizing noble gases [51, 56]. Hyperfine interaction and nuclear spin are not considered, rather just focused on the electron total angular momentum $j$. It is possible to ignore nuclear spin, because its only effect in practice is that it takes more photons in the beginning of the process to achieve the populated state, but it does not change the total electron spin polarization in the end. In addition, the pressure in the polarization cell in the SEOP method is at least on the order of 100 – 1000 mbars. This leads to a
pressure broadening of the $D_1$ transition wavelength and also makes the hyperfine structure unresolved, so it is a good approximation to consider nuclear spin $I = 0$. Thus, in figure 7, $^3S_{1/2}$ and $^3P_{1/2}$ states are only split due to the Zeeman interaction to $m_j = \pm 1/2$ sublevels.[51, 54]

Light is a form of electromagnetic radiation. It has a dual nature meaning that it is described by using both wave and quantum theory. Circularly polarized light can be considered as a transverse electromagnetic wave, in which an electric field vector is rotating in the plane perpendicular to wave propagation. Circularly polarized light is said to have “right-handed” or “left-handed” circular polarization depending on the direction in which the electric field vector rotates. In terms of quantum theory, a photon possesses a spin angular momentum $I_j = 1$. A photon of circularly polarized light with sufficient energy can cause a transition of the Rb valence electron from the ground state to the excited state. A change $\Delta m_j = \pm 1$ occurs depending if the light has right- or left-handed polarization in respect to the direction of the applied magnetic field. If the photon causes the transition $\Delta m_j = +1$, sign $\sigma^+$ is applied, as in figure 7.

![Figure 7. Simplified schematic of Rb energy levels and optical pumping process.](image)

Average lifetime of the excited state $^3P_{1/2}$ is very short (less than $10^{-8}$ s). However, due to the relatively high density excited Rb atoms experience collisional mixing and in spite of the short lifetime of the excited state, the populations of $^3P_{1/2}$ sublevels are even in practice. As an electron returns to its ground state by emitting a photon, it is equally likely for an electron to end up on either of the sublevels. The electron on the sublevel $m_j = -1/2$ rapidly absorbs another photon and again de-excitation is equally likely for either of the ground

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state sublevels. As a result of this optical pumping, sublevel \( m_J = -1/2 \) will eventually be almost empty. Atoms on the \( m_J = +1/2 \) sublevel cannot absorb \( \sigma^- \) polarized photons, but they can still depolarize to the \( m_J = -1/2 \) sublevel. One of the most efficient depolarization mechanisms is the absorption of photons from the radiative decay of the excited state. Other mechanisms are collisions between alkali-metal atoms, wall collisions, and interactions with the gases present in the mixture. All the processes mixing the ground levels \( m_J = -1/2 \) with \( m_J = +1/2 \) are summed up by a spin-destruction rate \( \gamma_d \). After a Rb atom is polarized it no longer absorbs photons, so the polarization cell can be completely illuminated. Almost 100% electron spin polarization is possible in the cell, except for in the regions close to walls, where relaxation is exceptionally rapid due to collisions between atoms and the wall. The efficiency of optical pumping is described by a factor \( \gamma_{opt} \) that describes the number of atoms pumped from the \( m_J = -1/2 \) to the \( m_J = +1/2 \) sublevel in one second. The time dependence of the Rb electron spin polarization can be expressed as

\[
P_{rb}(t) = \frac{\gamma_{opt}}{\gamma_{opt} + \gamma_d} \left[ 1 - \exp\left(-\left(\frac{\gamma_{opt}}{\gamma_{opt} + \gamma_d}\right)t\right) \right].
\]

Mixing of \( m_J = \pm 1 \) sublevels in the ground state is very slow compared to the same process in the excited state. This means that \( \gamma_d \) is very small compared to \( \gamma_{opt} \). Regularly it takes only 10 – 20 ms to achieve a steady state. Thus in the time scale of the SEOP experiment the Rb polarization can actually be described as

\[
P_{rb} = \frac{\gamma_{opt}}{\gamma_{opt} + \gamma_d}.
\]

Minimizing the spin destruction rate \( \gamma_d \) leads to maximal Rb polarization.[54, 56]

Buffer gases have a significant role in optical pumping. Collisions of Rb atoms with buffer gas atoms and molecules make possible the rapid collisional mixing of the excited state \( ^3P_{1/2} \) sublevels \( m_J = \pm 1/2 \), leading to the equal probabilities of de-excitation. When de-excitation occurs, photons causing depolarization are emitted. \( \mathrm{N}_2 \) is used as a quenching gas in SEOP systems, because the molecule has suitable vibrational energy levels to nonradiatively de-excite the excited atoms in collisions before they can reradiate a photon. Already 100 mbar partial pressure of \( \mathrm{N}_2 \) reduces the radiative decay to below 4% [57, 58].
Another advantage of using N₂ as a buffer gas is that the excited state lifetime of Rb is reduced from 28 ns to 1 ns [54]. Buffer gases, particularly helium, are responsible for the pressure broadening of the spectral lines of Rb mentioned earlier. This is a consequence of interaction between a Rb electronic cloud and the gases in the pumping mixture, resulting in a distortion of the Rb atomic energy levels. Pressure broadening for the Rb D₁ line is approximately 18 GHz/atm [59]. Hyperfine coupling between a Rb electron and a nucleus are less than 6.9 GHz, so coupling is already neglected at low pressures. When considered as a wavelength, this pressure broadening is approximately 0.038 nm/atm. Diode lasers used in optical pumping may have emission spectral lines of 2 – 3 nm, so the high pressure in the cell means that photons are absorbed much more efficiently by Rb electrons. In addition buffer gases also decrease the diffusion of Rb so that the wall relaxation of polarized Rb atoms is minimized. And as a final point, buffer gases are very useful when applying SEOP to xenon, as they have a significant role in the three-body collision mechanics that leads to the formation of van der Waals molecules.

5.2 Spin-Exchange

The Rb spin-destruction rate $\gamma_{sd}$ in the polarization cell is mainly influenced by the relaxation due to collisions, which is dependent on the density of the atoms and molecules inside the cell [60]. Wall relaxation is the dominant mechanism in the regions close to the wall. In fact, it is so efficient that there is a layer close to wall, where Rb polarization is close to thermal equilibrium [60, 61]. By optimizing cell geometry wall relaxation can be minimized. In a typical SEOP-experiment the effects of collisions with other Rb, He and N₂ atoms on the Rb spin-destruction rate $\gamma_{sd}$ are in the same order of magnitude [54]. However, spin relaxation caused by Rb-Xe collisions is even four orders of magnitude greater, so the Rb spin destruction is mainly caused by the collisions with Xe atoms [62].

Rb-Xe collisions can be either very short (~$10^{-12}$ s) binary collisions or so-called three-body collisions that include the formation of a van der Waals molecule. Because of collision to the third party, the kinetic energy of rubidium and xenon atoms before the collision is so low that the formation of a weakly-bonded van der Waals molecule is possible. On the other hand this molecule is “destroyed” as a result of a subsequent collision, so its lifetime is rather short (~$10^{-7}$-$10^{-11}$) as well [53, 54].
During the collisions and in the van der Waals molecule the distance between xenon and Rb atoms is so small that there is a certain probability density for a Rb valence electron to be found inside the xenon nucleus. At this point spin-exchange may occur between the electron and the nuclei through a Fermi-contact interaction. A more detailed description of the interaction requires the quantum mechanical approach presented by Appelt et al. [52]. All the interactions between Rb and Xenon atoms in collisions can be described by the Hamiltonian

$$H_{Rb-Xe} = \gamma(R)\mathbf{N} \cdot \mathbf{S} + \alpha(R)\mathbf{K} \cdot \mathbf{S} + AI \cdot \mathbf{S}. \quad (5-3)$$

The First term is the spin-rotation interaction between rotational angular momentum of the Rb-Xe van der Waals molecule $\mathbf{N}$ and Rb electron spin angular momentum $\mathbf{S}$. As a result of the interaction, the electron spin angular momentum transfers to the angular momentum of the molecule, and then to the kinetic energy of atoms as the molecule breaks up. To be exact, this spin-rotational relaxation is the same in binary collisions, but the molecule has an extremely short lifetime in that case. The third term corresponds to the hyperfine interaction between the electron and nucleus inside the Rb atom and is not significant for the SEOP process. The second term is the most interesting one, as it describes the hyperfine interaction between xenon nuclear spin $\mathbf{K}$ and Rb electron spin angular momentum $\mathbf{S}$ responsible for transferring the polarization from the Rb electron to the noble gas nucleus. The interaction is considered to be isotropic and
originating from the Fermi-contact interaction. \( \alpha(R) \) is known as the Fermi-contact strength coefficient and it is exceptionally large in the case of the Rb-Xe interaction.\[51, 52\]

Values of coefficients \( \gamma(R) \) and \( \alpha(R) \) in eq. (5-3) are dependent on the distance between the Rb and Xe atoms. The proportion of the coefficients is called the Breit-Rabi-parameter \( x = \gamma(R) / \alpha(R) \) and it can be used to calculate the efficiency of the spin-exchange \( 1/x^2 \), revealing the portion of Rb electron spin polarization that is transferred to the xenon nucleus.\[53\] Value \( x = 3.2 \pm 0.3 \) has been determined, meaning that the spin-rotation interaction restricts the efficiency of spin-exchange in van der Waals molecules and only 10% of the collisions lead to Rb spin polarization transfer to the xenon nucleus \[63\]. The spin rotation interaction is a major relaxation mechanism of Rb electron spin polarization. However, very high nuclear spin polarization is achievable if the Rb valence electrons are immediately repolarized after collisions via efficient optical pumping and if the nuclear spin relaxation rate of xenon is low.

Binary collisions are the dominant spin-exchange mechanism in the polarization cells at the pressure of several atmospheres. Three-body collisions are considered to be a more efficient mechanism, but high number of collisions is limiting the formation of van der Waals molecules at high pressure.\[51\] The efficiency of Rb-Xe spin-exchange in binary (two-body) collisions can be described by the equation

\[ \gamma_{SE}^{\text{bin}} = \kappa_{Rb\rightarrow Xe,SE} \frac{\text{[Rb]}}{\text{[Xe]}}, \]  

(5-4)

where the factor \( \kappa_{Rb\rightarrow Xe,SE} \) describing the cross section of binary collisions is determined to be \( 2.1 \cdot 10^{-16} \text{ cm}^3/\text{s} \) and \( [\text{Rb}] \) is the number density of Rb atoms \[64\]. Driehuys et al. suggested a way to calculate the proportion of three-body collisions forming the van der Waals molecules to spin-exchange rate in their SEOP system. Partial pressures of xenon and nitrogen in their system was so low that it was enough to consider three-body collisions with a helium atom as a third body.\[65\] The SEOP system introduced by Russet et al. applies higher partial pressures of xenon and nitrogen, so they modified the formula in the form

\[ \gamma_{SE}^{\text{vdW}} = \left[ \frac{\text{[Xe]}}{\gamma_{Xe}} + \frac{\text{[N}_2]}{\gamma_{N_2}} + \frac{\text{[He]}}{\gamma_{He}} \right] \frac{\text{[Rb]}}{\gamma_{SE}^{\text{bin}}}, \]  

(5-5)

where the factor \( \kappa_{Rb\rightarrow Xe,SE} \) describing the cross section of binary collisions is determined to be \( 2.1 \cdot 10^{-16} \text{ cm}^3/\text{s} \) and \( [\text{Rb}] \) is the number density of Rb atoms \[64\]. Driehuys et al. suggested a way to calculate the proportion of three-body collisions forming the van der Waals molecules to spin-exchange rate in their SEOP system. Partial pressures of xenon and nitrogen in their system was so low that it was enough to consider three-body collisions with a helium atom as a third body.\[65\] The SEOP system introduced by Russet et al. applies higher partial pressures of xenon and nitrogen, so they modified the formula in the form

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(5-5)
where $\gamma_{Xe}$, $\gamma_{N2}$ and $\gamma_{He}$ are the coefficients describing the efficiency of spin-exchange with Xenon, N$_2$ or Helium as a third party in the formation of van der Waals molecules [54]. The total efficiency of spin-exchange is

$$\gamma_{SE} = \left( \gamma_{SE}^{bin} + \gamma_{SE}^{vdW} \right).$$ (5-6)

Based on the values estimated in the literature $\gamma_{Xe} = 5230$ s$^{-1}$, $\gamma_{N2} = 5700$ s$^{-1}$ and $\gamma_{He} = 17000$ s$^{-1}$ [66, 67], the spin-exchange rates for binary and three-body collisions may be calculated for a typical polarization cell, where total pressure is 10 bars, gas mixture consists of 98% helium, 1% xenon and 1% N$_2$. If the temperature is estimated to be 150°C, the number density of rubidium [Rb] = $1.04 \times 10^{-14}$ cm$^{-3}$ [65]. Efficiency of spin-exchange due to binary collisions $\gamma_{SE}^{bin} = 0.0218$ s$^{-1}$ and three-body collisions $\gamma_{SE}^{vdW} = 0.00978$ s$^{-1}$. So the efficiency of spin-exchange via binary collisions is about two times higher than via spin-exchange and total efficiency of the spin-exchange $\gamma_{SE} = 0.032$ s$^{-1}$.

### 5.3 Xenon nuclear spin polarization

When estimating achievable nuclear spin polarization, it is necessary to consider different relaxation mechanisms for spin polarization in the cell. Interactions with Rb vapor, other buffer gases and the wall of the cell as well as chemical shift anisotropy and magnetic field inhomogeneity are all sources of relaxation [64]. According to a study by Chann et al. interactions with N$_2$ and helium are negligible compared to Xe-Xe spin-rotational relaxation [68]. Wall relaxation is dependent on cell geometry, proportion of wall area to cell volume, and properties of the wall material, i.e. paramagnetic impurities. Xenon wall relaxation has been successfully reduced using coatings. The advantage was considered to be significant only in low pressure systems, because spin-rotational relaxation was believed to dominate in high pressures (> 3 atm).[69, 70] However, simulations by Fink et al. suggest that the effect of wall relaxation could be significant in the modern high pressure systems due to convectional flow caused by the heating effects of high-power laser irradiation [58].

When Rb electron spin polarization $P_{Rb}$, Rb-Xe spin-exchange rate $\gamma_{SE}$ and total xenon spin relaxation rate $\Gamma$ are known, xenon nuclear spin polarization can be derived from [56, 71]
If time $t$ is long enough, steady-state is achieved, where

$$P_{\text{se}} = \frac{\gamma_{\text{se}}}{\gamma_{\text{se}} + \Gamma} P_{\text{se}} \left[ 1 - \exp[-(\gamma_{\text{se}} + \Gamma)t] \right].$$

(5-7)

Minimizing the relaxation mechanisms should lead to polarization close to that of Rb electron spin polarization. In practice, however, the highest polarization achieved is around 70\% \cite{72, 73}. The highest spin polarizations have been achieved with low partial pressure of xenon. As an example, Zook et al. observed that xenon spin polarization decreases to one third when partial pressure of xenon is increased from 0.6\% to 2\% \cite{72}. Increasing xenon partial pressure is so destructive to polarization, because Rb-Xe collisions are the dominant mechanism of relaxation for Rb and Xe-Xe collisions for Xe spin polarization as mentioned earlier. Increasing the efficiency of optical pumping by increasing the amount of laser power leads to higher Xe polarization, but it has limits. The amount of power required is dependent on the volume of the polarization cell, but considering a typical polarization cell (diameter of 2 – 5 cm), increasing laser power beyond 100 W does not give real benefit according to experiments and simulations \cite{58, 72}. During optical pumping Rb atoms absorb photons with high efficiency. Despite the relatively efficient spin-exchange, the largest portion of de-excitation happens via quenching N$_2$ gas and this energy is transferred to vibrational energy of N$_2$ molecules leading to increasing temperature inside the polarization cell. Walter et al. have shown that the temperature in the middle of the cell may be 200°C higher than near the walls \cite{74}. This increases Rb vapor pressure eventually leading to insufficient Rb electron spin polarization. High temperature gradients also cause convection flow inside the cell leading to faster spin destruction rates due to wall relaxation for both Rb and xenon. This is particularly disadvantageous for Rb electron spin polarization, because wall relaxation is very rapid and even coatings do not reduce it.

5.4 Continuous flow $^{129}$Xe hyperpolarizer

The availability of commercial hyperpolarizers has been severely limited and many research groups have chosen to construct their own. Driehuys et al. have
published a detailed description of a system capable of high-volume production of hyperpolarized xenon gas [65]. This type of design has since been widely used in systems around the world and it was the basis of the hyperpolarizer planned and constructed as a part of this work as well.

The main requirement for the hyperpolarizer was that it would produce highly nuclear spin-polarized xenon gas with a continuous flow. Composition of the gas mixture was selected to be the typical 1% xenon, 1% nitrogen and 98% helium (vol%). Naturally abundant xenon was used, so the amount of useful $^{129}$Xe isotope was only 26.4%. Gas was supplied by Messer Finland Inc. in a 50 L gas bottle pressurized to 150 bar. The gas bottle could not be taken in the NMR lab, so gas was supplied to the polarizer via Teflon tubing. Rb is very sensitive to impurities like water or oxygen, so the purity of the mixture was ensured using Messer Oxisorb purifier (that absorbed possible residues of H$_2$O and O$_2$). After passing through the purifier the gas flowed into the SEOP setup illustrated in figure 9.

Figure 9. Schematic of the constructed SEOP hyperpolarizer for xenon.

The gas mixture flowed through the system inside stainless steel and Teflon tubing. Commercial Swagelok fittings were mainly used to connect components together, but some home made connectors were used as well. Flow rate of the gas was monitored using an Aalborg GFM17A mass flowmeter located before the...
polarization cell in the system. Its accuracy was 0.01 L/min. Pressure in the front part of the system (before the polarization cell) was monitored by a Bourdon pressure gauge and in the part after the polarization cell by accurate digital pressure gauge (1 – 2000 mbar) supplied by YTM Industrial.

The polarization cell was prepared from Pyrex glass by a professional glassblower. The cell was illuminated by a 60 W Coherent Duo FAP laser system. The inner diameter of the cell was chosen to be exactly the same as the diameter of the laser beam passing through it: 18 mm. The laser beam was circularly polarized by an Opto Power RCP 025 circular polarizer and monitored with an Ocean Optics USB2000 near infra-red spectrometer (NIRS) located on the opposite side of the cell. The emission spectrum of the laser system was monitored, so that it could be tuned to match the Rb D1-wavelength. A drop (0.5 – 1 g) of rubidium was inserted directly into the cell in a glovebox under nitrogen atmosphere. The setup was simpler than the one with a separate Rb chamber and Rb vapor pressure was thought to be easier to adjust in this design. Outlet tubing of the cell formed a U-shape and a piece of glass wool was inserted there. Residue of the Rb vapor flowing out of the cell was efficiently accumulated in it, so that the Teflon needle valve controlling gas flow was not damaged. The teflon needle valve did not only control the flow, but it is also the part where pressure is reduced from 9 bar to below 2 bar used in experiments. From the polarization cell gas flow was directed into a xenon trap, a cold finger prepared by the glassblower. It was possible to separate xenon from the gas flow by freezing it, if the cold finger was immersed in liquid nitrogen.

Different designs to supply the polarized gas into sample were planned during the work. Two basic designs are shown in the figure 10. Type a) was useful, because it allowed a regular 10 mm sample tube to be attached in the system. The fitting was carefully machined out of Teflon so that the sample tube just fit around it when two layers of Teflon tape are used as a seal. The sample could be in any form from liquid to solid. Unfortunately, most of the gas flowing into the sample tube never entered the actual sample in this design. The outlet tubing leads to a vacuum pump controlling the pressure in the system and there was a direct flow from the inlet to outlet tubing past the sample. This setup was best suited for experiments where hyperpolarized xenon gas was accumulated using the freezing thawing method and then released into the sample. Unfortunately, even in that case most of the hyperpolarized gas was wasted due to extra volume in tubing coming and leaving from the sample and in sample tube itself.
So, generally the design in figure 10 b) was more useful as it made the flow through experiments possible, where all the hyperpolarized xenon atoms surely pass through the sample. Some constraints existed, as liquid samples could not be used in this setup. Gas flow in the system was controlled via numerous valves and adjustable needle valves. The whole system was designed so that the polarization cell can be “shut out” from the rest of the system in order to remove a cell or to pump out possible leaks from the rest of the line. The xenon trap could be removed from the setup, if xenon was not accumulated and in that case the polarized gas mixture flowed directly from the polarization cell to the sample.

If xenon was collected, a coil producing a homogeneous 650 G magnetic field was immersed into a liquid nitrogen bath. It was then possible to raise the coil around the cold finger so that the homogeneous magnetic field and liquid nitrogen surrounded it. The interior of the cold finger was treated with a coating supposedly prolonging $^{129}$Xe $T_1$ relaxation time [70]. Xenon was the only gas in the mixture that froze on the walls of the cold finger while helium and nitrogen flowed through it. In solid state and inside a strong enough homogeneous magnetic field ($>0.05$ T) the $T_1$ relaxation time of $^{129}$Xe is in the order of hours [75]. That should make the accumulation of xenon gas possible, without significant loss of polarization due to $T_1$. However, the freezing/thawing cycle led to some loss of polarization (30 – 50 %). The collector based on a spiral tubing slowly immersed
in liquid nitrogen was introduced by Ruset et al. and it is a more efficient solution [73]. The problem with the traditional method is that xenon is condensed on the first cold surface that the gas flows by. Xenon forms a thick layer close to the inlet tubing in the collector and xenon atoms on the surface of this layer are likely to be warmer than those close to the wall. Kuzma et al. observed in their experiments that a long accumulation period leads to decreased $^{129}$Xe polarization in frozen xenon [76]. The thick layer is problematic while warming the xenon back to gas phase as well, because phase transition is slower in this case. Warming is carried out by immersing a cold finger in warm water. Relaxation is especially rapid in temperatures close to phase transition and in the liquid phase, so the transition from solid to gas should be as fast as possible [76]. This problem is avoided by applying a spiral collector, because the total wall area where xenon is collected is larger leading to a thinner layer of frozen xenon. Xenon vaporizes rapidly when the spiral is immersed in water and pure hyperpolarized xenon is led to the sample without polarization losses due to the freezing/thawing cycle [73].

**Figure 11. Results of a hyperpolarizing experiment.**

Achieved polarization in the experiments was estimated by comparing intensities of spectra from thermally polarized and hyperpolarized xenon. As demonstrated in figure 11, the pressure in the reference sample containing xenon with thermal polarization has to be several magnitudes higher in order to make comparisons. In the spectra of figure 11, the intensity of the $^{129}$Xe NMR signal from hyperpolarized gas is 12-fold compared to the one from the reference sample. Considering the differences in pressure and abundance of the $^{129}$Xe isotope, polarization enhancement is almost 10000-fold. Using equation (2-4) it is possible to calculate thermal polarization to be 0.0007 % in the 7.04 T magnetic
field, so the nuclear spin polarization of the hyperpolarized sample is around 7% in this case. As the flow rate of gas mixture has been 0.32 L/min, it would be possible to produce 0.2 L of hyperpolarized xenon gas per hour.

According to equation (5-7) the achievable polarization rate in a continuous flow system is dependent on the Rb electron spin polarization, Rb-Xe spin-exchange rate, $^{129}$Xe relaxation rate in the cell and the time xenon atoms spend in the cell. In practice these variables could only be controlled by changing the flow rate of the gas and the temperature inside the oven. Laser power and the pressure of the gas mixture had to always be as high as possible to ensure efficient optical pumping and mixture ratio of the gas could not be modified in the current system. As partial pressure of Rb becomes higher, the probability of spin-exchange rises, but in order for this to be useful Rb electron spin polarization must remain high. This is only possible if high laser power is available. In addition, equation (5-7) is only valid if conditions are uniform within the cell. High laser power may lead to a rise in temperature especially in the middle of the polarization cell causing convectional flow in the cell [58]. This in turn leads to increased wall relaxation of the Rb electron spin polarization.

Figure 12 shows the results of the experiment where optimal temperature of the oven was determined. Maximal nuclear spin polarization of $^{129}$Xe achieved was 35.1% after five minutes of optical pumping at 170°C. Achieving maximal polarization is a slow process as optical pumping times of two and three minutes in the same temperature resulted in polarizations of 22.7% and 28.3%, respectively. Compared to these, the polarization of 11.1% after one minute of optical pumping is surprisingly low, but is easy to explain. The gas mixture was at room temperature, so rubidium vapor density dropped immediately after the gas flowed into the cell. It took some time before temperature and Rb vapor density inside the cell rose again causing some delay in the optical pumping process. This same problem was observed when operating in continuous flow mode. Based on the volume of the cell it was calculated that flow rates of 0.14, 0.28 and 0.55 L/min should correspond to the optical pumping times of 2, 1 and 0.5 minutes, when considering the time xenon nuclei spend inside the polarization cell on average. In practice, it was observed that nuclear spin polarizations as high as those presented in figure 12 were unachievable when continuous flow mode was applied. Especially with the high flow rates the achieved polarization was very low. Flow of “cold” gas efficiently reduces the density of Rb vapor especially near the inlet of the cell and this led to a decrease in spin-exchange rate.
Figure 12. The effect of oven temperature and optical pumping time on achieved polarization. Lines in the chart were not fitted, they just combine data in order to clarify temperature dependence.

and lower polarization. Increasing the cell temperature helped only little, because a too high Rb vapor density near the outlet was also an unwanted situation. The situation was particularly difficult, because the rubidium was placed directly inside the cell. Rb vapor pressure increased rapidly as the temperature inside the cell increased. Temperature rose rapidly due to heating by the high-power laser as mentioned earlier. As a result Rb polarization was low, although all the photons were absorbed. Only low xenon spin polarizations were attained with oven temperatures above 200°C. A series of experiments was carried out to find optimal conditions for continuous flow operation. Results of these experiments varied slightly, but it was confirmed that an oven temperature of 170° – 190°C should ensure an output of polarized xenon with a constant spin polarization, when flow rates up to 0.30 L/min were used. Achievable polarization was regularly 5 – 10 % depending on the purity of the Rb metal. Rb seemed to oxidize very easily and small leaks within the system led to the formation of an oxidized layer on the surface of the Rb metal in the cell. Rb vapor pressure was more difficult to control after this. The obvious solution for the uneven temperature between inlet and outlet regions inside the polarization cell is to warm the inflowing gas in advance. A heater consisting of copper tubing heated by a thermoelement was designed, though it was not efficient enough for high gas flow rates. A more efficient heating system is under construction, but there are many other improvements to also consider.
Earlier studies have shown that the highest polarizations are achieved in systems operating at low pressures [73, 77]. However, this requires laser light with a very narrow bandwidth. Zerger et al. have shown that broad spectral profiles of high-power laser diode arrays can be efficiently narrowed by external cavity configurations [78]. Even though they lead to a loss of laser power, more photons are actually absorbed by Rb atoms, because the spectral profile matches the Rb $D_1$-wavelength better. This leads to more efficient optical pumping resulting in higher achievable nuclear spin polarization. The diode laser is the most expensive component and the one with the most influence on the production rate of the system, so its power should not be wasted. Although being a commercial product, the circular polarizer in use is poorly planned for the current purpose. Circular polarization of the light is achieved by combining the linear polarizer and the quarter-wave ($\lambda/4$) plate. The linear polarizer in the setup is a beam splitter cube that divides the beam into two components with perpendicular linear polarizations. One component is simply blocked out, because it would produce circular polarization causing unwanted excitations if directed through a $\lambda/4$-plate. This means that half of the laser power is actually wasted. One of the most important steps in the further development of the current system would be to apply a better optical setup for narrowing the spectral profile and avoiding the wasting of laser light in the circular polarizer.

Recent simulations by Fink et al. [79] show that uneven spatial distribution of Rb vapor is a major factor restricting achievable $^{129}$Xe nuclear spin polarization in continuous flow systems. Most SEOP hyperpolarizers have a separate Rb presaturator where gas mixture is saturated with Rb vapor before the gas flows into the polarization cell illuminated by a laser. The effect of laser-induced heating is not as bad in this case and the gas is efficiently polarized throughout the volume of the cell.

If a higher production rate of polarized xenon is required, it might be useful to consider the ratios in a gas mixture. It has been shown that amount of He and $N_2$ in a gas mixture heavily influence achieved polarization [66, 80]. As the partial pressure of xenon increases, polarization rate goes down. However, total amount of polarized nuclei per time may still increase, so it can be useful to consider the production rate instead of just maximum polarization. Zook et al. were able to increase the production rate of polarized $^{129}$Xe nuclei by 40 %, when the partial pressure of xenon was increased from 0.6 % to 5 %, although polarization fell from 67 % to 12 % [72]. High partial pressure of xenon accelerates the Rb electron spin relaxation, so more laser power would be
required to maintain high polarization. Separate gas bottles for helium, nitrogen and xenon equipped with mass flow controllers would allow easy adjustment of the composition of the flowing gas.

In the current design, the gas flows out from the vacuum pump into the air. Wasting expensive gas should be avoided, so re-circulating systems for hyperpolarized gas have been introduced [81-83]. They are reported to have additional benefit in the form of higher polarization rates. There are a lot of nuclei in the gas mixture that are not depolarized during the actual measurement. This means that gas mixture is already prepolarized when it arrives back to the polarization cell.

In order to attain hyperpolarized gas in liter quantities, the design by Ruset et al. for a SEOP-based system should be adopted [54, 73]. The main difference is that their system operates in low pressure and the polarization cell has a larger volume than other designs. High efficiency of Rb-Xe spin-exchange is achieved via three-body collisions. The latest reports imply that a production rate of one liter per hour for xenon with a 50 % polarization rate is possible with reasonable 125 W laser power. They are also pursuing to commercialize this design.[84]

5.5 Applications of hyperpolarized $^{129}$Xe

Applying hyperpolarized xenon gas to LC studies was a logical interest, but it soon turned out to be unfeasible. There have been studies of hyperpolarized xenon dissolved in benzene [85] and it is possible to get some signal from the isotropic phase of an LC, if the sample was first degassed and hyperpolarized xenon gas collected in a cold finger was then released into sample. However, the self-diffusion of xenon atoms inside the LC mesophases was too slow even for the long $T_1$ relaxation time of $^{129}$Xe. An additional problem was that temperature of the gas should match that of the sample. Unmatched temperatures may lead to temperature gradients and broad spectral lines or even to a change of mesophase. Baumer et al. have proposed a solution based on hollow-fiber membranes that allow transfer of hyperpolarized gas to liquid solvents efficiently and without disturbing bubbling [86]. This extends the range of possible applications and could even be applied to LCs, if the problem regarding the temperature control of the flowing gas could be solved.

So far it has appeared that studies of different kinds of porous materials are the field of research where the real potential in materials research lies [87, 88]. Porous materials absorb a large amount of hyperpolarized gas and continuous
flow of gas can be directed through them leading to a strong NMR signal. Lung imaging with hyperpolarized xenon is still considered to be a promising technique in the field of medicine [89].
Magnetic resonance imaging is based on the use of gradients to spatially encode nuclei producing the observed NMR signal. Typical MRI experiments resulting in a 2D image include slice selection, phase encoding and frequency encoding gradients. A linear slice selection gradient is applied simultaneously with the RF pulse exciting observed nuclei. Its purpose is to alter the Larmor frequencies along the direction of the gradient, so that only the spins precessing with frequencies within the bandwidth of the applied RF pulse experience it. This means that only spins within a certain plane perpendicular to the direction of the gradient are excited. The NMR signal observed in MRI is actually spin or gradient echo. In a spin-echo sequence, a 180° RF pulse is applied in the middle of the time period between excitation and the observation of the echo signal. Creating phase encoding within the plane is not as simple to explain as slice selection. A short duration linear gradient is now produced in a direction of the selected plane creating a phase difference between spins in the direction of the gradient. Unlike in the diffusion encoding in the PGSE pulse sequence in figure 1, the gradient is only applied before the 180° RF pulse, so its effect is not refocused. Strength of the gradient is modified by constant steps between excitations, getting both positive and negative values, so that echo signals of excited spins with varying phase differences are acquired. During the observation of the NMR signal constant gradient is always applied in the direction orthogonal to the phase encoding gradient. This so-called readout gradient is again easy to understand as it creates linear variation to Larmor frequencies of the spins in the direction of the gradient. Measured echoes form a so called k-space, where the number of lines in the phase encoding direction reveals the resolution of the image in that direction. Adding more possible values for a phase encoding gradient (maintaining constant steps) increases resolution, but leads to longer experiment time as well. The signal from the frequency encoding direction is digitized as well and an actual image is formed from the k-space by applying 2D inverse Fourier transformation. The purpose of this very short description of MRI is to underline the importance of gradients in MRI. The topic is considered to be difficult, so familiarizing oneself with the literature is required for a more comprehensive understanding. [5, 90, 91]
6.1 Remote detection

Remote detection (RD) technique introduces an idea to separate the encoding and detection steps of NMR or MRI experiments both spatially and temporally [92]. This is usually done by rotating magnetization after phase encoding back to the direction of the $B_0$ field, where spins preserve the phase information from the spatial encoding. Because spins are moving, it is possible to measure encoding information later in a different location by just applying another excitation pulse. Different requirements are set for encoding and the detection coil, but compromises are not necessary if separate optimized coils can be used. A detection coil with an optimal filling factor increases the SNR of the observed signal [93] and even the use of an ultrasensitive superconducting quantum interference device (SQUID) or optical atomic magnetometer for detection is possible [94, 95]. It is not only possible to optimize coils, but applied magnetic field as well, because different magnetic fields for encoding and detection are possible with RD technique. NMR image information may be encoded at low field where better homogeneity is achieved and possible susceptibility gradients avoided [96, 97]. Demand for the high field homogeneity is not as strict for detection field, so even the less homogeneous ultra-high-field magnets can be used to achieve a better SNR [92]. However, RD technique works particularly well when combined with hyperpolarized noble gases, because their long $T_1$ relaxation times make possible to transport encoded nuclei over long distances and gas flow is relatively easy to control.

6.2 Combining hyperpolarization and remote detection techniques

As shown in figure 10 b) the most practical solution for leading the hyperpolarized xenon gas into the sample is a flow-through setup. It was rather simple to adapt this kind of design to be used in a remote detection setup as well. As seen in figure 13, the sample tube was replaced with a specially designed sample holder made of Teflon, where threads fitting to connectors were carved. This makes possible tight connections, but changing the sample is still rather easy.
6.3 Study of thermally modified wood

Applicability of the system was proven by time-of-flight remote detection measurements in wood samples. Thermal modification is a process where wood is heated for several hours at high temperature (180 – 250°C) using water vapor as a shielding gas [98]. The process increases the dimensional stability of wood,
lowers its equilibrium moisture content and increases resistance to biodegradation and weather [99]. As a part of this work the effects of thermal modification on Pinus Sylvestris were studied. The structure of Pinus Sylvestris is described in refs. [100, 101], but in summary, it is comprised of three different cell structures: longitudinal tracheids (93.0 volume percent of the wood), radial rays (6.4 %) and longitudinal resin canals (0.6 %). Studies applying methane gas had already given promising results of wood studies employing gaseous probe molecules [101, 102].

Constant gas flow from the polarizer was directed through the sample and a variety of Time-of-Flight measurements were carried out. The basic idea in these measurements is that encoded spins are detected in a series of excitations inside the detection coil. The encoding volume is larger than the volume inside the detection coil, so the gas encoded in different parts of the sample enters into the detection region at different times. A 90° detection pulse is repeated by a constant interval, so that observed signals are time labeled. The time interval is a critical parameter, because it has to be such that all the spins are excited by the detection coil, but only once. Time interval is calculated from the flow rate. Since the spins also contain the spatial information from the encoding, it is possible to analyze how fast spins from certain regions inside the encoding coil reach the detection coil. MRI sequences presented in article IV have fundamental differences when compared to a typical MRI sequence, because slice selection or readout gradients are not applied. This makes the used sequences simple and fast. An excellent temporal resolution of 31 ms was achieved in the experiments. In the case of wood structures this revealed the pathways of the gas flow and dispersion of the xenon atoms inside the wood. The study is presented in a more detailed manner in article IV.
This work has once again demonstrated the usefulness of a xenon atom as a probe in NMR spectroscopy of materials. The sensitivity of $^{129}$Xe NMR shielding arising from the large polarizable electron cloud makes possible the observation of even minimal changes in solvent densities, which in turn reveal the change in temperature of the sample. Exact determination of the sample temperature is often important in NMR spectroscopy and the accuracy of the xenon thermometer presented in this work exceeds, in optimal conditions, that of any other NMR thermometer. The xenon thermometer can be prepared in a capillary tube and inserted into the sample, so that temperature can be determined without inconvenient and time-consuming sample changes. In addition, even the sample itself could be turned into a xenon thermometer. The portion of the molecules under study is often small, so the density of the sample depends mainly on the used solvent. Thus, if the temperature dependence of the $^{129}$Xe shielding in the solvent is known, temperature can be determined with a rather high accuracy by just adding some xenon gas into the sample tube and sealing it. At least the temperature stability can always be monitored from the $^{129}$Xe spectrum.

The sensitivity of $^{129}$Xe shielding was used to derive information from a liquid crystal as well. 10B1M7 LC possess commercially interesting ferro-, ferri and antiferroelectric SmC* mesophases. $^{129}$Xe NMR spectra of xenon dissolved in 10B1M7 LC clearly reveal the isotropic - SmA and SmA - SmC*(ferroelectric) phase transitions. On the contrary, only small changes in the shielding were observed at the transitions within the different SmC* mesophases. Structural differences between these mesophases are small, but self-diffusion measurements of xenon revealed some additional information. Analysis of measurements revealed the layer structure of SmC* mesophases and the decrease in layer ordering of ferroelectric SmC* mesophase when compared to ferro- or antiferroelectric mesophases. Self-diffusion measurements of xenon were so time-consuming that the routine usability of these measurements is debatable. However, a series of studies in nematic and smectic LCs revealed that a strong $^{19}$F NMR signal observed from the SF$_6$ molecule allows fast and accurate self-diffusion measurements. On the basis of these promising results, SF$_6$ should be applied in a study of more demanding mesophases such as ferro- or antiferroelectric SmC* phases that are very interesting in a commercial sense. When comparing xenon and SF$_6$ as NMR probes, it is clear that SF$_6$ has an advantage in self-diffusion measurements. On the contrary, xenon is superior in its probing properties, such
as orientational order parameters in various mesophases and thermal expansion coefficients. Consequently, in most cases, it would be beneficial to use both xenon and SF₆ as probes. Since both gases are unreactive it is actually possible to use the same sample, only the gas needs to be changed between experiments. At least in some cases, it is possible to study samples with both gases dissolved.

A spin-exchange optical pumping hyperpolarizer for ¹²⁹Xe gas solves problems related to low signal intensity in ¹²⁹Xe NMR spectroscopy and MRI. The continuous flow SEOP system built in this work can produce approximately 0.2 L hyperpolarized xenon gas in an hour. This makes possible fast diffusion, flow or imaging experiments even in very low gas pressures. Combining hyperpolarized xenon with the novel remote detection technique allows a new approach to study any materials where xenon can flow through the sample. Time of flight remote detection magnetic resonance imaging of thermally modified Pinus Sylvestris proved the potential of this method. Wood as a sample is far from optimal for this kind of study, because flow through the sample is very restricted and the amount of gas is so low inside the sample that the signal needs to be accumulated even if using hyperpolarized xenon. Even so, it was still possible to derive information about the flow paths and acquire images of the inner structure of samples at the same time.
References


Original publications


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