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CHEMICAL SENSOR BASED ON NITROGEN-VACANCY CENTERS IN DIAMOND

by

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to qualify for the academic Master's degree in Physics.

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Abstract

During the last decade, the nitrogen-vacancy (NV) center in diamond has emerged as a solid platform for nanoscale quantum sensing, within which is electrometry and magnetometry. Owing to the NV center high sensitivity and the fact that the diamond withstands adverse environmental conditions, a chemical sensor based on NV centers is a promising candidate for measurements during mining processes. Here, we use a microfluidic confocal microscope and a shallow-implanted diamond with different implantation spots, which are circular areas of $\sim 35\text{ }\mu\text{m}$ diameter, to perform longitudinal spin relaxometry in the presence of sodium sulfate in aqueous solution in order to determine the T_1 relaxation time behaviour. We observed that by increasing sodium sulfate concentration, the longitudinal spin relaxation time decreases, being this effect more noticeable as the NV centers are closer to the diamond surface and, with respect to the $1/T_1$ parameter, it gives signs to exhibit a quadratic response with concentration. On the other hand, the T_1 values are distributed along the implantation spot diameter, reaching minimum values around the spot center and maximum values at the edges, which is evidence that NV centers with different orientations co-exist in the same implantation spot. These results lay the foundation for a possible second stage in our chemical sensor development in which, after certain set-up modifications, new pulse-sequence protocols could be tried.

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“A smooth sea never made a skilled sailor.”

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Chapter 1

Introduction to Shallow Nitrogen-Vacancy Center

Manipulation and control of isolated solid state systems are of vital importance for contemporary science related to quantum metrology[1] and quantum information[2] applications. There are several solid state systems that can be used for this purpose, being shallow Nitrogen-Vacancy centers the focus of this study. We want to use the Nitrogen-Vacancy center quantum properties to measure chemical compounds in aqueous solution by means of different pulse-sequence techniques —based on a combination of laser and microwave pulses— and a microfluidic confocal microscope specially designed for this task. The idea is to design an experimental protocol that allows us to determine the concentration of some chemical compounds —sodium and copper sulfates— in an aqueous sample. This thesis has been framed under the project FONDEF ID16I10214 “Chemical Reaction Sensor” and FONDECYT 1180673.

1.1 Thesis Structure

The present work is divided in four main chapters: The first chapter named “Introduction to Shallow Nitrogen-Vacancy Center” presents the theoretical background related to the Shallow Nitrogen-Vacancy centers and their sensitivity to external electric field fluctuations. The second chapter named “Experimental Set-Up for Microfluidic Sensing” focus

on all the necessary instrumentation in order to perform different kind of pulse sequence techniques over a diamond sample hosting Shallow Nitrogen-Vacancy centers. Chapter 3, named “Chemical Reaction Sensor: Results and Discussion”, includes all the experimental evidence recorded that supports the development of a quantum chemical sensor based on the Longitudinal Spin Relaxometry technique performed over Shallow Nitrogen-Vacancy centers. Chapter 4, named “Conclusions and Future Work”, summarizes the main achievements, their implications and possible methodology improvements that may lead to the next stages of sensor development. Finally, the author strongly recommends reading the “Appendix” because it contains complementary information related to software development, pulse-sequence techniques involving microwave radiation and a parallel research line based on this techniques.

1.2 Nitrogen-Vacancy Defects

The Nitrogen-Vacancy center is a point defect in the diamond lattice produced by replacement of a Carbon atom by a Nitrogen atom next to a vacancy. Diamond has many properties like thermal conductivity, high hardness index, optical properties and a wide band gap between valence and conduction bands. Because of this latter feature, these defects present a stable configuration, and moreover, they behave like trapped molecules. This is a great advantage because the electronic wavefunction is localized and, therefore, it can be studied and measured in a specific place. The NV center has a spin degree of freedom that can be measured and manipulated at room temperature (which is its main advantage over other point defects) and, depending on different external factors, the electronic decoherence time at this temperature can go from 1 μ s up to few ms [3]. This defect may appear naturally in diamonds (extracted from earth), however, we prefer to use synthetic diamonds implanted through ion implantation [4, 5] since these are cleaner in terms of impurities and cheaper.

1.2.1 Physic Structure of the Nitrogen-Vacancy center

In crystallography, a vacancy is a point defect in the crystal produced when a lattice atom is missing (it is also known as Schottky defect). The NV center is produced, as we said before, by a missing Carbon atom and a substitute Nitrogen atom in the diamond crystal lattice. The stable configuration has a trigonal symmetry C_{3v} , meaning that it has a triple rotation in the bisector plane and, further, three vertical planes of reflection.

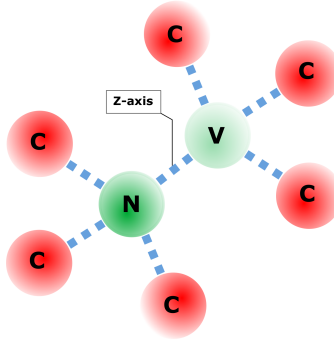


Figure 1.1: Nitrogen-Vacancy Center atomic configuration. The Nitrogen-Vacancy center is constituted by a Nitrogen atom (either ^{14}N or ^{15}N) next to a vacancy in the diamond lattice. Z-axis coincides with the C_{3v} symmetry axis of the defect.

1.2.2 Electronic Structure of the Nitrogen-Vacancy center

The Nitrogen-Vacancy defect can be found in three different total charge states: NV^+ , NV^0 y NV^- ; being the last two optically active, which means that they fluoresce under optical excitation[6] (NV^+ is known as a “dark state”). NV^0 has spin 1/2, with a neutral state that exhibits a zero-phonon line (ZPL) at 575 nm. On the other hand, NV^- has spin 1, with a ZPL at 637 nm[7]. In our case, we studied the NV^- which is more dominant in diamond and, from now, we are going to call it just NV center (for simplicity). This defect has the advantage that, through optical techniques, can be read the electronic spin sub-states $m_s = 0, \pm 1$ associated with the defect. Also, we can polarize the NV, leaving it in $m_s = 0$ sub-state and, radiating microwave pulses, the electronic spin can be manipulated.

It has been determined, through experiments, that the NV defect has a C_{3v} symmetry, a ZPL emission band associated with dipolar transition from A to E and its fundamental electronic state corresponds to a spin triplet [8–12]. This triplet is split due to spin-spin

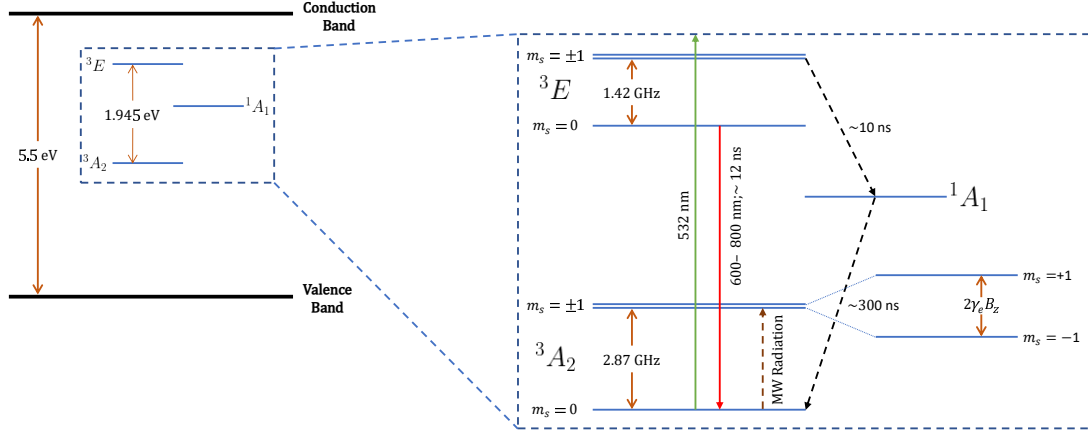


Figure 1.2: Nitrogen-Vacancy center electronic spin transitions. Energy levels schematic corresponding to the negatively charged Nitrogen-Vacancy center located in the band gap between the conduction and valence bands which is equal to 5.5 eV. In the ground state 3A_2 , $m_s = 0$ and $m_s = \pm 1$ presents a Zero Field splitting of 2.87 GHz. Green arrow indicate a transition owing to optical pumping from 3A_2 to 3E . In case of starting from $m_s = 0$, red arrow represents the spontaneous decay from 3E to 3A_2 emitting photons with wavelength between 600 nm and 800 nm. In case of starting from $m_s = \pm 1$, the decay from 3E to 3A_2 follows the black segmented line path through a meta-stable state 1A_1 and it is without photon emission. Once the system is fixed in 3A_2 sub-state $m_s = 0$, the electronic spin can be manipulated using microwave radiation (segmented brown arrow). A splitting between sub-states $m_s = \pm 1$ appears in presence of an external magnetic field due to Zeeman effect and it is equivalent to $2\gamma_e B_z$.

interaction, into a state S_z or $m_s = 0$ in A_1 and two states S_x , S_y or $m_s = \pm 1$ in E . These last ones are 2.87 GHz above in terms of energy and this zero-field splitting let us to identify the defect as a NV defect. ZPL is associated to the transition between 3A_2 and 3E .

Other perturbations, like strain, can cause shifting as mixing of the energy levels and states respectively. Even more, a meta-stable singlet state A_1 plays an important rol in the NV center dynamics under optical excitation[13]. Also, there is a vibronic state continuum which appear in the absorption at high frequencies and in the vibrational emission at low frequencies. When vibronic states are excited over the band (at $\lambda = 532\text{nm}$ laser), the phononic relaxation quickly leads the NV to one of the excited electronic states. The NV center fluoresces, mostly, in the phonon side-band wich extends from 630 nm to 800 nm. Even at low temperatures, the ZPL fluorescence only represents a small percentage of the emitted light[14]. The excited state 3E has a zero-field splitting of 1.42 GHz, with a Landé factor $g \approx 2$ for the fundamental and the excited states[15]. Nevertheless, if the defect is

excited from its sub-state $m_s = \pm 1$, the electron decays from 3E into a meta-stable singlet 1A_1 and then, decays to the sub-state $m_s = 0$ without photon emission[15, 16].

1.2.3 Ground-State Spin Hamiltonian

The Nitrogen-Vacancy center is immersed in a atomic lattice of nuclear spins, whereby it is important to understand the possible interactions between spins near the defect. The hyperfine structure results from an interaction between the electronic spin and the nuclear spins nearby. In terms of abundance, a 99.6% of NV defects are associated with ${}^{14}N$ ($I = 1$) isotopes and a 0.4% are associated with ${}^{15}N$ ($I = \frac{1}{2}$) isotopes. If we consider an external magnetic field applied, the NV fundamental state hamiltonian is $H_{Total} = H_S + H_{S-I} + H_I$, where H_S represents the electronic spin interaction, H_{S-I} corresponds to the hyperfine coupling with the nitrogen nuclear spin and H_I is related to the nuclear spin. The above can be summarized in the following equations:

$$\left. \begin{aligned} H_S &= DS_z^2 + E(S_x^2 - S_y^2) + \gamma_e \vec{B} \cdot \vec{S} \\ H_{S-I} &= A_{\parallel} S_z I_z + A_{\perp} (S_x I_x + S_y I_y) \\ H_I &= PI_z^2 - \gamma_N \vec{B} \cdot \vec{S}, \end{aligned} \right\} \begin{array}{l} \text{Electronic, nuclear} \\ \text{and hyperfine coupling} \\ \text{interactions.} \end{array} \quad (1.1)$$

where $D \approx 2.87\text{GHz}$ corresponds to the zero-field splitting owing to spin-spin interaction between unpaired electrons[17]. In the presence of a non-zero external magnetic field, a splitting between the sub-states $m_s = \pm 1$ appears due to Zeeman effect (see Figure 1.2), and each sub-state experiment a shift in $\gamma_e |\vec{B}_z|$, where $\gamma_e = 2.8 \text{ MHz/G}$ is the electron gyromagnetic ratio. On the other hand, E is the zero-field splitting transversal parameter[17, 18], $A_{\parallel} \approx -2.16 \text{ MHz}$ is the axial hyperfine constant[19] and $A_{\perp} \approx -2.7 \text{ MHz}$ is the transversal hyperfine constant[20]. Other structure due to the nitrogen nuclear spin coupling is shown with $m_I = 0$ separated from $m_I = \pm 1$ in $P \pm A_{\perp}$, where $P \approx -4.95 \text{ MHz}$ is the nitrogen quadrupolar splitting[19, 21].

The magnetic dipole transitions $m_s = \pm 1$ and $m_I = 0$ can be induced through an external oscillating magnetic field perpendicular to the NV z-axis. For a single NV center, there are six possible transitions as we can see in Figure 1.3. The above allows for diamond magnetometers, specially vector magnetic sensors, that can determine magnitude

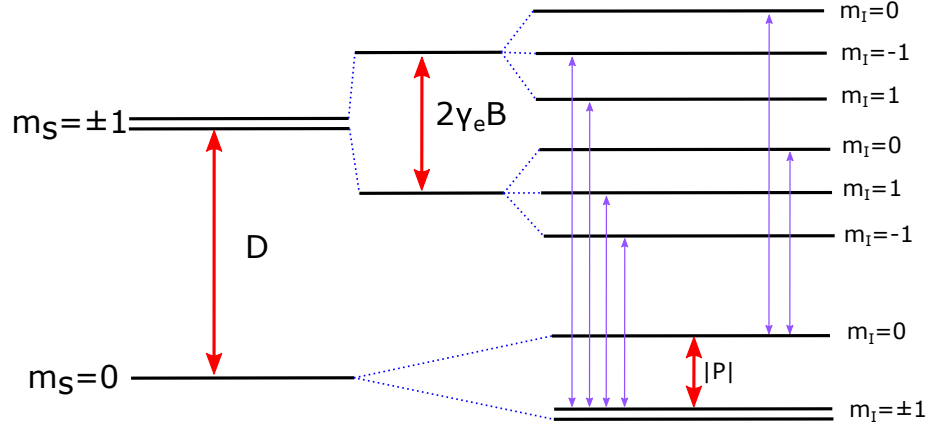


Figure 1.3: Energy levels scheme and possible transitions in C_{3v} symmetry. Ground state energy levels scheme and it possible transitions. It should be noted that, in presence of an external magnetic field, the hyperfine splitting of the Nitrogen nuclear spin can be seen, showing six transitions associated with $m_s = 0$ and $m_s = \pm 1$.

and direction of external magnetic fields.

1.3 Shallow Nitrogen-Vacancy Centers and Decoherence

In regard to sensitive capacity, the energy used during the implantation process plays a fundamental role because this parameter determines the implantation depth and, therefore, how exposed are the defects to the environment. According to [22], a very shallow NV center is the one who has a 5 keV implantation energy or below. When measuring photoluminescence intensity through 532 nm laser excitation within a range from 0.4 keV to 5 keV, reference [22] indicates that this value increases as energy does too. On the other hand, the peak depth related to every implantation energy were estimated using stopping and range of ions in matter (SRIM^I) Monte Carlo simulations, obtaining the following values: 5.0 ± 2.2 nm for 3 keV, 6.3 ± 2.6 nm for 4 keV and 7.7 ± 3.1 nm for 5 keV. An important result that emerges from this paper is that the very shallow NV centers are stable defects and, thus, they can be used as sensors.

Interactions with environment can cause decoherence which means, in simple words, that a superposition state of the system becomes into a complete mixed state[23, 24]. An im-

^IA group of computer programs which calculate interactions of ions with matter. SRIM is based on the binary collision approximation with a random selection of the impact parameter of the next colliding ion.

portant parameter closely related to this phenomenon is the coherence time T_2^* which, as exposed in [25], can be determined through measurements of the free-induction decay (FID) while applying the Ramsey sequence (more details in Section C.3). As indicated in the publication, this parameter can be defined as follows

$$T_2^* = \frac{1}{\sqrt{2}\pi\sigma_{\xi_{\perp}}} \sqrt{\frac{1 + \left(\frac{\beta_z}{\xi_{\perp}}\right)^2}{1 + \left(\frac{\beta_z}{\xi_{\perp}}\right)^2 \left(\frac{\sigma_{\beta_z}}{\sigma_{\xi_{\perp}}}\right)^2}}, \quad (1.2)$$

here β_z and $\xi_{\perp}$ are the magnetic and electric fields mean value, and $\sigma_{\beta_z}^2 = \langle \delta\beta_z^2 \rangle$ ($\sigma_{\xi_{\perp}}^2 = \langle \delta\xi_{\perp}^2 \rangle$) is the variance of the magnetic (electric) field fluctuation with $\delta\beta_z$ and $\delta\xi_{\perp}$ are random variables that represents magnetic and electric field fluctuations. This coherence time expression, according to [25], is simplified in a zero-magnetic-field regime, leading us to the following expression

$$T_2^* = \frac{1}{\sqrt{2}\pi\sigma_{\xi_{\perp}}}, \quad (1.3)$$

which means that the coherence time T_2^* , in absence of any external magnetic field, is limited by electric noise. In [26], spin coherence is increased by covering the diamond surface with high-dielectric-constant liquids which supports the electric noise influence over shallow nitrogen-vacancy centers and, thus, gave us the basis to create a chemical reaction sensor by quantizing the possible charge exchanges that may happen over the diamond surface.

Chapter 2

Experimental Set-Up for Microfluidic Sensing

Our set-up was specially designed in order to study shallow nitrogen-vacancy centers hosted in a single-plate diamond through different kind of spin-manipulation techniques, simulating what would be a first approximation to the real environment in which the sensor would be implemented. This set-up can be divided in four main parts: A home-made confocal microscope with a pulsed laser used to optically pump the sample, collect the emitted photons and, based on the above, understand the electronic spin behaviour of the NV center. A microwave circuit and a waveguide are used to manipulate the electronic spin. A microfluidic system that includes a microfluidic chamber to hold the sample, allows to expose the diamond to different chemical compounds and study how electronic spin behaviour changes. Finally, a coil connected to a power supply is used to cancel the earth magnetic field (everything related to the magnetic field generator system can be found in Appendix A). Every component of the set-up is connected to a computer and controlled by a single Matlab software developed by us.

2.1 Confocal Microscope

The Nitrogen-Vacancy center, as it was already mentioned in Chapter 1, is a defect in solid that fluoresces. In particular, it allows light excitation through photons with λ_1

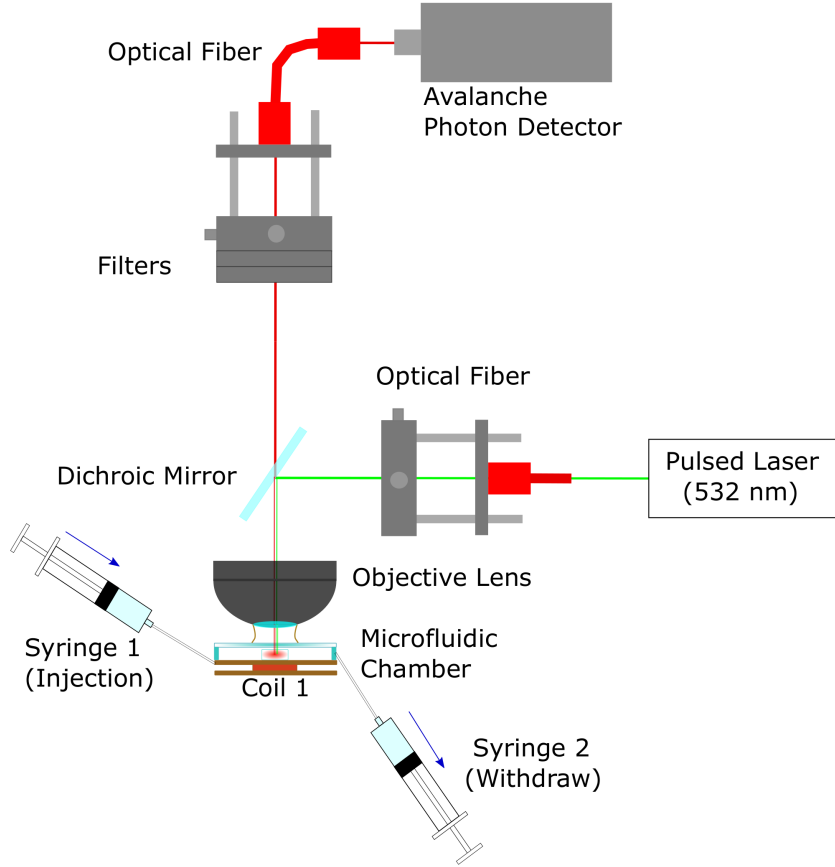


Figure 2.1: Confocal Microscope schematic. A basic representation of our home-made confocal microscope that includes a simplification of the microfluidic system and a coil. Green pulsed laser ($\lambda = 532$ nm) falls on the dichroic mirror, being deflected and impacting into the sample. The emitted photons pass through the mirror and are detected by an avalanche photon detector (APD). At the same time, an aqueous solution flows over the diamond surface inside the microfluidic chamber and it is regulated by a set of syringes. Finally, an electric current circulates through a coil in order to minimize the earth magnetic field.

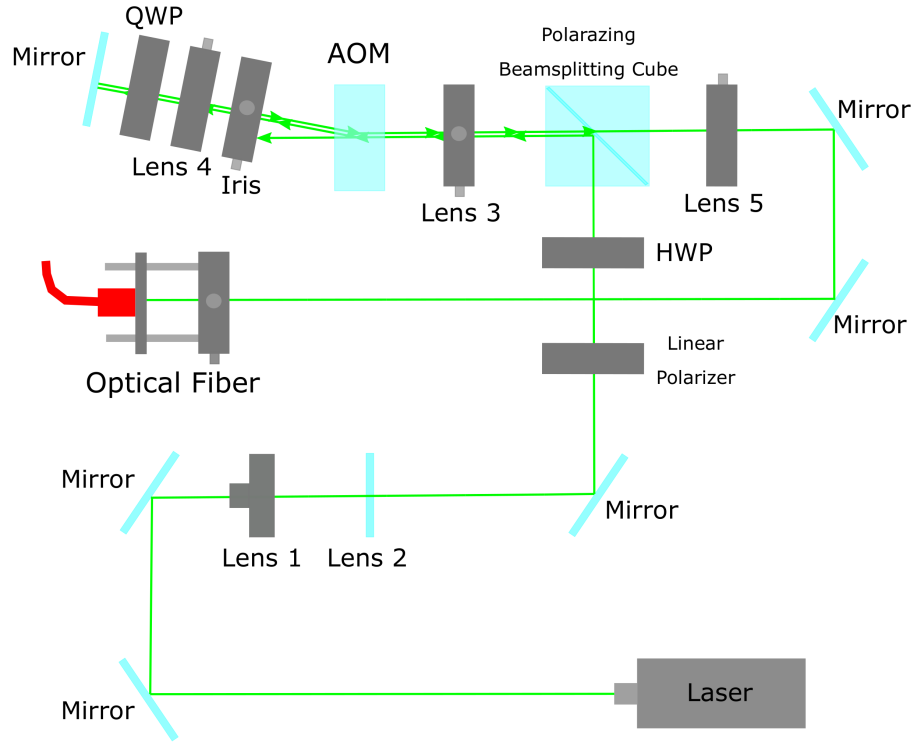


Figure 2.2: Optical circuit for laser pulsing. A basic representation of our pulsed laser control system. Green laser ($\lambda = 532$ nm) is collimated by lenses 1 and 2. Later, a linear polarizer and a half-wave plate rotates the polarization so that a polarizing beam splitter reflects the light. The polarizing beamsplitting cube allows to separate the laser, reflecting one of the polarizations and transmitting the other. The reflected beam pass through an acousto-optic modulator (AOM), diffracting the laser which is blocked by an iris except for the right first-order diffraction. The laser is reflected by a cat's eye retroreflector —formed by the Lens 4 and the mirror after the QWP— and a quarter-wave plate is used so as to rotate the polarization, letting the beam pass through the beamsplitting cube. After being collimated by lenses 3 and 5, the beam is coupled to an optical fiber and transmitted to our confocal microscope.

wavelength and light collection of emitted photons with $\lambda_2 > \lambda_1$ wavelength, like a confocal microscope, is mandatory.

Confocal microscopy principle is based on using an excitation light source and, by means of a dichroic mirror, make it impact on a objective lens which focuses light over the sample surface. The emitted photons pass through the objective lens and the mirror, being focused on the detector (in our case, an avalanche photon detector). Usually, lenses and pinholes are used to collimate the beam, and filters are used in order to ignore residual wavelengths. The optical arrangement used in this experiment can be divided in two parts:

- **Confocal Microscope:** Green laser (532 nm) is transmitted to our confocal microscope through an optical fiber. The light impacts over a Dichroic Mirror (532 nm BrightLine, laser dichroic beam splitter), being reflected towards the objective lens (depending on the experiment, it can be an air, oil or water immersion lens). After exciting the sample through optical pumping, emitted photons pass through Dichroic mirror and are filtered by a 600 nm long pass filter. Filtered light is collected by an APD (Perkin Elmer SPCM-AQRH-14-FC) through an optical fiber. The objective lens is mounted over a Piezoelectric stage (Physik Instrumente P-517), which allows to have a 3D sample scanning with a precision around 10 nm. For most of the experiment, a water dipping objective lens (Nikon NIR Apo 60X, NA: 1, WD: 2.8 mm) were used, having a resolution^I $R = 0.61 \frac{\lambda}{NA} = 0.32 \mu m$ (where λ is the wavelength in nanometers and NA is the numerical aperture). Considering that the objective lens captures around 17% of the emitted light, the optical fiber transmits around 50% of the photons and the APD photon detection efficiency is around 70% according to the manufacturer; the confocal light collection efficiency is around 6%. On the other hand, using an air objective lens (Nikon LU Plan Fluor 100x, NA: 0.90, WD: 1.0 mm) gives us a efficiency around 10% (the calculation details are in Appendix B).
- **Pulsed laser controller:** As long as to generate laser pulses, an acousto-optic modulator is used, which is based on the acousto-optic effect applied over a tellurium oxide (TeO_2) crystal, behaving like a diffraction grating. A double-path through

^IThe smallest resolvable distance between two objects.

an AOM[27] (i.e., acousto-optic modulator) is preferred over a single-path system because it has a better extinction ratio ($I_{off}/I_{on} \approx 10^{-6}$). As it is shown on Figure 2.2, a polarizing beamsplitting cube reflects one of the light polarizations in direction to a double-path system which consists in: an AOM, a quarter-wave plate and a cat's eye retroreflector. The AOM let us to create laser pulses with the needed length, this is due to a rise/fall time around 10 ns. The quarter-wave plate ensures that, after the double-path configuration, the beam will pass through the polarizing beamsplitting cube instead of being reflected. According to [27], a cat's eye retroreflector^{II} improves the AOM bandwidth compared to a flat-mirror retroreflector, which is a hit-or-miss configuration in terms of AOM diffraction efficiency and RF frequency.

Once the system is set in the sub-state $m_s = 0$ through laser excitation, a transition to the sub-states $m_s = \pm 1$ can be induced by transmitting microwave radiation to the sample with a frequency equal to the zero-field splitting—which, at room temperature, has a value of 2.87 GHz. Owing to this, a microwave control system that allows us to transmit microwave pulses to the sample is required.

2.2 Microwave Control System

As already mentioned, the transition between $m_s = 0$ and $m_s = \pm 1$ sub-states can be caused by microwave pulses, opening the possibility to perform pulse-sequence experiments by mixing laser and microwave pulses.

In order to produce microwave signals, we count with a signal generator (Rhode & Schwarz SMF100A Signal Generator), which has a frequency range between 100 kHz and 22 GHz. The signal passes through a circulator which has a 50 Ω -impedance load so as to dissipate the reflected signal (see Figure 2.3) and, then, to a switch connected to our pulse generator (PulseBlaster ESR 500 MHz). This pulse generator allows us to create microwave pulses using a Matlab software (developed in our lab). Later, the signal power is amplified around 30 dBm and it is transmitted to a waveguide.

^{II}A cat's eye retroreflector is a passive optical system consisting of a secondary mirror placed at the focal point of a primary lens.[28]

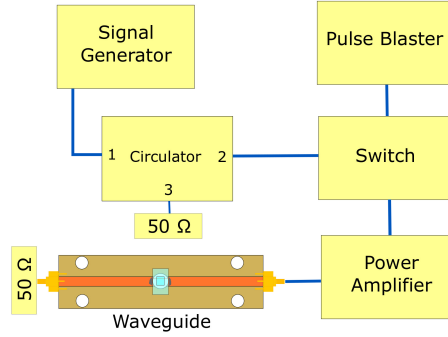


Figure 2.3: Microwave Circuit scheme. Graphic representation of the circuit between the signal generator and the microwave antenna. The signal passes through a circulator (port 1 input, port 2 output) and then through a switch controlled by a pulse blaster (and, therefore, by a computer). After that, the signal power is amplified in 30 dBm approximately and transmitted through a 50 Ω -impedance waveguide. The microwave signal is transmitted to the sample by a 25 μm -diamater gold wire.

The waveguide type used is manufactured through ferric chloride etching using as a base a copper circuit board and, as it is shown in Figure 2.3, a 50 Ω -impedance load is placed in the opposite side so as to transfer the maximum amount of power from the source to the load without signal reflection (which is known as Impedance Matching). A 25 μm -diamater annealed gold wire works as an antenna in order to transmit microwave radiation to the sample. Gold is preferred over copper because it is more resistant when in contact with the aqueous solutions used. With an annealing treatment, the electrical conduction is improved at the expense of thermal resistance, which represents a disadvantage when welding.

After being able to manipulate the NV center electronic spin, the following step is to expose our sample to chemical compounds in aqueous solution to observe the NV center quantum parameters behaviour using different pulse-sequence techniques. To be able to do this, a microfluidic system specially designed for our purpose is indispensable.

2.3 Microfluidic System

An important objective of this project is to take chemical compounds concentration measurements which means that our sensor has to be able to sense in an aqueous environment. In order to relate the NV center quantum parameters fluctuations with the chemical compounds concentration, we design and build an entire microfluidic system keeping in mind the following needs: To control which chemical compounds will interact inside the chamber, to control aqueous solutions flows and, if required, to measure mixture PH inside the chamber (or as close as possible). This Microfluidic System can be separated in two main parts: A Microfluidic Chamber and a Microfluidic Flow Control System.

2.3.1 Microfluidic Chamber

Throughout the project, we create a microfluidic chamber prototype and, as expected, it was updated as problems were found. The above led us to have several microfluidic chamber designs, which will be reviewed below:

- a) **Nanodiamond Chamber:** Since one of our main objectives was to take measurements with compounds which copper is soluble, a chamber design based on microwave resonators[29] was developed. Unfortunately, microwave signal was weaker than expected and, in consequence, no successfully experiment was ran, neither in nanodiamonds nor in our single-plate diamond. As a result of this, we created this “nanodiamond chamber” so as to recover the conventional microwave antenna (i.e., a $25\ \mu\text{m}$ diameter copper or gold wire). This is a hot-mount chamber because PARAFILM needs to be heated so as to act as a sealant. As it is shown in Figure 2.4, this microfluidic chamber needs around $15.46\ \mu\text{l}$ to be filled (considering a furrow depth of 1 mm), meaning a relative small sample volume. Unfortunately, the mounting method did not allow us to keep the wire tight, which is a mandatory condition to microwave transmission, and we were not able to re-tense the antenna. For that reason, “nanodiamond chamber” was discarded.
- b) **Diamond Chamber:** After the previous attempt, we focus on developing a demountable design so as to be able to fix or replace pieces instead building a new

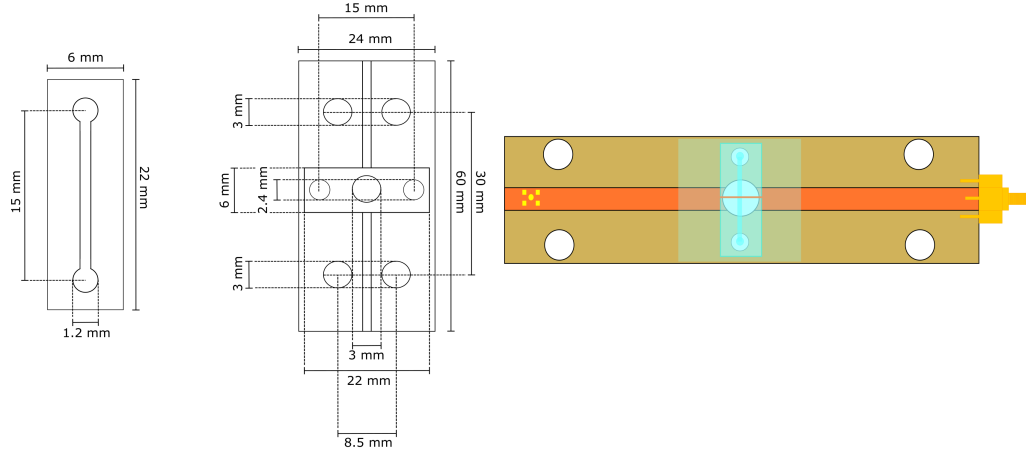


Figure 2.4: Nanodiamond Chamber. A detailed nanodiamond chamber and waveguide design plans (left figure), and a basic representation of the nanodiamond chamber final assembly (right figure). The chamber is covered by a 0.1 mm thickness cover glass and sealed using PARAFILM.

chamber. Also, we reconsider chamber dimensions in order to be able to use our main sample, which we will call “shallow-implanted diamond”. This chamber, shown in Figure 2.5, has a rubber o-ring as a sealant through mechanical pressure. A 0.1 mm thickness cover glass is used as a topping and it is fixed through pressure exerted by the upper “duraluminium” part, which is held by four screws. Except for a couple of leaks that we had at the very beginning, this chamber worked properly good from a microfluidic point of view. Regrettably, we cannot say the same in regard to the optics involved. An oil-immersion objective lens was used and, as you probably noticed, there is more than one propagation medium implicated (an aqueous solution, glass and oil). On the other hand, due to the o-ring thickness, defects barely fit inside the objective lens work distance (0.17 mm). Owing to these reasons, fluorescence signal was not high enough and, as a consequence, no experiment could be run.

- c) **Microfluidic Pool:** The installation of a water-immersion objective lens with a higher work distance (3 mm) allowed us to explore new configurations for the previous design. The cover glass was removed in order to eliminate the propagating medium issue, turning the chamber into a sort of microfluidic pool. Even though water evaporation was introduced as an issue, its effect is negligible since we are able to keep a continuous incoming aqueous solution flow and to control the environmental

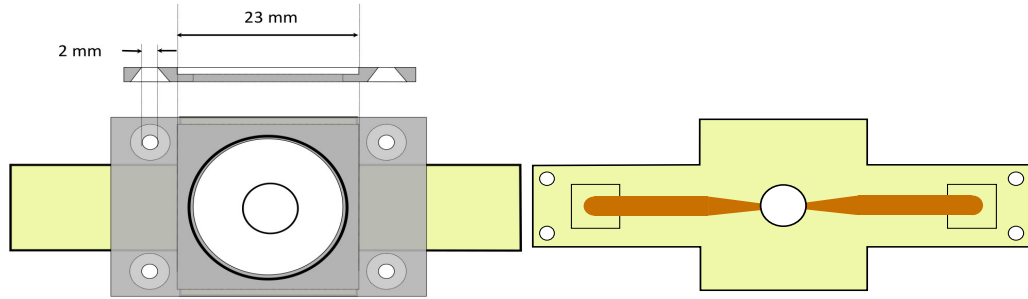


Figure 2.5: Diamond Chamber schematic. A basic representation of the chamber assembled (left figure) and its corresponding waveguide (right figure). Diamond chamber raw material is mostly “Duraluminium”, an aluminium-copper-magnesium-manganese alloy.

temperature. Different kind of experiments were ran using this chamber and positive results were obtained, setting it as the official design.

2.3.2 Microfluidic Flow Control System

A system focused on controlling the aqueous solution flow was designed and manufactured in our laboratory. This system consists of a pump station, a mixer and a pH sensor. All the above items are connected by teflon tubing (0.58 mm ID, 0.99 mm OD) owing to teflon chemical inertness related to the chemical compounds to use.

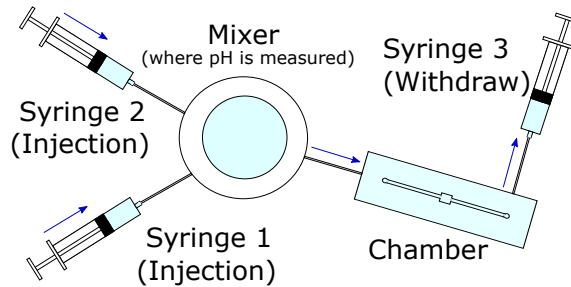


Figure 2.6: Microfluidic system. A basic representation of the system used to control the aqueous solution flow. Two syringes are used to inject solution into the mixer and the other one suck out in order to fill the chamber. Blue arrows indicate flow direction.

The pump station consists in a modular micro syringe pump (Chemyx Fusion 200) to which three syringe headers (NanoJet Stereotaxic Syringe Header) are connected, being possible to set different flow rates for every syringe. This system has flow rates ranging from $0.0001 \frac{\mu L}{min}$ to $84.7 \frac{mL}{min}$ and supports syringes up to 25 mL. Also, it is Matlab compatible

so it was possible to incorporate it to our main software.

Our mixer is a teflon cylinder that has, as Figure 2.6 shows, three connections (two inputs, one output). Inside of it, the pH meter is placed (Jenway 3520 pH meter) in order to record the pH of the mixture just before it flows inside the chamber. A teflon coated magnet is used in order to homogenize the mixture by means of an external magnetic field. The pH meter has an action range from -2.000 to 20.000 and an accuracy of ± 0.003 . It is also Matlab compatible, so the data can be recorded and stored into our computer.

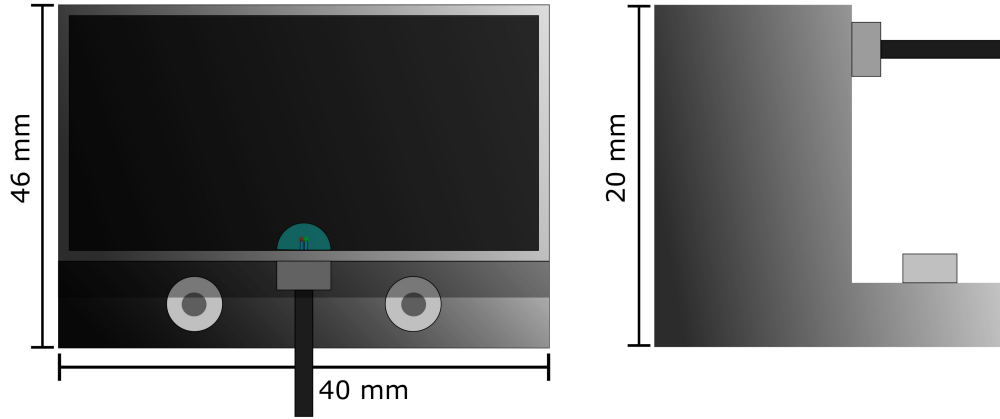


Figure 2.7: Water Level Module prototype. A basic representation of the first design of a duraluminium water level module in charge of hosting the water level sensor. The water level sensor placement is shown.

- **Prototype:** In order to take a step into the setup automation, a water level system has been designed. It is still in an experimental stage but the idea is shown in Figure 2.7. It will be a modular component coupled to our translation stage through two M6 screws and, as a first idea, the aqueous solution inside will have the same level compared to the chamber. A water level sensor (CQRobot Contact Water/Liquid Level Sensor) connected to our computer through an Arduino motherboard would indicate the fluid level with an accuracy of ± 0.5 mm and, if necessary, it would trigger the pump station in order to recover the referential level.

2.4 Shallow-Implanted Diamond

Once the confocal microscope and the microfluidic system were set up, we were able to perform a complete study over every implantation spot hosted in our sample. We used a $2 \times 2 \text{ mm}^2$ and 0.5 mm thick synthetic diamond which was implanted with Nitrogen by Jan Meijer (Universitat Leipzig), thus generating an implantation grid as it is shown in Figure 2.8. There are different implantation spots distributed along the rows by implantation dose and along the columns by implantation energy.

According to [30], the implantation energy and the NV centers average depth are closely related, following the rule of “grater energy, greater depth”. On the other hand, a greater nitrogen atoms dose implies a greater NV center density but limited by the yield^{III}. This quantity depends on the implantation energy because Nitrogen atoms create vacancies as they penetrate inside the diamond and the deeper they are, the more stable[30]. For instance, the 5 keV implantation energy spot with $7.64 \times 10^{12} \frac{N}{cm^2}$ dose has an average depth of 8 nm and a yield around 0.75%, which means that we have a surface NV centers density of $5.73 \times 10^2 \frac{NVs}{\mu m^2}$.

As we can see in Figure 2.9, a confocal image of a 5 keV implantation energy spot was taken, which appears as a $35 \mu m$ diameter fluorescent circle. According to our data, we can reach an emission peak of around 2×10^6 counts per second using a 1.5 mW laser power and an air objective lens. Considering an illumination spot diameter around $0.3 \mu m$, we are able to illuminate around 40 NV centers at the same time, which means that we have an emission peak of 50.000 counts/second per defect as a first approximation.

^{III}Ratio between active Nitrogen-Vacancy centers and the number of implanted Nitrogen atoms.

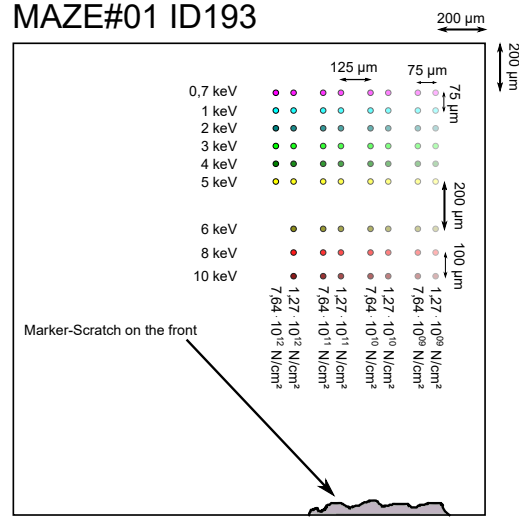


Figure 2.8: Diamond Implantation map. Implantation spots distribution over the diamond, ordered by implantation energy across the columns and by implantation dose across the rows. The implanted side is indicated by a mark on the bottom right corner, which can be seen through an optical microscope using a 4X magnification lens. The implantation was done by Jan Meijer, Nicole Raatz and Sebastien Pezzagna at Institut fur experimentelle Physik II - Universitat Leipzig.

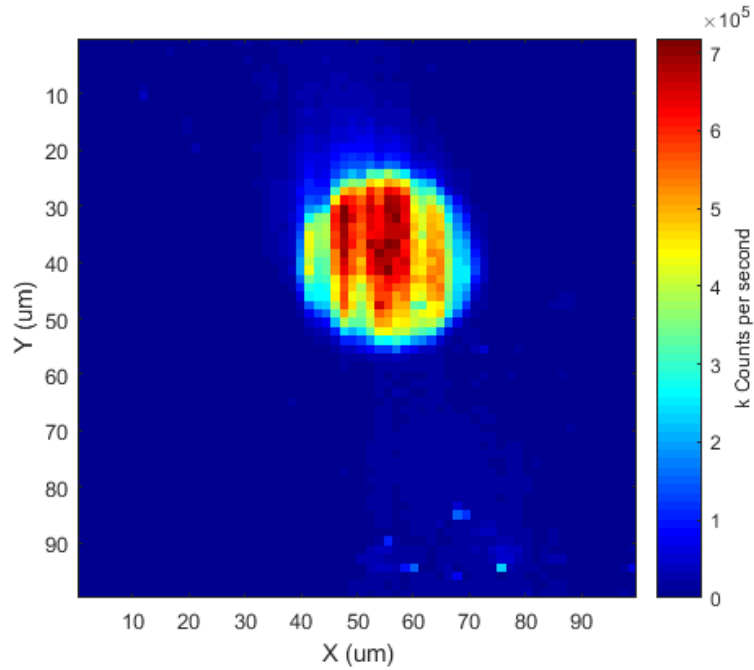


Figure 2.9: 5 keV Implantation Energy Spot Confocal Image. Confocal image of a 5 keV implantation energy spot with a dose of $7.64 \times 10^{12} \frac{N}{cm^2}$ using 0.3 mW green laser power and an air objective lens (Nikon LU Plan Fluor 100x, NA: 0.90, WD: 1.0 mm). The right side bar shows the counts per second scale detected by the APD.

Chapter 3

Chemical Reaction Sensor: Results and Discussion

As already mentioned, a Nitrogen-Vacancy center has an electronic spin that can be manipulated through either laser pulse or microwave pulse. The initial state, as it was explained in Figure 1.2, could be set in $m_s = 0$ by means of a 532 nm laser pulse with a minimum pulse length around 1 μs and. Afterwards, spin manipulation can be performed by different kind of microwave-pulse-sequence techniques (more information in Appendix C) using chemical compounds in aqueous solution as the measurements target. However, given that the chemical compound—both copper sulfate and sodium sulfate— was varying, the dielectric constant of the medium was modified and, therefore, a screening effect over the microwave radiation was present. Owing to that, it was opted for using a laser pulse technique so as to record the spin relaxation behavior in presence of different chemical compounds concentration.

3.1 Longitudinal Spin Relaxometry

An important phenomena involved in spin manipulation systems is the spin relaxation which is the tendency to recover the system natural spin state once it has been set in another state. In the Nitrogen-Vacancy center case, this experiment is performed by fixing the spin state in $|0\rangle$ or $|\pm 1\rangle$ and determine how long does relaxation take from the

detected fluorescence over time. In our case, we use $|0\rangle$ as initial state in order to run experiments without using microwave radiation. Figure 3.1 is a representation of the laser pulse sequence used to perform T_1 measurements. Fluorescence is recorded as a function of the time between polarization and read-out pulses ranging from 3 ns—the minimum time between laser pulses allowed by our setup—to, typically, 20 ms. According to [31], the fluorescence over time can be fitted by an exponential curve like the one shown below

$$y(t) = Ae^{-\frac{t}{T_1}} + C, \quad (3.1)$$

here T_1 corresponds to the spin relaxation, $(A + C)$ is the initial fluorescence value and C corresponds to the final fluorescence. This function is optimized, like the Equation C.1, through MatLab “fminsearch” function with respect to the Least-Squared method (more information in Appendix E). In order to determine how “soft” is the T_1 optimization, we calculated a minimum and a maximum T_1 value and, therefore, a T_1 range is created determined by a tolerance error respect to the sum of squared residuals—from the Least-Squared method.

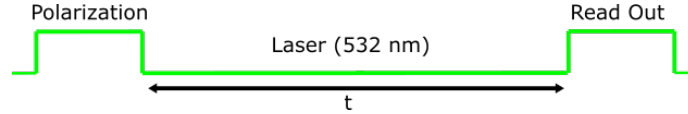


Figure 3.1: Longitudinal spin relaxometry: Laser pulse sequence. T_1 spin relaxometry experiment representation through a 532 nm laser pulse scheme. The first pulse fix the system in $m_s = 0$ and, after certain t time, a read-out is done so as to record the current fluorescence.

As it is shown in figure 3.2, the fluorescence over the time between pulses is plotted obtaining an exponential decay that can be described trough equation 3.1. Several relaxometry experiments were performed over the same spot; finding $T_{1,a} = 3.247$ ms, $T_{1,b} = 3.604$ ms and $T_{1,c} = 4.147$ ms relaxation time values for different positions inside the same 5 keV implantation spot. At first sight, this results may indicate an spacial dependence on spin relaxation time values measured over the same spot.

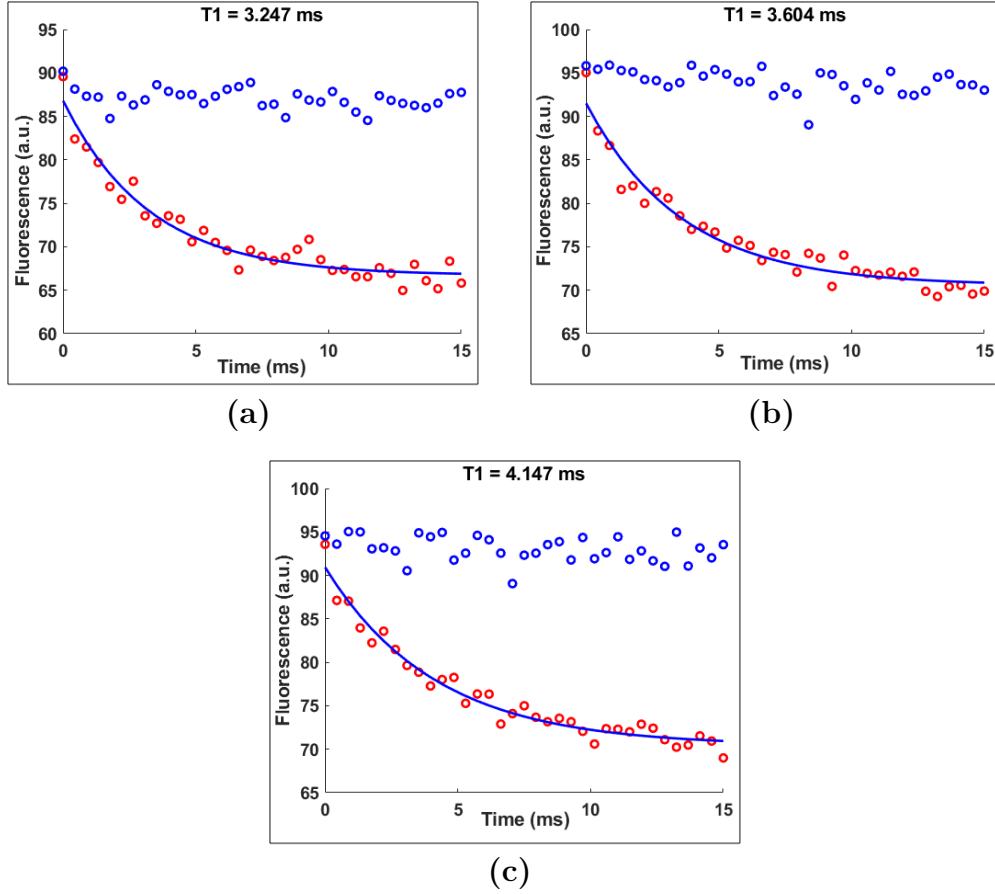


Figure 3.2: Longitudinal spin relaxometry for a 5 keV implantation spot. Fluorescence as a function of time for a T_1 spin relaxometry experiments performed in a 5 keV implantation energy spot with an ion fluence of $7.64 \times 10^{12} \frac{N}{cm^2}$ using 1.5 mW green laser power and air as optical medium. ((a), (b) and (c)) Red circles are the detected fluorescence, blue circles is the fluorescence right after polarizing and blue line correspond to an exponential curve fit. It is determined that $T_1 = 3.247$ ms ± 0.012 ms for (a), $T_1 = 3.604$ ms ± 0.013 ms for (b) and $T_1 = 4.147$ ms ± 0.012 ms for (c) with a 5% tolerance error.

3.2 Longitudinal Spin Relaxation Time Spatial Distribution

As already mentioned, we found clues about a possible space distribution over the NV centers implantation spot. In order to corroborate this, we make the following updates to our Matlab software: The implementation of a new tracking system based on image comparison so as to correct the drifting effect over the sample and a path tracing system that recognizes the implantation spot geometric center, which serves as a reference point to trace different paths over the spot (further information in Appendix F).

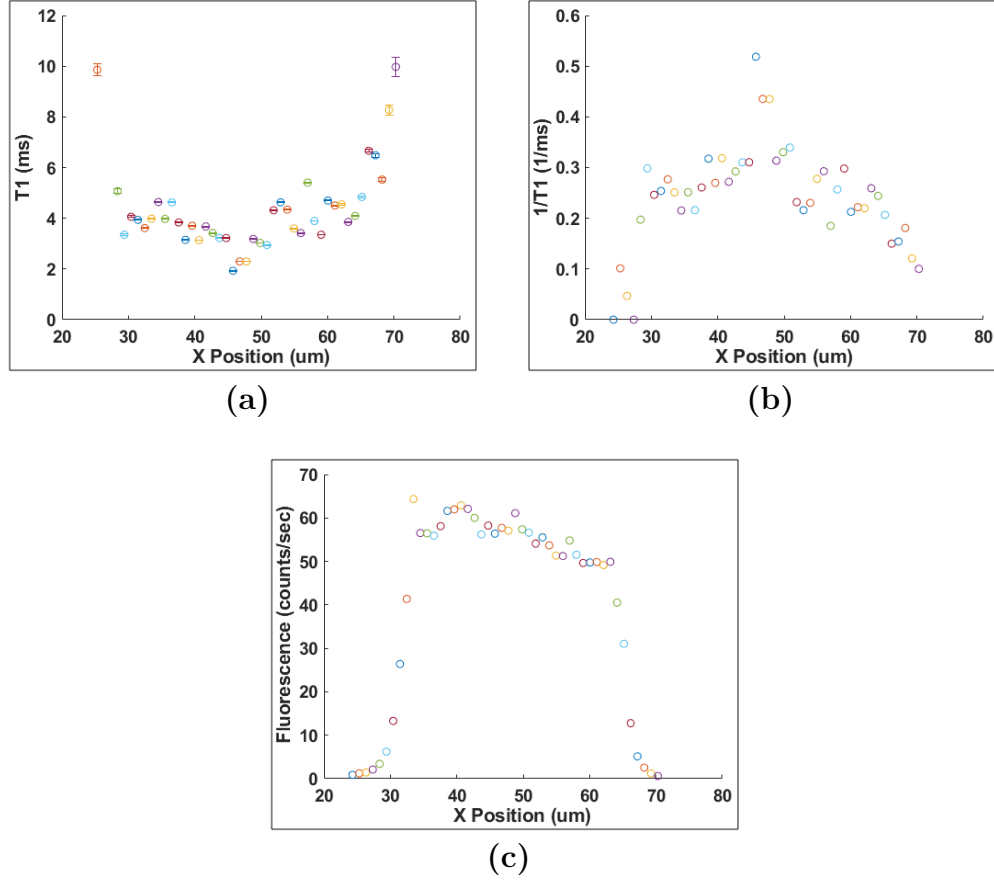


Figure 3.3: T_1 spin relaxation time distribution over a 5 keV implantation spot. (a) Spin relaxation time of the $m_s = 0$ sub-state as a function of the position over a straight line path of $46 \mu\text{m}$ length for a 5 keV implantation energy spot with an ion fluence of $7.64 \times 10^{12} \frac{\text{N}}{\text{cm}^2}$ using 1.5 mW green laser power and air as optical medium. (b) $1/T_1$ distribution over the implantation spot diameter (x-axis) and (c) is the fluorescence distribution over the spot diameter, both maintaining the same conditions of (a) with a tolerance error of 5%.

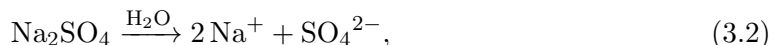
As it is shown in Figure 3.3, the spin relaxometry experiment was performed several times following a straight line path over the sample which corresponds to the 5 keV implantation energy spot equator line. The fluorescence variation across the path is minimum for the zone corresponding to the implantation spot and much more noticeable on the spot edges. Regarding the spin relaxation time distribution, we can see that the T_1 time reaches the highest values around the implantation spot edges. This behaviour would be related to the low NV centers concentration at the edges since it was the only modified parameter during the experiment and this behaviour was also present in other spin relaxation time

distribution experiments performed over the same implantation spot. On the other hand, we can see that the minimum T_1 value is reached around the spot geometric center which is one of the zones with the highest fluorescence and, therefore, with a high NV centers quantity. According to [32], this spin relaxation time distribution over the spot can be explained through the cross-relaxation phenomenon which is a collective effect characteristic of NV centers ensembles with different orientations and it is proportional to the NV^- concentration—explaining the higher T_1 values at the spot edges. Also, we never achieve a 100% NV polarization what contributes to the T_1 decrease as well. These results support the need to take into account the spin relaxation time space distribution since, as can be seen in Figure 3.3, the T_1 values range between 2 ms and 10 ms which is something that cannot be ignored.

After finding evidence of the T_1 distribution, including minimum and maximum values zones, it is necessary to determine if the relaxation of the sub-state $m_s = 0$ is influenced by the presence of nearby ions in aqueous solution.

3.3 Longitudinal Spin Relaxometry in Presence of Sodium Sulfate

The main objective of this work is to find sufficient evidence to link the NV center quantum parameters behaviour in presence of different chemical compounds in aqueous solution. For this, the microfluidic chamber was filled with sodium sulfate in aqueous solution in order to expose the diamond surface to it. In this state, the sodium sulfate descomposes as follows



which means that the diamond is exposed to moving ions. We performed several spin relaxometry experiments based on the $m_s = 0$ sub-state varying the sulfate sodium concentration, which is represented in Figure 3.4. As it is shown, the $1/T_1$ data has a quadratic behaviour represented by the fitting curve which is supported by a low norm of residuals.

This result indicates that, for 5 keV implantation energy NV centers, an increase in the ion concentration leads to a stronger spin relaxation.

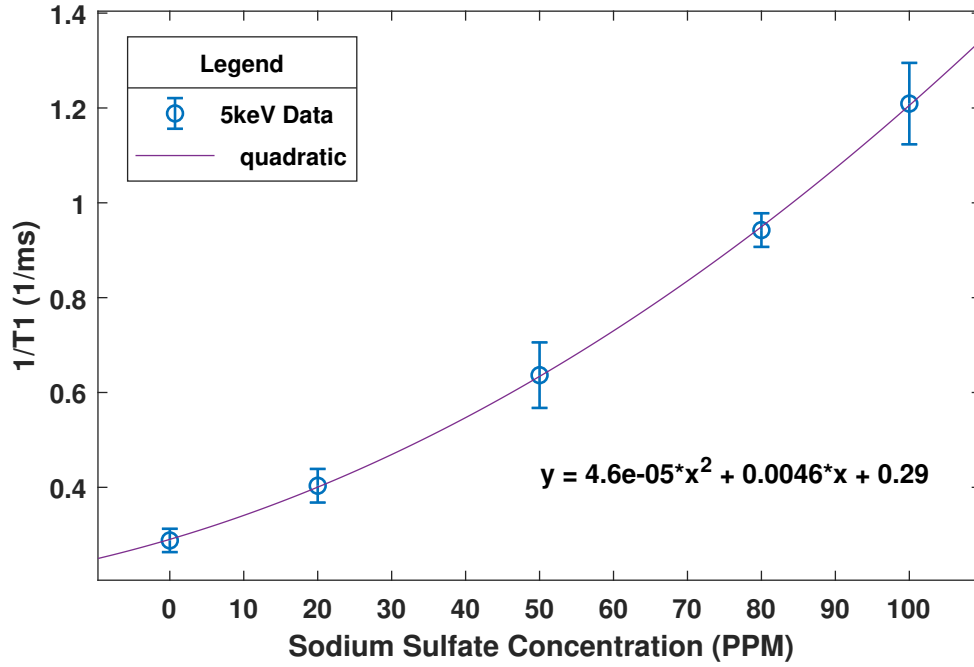


Figure 3.4: $1/T_1$ as a function of sodium sulfate concentration for a 5 keV implantation spot. $1/T_1$ as a function of the sodium sulfate concentration for a 5 keV implantation spot with an ion fluence of $7.64 \times 10^{12} \frac{N}{cm^2}$ using 1.5 mW green laser power and water as optical medium. A quadratic fitting curve is plotted over the data with a norm of residuals of 0.00915 and with $y = 4.6 \times 10^{-5}x^2 + 0.0046x + 0.29$ as the associated equation.

After determining a relation between the longitudinal spin relaxation time fluctuation and the sodium sulfate concentration in aqueous solution, it is worth wondering what role does the proximity of the NV centers to the diamond surface play. As it is shown in Figure 3.5, several longitudinal spin relaxometry experiments were performed over implantation spots with implantation energies 5 keV, 4 keV and 3 keV and with the same ion fluence. The first thing that can be observed is that, apparently, the relation between the implantation energy and the sodium sulfate concentration is somewhat weak for concentrations below 50 PPM—or 50 mg/L. For concentrations over 50 PPM, the results go according to the theoretical background because the effect is higher for NV centers closer to the surface. However, Figure 3.5c shows that, unlike 5 keV and 4 keV data, quadratic fit does not fit

very well over the 3 keV data —its norm of residuals is two orders of magnitude larger than the other two data sets— which may indicate the need to increase the average number per point and to include intermediate concentrations.

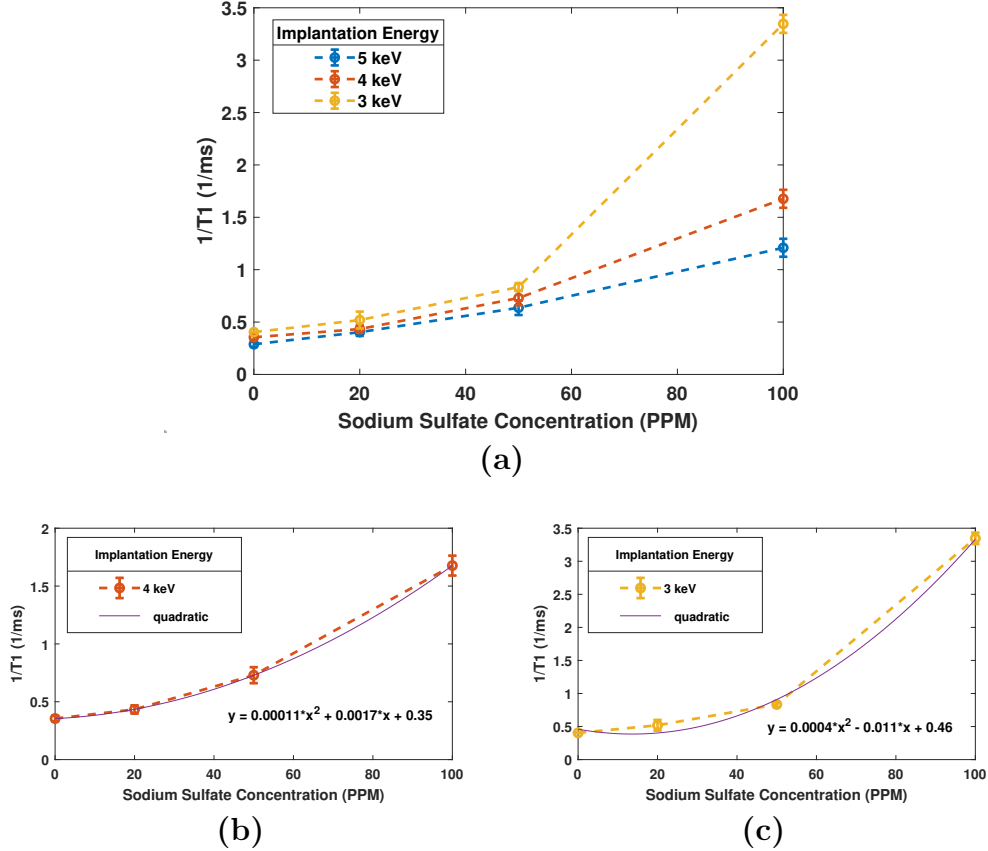


Figure 3.5: $1/T_1$ as a function of sodium sulfate concentration for different implantation spots. (a) $1/T_1$ as a function of the sodium sulfate concentration for a 5 keV (blue), 4 keV (orange) and 3 keV (yellow) implantation spots with an ion fluence of $7.64 \times 10^{12} \frac{N}{cm^2}$ using 1.5 mW green laser power and water as optical medium. (b) Quadratic fitting curve plotted over the 4 keV data with a norm of residuals of 0.00203 and with $y = 1.1 \times 10^{-4}x^2 + 0.0017x + 0.35$ as the associated equation. (c) Quadratic fitting curve plotted over the 3 keV data with a norm of residuals of 0.14991 and with $y = 4 \times 10^{-4}x^2 - 0.011x + 0.46$ as the associated equation.

In [33], they developed a pH sensor based on functionalized nanodiamonds which attract charged molecules to the surface in basic medium and, based on the T_1 time decay, they determine how strong is the base. Unlike the aforementioned, we determined that T_1 longitudinal spin relaxation time is affected by the presence of sodium sulfate in aqueous

solution despite not having the diamond surface functionalized. Nevertheless, references [34] and [35] performed longitudinal spin relaxometry in presence of ionic atoms in aqueous solution —something more similar to what we did— and the T_1 decay recorded is more related to magnetic fluctuations than electrical fluctuations, specially when performing relaxometry experiments based on the $m_s = 0$ sub-state. Although in [34] they focused their study on Gd_3^+ in aqueous solution, the magnetic dipole moment of the Na^+ is the third part of it, meaning that the magnetic fluctuations due to the sodium ions movement would be the main external longitudinal spin relaxation source. The above leads us to re-evaluate how our sensor is defined, considering that now we have protocols more sensitive to electrical fluctuations (more information in Appendix C) and the longitudinal spin relaxometry which is more sensitive to magnetic fluctuations.

Chapter 4

Conclusions and Future Work

Based on the results presented during this thesis, we can conclude that the Longitudinal Spin Relaxometry protocol presents itself as a strong candidate on which to base the operation of our chemical sensor as long as the following limitations are taken into account: Measurements are limited to chemical compounds in aqueous solution that decompose into ions and, at the same time, these ions must be in motion in order to generate magnetic fluctuations to which the protocol is sensitive.

It was found that the effect of increasing sodium sulfate concentration on longitudinal relaxation time T_1 is greater as NV centers are closer to the surface (i.e., for lower implantation energies). Regarding the relation between $1/T_1$ and the sodium sulfate concentration, it can be said that it is quadratic since two of the three implantation spot studied presented this kind of dependence but, of course, more data is needed in this regards in order to determine the type of curve fit and to quantify this relation more accurately —this last step is crucial to establish a theoretical model based on the presence of Na^+ and SO_4^{2-} close to the diamond surface. Another important factor to consider is the existence of a T_1 distribution over the implantation spots what could be corroborated experimentally, having higher spin relaxation time values at the edges of the spot and lower values around the center. This last result is relevant because it helps us to reduce the longitudinal spin relaxation time fluctuation owing to the position over the spot, thus achieving a clearer vision of the phenomenon of interest.

With regard to improvements to the experimental set-up, change the syringe pump station for a much larger reservoir, like a container of around ~ 5 L, actuated by an electric solenoid valve would give the set-up much more independence when performing experiments. This is complementary to the prototype presented in Chapter 2 and, all this together, would allow to perform experiments during days without any physical intervention by researchers. Another interesting set-up improvement would be to use a thinner diamond to host the shallow NV centers in order to perform experiments from the back of the sample. For instance, a ~ 20 μm thick diamond is thin enough to take NV centers confocal images from the back and, even more important, it is thin enough to transmit microwave radiation to the defects. This improvement would allow us to expose the diamond front side to the aqueous solution and perform the experiments from behind, automatically correcting all issues that arose during the comparative study using different chemical compounds by pulse-sequence techniques that use microwave radiation (further information in Appendix D) and, therefore, allowing these pulse-sequence techniques to become viable again (more information in Appendix C)—this last implication is very important because, according to [25], it would give our sensor electric field fluctuation sensitivity.

The next step in our quantum chemical sensor development considers using diamond with functionalized surfaces with which it is intended to capture molecules of interest for the study, positioning them just above the surface as it was done in [33]. This would lead us to implement new experimental techniques and, with all certainty, to introduce new possible complications like inducing a change in the shallow NV centers charge state due to the surface functionalizing process. In order to correct this, a photo-induced ionization protocol based on a multi-wavelength optical array is what we propose (further information in Appendix G). We consider that, owing to the fact that our sample contains plenty implantation spots with different NV centers concentrations, this proposal opens a wide range of possibilities regarding experimental techniques that can be applied and future results with respect to chemical sensing through shallow NV centers.

Appendix

A Magnetic Field Generation System: Characterization using the Nitrogen-Vacancy center

As it was already mentioned in Chapter 1, reaching a zero-magnetic-field regime is a mandatory condition to achieve that the system coherence time T_2^* only be affected by external electric field fluctuations.

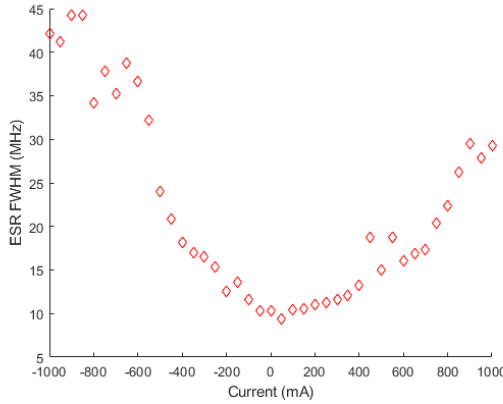


Figure A.1: FWHM as a function of Electric Current. Electron Spin Resonance FWHM in MHz as a function of the coil circulating electric current in mA. Electric current step is 49 mA approximately.

In order to fulfill the previous condition by cancelling the earth magnetic field ($|\vec{B}_{Earth}| \approx 0.45$ G), a simple magnetic field generator system was designed. This system is composed of a DC one-channel programmable power supply (Korad KD3005D) which has a real current precision of ± 1.5 mA, and an enamel copper wire coil. This last was calibrated throughout magnetometry using Electron Spin Resonance technique (see Section C.1) over

NV centers. As it can be seen in Figure A.1, ESR Full Width at Half Maximum as a function of the coil circulating current was graphed and, based on [25, 36], the magnetic field-electric current equivalence is $1 \text{ mA} \approx 1 \text{ mG}$.

Unfortunately, the research line based on microwave pulse sequence techniques was discarded due to the microwave radiation was screened by the optical medium and it was replaced by a Longitudinal Spin Relaxometry protocol based on the $m_s = 0$ sub-state which is independent of the external magnetic field, meaning that there is no longer a need to generate this kind of fields.

B Confocal Light Collection Efficiency

Based on the confocal microscope structure shown in Figure 2.1, three photon loss sources are considered: the collection efficiencies of the objective lens, the single-mode fiber and the APD.

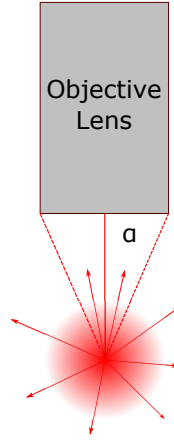


Figure B.1: Objective lens light collection scheme. Representation of the light collection efficiency of an objective lens relating to a spherical light emission. The α -angle describes a cone that represents the effective sphere fraction collected by the lens.

As it is shown in Figure B.1, the effective light collected by the lens is a fraction of the total emission determined by an α -angle cone. This angle can be calculated from the following equation

$$Na = \eta \sin(\alpha), \quad (\text{B.1})$$

here Na corresponds to the lens numerical aperture—which is a dimensionless number that characterizes the range of angles over which the system can accept or emit light—, and η is the medium refractive index—which is a dimensionless number that describes how fast the light travels through the material. Considering that the solid angle described by the α -angle is $\Omega = 2\pi(1 - \cos(\alpha))$ and, therefore, the light collected percentage relating to the full solid angle 4π is

$$\% = \frac{1}{2}(1 - \cos(\alpha)) \times 100. \quad (\text{B.2})$$

The second limiting factor is the optical fiber coupling. According to our experimental experience, the maximum efficiency in the light transmission through a single-mode optical fiber is around 50%.

Figure 3. Typical Photon Detection Efficiency (PDE) vs. Wavelength

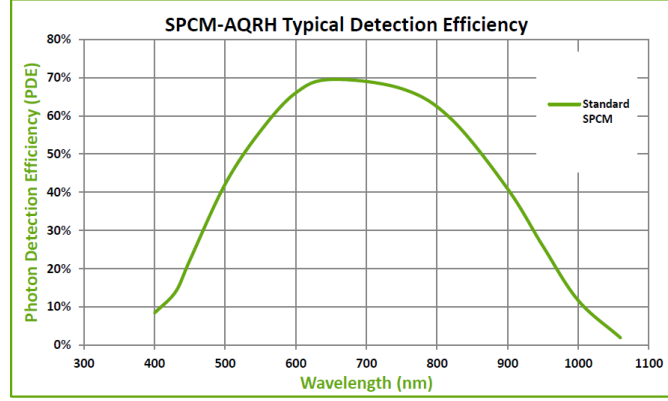


Figure B.2: APD photon detection efficiency as a function of wavelength. Graphic extracted from *Perkin Elmer SPCM-AQRH-14-FC* user manual that shows the detection efficiency respect to the photons wavelength.

According with Figure B.2 and considering that the emission spectrum of the NV^- goes from 600 nm to 800 nm, the APD detection efficiency is around 70%.

C Characterization Techniques

C.1 Electron Spin Resonance (ESR)

Electron Spin Resonance (ESR), or also called Electron Paramagnetic Resonance (EPR), is a spectroscopy method for studying materials with unpaired electrons. After polarizing the electronic spin at $m_s = 0$, a microwave sweeping is applied over the defect in order to obtain the right transition frequency to the state $m_s = \pm 1$. At room temperature and without an external magnetic field, the transition frequency between this substates is 2.87 GHz. If we plot the detected photons flux as a function of the microwave frequency, we are going to obtain a graphic similar to Figure C.1, which has a Lorentzian fit curve according to

$$y(x) = x_0(4) - \frac{x_0(2)}{1 + \left(\frac{x - x_0(1)}{x_0(3)}\right)^2} + x_0(5)(x - x(1)), \quad (\text{C.1})$$

where $x_0(1)$ is the transition frequency in GHz, $x_0(2)$ is the fluorescence contrast, $x_0(3)$ is the Full Width at Half Maximum (FWHM) in MHz, $x_0(4)$ is the average fluorescence and $x_0(5)$ is a linear correction term used so as to correct possible drifting in the data. Variables $y(x)$ and x represent fluorescence and frequency data vectors. The equation C.1 can be extended in case of having two different transition frequencies by duplicating the middle term and replacing with $x_0(1)$, $x_0(2)$ and $x_0(3)$ associated with the second trough. This function is optimized through MatLab “fminsearch” function with respect to the Least-Squared method (more information in Appendix E).

The $m_s = \pm 1$ is a degenerated state whose degeneracy usually breaks by an external magnetic field, causing that $m_s = 1$ and $m_s = -1$ separate in $2\gamma_e B_z$ (Zeeman effect). However, Figure C.1 data was taken without an external magnetic field and, despite this, a $m_s = \pm 1$ non-negligible splitting appears with a value around 19 MHz. This is due to the data was taken over a NV center ensemble and, according to [18], it means that the local axial symmetry ($C_{3\nu}$) of most of defects is broken at the ground state.

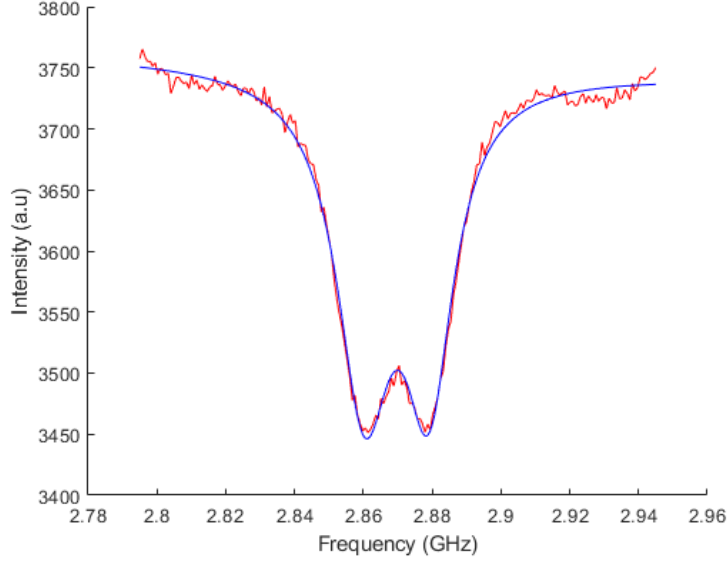


Figure C.1: Electron Spin Resonance for a 10 keV Implantation Spot. ESR over a 10 keV implantation energy spot with a dose of $1.27 \times 10^{12} \frac{N}{cm^2}$ using 1 mW green laser power and 30 dBm microwave signal potency. Transition between $m_s = 0$ and $m_s = \pm 1$ occurs at frequencies 2.860 GHz and 2.879 GHz. The first trough (from left to right) has a 19.48 MHz FWHM and 6.95% fluorescence contrast while the second one has a 17.46 MHz FWHM and 6.52% fluorescence contrast. Nanopurified water were used as optical medium.

An experimental result, as it can be seen in Figure C.2, is the existing relation between the ESR contrast and the incoming photon flux while keeping the microwave signal power constant. The objective of this experiment was to determine the optimal laser power for this shallow NV centers. We were not able to reach laser power over $2500 \mu W$, regime in which the contrast appears to markedly decrease it rise rate. Notwithstanding it seems that $2000 \mu W$ is the optimal power, it was decided to work around $1500 \mu W$ owing to over that point, the laser output power is unstable.

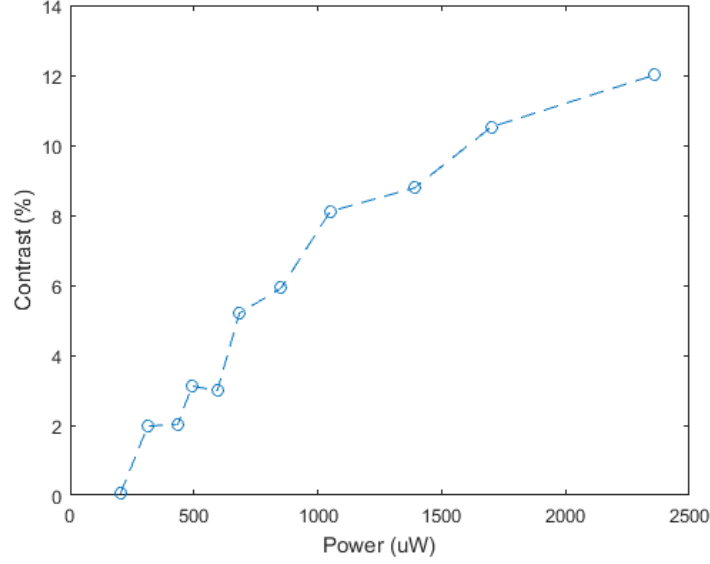


Figure C.2: Electron Spin Resonance Contrast. ESR contrast as a function of laser power for a 10 keV implantation energy spot with a dose of $1.27 \times 10^{12} \frac{N}{cm^2}$ using 25 dBm microwave signal potency.

C.2 Rabi Oscillations

Once the transition frequency from $m_s = 0$ to $m_s = \pm 1$ is known, the next step is to determine how long it takes to rotate from one state to the other one. Rabi oscillations is a good experimental method to determine this by the application of variable-duration microwave pulses. In Figure C.3, it is exemplified how the experiment is performed: The system is set in the $m_s = 0$ state by a polarization pulse. Afterward, a microwave pulse is sent to the sample and, then, a read out is done by a laser pulse. This is repeated for different microwave pulse lengths while keeping the frequency fixed so as to determine three significant outputs: Rabi frequency, π -pulse length (i.e., how long takes the transition between $m_s = 0$ and $m_s = \pm 1$) and $\frac{\pi}{2}$ -pulse length (i.e., how long takes the transition from the Bloch sphere top to the equator shown in Figure C.3).

Figure C.4 shows fluorescence as a function of the microwave pulse length for a Rabi oscillation experiment which has a damped sinusoidal fit curve according to

$$y(x) = x_0(1) + x_0(2) \cos(2\pi x_0(3)x + x_0(5)) e^{\frac{-x}{x_0(4)}}, \quad (\text{C.2})$$

here $x_0(1)$ is a vertical displacement, $x_0(2)$ is the initial amplitude, $x_0(3)$ is the initial frequency, $x_0(4)$ is a characteristic time and $x_0(5)$ is the sinusoidal phase. This function is optimized, like the Equation C.1, through MatLab “fminsearch” function with respect to the Least-Squared method (more information in Appendix E). Variables $y(x)$ and x represent fluorescence and microwave pulse length data vectors. This experiment was performed choosing arbitrarily one of the transition frequencies -2.860 GHz of the ESR experiment shown in Figure C.1 (no matters which transition frequency is used, it always has the same output values), having the following output values: a π -pulse of $0.082 \mu\text{s}$, a $\frac{\pi}{2}$ -pulse of $0.041 \mu\text{s}$ and a Rabi frequency of 6.099 MHz. The damping effect over the sinusoidal amplitude is strongly noticeable because of the studied NV centers are very close to the surface (below 10 nm from it) which facilitates environmental interactions[37].

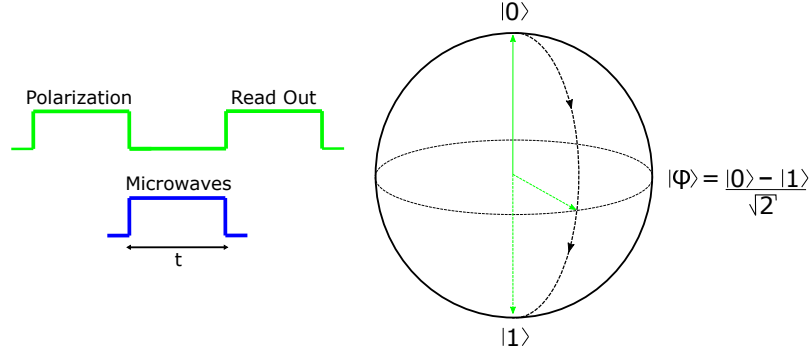


Figure C.3: Rabi Pulse Sequence and Bloch Sphere Representation. Left side: Rabi laser (532 nm) and microwave (blue) pulses sequence basic representation. A $1.5 \mu\text{s}$ laser pulse set the system initial state as $m_s = 0$ and, after the microwave pulse, a read out is done by a $0.5 \mu\text{s}$ laser pulse. Right side: Bloch sphere representation of a two-level quantum system. Black dotted arrows indicates the transition direction and green arrows indicates the main quantum states — $m_s = 0$, $m_s = 1$ and $\frac{|0\rangle - |1\rangle}{\sqrt{2}}$ — studied during a Rabi oscillations experiment.

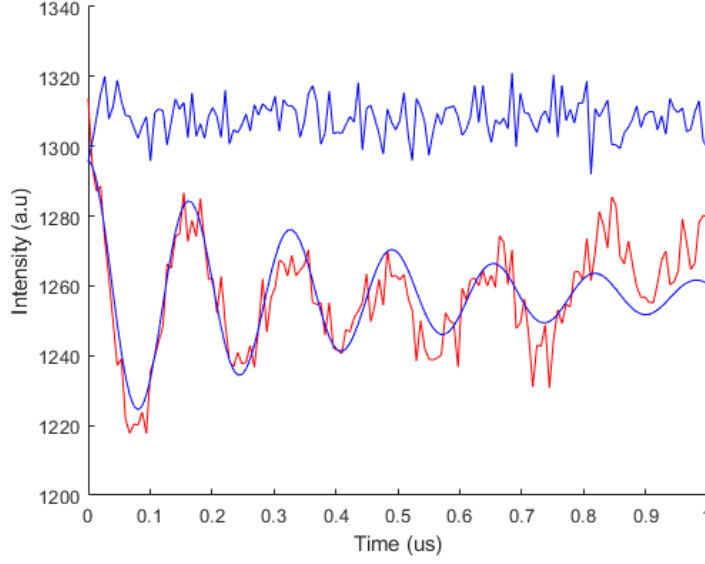


Figure C.4: Rabi Oscillation for a 10 keV Implantation Spot. Fluorescence as a function of the microwave pulse length for a Rabi oscillation experiment over a 10 keV implantation energy spot with a dose of $1.27 \times 10^{12} \frac{N}{cm^2}$ using 1 mW green laser power and 30 dBm microwave signal potency. Upper blue line shows maximum fluorescence, red line is the detected fluorescence and blue line –over the red one– is a damped sinusoidal fitting. Microwave frequency is 2.860 GHz, π -pulse is $0.082 \mu s$, $\frac{\pi}{2}$ -pulse is $0.041 \mu s$ and Rabi frequency is 6.099 MHz. Nanopurified water were used as optical medium.

C.3 Ramsey Spectroscopy

Once both the transition frequency and the microwave pulse length enough to induce it are determined, Ramsey spectroscopy experiments can be performed. This kind of experiment focus on free-spin dynamic, which can be studied through the typical Ramsey microwave pulse sequence $\frac{\pi}{2} - \tau - \frac{\pi}{2}$ applied over the system to later measure the probability of recovering the initial state. Starting from $m_s = 0$, the first $\frac{\pi}{2}$ -pulse is applied in order to lead the system into a superposition state $|\varphi\rangle = \frac{|0\rangle - |1\rangle}{\sqrt{2}}$. Then, the system evolves freely –without any laser or microwave pulse interaction– during a time τ , which is known as free-precession time, making the system acquire a phase $|\varphi\rangle = \frac{|0\rangle - e^{i\phi(\tau)}|1\rangle}{\sqrt{2}}$. Finally, the last $\frac{\pi}{2}$ -pulse is applied making the spin rotate back to $|0\rangle$ as it is shown in Figure C.5. According to [38], this Ramsey sequence can be seen as a $\frac{\pi}{2}$ -rotation operator applied over the system followed by a temporal evolution operator and, to end, another $\frac{\pi}{2}$ -rotation operator making the spin goes back to the north pole in a Bloch sphere scheme. From this,

it follows that

$$|\varphi(\tau)\rangle = \frac{1}{2} \left(\left(1 - e^{i\phi(0,\tau)}\right) |0\rangle + \left(1 + e^{i\phi(0,\tau)}\right) |1\rangle \right), \quad (\text{C.3})$$

here $\phi(0, \tau) = \int_0^\tau \langle m_s | \frac{H_{\text{Interaction}}}{\hbar} | m_s \rangle dt$. The probability of returning to $|0\rangle$ state as a function of τ can be determine through the NV center fluorescence level and, according to [39], it can be fitted by

$$P(\tau) = \frac{1}{2} - \frac{e^{-\left(\frac{\tau}{T_2^*}\right)^2}}{2} \sum_{j=1}^N \alpha_j \cos(2\pi f_j \tau + \phi_j), \quad (\text{C.4})$$

here f_j corresponds to the frequencies extracted from the power spectrum and, depending on whether the external magnetic field projection B_z is zero or not, it can be three or six frequencies—which are associated with the electronic levels $m_s = \pm 1$ and, for each one, nuclear hyper-fine states associated $m_I = 0, \pm 1$. The terms α_j and ϕ_j are associated with every frequency, and N corresponds to the number of frequencies involved. It is easy to notice that the equation C.4 describes a sinusoidal-type curve with an exponential damping factor which depends on T_2^* —better known as coherence time.

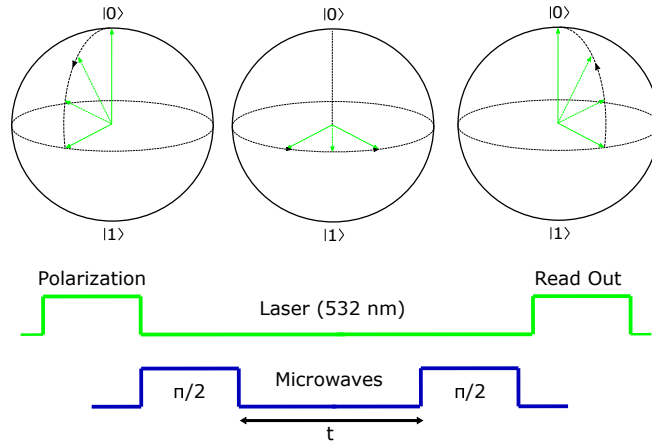


Figure C.5: Ramsey Spectroscopy: Bloch Sphere Representation and Pulse Sequence Scheme. Free-induction decay (FID) experiment representation through a Bloch sphere diagram and the necessary laser (green)/microwave (blue) pulse sequence to perform it. After the system polarization through a 532 nm laser pulse, the transition from $|0\rangle$ to $\frac{|0\rangle - |1\rangle}{\sqrt{2}}$ —represented on the first sphere (left)—takes place owing to a microwave $\frac{\pi}{2}$ -pulse. The second sphere (middle) represents the system evolution during a τ time without any microwave pulse. The third sphere (right) represents the transition back to the initial state through a microwave $\frac{\pi}{2}$ -pulse.

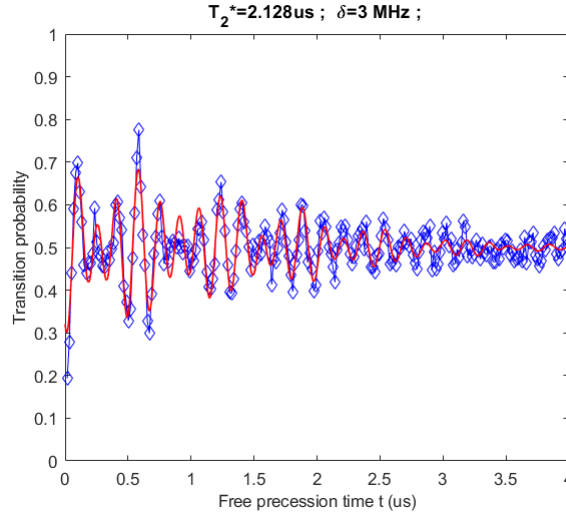


Figure C.6: Transition Probability for a 10 keV Implantation Spot. Transition probability from $\frac{|0\rangle - |1\rangle}{\sqrt{2}}$ to $|0\rangle$ as a function of free precession time τ for a 10 keV implantation energy spot with a dose of $1.27 \times 10^{12} \frac{N}{cm^2}$ using 1 mW green laser power, 30 dBm microwave signal potency and 3 MHz of detuning. Blue diamonds corresponds to experimental data and red line represents a curve fitting according to equation C.4. The coherence time is $T_2^* = 2.128 \mu s$. Nanopurified water were used as optical medium.

Based on the recorded fluorescence as a function of the free evolution time of the system, a transition probability over the evolution time can be plotted as it is shown in Figure C.6. Red line represents a curve fitting according to equation C.4, which has a damping term $e^{-\left(\frac{\tau}{T_2^*}\right)^2}$ from where it can be extracted the coherence time of the system. A detuning $\delta = 3$ MHz—which is the difference between the transition frequency of the system and the microwave pulse frequency—was used in order to increase the oscillations number (i.e., the time needed to observe the amplitude decay) obtaining a better curve fitting and, therefore, a more exact coherence time determination. This experiment was performed using nanopurified water as optical medium in order to define a referential coherence time for every implantation spot. Nevertheless, it could only be determined the coherence time for a 10 keV implantation spot ($T_{2,10keV}^* = 2.128 \mu s$) and for a 8 keV implantation spot ($T_{2,8keV}^* = 1.522 \mu s$), both with $1.27 \times 10^{12} \frac{N}{cm^2}$ ion fluence. This gives us a lead that the NV coherence time and the implantation energy may be related, but the results are not conclusive.

D Chemical Reaction Sensor: Copper Sulfate and Sodium Sulfate Comparative Study

Following what was presented in Section 1.3, shallow NV centers coherence time should be affected by nearby electric fluctuations. In order to prove the nitrogen-vacancy center electrical sensitivity, different kind of pulse-sequence experiments were performed in presence of copper sulfate and sodium sulfate in aqueous solution. In this state, this chemical compounds dissociate into a sulfate group and a Cu^{2+} ion (or a Na^+ ion in case of sodium sulfate). Due to the ionic copper atom has higher charge than the ionic sodium atom, the effects over the NV center quantum parameters are expected to be more noticeable for the first one.

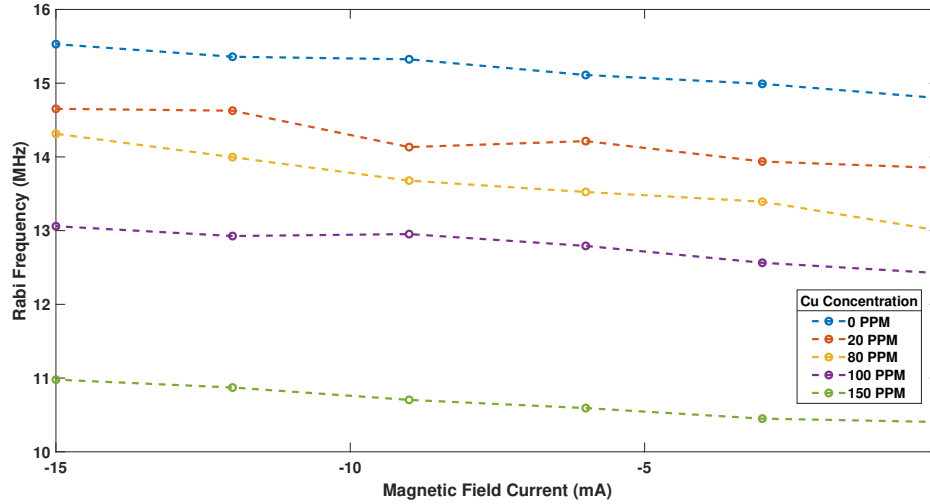


Figure D.1: Rabi Frequency as a Function of the Coil Electric Current. Rabi frequency as a function of the circulating electric current through a coil in presence of different copper sulfate concentrations. This measurements were taken over a 5 keV implantation energy spot with an ion fluence of $7.64 \times 10^{12} \frac{N}{cm^2}$ using 1.5 mW green laser pulses and 30 dBm microwave radiation.

A coil electric current sweeping were performed over a 5 keV implantation energy spot using our magnetic field generation system (more details in Appendix A). In Figure D.1, the Rabi frequency (more details in Appendix C) as a indirect function of the coil magnetic field is plotted for different copper sulfate concentrations.

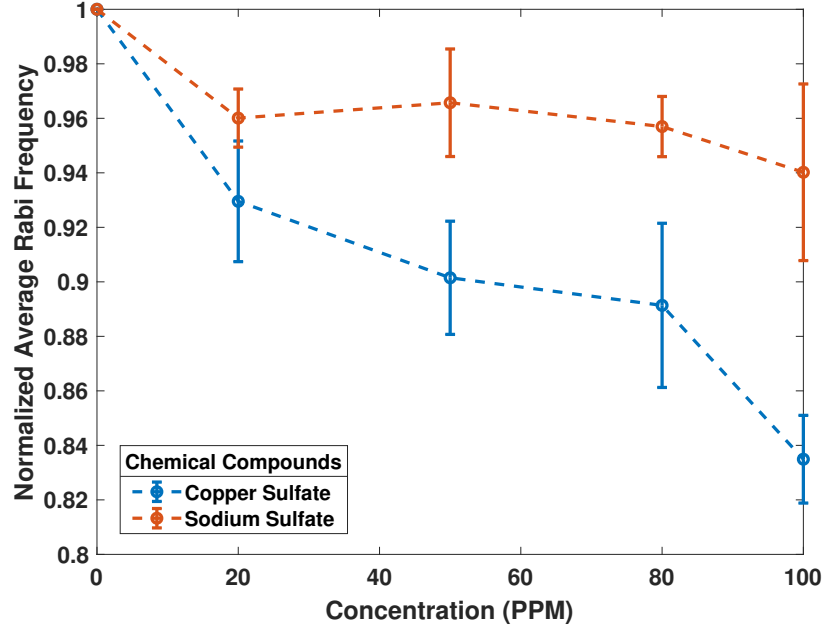


Figure D.2: Normalized average Rabi frequency as a function of chemical compounds concentration. Average Rabi frequency as a function of the chemical compounds concentration for a 5 keV implantation energy spot with an ion fluence of $7.64 \times 10^{12} \frac{N}{cm^2}$ using 1.5 mW green laser pulses and 30 dBm microwave radiation. Orange line corresponds to sodium sulfate, blue line corresponds to copper sulfate and the normalizing factor is the rabi frequency at 0 PPM (nanopurified water).

This experiment was repeated also for sodium sulfate and, after averaging the Rabi frequencies over every concentration and normalizing by the reference (water), an average Rabi frequency as a function of the concentration graphic for both copper sulfate and sodium sulfate was plotted as it is shown in Figure D.2. As it was expected, the effect of the Cu^{2+} copper ions is more noticeable than the effect of the Na^{+} sodium ions over the Rabi frequency. However, before any Ramsey experiment was performed in order to determine T_2^* , we realized that changing the copper/sodium concentration in aqueous solution means changing the dielectric constant of the medium and, in consequence, an screening effect over the microwave radiation contributes to the Rabi frequency decay. Due to this, the procedure was rethought so as to use NV center quantum parameters whose way of measuring does not require any microwave pulse (more details in Chapter 3).

[illegible]

```

26 end
27 x2 = [xT1(:), xA(:), xC(:), res2(:)];
28 obj.ER = 0.05; % Tolerance Error
29 x2(x2(:,4)>(1+obj.ER)*res,:) = [];
30 T1min = x2(1,1); %T1 minimum value
31 T1max = x2(end,1); %T1 maximum value
32 x = fminsearch(@(x) obj.myT1fun(x),x0); % Re-Optimize to recover X
    vector
33
34 end

```

Listing E.1: T_1 Fitting Matlab code.

As it is shown in Listing E.1, data is extracted from our report file, creating a `obj.Xf2` equal time partition (which will be used for drawing the fitting curve). After building a `X0` vector with the parameters to optimize, the optimization takes place over the vector with respect to a function called `myT1fun(x)` (code displayed in Listing E.2). As it is shown in Listing E.2, the optimization is applied over the summation

$$res = \sum_{i=1}^N (Yf_i - Yf2_i)^2, \quad (\text{E.1})$$

here `Yf` corresponds to the original data and `Yf2` corresponds to the fitting time partition. This method return the optimal parameters `A`, `C` and `T1`.

```

1 function [res] = myT1fun(obj,x)
2     % LEAST SQUARES METHOD (By Vicente Santibanez, 2019)
3     T1 = x(1);
4     A = x(2);
5     C = x(3);
6
7     obj.Yf = A.*exp(-obj.X/T1) + C; %Using Time Data
8     obj.Yf2 = A.*exp(-obj.Xf2/T1) + C; %Using Time Partition
9     res = sum((obj.Y-obj.Yf).^2);
10 end

```

Listing E.2: Least Squares Method for an exponential decay.

Going back to Listing E.1, from the code line 18 until the code line 31 a process to determine how “soft” is the approach to the optimal value is carried out, creating a minimum and maximum T_1 value with a tolerance error of 5%. This optimization method is also valid for the experiments in Appendix C.

F Matlab Software Improvements

Until before we start to study this shallow implanted diamond, a tracking system based on finding the maximum fluorescence was used. This system works fairly good for singles NV centers but it does not work correctly for a NV centers ensemble—which is our case. On the other hand, and as it was exposed in Chapter 3, spin relaxation time values and the position over an implantation spot are related, which means that a script for tracing a path on the ensemble is required. Based on this two limitations, the following upgrades to our Matlab software were implemented:

- **Image comparison tracking system:** As it is shown en Figure F.1, a drifting effect over the sample was present during the experiments owing to the way we performed the tracking.

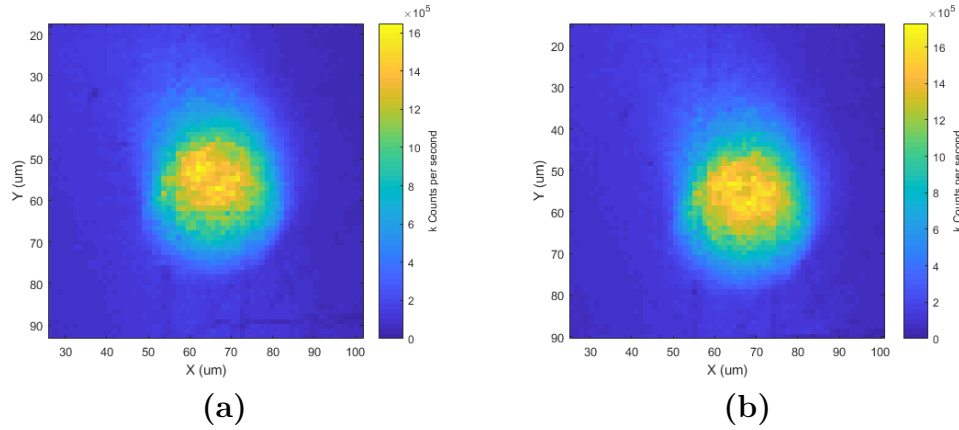


Figure F.1: Drifting effect over the sample. Confocal images taken before and after performing a spin relaxometry experiment over a 6 keV implantation energy spot with an ion fluence of $1.27 \times 10^{12} \frac{N}{cm^2}$.

In consequence, we implement a new tracking system which takes periodically confocal images of the spot and extract the fluorescence data matrix associated to each picture. These matrices are the input for the script presented in Listing F.1, which is the responsible for calculating a shift vector.

```

1 function DX = getShift(obj,D1,D2)
2 Gray1 = D1;
3 Gray2 = D2;
4 L1 = size(D1,1);
5 L2 = size(D1,2);
6 C = obj.myxcorr2(Gray1,Gray2);
7 [max1, Ind1] = max(C, [], 1);
8 [max2, Ind2] = max(max1);
9 DIndY = Ind2 - L1;
10 DIndX = Ind1(Ind2) - L2;
11 DX = [DIndX DIndY 0];
12 end

```

Listing F.1: Shift calculation script.

The core of this script is the determination of a 2D cross-correlation matrix through the “myxcorr2” function which is based on the following equation

$$C(k, l) = \sum_{m=0}^{M-1} \sum_{n=0}^{N-1} A(m, n) B(m - k, n - l), \quad (\text{F.1})$$

here A is a M×N data matrix and B is a P×Q data matrix—we use same-size images but the script allows images with different sizes. The conditions over k and l in the equation F.1 are $-(P-1) \leq k \leq M-1$ and $-(Q-1) \leq l \leq N-1$ respectively. Once the C cross-correlation matrix of size (M+P-1)-by-(N+Q-1) is obtained, a row vector with the position of the maximum value of each column is generated and, from these values, the shift vector is established. Finally, using the shift vector, the tracking system gives the order to the nanopositioning linear piezo stage so as to recover the initial X-Y position over the sample.

This new tracking system allows us to perform experiments over the same point over the sample, thus reducing fluctuations in the parameters of interest due to a drifting effect.

- **Path tracing system:** As it is shown in Listing F.2, the function receive the image data matrix which, as a first step, is turned into a column vector using “reshape”

Matlab function. After normalizing, the column vector is used to find the data threshold so as to create a binarized image.

```

1 function Stats = ImageStats2(obj, D)
2 %From 2D to 1D
3 flatten = reshape(D.',1, []);
4 %Normalizing Data
5 DataNorm = uint8(255*(D-min(flatten))/(max(flatten)-min(flatten)));
6 %Binarizing image by an iterative thresholding script
7 [DataNorm, level] = obj.ksbinaryMS(DataNorm);
8 [y, x] = ndgrid(1:size(DataNorm, 1), 1:size(DataNorm, 2));
9 %Geometric center
10 center = mean([x(logical(DataNorm)), y(logical(DataNorm))]);
11 %Equator Line
12 xcenter = int16(round(center(2)));
13
14 sum = double(0);
15 N = 0;
16 for i = 1: 64
17     v = double(DataNorm(i,xcenter));
18     sum = sum + i*v;
19     N = N + v;
20 end
21
22 mymean = sum/N; % Average
23 sum = double(0);
24 for i = 1:64
25     v = double(DataNorm(i,xcenter));
26     sum = sum + ((i - mymean)^2)*v;
27 end
28
29 sigma = sqrt(sum/N); % Standard Deviation
30 Stats.center = center;
31 Stats.sigma = sigma;
32 end

```

Listing F.2: Geometric center calculation script.

The binarizing threshold and, thus, the binarized data matrix are determined through the “ksbinaryMS” function. This function is based on an iterative optimal thresholding method[40] which follows the following steps: Find the initial threshold, perform an iterative approach to find the optimal threshold, normalize the optimal threshold and create a binary image using the optimal threshold. The following code lines determine the geometric center of the image and the data standard deviation, returning the center coordinates.

Finally, we have an script that allows us to perform different kind of experiments individually or in sequences. This software upgrade allows us to determine, for example, the longitudinal spin relaxation time distribution over an implantation spot and, thus, determine minimum/maximum time value regions.

G Multi-Wavelength Optical Array for Photo-Induced Ionization

When considering functionalizing the surface, a possible future issue is related to the shallow NV centers charge state due to their proximity to the diamond surface and, therefore, their exposure to changes in it. As it was exposed in [41] and delved in [42], the NV center charge state can be temporarily change by means of lighting the sample with beams with different wavelengths and thus be able to control the NV^- concentration.

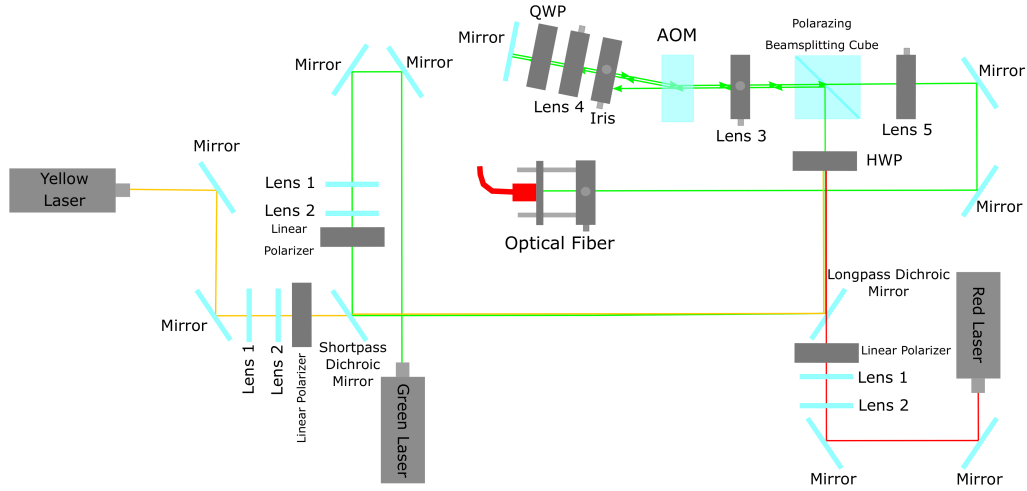


Figure G.1: Multi-wavelength pulsed laser controller for NV center photo-induced ionization. Improvement proposal to the pulsed laser controller (Figure 2.2) presented in Chapter 2. Three red ($\lambda = 633 \text{ nm}$), yellow ($\lambda = 594 \text{ nm}$) and green ($\lambda = 532 \text{ nm}$) lasers are included in order to perform photo-induced ionization experiments. Before the half-wave plate (HWP), every optical path consider the following elements: A couple of mirrors, a telescope (lens 1 and 2) and a linear polarizer. Two shortpass and longpass dichroic mirrors are used to reflect some wavelength and transmit others. The rest of the system works as usual.

As it is shown in Figure G.1, our modification proposal is based on including two extra lasers with wavelengths $\lambda_y = 594 \text{ nm}$ and $\lambda_r = 633 \text{ nm}$ in order to perform photon-induced ionization experiments. Every optical path has a couple of mirrors to align, a telescope to collimate the beam and a linear polarizer to, as it can be inferred from the name, linearly polarize the beam. All beams converges to the same optical path by means of a shortpass dichroic mirror (Thorlabs – DMSP567T 567 nm Cutoff Wavelength) that reflects(transmits) the green(yellow) beam and a longpass dichroic mirror (Thorlabs

– DMLP605T 605 nm Cut-on) that transmits(reflects) the red(green and yellow) beam. Modify this system in this way necessarily implies having to replace the confocal microscope dichroic mirror (see Figure 2.1) for a 50:50 beam splitter in order to reflect beams independent of its wavelength.

We consider that this would be a positive set-up improvement inasmuch as our sample has several implantation spots where the NV^- can be turned into NV^0 and vice versa.

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