Doctoral Thesis

High-resolution spectroscopy of praseodymium ions in a solid matrix
Towards single-ion detection sensitivity

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High-resolution spectroscopy of praseodymium ions in a solid matrix: towards single-ion detection sensitivity

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presented by

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Summary

This thesis investigates the possibilities of optically detecting single rare-earth ions doped into solid-state crystals. These systems appear promising for future optical quantum information processing applications, which require multiple optically addressable levels and long coherence times. Experiments carried out on praseodymium-doped yttrium orthosilicate (Pr:YSO) suggest that single-ion detection is possible using state-of-the-art detection techniques.

The visible spectrum of the trivalent rare-earth ions $\text{RE}^{3+}$ is known to exhibit very narrow transition lines, which emerge as a consequence of the long radiative lifetimes ranging between several microseconds and tens of milliseconds. Corresponding transitions take place within the 4f electronic shell, shielded from the immediate environment of a rare-earth ion by its outer 5s and 5p orbitals. For this reason, rare-earth ions may behave like isolated quantum emitters even in a solid-state host, provided that phononic interactions with the host are frozen out at cryogenic temperatures ($T \approx 4\,\text{K}$).

While detection of single rare-earth ions is straightforward from a theoretical viewpoint, its experimental implementation is technically demanding for two reasons. On the one hand, transition lines may be as narrow as a few kilohertz, which requires frequency-stabilizing the excitation laser source to the kilohertz level on both short and long timescales. On the other hand, long radiative lifetimes impose upper limits on the detectable signal, so that appropriate detectors must be chosen wisely.

We first characterize the spectroscopic properties of Pr:YSO using absorption and fluorescence measurements, spectral holeburning, and lifetime studies. By deriving important quantities such as the absorption cross-section and the saturation intensity, we determine numbers for the signal-to-noise ratio both theoretically and experimentally.
Zusammenfassung


Das sichtbare Spektrum der dreiwertigen Seltenerdionen $\text{RE}^{3+}$ ist geprägt durch sehr schmale Linien, welche auf entsprechend lange Lebensdauern der angeregten Zustände zwischen einigen Mikrosekunden bis hin zu mehreren zehn Millisekunden zurückzuführen sind. Die entsprechenden Übergänge finden innerhalb der $4f$-Schale statt und sind durch die weiter außen liegenden $5s$- und $5p$-Orbitale von der unmittelbaren Umgebung abgeschirmt. Wenn phononische Wechselwirkungen außerdem durch Herabkühlen auf kryogene Temperaturen ($T \approx 4 \, \text{K}$) ausgefroren werden, können sich die Ionen der seltenen Erden daher auch in einer Festkörpermatrix wie isolierte Quantensysteme verhalten.

Theoretisch betrachtet erscheint der Nachweis einzelner Seltenerdionen nicht sonderlich schwierig, die experimentelle Umsetzung gestaltet sich jedoch anspruchsvoll: Einerseits sind die Übergänge nur einige Kilohertz breit, was einen Anregungslaser erfordert, der auf kurzen wie auch auf langen Zeitskalen auf wenige Kilohertz frequenzstabilisiert ist. Andererseits begrenzen die langen Lebensdauern der angeregten Zustände jedes detektierbare Signal und stellen so hohe Anforderungen an die eingesetzten Detektoren.

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1. Introduction

Fundamental studies of light-matter interactions have been the subject of very lively research in the past three decades. Some of the most impressive accomplishments of this activity have been experiments on single optical emitters such as atoms and ions in traps, or molecules, quantum dots, and color centers in the condensed phase. While the early spectroscopy of single atoms was motivated by academic interest and curiosity, single dye molecules, quantum dots, and color centers have attracted immense attention for their broad range of applications in biophysics, optoelectronics, and quantum cryptography. Single emitters are considered as biological label [1], point-like source of light [2,3], nanoscopic magnetometer [4], source of single photons [5], subwavelength mirror [6], and nano-optical transistor [7]. In addition, the discovery of each system has fueled new activities in other areas of research such as material science, chemistry, and engineering.

A significant impulse of current interest is in the use of single emitters for quantum engineering and information processing because they possess well-defined quantum features that can be manipulated and probed by light. Furthermore, these tiny building blocks have great potential for high-density packaging and miniaturization of both quantum and classical optical circuits to the nanometer scale. Therefore, scientists have devised schemes where single emitters serve as optical quantum memories, gates, switches, or other logic elements such as transistors.

Concrete applications of single emitters call for a large palette of various wavelengths, linewidths, and tunability, as well as spatial and temporal modes. So far, only a “handful” of systems have been demonstrated. They may be divided into two classes: emitters in the gas phase such as ions and atoms on the one hand and emitters in the solid state such as quantum dots, molecules or diamond color centers on the other. The technical advantages of each of these systems have been accompanied by various inconveniences and experimental hurdles. For example, single atoms in a gas phase are truly isolated quantum emitters, but it is difficult to control their position with nanometer accuracy or to approach them in the near field. As a result, one cannot
package single atoms densely or address them easily. Semiconductor quantum dots, on
the other hand, are fixed in space, but they have a complex interaction with their envi-
ronment, and their fabrication requires a great deal of material optimization and heavy
equipment. Single dye molecules are very bright, cheap, and easy to handle, and satisfy
most of the requirements for quantum optical experiments. However, so far, there has
been no report on the spectroscopy of single molecules with spin multiplicity in the
ground state. As a result, all operations have to be performed within a fluorescence
lifetime of a few nanoseconds, severely limiting their use in practice. Single nitrogen-
vacancy color centers in diamond have offered an attractive compromise among these
considerations, but their fabrication and material properties remain challenging even
after more than ten years of work by several groups. Despite the various shortcomings,
researchers are currently pursuing all these systems fiercely in order to overcome the
difficulties.

In this work, we aim to explore a new class of single emitters, namely the rare-
earth ions embedded in crystals. These emitters marry many advantages of gaseous
atoms with those of crystal-embedded dye molecules and color centers. In particular,
they provide well-defined magnetic sublevels, which pave the way for sophisticated
quantum-state preparation schemes, e.g. in a Λ configuration \[8–11\]. Moreover, the
abundance of optical transitions provides many avenues for manipulating the ion’s
populations and coherences. Furthermore, their long coherence times of the excited
state facilitate multiple operations. In contrast to organic dye molecules, they are
nearly indefinitely photostable and compatible with durable dielectric environments.
Their advantage over color centers is that a particular ion is a well-defined entity that
can be incorporated in different hosts as an impurity.

The downside of the rare-earth ions is their long fluorescence lifetimes. On the exci-
tation side, this means that one requires extremely narrowband laser sources, whereas
on the detection side, slow fluorescence decay results in low signal. Consequently, vari-
ous attempts to detect them at the single ion level \[12–16\] have been hampered by tech-
nical difficulties. However, two decades of progress in single molecule spectroscopy,
cavity quantum electrodynamics, scanning probe technology, and plasmonics provide
several solutions for detecting single ions in the solid state.

Single-ion spectroscopy will open many doors to classical and quantum optical sig-
nal processing at the nanometer scale. Recent proposals have suggested that a single
emitter can block light travelling in a dielectric waveguide \[17\] or perform nonlinear
operations on different laser beams \[18\]. Furthermore, integration of single emitters
in microcavities and photonic crystals has been discussed \[19]. However, realization of these ideas has only been possible in the semiconductor community and only in a few select materials. Many years of experience in the optical industry on nonlinear and laser crystals makes rare-earth ions an attractive candidate for these applications. Furthermore, compared to semiconductor quantum dots, the well-defined energy levels of ions allow a much simpler implementation of optical coherent control schemes such as electromagnetically induced transparency.

Studies of single ions are also of fundamental interest to solid-state spectroscopy because they eliminate the need for averaging processes in ensemble measurements and provide new insights into the material and optical properties of the guest-host system. Indeed, while atoms in vacuum chambers can be analyzed exactly, very basic information such as natural linewidths and fine and hyperfine splittings are still missing for most solid-state systems. Single-ion spectroscopy will provide direct insight into questions about the interaction with neighboring host atoms and with the phononic modes of the matrix. This knowledge allows optimization of the optical properties of ion-doped crystals and is of central importance to the optical industry.
2. Rare-earth ions in a solid-state matrix

The discovery of the 17 rare-earth elements is very closely linked to the spectroscopy of their compounds. While it took almost 100 years to isolate the first six rare earths (Y, Ce, La, Tb, Er, Yb), the advent of optical flame spectroscopy in the 1870s gave a boost to the quest for new elements. Only seven years after the first time that this new technique was applied to rare-earth compounds, researchers had discovered another eight rare-earth elements (Sm, Sc, Tm, Ho, Dy, Gd, Pr, Nd) \[20\]. The origin of their spectral lines however was not well understood.

The solution had to wait until 1937, when the unusually narrow spectral lines at visible wavelengths could be attributed to 4f intra-shell electronic transitions \[21\]. However, it took another three decades until the problem was also solved in a quantitative fashion \[22, 23\]. Since the 1960s, dye lasers have been used to experimentally obtain high-resolution spectra of rare-earth compounds. The results of these experiments provide insights into emitter-emitter and emitter-matrix interactions that were not observable before.

In this chapter, we will start with an outline about the rare-earth electronic level structure. In what follows, we shall review electronic transitions between 4f levels and their respective intensities. We also describe different sources of spectral broadening. Experiments on the single-emitter level usually suffer from spectral broadening, which is why we will review measures to counteract these effects.

2.1. Electronic structure

2.1.1. Electron configuration

The lanthanide series of chemical elements is characterized by consecutive filling of the 4f electronic shell. Together with scandium and yttrium they are often referred to as “rare earth elements” or simply “rare earths”. Fig. 2.1 shows their location within the periodic table of the elements. All the lanthanides can be found as trivalent cations
2. Rare-earth ions in a solid-state matrix

RE\(^{3+}\) characterized by a \([\text{Xe}]4f^n\) electron configuration where \(n\) ranges between zero (lanthanum) and fourteen (lutetium). Fig. 2.2 gives a graphical representation. Fig. 2.3 depicts the RE\(^{3+}\) 4f radial wave functions. Its bigger part extends much less than the wave functions of the 5s and 5p electrons. This fact has two important consequences: First, since the chemical behavior is governed by the outermost electrons, the lanthanides behave very similarly. This makes it easy to substitute rare-earth elements against each other in chemical compounds. The most distinctive feature is actually the ionic radius which ranges between 102 pm (La\(^{3+}\)) and 86 pm (Lu\(^{3+}\)). Ho\(^{3+}\) with its 90 pm ionic radius for example has the same size as Y\(^{3+}\) which it can thus ideally substitute. As long as the doping concentration remains below reasonable limits however, it is also possible to very efficiently substitute Y\(^{3+}\) with larger RE\(^{3+}\) ions like Pr\(^{3+}\). [24].

Secondly, the 5s and 5p orbitals provide a shielding for the beneath lying 4f electrons. Processes taking place within the 4f shell are thus not disturbed by the immediate environment surrounding RE\(^{3+}\) ion. Transitions within the 4f shell thus exhibit very sharp, atomic-like spectra. Respective linewidths may approach the Fourier limit even in chemical compounds. Due to the weak interaction with the environment, the 4f energy levels vary by not more than 1% for different host matrices.

2.1.2. Free-ion interactions

The free-ion Hamiltonian \(\hat{H}_{\text{free}}\) of a trivalent rare-earth ion can be decomposed into several components [25]:

\[
\hat{H}_{\text{free}} = \hat{H}_0 + \hat{H}_C + \hat{H}_{SO}
\]  

(2.1)

where \(\hat{H}_0\) comprises the kinetic and potential energies of all the electrons in the field of the bare nucleus, \(\hat{H}_C\) describes the Coulomb interactions between them and \(\hat{H}_{SO}\) takes care of their spin-orbit coupling. Hartree-Fock methods can commonly be used to obtain solutions for such multi-electron systems.

In this context it is interesting to note that both LS (Russell-Saunders) coupling and \(jj\) coupling schemes fail to adequately describe the spin-orbit coupling mechanism in RE\(^{3+}\). This is due to the fact that \(\hat{H}_C\) and \(\hat{H}_{SO}\) have comparable magnitudes. The correct way to handle this intermediate coupling regime is to start out with eigenstates obtained from the Russell-Saunders coupling scheme, i.e. states which can be characterized by their quantum numbers \(n\) (principal quantum number), \(l\) (azimuthal quantum number), \(L\) (orbital angular momentum), \(S\) (total spin angular momentum),
**Figure 2.1.** Periodic table of the chemical elements. The lanthanide series of elements is highlighted with a dark gray background. Together with scandium (#21) and yttrium (#39) they form the series of the rare earths.
Figure 2.2. Graphical representation of the electron configuration for the trivalent rare-earths. The principal quantum number $n$ is plotted on the vertical axis while the azimuthal quantum number $l$ is tied to the horizontal axis. Boxes represent spatial electron orbitals that may be filled with up to two electrons of opposite spin. Electrons depicted as black arrows make part of the xenon electron configuration. Trivalent rare earths fill the empty orbitals outlined in red.

Figure 2.3. **Bold trace:** Radial wave function $r^2 \psi^2$ as a function of the distance from the nucleus $r$ in units of the atomic radius for the 4f electrons in Nd$^{3+}$. **Narrow trace:** Charge distribution of the core xenon electron configuration. Reproduced from [25] with kind permission from Springer Science+Business Media.
2.1. Electronic structure

\( J \) (total angular momentum), \( M \) (magnetic quantum number), and \( \tau \) (seniority number used to distinguish states with identical \( L \) and \( S \)). Commonly, these states are denoted by \( |nl\tau LSJM\rangle \). A set of eigenfunctions for \( \hat{H}_{\text{free}} \) may then be generated by linear combinations of these Russell-Saunders eigenstates.

It turns out that \( n, l, \) and \( J \) are the only good quantum numbers for \( \hat{H}_{\text{free}} \). Therefore, the free-ion eigenstates \( \Psi(nlJ) \) can be expressed as

\[
\Psi(nlJ) = \sum_{\tau L SM} a_{\tau LSJ} |nl\tau LSJM\rangle .
\] (2.2)

Note that neither \( \Psi(nlJ) \) nor the coefficients \( a_{\tau LSJ} \) depend on \( M \). Consequently, there are \( 2J+1 \) Russell-Saunders eigenstates \( (M = -J \cdots + J) \) contributing to a new free-ion eigenstate which is thus \( 2J+1 \)-fold degenerate.

Coulomb interactions alone cause energy splittings on the order of \( 10,000 \text{ cm}^{-1} \) corresponding to transitions in the uv/vis. Spin-orbit interactions are on the order of \( 1,000 \text{ cm}^{-1} \), which equals tens of nanometers at visible wavelengths.

2.1.3. Crystal-field interaction

A \( \text{RE}^{3+} \) that is embedded into a crystalline environment experiences electrostatic perturbations which will lift the spherical symmetry of its potential and, as a consequence, also the \( 2J+1 \) fold degeneracy of the \( \hat{H}_{\text{free}} \) eigenstates. It is relatively easy to predict the degree to which this degeneracy is lifted since this depends exclusively on the point symmetry of the crystal site where the \( \text{RE}^{3+} \) resides \[26\]. It is difficult, however, to obtain actual values for the respective crystal-field splittings because there are a number of interactions influencing the electronic states that cannot be accurately taken care of in \textit{ab initio} calculations.

It is not clear from the very beginning how to correctly model the crystal-field interactions mathematically. However, since the crystal-field interaction may be approximated as point charge perturbations, one may define a very general interaction Hamiltonian on the basis of spherical harmonic functions \[27\]

\[
\hat{H}_{\text{CF}} = \sum_{k,q} A_{kq} \sum_{i} r_{i}^{k} Y_{kq}(\theta_{i}, \phi_{i})
\] (2.3)
2. Rare-earth ions in a solid-state matrix

where \( i \) indexes all the \( 4f \) electrons, \( Y_{kq} \) are the spherical harmonics, \( r_i \) is the position vector modulus of the \( i \)th electron, and \( A_{kq} \) are the structural coefficients parametrizing the crystal field.

In general, such a Hamiltonian mixes states of different \( J \) and \( M \) so that a crystal-field eigenfunction \( |\mu\rangle \) can be decomposed as

\[
|\mu\rangle = \sum_{J,M} a_{JM} |JM\rangle .
\]

It is obvious that neither \( J \) nor \( M \) constitute good quantum numbers for a crystal-field level \( \text{(2.4)} \). However, as long as the energy separation of the multiplets is much greater than the resulting crystal-field splitting, \( J \) mixing usually remains negligible.

So far, the most reliable results for crystal-field parameters have been obtained by fitting them to experimentally observed spectra \( \text{(2.5)} \). Crystal-field interactions commonly amount to splittings on the order of 100 cm\(^{-1}\) or 1 nm at visible wavelengths. See Fig. 2.4 for a comprehensive illustration of the energy splittings handled so far.

2.1.4. Hyperfine interaction

Just as in atoms, the total spin \( J \) of the \( 4f \) electrons may interact with the \( \text{RE}^{3+} \) nuclear spin \( I \) by magnetic field coupling. This will give rise to magnetic hyperfine splittings, which can be described by the effective spin Hamiltonian

\[
\hat{H}_{\text{HF}} = A_\parallel \hat{J}_z \hat{I}_z + A_\perp (\hat{J}_x \hat{I}_x + \hat{J}_y \hat{I}_y)
\]

(2.5)

where \( \hat{J}_{x,y,z} \) and \( \hat{I}_{x,y,z} \) are the electronic and nuclear spin operators in the respective crystal directions, and \( A_\parallel \) and \( A_\perp \) give the interaction coefficient along and perpendicular to the \( z \) direction, respectively. Usually, \( A_\parallel \) and \( A_\perp \) are specified in a reference frame where \( z \) coincides with the crystal axis denoted by \( c \).

An important exception arises for non-Kramers ions (ions with an even number of \( 4f \) electrons) such as \( \text{Pr}^{3+} \). At crystal sites with a low symmetry, the diagonal elements of \( \hat{H}_{\text{HF}} \) vanish for non-Kramers ions, i.e. there is no first-order magnetic hyperfine interaction. In this case, the contributions to hyperfine splitting are solely due to off-diagonal matrices between different multiplets \( J \) and \( J' \). The leading component is of second order and can be described by a Hamiltonian that takes the same form as the Hamiltonian for electric quadrupolar interactions \( \text{(2.8,2.9)} \). For this reason, second-
order magnetic hyperfine interactions are also called “pseudo-quadrupole”. It is convenient to combine both electric and magnetic effects into one effective Hamiltonian \[ \hat{H}_Q = D \left( \hat{I}_z^2 - \hat{I}(\hat{I} + 1)/3 \right) + E \left( \hat{I}_x^2 - \hat{I}_y^2 \right) \] (2.6)

where \( D \) is the combined quadrupole coupling constant and \( E \) is the combined gradient parameter. For \( E = 0 \) it is clear that the hyperfine levels \( \pm I_z \) are doubly degenerate since \( H_Q \) only depends on \( I_z^2 \) and \( I \). In the case of half-integral \( I \) however, group theoretical treatments \[30\] show that the \( \pm I_z \) degeneracy remains even for \( E \neq 0 \). Typical splittings are on the order of \( 10^{-3} \text{ cm}^{-1} \) or tens of megahertz.

### 2.2. Transition probabilities

Within the context of this work, we will mainly be concerned with electronic transitions between states of the 4f manifold, i.e. with intra-shell transitions. According
2. Rare-earth ions in a solid-state matrix

To Laporte’s rule \([31]\), electric dipole transitions can only connect states with opposite parities. Obviously, this condition is not met for intra-shell transitions, since the parity \((-1)^{\sum \ell_i}\) is the same for all states within the 4f manifold.

However, this conclusion is only true for the free \(\text{RE}^{3+}\). The crystal-field Hamiltonian \([2.3]\) may admix states of opposite parity into the crystal-field levels and thus enable electric dipole transitions between them. This can easily be seen from the respective matrix elements. They involve expressions of the form

\[ B_{kq} = A_{kq} \langle f | r^k | i \rangle \]  

where \(|i\rangle\) and \(|f\rangle\) represent the initial and final states, respectively. From symmetry considerations it is clear that \(B_{kq}\) connects states of opposite parity for odd \(k\) and states of equal parity for even \(k\). Thus, it is the crystal-field components \(B_{kq}\) with odd \(k\) that will enable electric dipole transitions within the 4f manifold. They are generated by a non-centrosymmetric crystal field around the \(\text{RE}^{3+}\). (In a centrosymmetric field the Hamiltonian would be invariant under coordinate inversion, thus preserving parity.)

The admixture of opposite parity must somehow involve states outside the 4f manifold. These are higher-lying states such as 5d (even parity) which can be mixed into the excited 4f states due to their energetic proximity.

2.2.1. Judd-Ofelt theory

Independently from each other, Judd \([22]\) and Ofelt \([23]\) have derived a theory that calculates the line strength

\[ S = \sum_{M,M'} | \langle \alpha J M | \hat{P} | \alpha' J' M' \rangle |^2 \]  

between two manifolds characterized by their total angular momenta \(J, J'\) and additional quantum numbers \(\alpha, \alpha'\). Note that the summation includes all \(M\) and \(M'\) values from the respective manifolds. This means that the Judd-Ofelt theory will not provide line strengths between individual crystal-field-split levels. Instead it will give \(S\) values for transitions between different \(J\) manifolds. This is due to an approximation in the theory which states that the \(J\) and \(J'\) manifolds are completely degenerate in \(M\) and \(M'\), respectively.
The main result of Judd and Ofelt is to express any 4f intra-shell line strength as

\[
S = e^2 \frac{2}{3} \sum_{\lambda = 2,4,6} \Omega_\lambda \left| \langle \alpha J \| \hat{U}^{(\lambda)} \| \alpha' J' \rangle \right|^2
\]  

(2.9)

where the three Judd-Ofelt parameters \( \Omega_{2,4,6} \) are specific to a particular system of rare-earth ion and host matrix, and the term in brackets encapsulates the dynamics between the manifolds \( \alpha J \) and \( \alpha' J' \). Actually, the latter term is a reduced matrix element of the unit tensor operator \( \hat{U}^{(\lambda)} \). (It is considered reduced because any dependence on \( M \) has been removed using the Wigner-Eckart theorem \cite{32}.) Ref. \cite{33} tabulates actual values for the reduced matrix elements.

As we have seen with the calculation of crystal-field splittings, it is difficult to obtain reliable values for \( A_{kq} \) from \textit{ab initio} calculations. The same is true for the Judd-Ofelt parameters \( \Omega_{2,4,6} \) of Eq. (2.9). Therefore, the common procedure is to fit these parameters to experimentally observed absorption spectra, or more precisely: to the integrated absorption cross-sections \( \int \sigma(\lambda) \, d\lambda \) contained therein. For unpolarized measurements these are related to the line strength by \cite{34}

\[
S = \frac{3e_0 \hbar c}{n \bar{\omega}} (2J + 1)n \left( \frac{3}{n^2 + 2} \right)^2 \int \sigma(\lambda) \, d\lambda \frac{\Delta \lambda}{\lambda} 
\]  

(2.10)

where \( e_0 \) is the vacuum permittivity, \( \hbar \) is Planck’s constant, \( n \) is the refractive index, \( \bar{\omega} \) is the mean angular frequency of the transition under consideration, and the integration runs over an entire \( J \) manifold. Since the number of fitting parameters is three, the number of absorption observations should exceed three to obtain a proper fit.

Once the \( \Omega_{2,4,6} \) parameters have been found, Eq. (2.9) allows one to calculate \( S \) values for any 4f transition within the same guest-host system. It is then straightforward to obtain the corresponding Einstein \( A \) coefficients \cite{34} and from these the radiative lifetime for the \( J' \) manifold

\[
\tau = \frac{1}{\sum_{J''} A_{J' \rightarrow J''}} 
\]  

(2.11)

and the branching ratio for the transition between the manifolds \( J' \) and \( J \)

\[
\beta = \frac{A_{J'' \rightarrow J}}{\sum_{J''} A_{J'' \rightarrow J''}}. 
\]  

(2.12)
There are two important exceptions that the standard Judd-Ofelt model fails to explain satisfactorily. One is europium, which experimentally exhibits transitions that are forbidden in theory. Such transitions often occur with only low intensities, still this implies that the Judd-Ofelt theory is incomplete in its standard form. The other case which commonly causes problems is praseodymium. There are often large deviations between calculations and experimental observations, which are usually explained by the exceptionally small energy difference between the $4f^n$ and $4f^{n-1}5d$ configurations in Pr$^{3+}$ [27]. In such a case, $4f^{n-1}5d$ contributions cannot really be handled as small perturbations to the $4f^n$ states.

2.2.2. Selection rules

The electric dipole operator $\hat{P}$ is spin-independent so that it should ensure $\Delta S = 0$. However, in the framework of intermediate coupling where spin-orbit interactions are not negligible, we operate on states with a mixture of different $S$ and $L$ to begin with. Therefore, it is possible and common to observe transitions with $\Delta S = \pm 1$ violating the spin selection rule.

This leaves us with possible selection rules on $J$. Since $J$ is a good quantum number even in the intermediate coupling regime, we may expect some stricter selection rules here. Expressing both the electronic states and the dipole operator of Eq. (2.8) in terms of tensor operators (spherical harmonics) and applying the Wigner-Eckart theorem allows us to derive restrictions for $\Delta J$, which arise from the arithmetic properties of the Wigner $3j$ symbols. To be precise, electric dipole transitions should be restricted to $\Delta J \leq 6$ with $0 \leftrightarrow 2, 4, 6$ only [32]. It turns out, however, that even these selection rules are commonly violated. This cannot be explained in a thorough manner, but is usually attributed to $J$ mixing introduced by the crystal field.

2.3. Spectroscopic properties

We have seen that the Judd-Ofelt model can provide us with transition intensities and radiative lifetimes. Aside from the fact that the theory only gives estimate values, there are a number of practical limitations though. On the one hand, the Judd-Ofelt theory is unable to calculate line strengths for transitions between specific crystal-field or hyperfine levels. After all, it merely handles transitions between distinct $J$ multiplets.
2.3. Spectroscopic properties

Other effects such as spectral diffusion or dephasing are simply beyond the scope of this theory. Spectroscopy is able to provide deeper insights into these specific effects.

2.3.1. Inhomogeneous broadening

RE$^{3+}$ that are embedded in a crystalline host matrix experience individual shifts of their transition frequencies (see Fig. 2.5). These shifts are usually explained by the fact that the crystalline lattice underlies strain and exhibits defects, something that is ultimately dictated by thermodynamics. Therefore, each ion finds itself in a different local environment and experiences different local electric and magnetic fields, which will accordingly shift its transition frequency. The resulting distribution of frequencies gives rise to an inhomogeneously broadened line, where the term “inhomogeneous” suggests that the broadening is due to shifts that are not equal for all the RE$^{3+}$.

For rare-earth doped inorganic crystals the shape and width of the inhomogeneous line strongly depend on the crystal growth parameters. While for high-quality crystals common inhomogeneous linewidths are on the order of 10 GHz or less, lower-quality samples may exhibit broadenings of 1 THz or more. The lower end of this scale is marked by Nd:YLiF$_4$ which has been shown to broaden by 10 MHz at very low doping levels.

2.3.2. Non-inhomogeneous line shape

We have already seen that the spectra of RE$^{3+}$ exhibit a wealth of energy level splittings. The respective spectral lines all have a particular shape which can be divided into a zero-phonon part and a phononic sideband (see Fig. 2.6). The zero-phonon line is unaffected by lattice phonons and may be regarded as a purely electronic transition. The phononic sideband on the other hand involves coupling to all lattice phonon modes of the crystalline host.

Maximizing the zero-phonon line over the phononic sideband can usually be quite an involved task. This is especially true for dye molecules in organic host matrices [35]. RE$^{3+}$ on the other hand – if cooled down to cryogenic temperatures – usually feature sharp zero-phonon lines within their 4f intra-shell spectra, and the phonon sideband can most often be neglected [36].
2. Rare-earth ions in a solid-state matrix

Figure 2.5. Left: In a perfect crystal lattice, non-interacting emitters exhibit identical transition frequencies. The ensemble absorption profile thus has the same shape as the single emitter absorption line. Right: Crystal defects and strain introduce individual shifts to the single emitter absorption lines (gray) so that the ensemble absorption profile (blue) becomes inhomogeneously broadened.

Figure 2.6. Sketch of high-resolution fluorescence spectra for two typical kinds of emitters. Type 1 emitters exhibit strong zero-phonon lines, coupling to lattice phonons is accordingly small. In type 2 emitters only a small contribution of the total emission goes into the zero-phonon line. Most of the emitted radiation is found in the phonon wing at higher wavelengths.
2.3. Homogeneous broadening

Dynamical processes taking place on the microscopic level of the embedded RE$^{3+}$ emitters will give rise to homogeneous broadening. “Homogeneous” in this context refers to the fact that the transition line of every single emitter underlies the same broadening effects. Note that most effects will broaden the transition line, narrowing in this sense is hardly possible. In other words, the undisturbed line dictates a lower limit on the linewidth, the Fourier limit. This term arises from the fact that the undisturbed linewidth is exclusively determined by population relaxation (usually a single exponential decay), which is why a Fourier transformation will directly yield the lineshape and its width.

In order to make clear how the different effects contribute to the homogeneous linewidth $\Gamma_h$, we introduce its decomposition as

$$\Gamma_h = \frac{1}{2\pi T_1} + \frac{1}{2\pi T_1^*} + \frac{1}{\pi T_2} = \frac{1}{\pi T_2}$$

where $T_1$ denotes the population decay time associated with undisturbed radiative transition, $T_1^*$ characterizes non-radiative decay channels, and $T_2^*$ is the relaxation time arising from pure dephasing processes. An undisturbed system with $T_{1,2} \to \infty$ is called $T_1$-limited, lifetime-limited, or Fourier-limited. Alternatively, the homogeneous linewidth may be associated with an overall dephasing time $T_2$ that incorporates both population decay and pure dephasing processes.

2.3.3.1. Ion-phonon interactions

Interactions with host matrix phonons constitute an important source of homogeneous broadening. Typical phonon energies within crystalline materials are comparable to the energy splittings within one $J$ multiplet, i.e., the energy splittings due to the presence of a crystal field (described by $\hat{H}_{\text{CF}}$). As a consequence, phononic broadenings are most apparent on the energy scale of crystal-field split levels. We may distinguish three prominent effects:

1. Within one $J$ multiplet, higher-lying crystal-field levels are more severely broadened than the lower-lying ones (see Fig. 2.7). This is due to direct phonon coupling between individual levels which eventually causes any population to decay into the lowest crystal-field level. Higher levels may couple to any lower-lying
2. Rare-earth ions in a solid-state matrix

level; thus, their decay generally involves multiple phonons, which contribute additively to the observed linewidth. Since they directly affect the electronic populations, these processes are $T_1^*$ processes. In the Debye limit $T \ll T_{\text{Debye}}$, where only acoustic phonon modes are populated, the phonon density can usually be expressed as $\rho(\omega) \propto \omega^2$. Therefore, the resonant phonon transition rate behaves as $R_{\text{ph}} \propto \omega^3$ where $\omega$ is the phonon transition frequency \[36\].

2. Electronic transitions between the lowest crystal-field levels of different $J$ multiplets are usually not affected by direct phonon coupling because the respective energy gap is too large. However, higher-order phonon processes may still individually broaden the involved crystal-field levels by elastic Raman scattering (see Fig. 2.8). It has been shown \[37\] that at low temperatures $T \ll T_{\text{Debye}}$ the contribution from two-phonon Raman processes exhibits a $T^7$ temperature dependence. They are purely dephasive in nature and as such they are $T_2^*$ processes. Their magnitude depends on the respective host material; in most cases however, they can be neglected at temperatures $T < 6 \text{K} \[38\].

3. Multi-phonon processes may also couple levels from different $J$ manifolds as $T_1^*$ processes. Empirically, phonon emission processes up to fifth order (involving five phonons) are comparable to radiative emission probabilities \[39\]. Given

Figure 2.7. Left side: Schematic illustration of a $J$ multiplet with its different crystal-field split levels labeled 1 through 4. Higher lying levels decay into the lower lying ones by phononic interaction (gray). Right side: Sketch of the corresponding absorption spectrum caused by an electronic transition originating at a lower-lying $J$ multiplet. Higher-lying crystal-field levels are more severely broadened due to the phonon-mediated decay channels.
2.3. Spectroscopic properties

Figure 2.8. Phonon-induced dephasing mechanisms. Three crystal-field levels are labeled by a, b, and c. Direct phonon relaxation, Orbach, and inelastic Raman scattering can be identified as population decay processes. The lowest crystal-field level in a $J$ manifold is usually not phonon-coupled to lower-lying levels. Therefore, it is solely subject to elastic Raman scattering processes associated with $T_2^*$ dephasing.

A typical maximum phonon energies on the order of 500 cm$^{-1}$ (see Tab. 2.1), electronic transitions should thus span more than 2, 500 cm$^{-1}$ in order to be unaffected by phonon relaxation. This is especially important for the excited-state level. Its energy spacing to the next lower-lying $J$ manifold must be large enough to avoid non-radiative phononic relaxation.

In summary, ion-phonon interactions can basically be frozen out at low temperatures for transitions involving the lowest crystal-field levels as long as the excited-state level is well isolated in frequency space.

2.3.3.2. Ion-ion interactions

Mutual electronic spin-flip interactions between the RE$^{3+}$ emitters will instantaneously shift their optical transition frequencies, the average of which results in a broadening of the observed line. As one would expect, this effect is more severe for Kramers ions, which all carry a magnetic moment. Even at impurity concentrations of less than 0.1%, spin flips may introduce broadenings on the order of 10 MHz. Although it is possible to suppress these spin flips in strong magnetic fields of several teslas, lifetime-limited linewidths are much more easily observed in non-Kramers ions (that do not carry any magnetic moment).
2. Rare-earth ions in a solid-state matrix

<table>
<thead>
<tr>
<th>Host</th>
<th>( \omega_{\text{max}} ) cm(^{-1} )</th>
<th>( \omega_{\text{max}} ) THz</th>
<th>K</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>LaF(_3)</td>
<td>350</td>
<td>10.5</td>
<td>500</td>
<td>40</td>
</tr>
<tr>
<td>LaCl(_3)</td>
<td>260</td>
<td>7.8</td>
<td>370</td>
<td>40</td>
</tr>
<tr>
<td>Y(_2)O(_3)</td>
<td>550</td>
<td>16.5</td>
<td>790</td>
<td>40</td>
</tr>
<tr>
<td>Y(_2)SiO(_5)</td>
<td>400</td>
<td>12.1</td>
<td>580</td>
<td>41</td>
</tr>
</tbody>
</table>

Table 2.1. Maximum phonon energies for different common crystalline host materials. The second column holds the value in units of inverse centimeters, the third column in terahertz, and the fourth column in kelvin, which is equal to the Debye temperature. As the Debye temperature is directly proportional to the effective sonic velocity \([42]\), these values represent a measure for the hardness of the respective host material.

At higher excitation intensities, so-called excitation-induced frequency shifts (efs) may contribute significantly to homogeneous broadening. In this case, the difference in the electronic dipole moments of the ground and excited states of an ion causes a shift in the transition frequency of its neighbors. As the excitation power is increased, more ions are transferred to the excited state, which in turn will cause more severe broadening. For weak excitation intensities of several W \( \cdot \) cm\(^{-2} \) it has been shown that efs can be neglected \([44]\).

2.3.3. Ion-nuclear spin interactions

The constituents of the host material may undergo nuclear spin flips, thereby instantaneously shifting the transition frequency of the embedded RE\(^{3+}\). As we have seen before, the result of such shifts is a broadened homogeneous line. This effect is kept low by choosing a host material whose constituents minimize the total nuclear magnetic moment, thus also minimizing local (magnetic) field changes associated with nuclear spin flips. Y\(_2\)SiO\(_5\) has turned out to be a particularly well suited material in this regard (see subsection 3.2.1).

For one particular RE\(^{3+}\) hyperfine transition, it is possible to entirely cancel the susceptibility to local field changes if the differential first-order Zeeman shifts of both the upper and lower hyperfine levels vanish, i.e. \( \frac{dE_{1,2}}{dB} = 0 \) where \( E_1 \) denotes the energy of the lower hyperfine level, \( E_2 \) is the energy of the upper hyperfine level, and \( B \) is the local magnetic field. Such a situation is achieved by applying a specific
homogeneous magnetic field controlled in both strength and direction. In combination with a low-magnetic-moment host, this technique has facilitated very long coherence times, equivalent with very narrow homogeneous lines\cite{45}.

The \textsuperscript{3+} electronic spin may moreover interact with nuclear spins of the surrounding crystal ligands to give rise to instantaneous frequency shifts caused by nuclear spin flips. Nearest neighbor interactions cause shifts on the order of 10 MHz, comparable to the contribution of electron spin-spin interactions. Freezing out nuclear spin flips by energetically separating the spin orientations in a strong magnetic field is hardly possible however. The Zeeman shifts of around 100 kHz/T are simply not sufficient for this purpose at liquid helium temperatures. In analogy to the case of electronic spin-spin interactions, the broadening due to interactions with surrounding nuclear spins is only an issue with Kramers ions.

A process that will also affect the linewidth of non-Kramers ions is mutual nuclear spin flips of the \textsuperscript{3+} optical center and surrounding ligands, called \textit{superhyperfine interaction}. This is even true for optical centers with vanishing nuclear magnetic moments since their quadrupole moments can still couple to surrounding nuclei. For non-Kramers ions, these effects usually impose a lower limit to the homogeneous linewidth since they cannot be easily suppressed (except at ultra-low temperatures and very strong magnetic fields).

The homogeneous broadening effects considered so far all become apparent on the timescale of the radiative decay rate. Both interactions with electronic and nuclear spins may, however, shift the transition frequencies of surrounding nuclei also on longer timescales. This effect is called \textit{spectral diffusion}. Although spectral diffusion is usually handled separately from homogeneous broadening, the underlying principles and interactions are actually the same: instantaneous shifts of particular transition frequencies give rise to spectral dynamics. However, while it is usually impossible to observe the dynamics causing homogeneous broadening, spectral diffusion can be observed experimentally in terms of the dynamics of the inhomogeneously broadened line. Most commonly, spectral diffusion will cause a narrow spectral feature to broaden over time. Spectroscopy on the single-emitter level may reveal the individual frequency shifts over time.

In order to suppress spectral diffusion for a particular guest/host system, the same criteria apply as for the reduction of homogeneous line broadening: non-Kramers ions, low impurity concentrations, modest magnetic fields, and low nuclear spin hosts will each reduce the possibility of extended spectral diffusion.
3. **Praseodymium-doped yttrium orthosilicate**

From Fig. 3.1 it is immediately clear that RE$^{3+}$ provide a wealth of electronic transitions in the infrared, visible and ultraviolet parts of the spectrum. Refs. 46 and 47 have compiled extensive overviews on the most prominent transitions that have been investigated in the past. In what follows, we shall isolate a transition that is suitable as a candidate for single ion detection.

### 3.1. Requirements

The optimum transition can be characterized as follows:

1. **The transition is in the vis spectral range.** This allows one to detect photons very efficiently using silicon detectors, which reach single-photon sensitivity.
2. **The excited state fluoresces,** thus facilitating fluorescence detection.
3. **The radiative lifetime of the excited state is as short as possible.** That way, a large amount of fluorescent photons can be generated.
4. **The excited state relaxes merely by radiative $T_1$ processes.** This is important because non-radiative decay processes – termed $T_1^*$ in Eq. (2.13) – do not contribute to the light-matter interaction process and accordingly diminish the absorption cross-section.
5. **The lower level is the spectroscopic ground state.** By meeting this requirement we avoid complicated optical pumping procedures. Furthermore, we may expect narrow lines for transitions into the ground state.
6. **Dephasing for the transition (expressed by the $T_2^*$ term in Eq. (2.13)) is negligible,** i.e. the homogeneous linewidth is as close to the Fourier limit as possible in order to maximize the absorption cross-section 49.
3. Praseodymium-doped yttrium orthosilicate

Figure 3.1. Calculated energy levels for the $J$ manifolds of trivalent rare-earth ions in LaF$_3$. The individual levels within a $J$ manifold are too dense to be resolved in this graph; white space indicates an energy gap of at least 400 cm$^{-1}$. Highlighted in green is the range of levels whose decay into the ground state is associated with visible transitions. Reprinted with permission from [48]. Copyright 1989, American Institute of Physics.
3.1. Requirements

7. Spectral diffusion does not exist on the characteristic timescales of an experiment.

8. The ratio of inhomogeneous and homogeneous linewidths $\Gamma_{\text{inh}}/\Gamma_{\text{hom}}$ is large in order to facilitate spectral selection.

While requirements 1 through 7 restrict the choice of possible impurity ions, requirements 6 through 8 narrow the range of possible host materials.

3.1.1. Host material

Requirements 6 and 7 basically tell us to choose a host material in which the amount of dynamical processes is constrained to a minimum. Dynamical processes in this sense comprise any effects which would cause instantaneous frequency shifts to the optical transition of the guest ion. From this viewpoint, crystalline materials are well suited as a host material, since at low temperatures their only excitations are acoustic lattice vibrations. In addition, the crystal constituents should preferably have a low nuclear magnetic moment in order to minimize guest-host interactions due to nuclear spin flips. In the late 1980s, yttrium orthosilicate has been discovered as the best material currently available for these purposes $^{50,51}$. Owing to its comparatively low melting point of 2070 °C $^{52}$, bulk samples can be grown at high qualities. Since oxygen and most silicon isotopes carry a nuclear spin of zero, the total nuclear magnetic moment is minimized.

3.1.2. Impurity ion

When it comes to finding a good impurity ion, requirement 6 already rules out Kramers ions as possible candidates. While it is true that lifetime-limited linewidths can be achieved with Kramers ions under strong magnetic fields, these systems are still plagued by spectral diffusion $^{43}$. Item 4 dictates that we should look for an excited state which is the lowest crystal-field level of an otherwise well isolated $J$ manifold. Radiation from higher-lying levels within the $J$ manifold would most certainly be quenched due to phonon-assisted relaxation. This way, we can rule out holmium, for example. Looking at Fig. 3.1, requirement 1 basically leaves us with the candidates listed in Tab. 3.1.
3. Praseodymium-doped yttrium orthosilicate

<table>
<thead>
<tr>
<th></th>
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<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Pr$^{3+}$</td>
<td>$^{3}H_{4}$</td>
<td>$^{3}P_{0}$</td>
<td>488</td>
<td>3</td>
<td>[53]</td>
</tr>
<tr>
<td>Pr$^{3+}$</td>
<td>$^{3}H_{4}$</td>
<td>$^{1}D_{2}$</td>
<td>606</td>
<td>164</td>
<td>[54]</td>
</tr>
<tr>
<td>Eu$^{3+}$</td>
<td>$^{7}F_{0}$</td>
<td>$^{5}D_{0}$</td>
<td>580</td>
<td>1900</td>
<td>[55]</td>
</tr>
<tr>
<td>Tb$^{3+}$</td>
<td>$^{7}F_{6}$</td>
<td>$^{5}D_{4}$</td>
<td>486</td>
<td>3140</td>
<td>[56]</td>
</tr>
<tr>
<td>Tm$^{3+}$</td>
<td>$^{3}H_{6}$</td>
<td>$^{1}G_{4}$</td>
<td>468</td>
<td>432</td>
<td>[57]</td>
</tr>
<tr>
<td>Tm$^{3+}$</td>
<td>$^{3}H_{6}$</td>
<td>$^{3}H_{4}$</td>
<td>790</td>
<td>134</td>
<td>[46, 57]</td>
</tr>
</tbody>
</table>

Table 3.1. Transitions of trivalent rare earth ions in Y$_2$SiO$_5$ possibly facilitating both detection by fluorescence and absorption down to the single-emitter level. Pm$^{3+}$ is not listed here because its radioactivity limits the total abundance in the earth’s crust to less than 600 grams [58].

3.2. Trivalent praseodymium in yttrium orthosilicate

For this work, we decided to work with trivalent praseodymium in yttrium orthosilicate (Pr:YSO). Tab. 3.1 lists two prominent transitions in the vis spectral range one of which, the $^{3}H_{4} \leftrightarrow ^{3}P_{0}$ transition, exhibits a very short lifetime of about 3 µs. This transition thus promises to be a good candidate for single ion experiments. In what follows, we will first provide some more details on YSO as a host material. Some general remarks on Pr$^{3+}$ will then be concluded by details on the two vis transitions in Pr:YSO.

3.2.1. Yttrium orthosilicate

We have already seen that the most prominent property of yttrium orthosilicate (YSO) is its low nuclear magnetic moment. While oxygen, silicon-28, and silicon-30 have a vanishing nuclear magnetic moment, yttrium contributes $-0.23\mu_N$, and silicon-29 contributes $-0.56\mu_N$. The interaction of rare-earth impurities with both of these isotopes is comparatively weak however. For silicon-29, the natural abundance is a mere 4.7%, limiting the impact on line broadening or spectral diffusion. Yttrium on the other hand is the crystal component that gets substituted by rare-earth impurities. That way, yttrium ions will never sit right next to an impurity ion. Nearest neighbor Y$^{3+}$ ions will however induce magnetic fields on the order of 0.1 G causing frequency shifts of the order of hundreds of hertz [45].
3.2. Trivalent praseodymium in yttrium orthosilicate

Figure 3.2. The monoclinic $\text{Y}_2\text{SiO}_5$ unit cell with axes labeled $a$, $b$, and $c$. $a$ and $c$ enclose an angle of $\beta = 102.65^\circ$. The axes of the optical indicatrix are $b$, $D_1$, and $D_2$. They are mutually perpendicular.

<table>
<thead>
<tr>
<th>axis</th>
<th>$A$</th>
<th>$B$</th>
<th>$C$</th>
<th>$D$</th>
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<tr>
<td>$b$</td>
<td>3.0895</td>
<td>0.0334</td>
<td>0.0043</td>
<td>0.0199</td>
</tr>
<tr>
<td>$D_1$</td>
<td>3.1173</td>
<td>0.0283</td>
<td>$-0.0133$</td>
<td>0.00</td>
</tr>
<tr>
<td>$D_2$</td>
<td>3.1871</td>
<td>0.03022</td>
<td>$-0.0138$</td>
<td>0.00</td>
</tr>
</tbody>
</table>

Table 3.2. Sellmeier coefficients for light polarized along the three principal axes of YSO.

YSO crystallizes in a monoclinic cell of $C_{2h}^6$ symmetry. Its lattice constants are $a = 1.041 \text{ nm}$, $b = 0.6726 \text{ nm}$, $c = 1.249 \text{ nm}$, where the $a$ and $c$ directions enclose an angle of $\beta = 102.65^\circ$. Monoclinic crystals are birefringent in general. Thus, the principal axes of the optical indicatrix do not coincide with the crystal axes. However, the crystal $b$ axis is certainly also a principal axis for symmetry reasons. The other two principal axes are commonly labeled $D_1$ and $D_2$ [59] (see Fig. 3.2). The refractive indices for polarizations along these principal axes are described by the Sellmeier dispersion equation

$$n^2 = A + \frac{B}{\lambda^2 + C} + D\lambda^2$$  \hspace{1cm} (3.1)

where $\lambda$ is the wavelength in microns, and the dimensionless coefficients $A$ through $D$ are listed in Tab. 3.2.
3. Praseodymium-doped yttrium orthosilicate

A rare-earth impurity in YSO substitutes one of the two yttrium ions Y$^{3+}$, which each occupy a crystal site with distinct C$_1$ symmetry. While europium ions, for example, are incorporated into both sites with almost equal probability [52], praseodymium ions preferably substitute yttrium at only one site [46].

3.2.2. Trivalent praseodymium

Trivalent praseodymium Pr$^{3+}$ has two electrons in its 4f shell, which give rise to the term symbols (in ascending order of their respective energy) $^3$H$_{4,5,6}$, $^3$F$_{2,3,4}$, $^1$G$_4$, $^1$D$_2$, $^3$P$_{0,1,2}$, $^1$I$_6$, and $^1$S$_0$. The corresponding energy level diagram is depicted in Fig. 3.3. It shows an energy gap of 6000 cm$^{-1}$ between the $^1$D$_2$ state and the adjacent lower-lying $^1$G$_4$. Equivalently, there is a 4000 cm$^{-1}$ gap between $^3$P$_0$ and the next lower-lying manifold $^1$D$_2$. These energy gaps are about an order of magnitude larger than what is to be expected as the maximum phonon energy in typical crystals (see Tab. 2.1). Hence, at cryogenic temperatures the radiative decay from these levels should not be quenched by phononic interaction.
3.2. Trivalent praseodymium in yttrium orthosilicate

Due to the early availability of dye lasers from the late 1960s, the spectroscopic properties of the $^3\text{H}_4 \leftrightarrow ^1\text{D}_2$ transition have been extensively studied \cite{47} in the wavelength range between 592 nm and 610 nm, depending on the host material. Apart from determining important parameters such as absorption cross-sections, radiative lifetimes, and coherence times, a number of experiments have been carried out making use of the long hyperfine coherence times \cite{60-67}.

There have also been some reports on spectroscopy of the $^3\text{P}_0$ level in Pr$^{3+}$ \cite{47}. With respective wavelengths ranging between 478 nm and 495 nm however, its transition is not as easily accessible to dye lasers. This is perhaps why high-resolution spectra have not been measured for the $^3\text{P}_0$ level. Transition properties for the $^3\text{H}_4 \leftrightarrow ^3\text{P}_0$ can be estimated using Judd-Ofelt theory. It is well known however that these calculations will partially fail to reproduce the experimentally observed transition intensities in Pr$^{3+}$ \cite{68,69}. This shortcoming is commonly explained by the close proximity of the $^3\text{P}_J$ manifolds.

The praseodymium nucleus carries a spin of $I = \frac{5}{2}$ which gives rise to distinct hyperfine levels even at zero magnetic field. Depending on the site symmetry of the surrounding crystal each crystal-field level will split into either six non-degenerate (e.g. in LaCl$_3$) or three doubly degenerate (e.g. at low-symmetry sites such as in LaF$_3$) hyperfine levels. In the former case, the interaction is mostly due to the first-order effect described by \textbf{Eq. (2.5)} and the splittings are on the order of 1 GHz. Hyperfine interactions in the doubly degenerate case emerge due to the second-order hyperfine effect of \textbf{Eq. (2.6)}. The respective splittings are accordingly smaller, around 10 MHz.

3.2.3. Pr:YSO

From the numerous rare-earth doped materials that have been investigated with regard to coherent processes, Pr:YSO and Eu:YSO are among the two most thoroughly studied ones. \textbf{Tab. 3.3} gives a comprehensive overview on the properties of the $^3\text{H}_4 \leftrightarrow ^1\text{D}_2$ transition in Pr:YSO. As stated earlier, data records on the $^3\text{H}_4 \leftrightarrow ^3\text{P}_0$ transition are much more sparse because tunable laser sources required for high-resolution spectroscopy are not commonly available at that wavelength ($\lambda = 488$ nm). \textbf{Tab. 3.4} lists available data.

We have already seen that the crystallographic sites in YSO both feature a $C_1$ symmetry. As a consequence of this low symmetry, the praseodymium hyperfine levels are all doubly degenerate. Hyperfine parameters for the $^3\text{H}_4$ ground state and the $^1\text{D}_2$ excited
3. Praseodymium-doped yttrium orthosilicate

<table>
<thead>
<tr>
<th>Property</th>
<th>Site 1</th>
<th>Site 2</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
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<td>Wavelength</td>
<td>605.977 nm</td>
<td>607.934 nm</td>
<td>54</td>
</tr>
<tr>
<td>Inhomogeneous linewidth $\Gamma_{\text{inh}}$</td>
<td>4.4 GHz</td>
<td>2.5 GHz</td>
<td>54</td>
</tr>
<tr>
<td>Absorption coefficient</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>polarization along $D_1$</td>
<td>72 / (cm · %)</td>
<td>120 / (cm · %)</td>
<td>46</td>
</tr>
<tr>
<td>polarization along $D_2$</td>
<td>940 / (cm · %)</td>
<td>42 / (cm · %)</td>
<td>46</td>
</tr>
<tr>
<td>polarization along $b$</td>
<td>&lt; 2 / (cm · %)</td>
<td>12 / (cm · %)</td>
<td>46</td>
</tr>
<tr>
<td>Population decay time $T_1$</td>
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<td>222 µs</td>
<td>54</td>
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<td>Optical coherence time $T_2$</td>
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<td>377 µs</td>
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</tr>
<tr>
<td>Homogeneous linewidth $\Gamma_{\text{hom}}$</td>
<td>1.8 kHz</td>
<td>850 Hz</td>
<td>54</td>
</tr>
</tbody>
</table>

Table 3.3. Characteristic parameters of the $^3H_4 \leftrightarrow ^1D_2$ transition in Pr:YSO.

<table>
<thead>
<tr>
<th>Property</th>
<th>Site 1</th>
<th>Site 2</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wavelength</td>
<td>487.7 nm</td>
<td>482.9 nm</td>
<td>70</td>
</tr>
<tr>
<td>Absorption coefficient</td>
<td>210 / (cm · %)</td>
<td></td>
<td>53</td>
</tr>
<tr>
<td>Population decay time $T_1$</td>
<td>2.7 µs</td>
<td></td>
<td>53</td>
</tr>
<tr>
<td>Fourier-limited homogeneous linewidth $\Gamma_{\text{hom}}$</td>
<td>59 kHz</td>
<td></td>
<td>53</td>
</tr>
</tbody>
</table>

Table 3.4. Characteristic parameters of the $^3H_4 \leftrightarrow ^3P_0$ transition in Pr:YSO.

state are summarized in Tab. 3.5. Also consult Fig. 3.4 for a graphical representation of the energy splittings.
3.2. *Trivalent praseodymium in yttrium orthosilicate*

<table>
<thead>
<tr>
<th>Splitting</th>
<th>Site 1</th>
<th>Site 2</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^3\text{H}_4$ ground state</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\pm 1/2 \leftrightarrow \pm 3/2$</td>
<td>10.19 MHz</td>
<td>3.78 MHz</td>
<td>54</td>
</tr>
<tr>
<td>$\pm 3/2 \leftrightarrow \pm 5/2$</td>
<td>17.30 MHz</td>
<td>4.93 MHz</td>
<td>54</td>
</tr>
<tr>
<td>$</td>
<td>D</td>
<td>$</td>
<td>4.44 MHz</td>
</tr>
<tr>
<td>$</td>
<td>E</td>
<td>$</td>
<td>0.564 MHz</td>
</tr>
<tr>
<td>$^1\text{D}_2$ excited state</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\pm 1/2 \leftrightarrow \pm 3/2$</td>
<td>4.59 MHz</td>
<td>2.29 MHz</td>
<td>54</td>
</tr>
<tr>
<td>$\pm 3/2 \leftrightarrow \pm 5/2$</td>
<td>4.84 MHz</td>
<td>2.29 MHz</td>
<td>54</td>
</tr>
<tr>
<td>$</td>
<td>D</td>
<td>$</td>
<td>1.36 MHz</td>
</tr>
<tr>
<td>$</td>
<td>E</td>
<td>$</td>
<td>0.425 MHz</td>
</tr>
</tbody>
</table>

Table 3.5. Hyperfine splittings and quadrupole parameters for the $^3\text{H}_4$ ground state and the $^1\text{D}_2$ excited state in Pr:YSO. The quadrupole parameters $D$ and $E$ are defined in Eq. (2.6).

**Figure 3.4.** Hyperfine splittings for the $^3\text{H}_4$ ground state and the $^1\text{D}_2$ excited state in Pr:Y$_2$SiO$_5$. 
4. Solid-state single emitter spectroscopy

The first emitters to be detected as single entities in the solid state were organic dye molecules [71]. Since then, many more solid-state systems have been observed on the single emitter level, including quantum dots [72], diamond NV centers [73], and carbon nanotubes [74]. Although single rare-earth ions in the solid state appear very attractive for quantum information applications, the reliable isolation of a single ion has not been reported. This fact must be attributed to their comparatively long radiative lifetimes which impose limits to the detectable photon rate. Also, their oscillator strengths are some three to four orders of magnitude lower compared to e.g. organic dye molecules, thus complicating efficient light-matter interaction processes.

The question thus arises how to most efficiently detect a single ion in the solid state. We will review some important quantities relevant for single emitter detection and investigate different detection techniques. Furthermore, we describe experiments that unambiguously prove that interaction takes place on a single-emitter level.

4.1. Relevant quantities

4.1.1. Absorption cross-section

A quantity of paramount importance in single-emitter studies is the absorption cross-section $\sigma_{\text{abs}}$. In an intuitive picture it describes the conversion of incident electromagnetic radiation into electronic excitations of an emitter of interest. It will thus cause an attenuation of the incident light. However, an analysis of the light-matter interaction at the single-emitter level reveals [75] that this picture is all too simple, as it does not account for the fact that the incident electromagnetic power may also be scattered off the emitter. In fact, an idealized two-level system never really absorbs light. Instead, it scatters 100% of the interacting radiation with a phase shift of $\pi$. In this particular
case, the attenuation of light behind the emitter is caused by destructive interference of the incident beam and the scattered radiation. In general though, any light attenuation is caused by both absorption and scattering processes, commonly combined into the so-called extinction. It would thus be more appropriate to talk about the extinction cross-section $\sigma_{\text{ext}}$ instead of the absorption cross-section. However, since the spectroscopic literature on the subject is clearly dominated by the term absorption cross-section, we will also use it in the following section.

No matter which technique is used to detect a single emitter, the signal will crucially depend on the respective absorption cross-section at saturation, since its magnitude determines the first step of any single-emitter detection experiment: the interaction of light with the emitter. Its value can easily be determined from a standard extinction experiment (see Fig. 4.1). Knowing the sample thickness $l$ and the optical powers without sample ($P_0$) and with the sample ($P$), Beer’s law allows us to first calculate the attenuation coefficient from

$$P = P_0 e^{-\alpha l}. \quad (4.1)$$

Assuming that all emitters in our sample interact identically with the incident beam of light and neglecting any wavelength dependence, the absorption cross-section is then determined by

$$\sigma_{\text{abs}} = \frac{\alpha}{N}. \quad (4.2)$$

where $N$ is the number of emitters per unit volume. Note that both $\alpha$ and $\sigma_{\text{abs}}$ depend on the polarization of the incoming light in general. The absorption cross-section thus cannot be specified without also considering the relative orientations of emitter dipoles and the incoming polarization direction. This becomes especially important for randomly oriented single emitters: Their individual absorption cross-sections will all be different for a fixed polarization of the excitation beam. In extended crystalline structures however, we may assume that all emitter dipoles are oriented in the same direction with identical individual absorption cross-sections.

In this context, we also note that there is some confusion in the literature about the absorption cross-section $\sigma_{\text{abs}}$ and its integral over a certain frequency range $\int \sigma_{\text{abs}}(\nu) d\nu$, which is sometimes also denoted $\sigma$. We will stick to the notation introduced in Ref. [77] where $\sigma_{\text{abs}}$ represents the (frequency-dependent) absorption cross-section in units of area, and the integral is written in an explicit form.
4.1. Relevant quantities

Care must be taken when evaluating the number density \( N \) to only account for those emitters that the excitation light is actually interacting with. Since we are usually dealing with inhomogeneously broadened samples, the number density is calculated by

\[
N = N_{\text{tot}} \frac{\Gamma_{\text{hom}}}{\Gamma_{\text{inh}}}
\]  

(4.3)

for spectrally narrow light sources satisfying \( \Delta\nu_{\text{source}} < \Gamma_{\text{hom}} \). Here, \( N_{\text{tot}} \) specifies the total number of emitters within the illuminated volume (no matter whether they are resonant with the light source or not), while \( \Gamma_{\text{hom}} \) and \( \Gamma_{\text{inh}} \) denote the homogeneous and inhomogeneous linewidths, respectively. For light sources with a broader spectrum \( \Delta\nu_{\text{source}} > \Gamma_{\text{hom}} \) however, we should calculate

\[
N = N_{\text{tot}} \frac{\Delta\nu_{\text{source}}}{\Gamma_{\text{inh}}}
\]  

(4.4)

Single-emitter studies typically operate in a regime where \( N \approx 10^{10} \text{ cm}^{-3} \). The actual density of emitters \( N_{\text{tot}} \) may be orders of magnitude larger though, provided that both the laser and the homogeneous linewidth are narrower than the inhomogeneous broadening. This is typically true for solid-state single emitter experiments at cryogenic temperatures, where resonant light-matter interaction can be constrained to a subset of emitters using the spectral selection processes \([4.3]\) or \([4.4]\). At ambient temperatures however, the homogeneous lines of many solid-state emitters are broadened beyond

![Schematic of a typical setup used to measure the extinction coefficient \( \alpha \) from Beer’s law (4.1).](image)
4. Solid-state single emitter spectroscopy

Figure 4.2. Three-level system consisting of ground state $|1\rangle$, excited state $|2\rangle$, and the additional level $|3\rangle$. For single molecules, this third level can often be identified with the triplet state.

the inhomogeneous profile. Single-emitter experiments at room temperature thus have to work with an accordingly smaller density $N_{\text{tot}}$ of emitters.

4.1.2. Saturation intensity

In general, the absorption cross-section depends on the applied excitation intensity. For a single emitter, it behaves according to \( (76) \)

$$\sigma_{\text{abs}}(I) = \frac{\sigma_{\text{abs},0}}{1 + II_{\text{sat}}} \quad (4.5)$$

where $I_{\text{sat}}$ denotes the saturation intensity and $\sigma_{\text{abs},0}$ is the maximum absorption cross-section as $I$ approaches zero. Thus, at saturation, the absorption cross-section drops to half the maximum value. For a two-level system with levels labeled $|1\rangle$ and $|2\rangle$, this means that 1/4 of the electronic population is in the excited state while 3/4 remain in the ground state. The presence of a lower-lying third level $|3\rangle$ changes $I_{\text{sat}}$ according to \( (78) \)

$$I_{\text{sat}} \rightarrow I_{\text{sat}} \cdot \frac{1 + k_{23}/k_{21}}{1 + k_{23}/(2k_{31})} \quad (4.6)$$

where the meaning of the transition rates $k_{ij}$ is depicted in Fig. 4.2. The lifetime of $|3\rangle$ is often considerably longer than the one of $|2\rangle$, which will accordingly reduce $I_{\text{sat}}$.

4.1.3. Oscillator strength

When it comes to comparing the magnitude of light-matter interaction for different materials, the absorption cross-section might be an unhandy measure due to its notori-
ous small values. A more convenient gauge is provided by the dimensionless oscillator strength $f$, which is closely linked to the integral over an absorption line

$$\int \sigma_{\text{abs}}(\nu) d\nu = \frac{1}{4\pi\varepsilon_0} \frac{\pi e^2 F}{mc} f$$

(4.7)

where $c$ is the speed of light in vacuum, $m$ is the effective electron mass, $e$ is the unit charge, $n$ is the refractive index and $F$ is the local field factor given by

$$F \approx \left(\frac{n^2 + 2}{3}\right)^2$$

(4.8)

When dealing with single emitters we are mainly concerned with absorption profiles that have a Lorentzian lineshape

$$\sigma_{\text{abs}}(\nu) = \frac{\sigma_p}{1 + 4(\nu - \nu_0)^2/w^2}$$

(4.9)

with peak absorption cross-section $\sigma_p$, center frequency $\nu_0$, and full width half maximum (FWHM) $w$. Integration then yields

$$f = \frac{2\pi\varepsilon_0 mc n}{e^2 F} \sigma_p w = \frac{2\varepsilon_0 mc n \sigma_p}{e^2 F T_2}$$

(4.10)

where the last equality relates to the overall dephasing time $T_2$ of the transition of interest using Eq. (2.13). It is already clear from these considerations that the oscillator strength is maximized as $T_2$ is minimized, i.e. as $T_2$ approaches the $T_1$ limit and dephasing becomes negligible.

Allowed electric dipole transitions feature oscillator strengths of $f \approx 1$. Assuming a Lorentzian lineshape with a linewidth of 20 MHz, the corresponding peak absorption cross-section is on the order of $10^{-10}$ cm$^2$. Experimentally observed values for single molecules at low temperatures can come quite close to this value. Pentacene for example has an estimated peak absorption cross-section of $\sigma_{\text{abs}} = 9 \cdot 10^{-12}$ cm$^2$ [76].

On the other hand, transitions in rare-earth ions are very weak compared to those in organic dye molecules. Typical oscillator strengths are on the order of $10^{-7}$ [54,55], some six orders of magnitude below the value of reasonable single molecule candidates. Note however that the $T_2$ values for rare-earth ions are usually four to five orders of magnitude larger compared to organic molecules. The respective peak absorption
cross-sections may thus still be largely comparable (to within one or two orders of magnitude).

### 4.1.4. Fluorescence quantum yield

Taking absorption one step further we may look at samples that fluoresce. Excluding some contributions of resonance fluorescence \[80\], the emitted fluorescence can be regarded as a secondary process that follows excitation. In general however, not every absorption process will generate a fluorescent photon. The probability that an excitation will subsequently lead to fluorescent photon emission is described by the fluorescence quantum yield $\Phi_F$. Common laser dyes for instance may feature quantum yields in excess of 95%.

### 4.2. Detection techniques

In the context of this work we distinguish two different experimental techniques to detect single emitters. The first is absorption, or strictly speaking: extinction. Aside from the complication that the interaction volume has to be constrained to a small volume around the emitter, extinction detection is basically as straightforward as its ensemble analogue: The presence of a single emitter will attenuate an incident laser beam whose transmitted power is monitored on a photodetector. The second technique is fluorescence excitation spectroscopy whose signal is generated by red-shifted fluorescence photons. Spectral selectivity of this scheme usually takes place solely on the excitation frequency axis, i.e. any spectral information of red-shifted fluorescence is neglected. Therefore, extinction and fluorescence excitation spectroscopy both feature the same excitation process and the same spectral selectivity.

#### 4.2.1. Absorption detection

As one of the simplest spectroscopic experiments, an absorption measurement detects the absorbance of a sample over a particular spectral range using an incoherent light source. A typical setup is depicted in Fig. 4.3. The interaction of light with matter on the scale of a single emitter largely follows the description of the ensemble. To this end,
4.2. Detection techniques

Figure 4.3. Typical absorption setup operating with incoherent light on a sample cooled to liquid helium temperatures. The absorbance of a particular sample is given by the ratio of (wavelength-dependent) intensities with and without sample.

\[
\sigma_{\text{ext}} = \sigma_{\text{scat}} + \sigma_{\text{abs}} \tag{4.11}
\]

where \(\sigma_{\text{scat}}\) denotes the scattering cross-section, i.e. conversion of incident radiation into elastically scattered photons, and \(\sigma_{\text{abs}}\) is the absorption cross-section, i.e. conversion of incident radiation into inelastically scattered photons or other forms of energy. As we have noted earlier, the terms absorption and extinction are often used interchangeably in the literature though.

Taking into account Eq. (4.5), the extinguished optical power \(P_{\text{ext}}\), i.e. the reduction of power in the transmitted laser beam, behind a single emitter is determined by

\[
P_{\text{ext}} = \sigma_{\text{ext}} I_0 = \sigma_{\text{ext},0} \frac{I_0}{1 + I_0/I_{\text{sat}}} = \sigma_{\text{ext},0} \frac{P_0}{A + P_0/I_{\text{sat}}} \tag{4.12}
\]

where \(I_0\) and \(I_{\text{sat}}\) are the excitation and saturation intensities, \(\sigma_{\text{ext},0}\) denotes the maximum extinction cross-section, \(P_0\) is the excitation power, and \(A\) is the effective area that the excitation light is confined to at the position of the emitter. By definition, \(A\) will depend on the details of the intensity distribution. In single-emitter studies we are usually operating with a focused plane wave (FPW), i.e. a collimated laser beam that
4. Solid-state single emitter spectroscopy

Figure 4.4. Typical fluorescence excitation setup at cryogenic temperatures. Excitation light is colored blue, while fluorescence is colored red. A longpass filter separates fluorescence from the excitation light so that only fluorescent light impinges on the detector SIG. Spectroscopy is carried out by scanning the excitation frequency.

is focused onto the emitter at an aperture angle of $2\alpha$ (see Fig. 4.3). The area measure that will correctly reproduce Eq. (4.12) is given by

$$A_{FPW} = \frac{225\lambda^2}{256\pi} \left( \frac{\sin \alpha}{1 - \cos^{3/2} \alpha (5 + 3 \cos \alpha)/8} \right)^2. \quad (4.13)$$

4.2.2. Fluorescence detection

When we talk about fluorescence detection, we actually mean detection of fluorescence in fluorescence excitation spectroscopy. Consider a setup like the one depicted in Fig. 4.4. A longpass filter or dichroic mirror blocks the detection path for radiation at the excitation wavelength. That way, only red-shifted fluorescence will arrive at the detector. However, since fluorescence only emerges upon resonance with an absorption feature, we are actually probing the absorption spectrum. Photons incident on the detector usually cover a broad wavelength range, the specific spectrum of which depends on the energy level structure of the fluorescent emitter.

Considering Eq. (4.11), the appearance of red-shifted fluorescence must be attributed to an absorption term $\sigma_{abs}$, since it is certainly distinct from elastic scattering. The actual amount of red-shifted fluorescence is furthermore determined by the fluorescence quantum yield $\Phi_F$, which describes the probability of photon emission after successful
4.3. Low-temperature spectroscopy

Absorption of an incoming excitation photon. Together with Eq. (4.5) the amount of red-shifted fluorescence can then be evaluated as

\[ P_{\text{red}} = \sigma_{\text{abs}} \frac{P_0}{A + P_0/I_{\text{sat}}} \Phi_F \frac{\langle \nu_{\text{red}} \rangle}{\nu} \]  \hspace{1cm} (4.14)

where \( A \) is the area measure from Eq. (4.13), \( P_0 \) is the excitation power, \( I_{\text{sat}} \) is the saturation intensity, \( \nu \) denotes the optical excitation frequency, and \( \langle \nu_{\text{red}} \rangle \) is the average frequency of the observed fluorescence spectrum \( S_F(\nu) \) according to

\[ \langle \nu_{\text{red}} \rangle = \frac{\int S_F(\nu) \nu d\nu}{\int S_F(\nu) d\nu}. \]  \hspace{1cm} (4.15)

4.3. Low-temperature spectroscopy

Interactions of matrix phonons with the embedded guest emitter usually cause line broadening by means of dephasing mechanisms (see Eq. (2.13)). At cryogenic temperatures around 4 K, it is possible to freeze out phononic interactions. The homogeneous linewidth may consequently approach the Fourier limit: \( \Gamma_{\text{hom}} = 1/(2\pi T_1) \). This situation is interesting for two reasons. On the one hand, the absorption cross-section may come close to the limit of an ideal quantum system

\[ \sigma_{\text{abs}}^{\text{lim}} = \frac{3\lambda^3}{2\pi} \]  \hspace{1cm} (4.16)

thus facilitating absorption experiments featuring extinction ratios on the order of 20\% \cite{81}. On the other hand, negligible dephasing means that the coherence time of the emitter is maximized, i.e. the light-matter interaction is coherent until the excited state decays spontaneously. Although this timespan is often shorter than 100 ns, coherent optical Rabi oscillations have been experimentally demonstrated \cite{82}.

Most importantly however, narrow homogeneous linewidths make it possible to efficiently address different subsets of emitters within an inhomogeneously broadened band. The number of individually addressable channels

\[ N_{\text{ch}} = \frac{\Gamma_{\text{inh}}}{\Gamma_{\text{hom}}} \]  \hspace{1cm} (4.17)
is maximized as the homogeneous linewidth $\Gamma_{\text{hom}}$ becomes Fourier-limited. Depending on the disorder within the host matrix, $N_{\text{ch}}$ may reach values of $10^6$ or more \[36\].

### 4.4. Experiments with a small number of emitters

Before one tries to isolate a single emitter within a solid-state medium, it is very helpful to have some techniques at hand which bridge the gap between ensemble measurements and the detection of single emitters. They allow us, for example, to reliably determine the homogeneous linewidth and the spectral stability of the emitters. Furthermore, we can estimate the signal-to-noise ratio for single-emitter detection from the spectroscopy of a small number of emitters.

#### 4.4.1. Spectral holeburning

Spectral holeburning is a process that removes a subset of emitters from the inhomogeneously broadened absorption line by selective excitation. The optical sample will become less absorptive around the excitation frequency, thus creating a “hole” in a subsequently acquired absorption spectrum. In principle, the holeburning process is based on a mechanism that transfers the electronic population of excited emitters into a different state, which do not contribute any more to absorption at the excitation frequency. In the case of rare earths in inorganic crystals, the mechanism is often a redistribution of electronic population into different hyperfine levels of the ground state. At cryogenic temperatures where the homogeneous lines of the individual hyperfine levels do not overlap, respective lifetimes may be on the order of days \[83\]. Accordingly, holeburning spectra may persist for very long times at modest magnetic fields.

The holeburning process removes electronic population from the respective hyperfine level in the ground state. As the excited state decays back into the ground state, the non-excited hyperfine levels in the ground state become populated. Thus, the absorption spectrum in the vicinity of the burning wavelength will exhibit antiholes of increased absorption. The hyperfine level structure of the excited state on the other hand will give rise to sideholes next to the central hole. See Figs. 4.5 and 4.6 for an illustrative explanation.

The spectral width of a hole burnt at very low intensities is given by twice the homogeneous linewidth \[84\]: One homogeneous linewidth stems from the burning process, since the emitters burnt away are characterized by the homogeneous linewidth.
4.4. Experiments with a small number of emitters

Figure 4.5. Schematic illustrating the appearance of sideholes (solid black arrows) and antiholes (dashed black arrows) upon burning a central hole (bold arrows) into a material featuring two hyperfine levels in both ground and excited states with splittings of $\Delta_g$ and $\Delta_e$, respectively. Cases $a$ through $d$ represent the four possibilities of burning a hole into an inhomogeneously broadened medium. Each case gives rise to one sidehole (less absorption due to decreased population in the ground state) and one antihole (more absorption due to increased population in the respective ground state). As the total holeburning spectrum includes all four cases, it will exhibit a symmetric structure of one sidehole and one antihole on each side of the central hole (see Fig. 4.6). More complicated structures arise in the case of more than two hyperfine levels.

Figure 4.6. Sketch of a holeburning spectrum for the system illustrated in Fig. 4.5. First, a central hole is burnt at frequency $v_0$. What is illustrated here is the subsequently acquired absorption spectrum, which exhibits sideholes at frequencies $v_0 \pm \Delta_e$ and antiholes at frequencies $v_0 \pm \Delta_g$. Vertical lines indicate the respective frequency positions, while letters next to a line correspond to the cases of Fig. 4.5 which cause the appearance of the respective feature.
Another homogeneous linewidth is introduced during the readout process as the spectrum of the remaining emitters in the hole is convolved with their inherent, i.e. homogeneous, linewidth. Furthermore, this result has to be convolved with the linewidths $\Delta \nu_{\text{burn}}$, $\Delta \nu_{\text{read}}$ of the burning and readout lasers, respectively. In the case of Lorentzian lineshapes for all three contributions, we derive

$$\Gamma_{\text{hole}} = 2\Gamma_{\text{hom}} + \Delta \nu_{\text{burn}} + \Delta \nu_{\text{read}}. \quad (4.18)$$

This equation is only valid in the case of vanishing burning fluence $F$ however, the fluence being the product of burning intensity and duration. At higher burning fluences, the hole width will broaden, because, at some point, there are no more resonant emitters in the center of the hole. As a result, the burning process affects an increasing amount of emitters in the wings of the hole, thus broadening the hole according to $\Gamma_{\text{hole}} \propto F^\alpha$ where the exponent $\alpha$ takes values between 0.25 and 1 \cite{85, 86}. Even at constant low burning fluences it is possible to broaden the spectral hole by means of power broadening \cite{86}. Thus, both burning fluence and burning power should be kept low if one wants to measure the homogeneous linewidth.

### 4.4.2. Statistical fine structure

When one tries to isolate a single emitter from within an inhomogeneously broadened ensemble, one usually starts carrying out spectroscopy either by decreasing the number of resonant emitters, reducing their concentration, decreasing the interaction volume, or by spectral selection. At some point, a reproducible fluctuating signal will emerge in the detected signal (see Fig. 4.7). The signal excursions of this co-called statistical fine structure (sfs) occur due to the number fluctuations of emitters in resonance. Since these number fluctuations follow Poisson statistics, the sfs signal excursions scale as $\sqrt{N}$ where $N$ is the number of molecules in resonance \cite{76}. Note however that this statement only applies to the absolute sfs fluctuations. There are a number of experimental techniques, e.g. classical absorption measurements, which do not determine the absolute fluctuations; instead, they yield the relative signal fluctuations, which scale as $1/\sqrt{N}$, since, as a first approximation, the average signal scales as $N$.
4.4. Experiments with a small number of emitters

Figure 4.7. Simulated fluorescence spectra of inhomogeneously broadened ensembles of $N$ emitters, which each have a Lorentzian homogeneous lineshape of $\Gamma_{\text{hom}} = 20$ MHz. The inhomogeneous broadening $\Gamma_{\text{inh}}$ is assumed to be much larger than $\Gamma_{\text{hom}}$. The graphs in the left column show the absolute fluorescence signal of (a) $N = 10^7$, (b) $N = 10^5$, (c) $N = 10^3$, (d) $N = 10$ emitters. The two graphs in the right column are zooms into the traces on the left, i.e. (a') $N = 10^7$, (b') $N = 10^5$ emitters. While the relative signal fluctuations in the left column behave as $1/\sqrt{N}$, the absolute signal fluctuations grow as $\sqrt{N}$. 

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4. **Solid-state single emitter spectroscopy**

### 4.4.3. Photon correlations

When we carry out spectroscopy on a small number of emitters, at some point the question arises whether the signal stems from a single emitter or from multiple ones. To answer this question, we look at the photon statistics of the detected radiation. Mathematically, this statistics is described by the second-order autocorrelation function of the emitted electric field $E$. In its normalized form it reads

$$g^{(2)}(\tau) = \frac{\langle I(t)I(t+\tau) \rangle}{\langle I(t) \rangle \langle I(t+\tau) \rangle}\quad (4.19)$$

where $I(t)$ denotes the intensity (which is proportional to $E^2$) and the brackets indicate the average over $t$. An equivalent description uses the correlation of photon numbers in a particular mode instead of intensities [88].

For a single quantum emitter, any emission of a photon is associated with the transition of electronic population into a lower-lying state. Since it takes a finite time to transfer this population back into the excited state, there is a zero probability that two photons are emitted on one transition at the same time. Accordingly, the second-order autocorrelation function should be zero at $\tau = 0$ for a single quantum emitter. We call such a feature **antibunching** to reflect the fact that the photons originating from a single quantum emitter do not come in bunches: small time intervals between adjacent photons are rare.

The presence of two identical emitters will lead to an antibunching of $g^{(2)}(0) = 0.5$. Thus, measuring $g^{(2)}(0) < 0.5$ is sufficient as a proof for a single emitter.
5. Experimental techniques

5.1. Laser source

5.1.1. Requirements

As we have seen in section 4.2 both absorption and fluorescence excitation spectroscopy aim to gather information about an emitter’s absorption spectrum. In contrast to conventional spectroscopy, high-resolution techniques do not require any dispersive element in the beamline. Instead, they scan the excitation frequency $\nu$ directly to gather the spectroscopic signal $S(\nu)$. Being interested in the selective excitation of the $^3P_0$ level of Pr:YSO, we will thus need a frequency-tunable laser source operating around 488 nm (see Tab. 3.4).

From the data on the $^3H_4 \leftrightarrow ^1D_2$ transition (Tab. 3.3) we may expect inhomogeneous broadenings on the order of a few gigahertz. The tuning abilities of our laser source should be large enough to cover that range. This requirement should be easy to meet as most spectroscopic laser sources nowadays feature mode-hop free tuning ranges of some tens of gigahertz.

Furthermore, our laser source should be narrower in frequency than the homogeneous linewidth of the transition. Only then will we be able to scan across the absorption line and determine its shape and width. We have seen in Tab. 3.4 that the homogeneous linewidth of the $^3H_4 \leftrightarrow ^3P_0$ transition is on the order of a few tens of kilohertz, provided that pure dephasing processes do not broaden the homogeneous line. The excitation laser should thus have a linewidth of around 10 kHz.

Last but not least, the laser’s center frequency should ideally not drift by more than one homogeneous linewidth between consecutive experimental runs. This property will allow us to easily repeat experiments and to directly compare their results. We may expect integration times on the order of a second due to the excited-state lifetimes on the order of microseconds (see Tabs. 3.3, 3.4). Thus, for an estimated number
5. Experimental techniques

of 100 samples per experiment, we require the laser frequency drift to be better than 1 kHz/min.

5.1.2. Quick overview

We have decided to realize the laser system outlined above using a continuous wave titanium-sapphire laser (*Sirah Matisse*) operating near 976 nm and frequency doubling that to 488 nm in an external home-built cavity. The *Matisse* is optically pumped by a 532 nm *Laser Quantum Finesse* with a maximum optical power of 10 W.

Intensity and linewidth of the frequency-doubled radiation are largely determined by the fundamental Ti:Sa laser source, which is why the spectral properties of the fundamental laser light should be accurately controlled. The frequency-stabilized *Matisse TS* version comes with a linewidth of 100 kHz, which is a sufficient value for certain experiments. Resolving the homogeneous line in Pr:YSO, however, requires a linewidth that is an order of magnitude less. At the same time, drift of the laser should be reduced to less than 10 kHz. In order to meet these goals, we have implemented an alternative stabilization scheme which involves locking the Ti:Sa to an external cavity whose long-term drift is minimized by appropriate temperature stabilization. Fig. 5.1 shows an overview of the laser setup.

5.1.3. Frequency stabilization

An unstabilized, free-running laser will usually have a linewidth that is much broader than the ultimate, standard quantum limit which is dictated by the Schawlow-Townes relationship. The reason for this broadening is external noise sources with bandwidths up to several megahertz, which introduce length changes to the laser cavity. As a result, the laser frequency is constantly modulated at these frequencies. Depending on the integration time used to measure the fluctuating laser frequency, one will observe a more or less broadened line. Examples of prominent noise sources are mechanical vibrations (up to several tens of kilohertz in bandwidth) or intensity fluctuations of pump lasers (up to several megahertz). It is the goal of any frequency stabilization technique to reduce these fluctuations, thereby narrowing the linewidth.

Passive frequency stabilization encompasses measures such as a rigid mechanical construction of the laser cavity, its mechanical decoupling from the surrounding (vibration isolation), and ensuring that the index of refraction within the cavity does not
5.1. Laser source

Figure 5.1. Schematic overview of the laser setup used for high-resolution spectroscopy of the $^3\text{H}_4 \leftrightarrow ^3\text{P}_0$ transition within Pr:YSO. A commercial cw Ti:Sa laser is frequency-doubled using an LBO crystal in an external cavity. At the same time, the laser frequency is stabilized to an external temperature-stabilized high-Q cavity using the Pound-Drever-Hall (PDH) locking scheme. In a situation when the laser is locked to the high-Q cavity, tuning abilities are provided by the two acousto-optic modulators $\text{AOM}_1$ and $\text{AOM}_2$. They are both operated in a double-pass configuration using two deflection prisms. EOM: electro-optic modulator, PBS: polarizing beamsplitter, $\lambda/4$: quarter waveplate.
fluctuate. However, even the best passive stabilization is not effective against frequency modulations at frequencies beyond the acoustic regime. This is why laser frequency stabilization is usually achieved by applying an active feedback to the length of the laser cavity.

The error signal required for active feedback is generated with the help of a frequency reference whose spectral properties will more or less dictate the frequency response of the laser. A more stable reference will thus allow us to build a more stable laser source. Common frequency references used for laser stabilization include Fabry-Perot cavities and atomic resonances. The fringes of Fabry-Perot cavities can be made as narrow as a few kilohertz by using highly reflecting mirrors. Accordingly, the short-term linewidth of such-stabilized lasers may reach the regime of less than one hertz \[^90\]. Atomic resonances, on the other hand, are usually several megahertz wide, but they feature an exquisite long-term stability, which allows one to compensate drifts of the laser frequency. However, atomic resonances are not always available at the precise wavelength of laser operation, which is why in the following we will focus on locking to Fabry-Perot cavities. Two standard techniques have evolved to generate an appropriate error signal for laser stabilization from a fringe of the reference.

5.1.3.1. Side-of-fringe locking

Side of fringe locking is probably the simplest scheme to lock the laser frequency to a Fabry-Perot fringe. The error signal is generated by subtracting a constant setpoint value from the transmission signal through the stabilization cavity (see Fig. 5.2). As with most locking techniques, the locking point is defined as the laser frequency where the error signal vanishes. We can see from Fig. 5.3 that this point is on one side of the fringe, depending on the sign of feedback applied to the laser cavity. This stabilization scheme can be implemented quite easily for cavities with broad and medium linewidths of down to several megahertz. Since the locking bandwidth to one side of the locking point is limited by the cavity linewidth (again see Fig. 5.3), this scheme cannot be exclusively used with narrower resonances however: Negative frequency deviations greater than the FWHM resonance linewidth will cause a loss of the lock if they happen too quickly, i.e. faster than the servo bandwidth. Furthermore, intensity fluctuations of the laser shift the position of the error signal on the frequency axis, an effect that is not desired when stabilizing the laser’s frequency.
5.1. Laser source

Figure 5.2. Schematic of the laser system stabilized using the side-of-fringe locking technique. See the text for further details and explanations. OC: fiber output coupler, L: mode-matching lens, PD: photodiode, amp: amplifier, PZT: piezoelectric actuator. The confocal cavity is tunable by mounting one of the mirrors onto a PZT.

Figure 5.3. Error signal for the side-of-fringe locking technique. The horizontal axis specifies the laser frequency offset $\omega$ in units of the cavity linewidth $\Delta \nu$. A constant value of 0.5 has been subtracted as a set-point value from the cavity fringe observed in transmission to generate the error signal. The shaded region highlights the frequency range where a positive feedback will maintain a stable lock to the frequency indicated by the blue dot. An increase in laser intensity of 50% will alter the error signal as indicated by the red line. Accordingly, the locking point will shift towards the higher frequency marked by the red dot.
5. Experimental techniques

5.1.3.2. Pound-Drever-Hall locking

The limitations of a side-of-fringe locking technique are lifted in a frequency-modulation locking scheme named after its inventors R. V. Pound, R. Drever, and J. L. Hall. Their locking technique is superior to the side-of-fringe technique in the sense that the position of a Pound-Drever-Hall (PDH) error signal is not subject to intensity fluctuations at first order and that the locking range is increased. Fig. 5.4 illustrates the setup used in our experiments. The electric field incident on the stabilization cavity $E_{\text{inc}}$ is phase-modulated by a local oscillator (LO) running at (angular) frequency $\Omega$. This way we imprint sidebands to the carrier laser frequency $\omega$ according to

$$E_{\text{inc}} = E_0 \left( J_0(\beta) e^{i\omega t} + J_1(\beta) e^{i(\omega+\Omega)t} - J_1(\beta) e^{i(\omega-\Omega)t} \right)$$

where $J_i(\beta)$ denote the Bessel functions for the modulation depth $\beta$ and we have neglected higher-order terms (which is a good approximation for $\beta \lesssim 1$). The modulation depth $\beta$ parametrizes the amplitude of phase modulation. Thus, $\beta = \pi$ means that the phase is modulated between $-\pi$ and $\pi$ at a frequency of $\Omega$.

Now let $F(\omega)$ denote the reflection coefficient of the electric field for the Fabry-Perot cavity ($F = 0$ on resonance for a lossless cavity, $|F| = 1$ off resonance). The power reflected off the cavity $P_{\text{ref}}$ then reads

$$P_{\text{ref}} = \left| E_0 \left( J_0(\beta) F(\omega) e^{i\omega t} + J_1(\beta) F(\omega + \Omega) e^{i(\omega+\Omega)t} - J_1(\beta) F(\omega - \Omega) e^{i(\omega-\Omega)t} \right) \right|^2$$

$$= P_c |F(\omega)|^2 + P_s \left( |F(\omega + \Omega)|^2 + |F(\omega - \Omega)|^2 \right)$$

$$+ 2 \sqrt{P_c P_s} \Re [F(\omega) F^*(\omega + \Omega) - F^*(\omega) F(\omega - \Omega)] \cos \Omega t$$

$$- 2 \sqrt{P_c P_s} \Im [F(\omega) F^*(\omega + \Omega) - F^*(\omega) F(\omega - \Omega)] \sin \Omega t$$

$$+ \mathcal{O}(2\Omega)$$

where $\Re$ and $\Im$ are the real and imaginary parts of the enclosed expressions, $P_0$ denotes the total incident optical power and we have introduced the optical powers in the carrier $P_c = f_0^2(\beta) P_0$ and in the sidebands $P_s = f_1^2(\beta) P_0$. Fig. 5.5 shows a time-averaged spectrum of the power reflection coefficient.

If $\Omega$ is much larger than the linewidth of the Fabry-Perot cavity, it can be shown that the cosine term in Eq. (5.2) vanishes [91]. Using a fast photodetector we can monitor the sine oscillation and mix it down using the LO frequency. Discarding any oscillations...
5.1. Laser source

Figure 5.4. Schematic of the laser system stabilized using the Pound-Drever-Hall locking technique. See the text for further details and explanations. EOM: electro-optic modulator, λ/4: quarter-wave plate, L1,2: mode-matching lens pair, PBS: polarizing beam splitter, PD: photodiode, LO: local oscillator, PS: phase shifter, M: mixer, amp1,2: amplifiers, PZT: piezoelectric actuator, AOM: acousto-optic modulator.

At 2Ω the resulting error signal will be proportional to the respective coefficient of Eq. (5.2)

\[ \epsilon = -2\sqrt{P_c P_s} \Im [F(\omega)F^*(\omega + \Omega) - F^*(\omega)F(\omega - \Omega)]. \quad (5.3) \]

Fig. 5.6 shows a plot of this error signal. It consists of three characteristic dispersive "resonances" produced by the cavity reflections of the carrier and the two sidebands, the locking point being the zero-crossing of the central dispersive feature. The slope of the two outer resonances is reversed compared to the central slope. This is why appropriate feedback will maintain a stable lock to the central zero-crossing, not the outer ones.
5. Experimental techniques

Figure 5.5. Time-averaged reflected power $P_{ref}/P_0$ of a phase-modulated beam ($\beta = 1.08$, $\Omega = 2\pi \cdot 5$ MHz) incident on a Fabry-Perot cavity (free spectral range FSR = 1.5 GHz, finesse $\mathcal{F} = 10,000$). Note the appearance of sidebands at $\omega = 2\pi \cdot 5$ MHz. The phase modulation process re-distributes optical power into both the carrier and the sidebands, which is why the sum of all dips should yield a dip that goes to zero.

Figure 5.6. Calculated PDH error signal $\epsilon/(4\sqrt{P_cP_s})$ for a beam modulated at 5 MHz (modulation depth $\beta = 1.08$) incident on a Fabry-Perot cavity with free spectral range FSR = 1.5 GHz and finesse $\mathcal{F} = 10,000$. The shaded region specifies the locking bandwidth. Within this region, a negative feedback will maintain a stable lock at $\omega = 0$. 

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5.1. Laser source

<table>
<thead>
<tr>
<th>cavity type</th>
<th>A</th>
<th>B</th>
</tr>
</thead>
<tbody>
<tr>
<td>material</td>
<td>Invar</td>
<td>Corning ULE</td>
</tr>
<tr>
<td>radius of curvature</td>
<td>250 mm</td>
<td>500 mm</td>
</tr>
<tr>
<td>free spectral range</td>
<td>600 MHz</td>
<td>1.5 GHz</td>
</tr>
<tr>
<td>finesse at $\lambda = 976$ nm</td>
<td>43</td>
<td>12,000</td>
</tr>
<tr>
<td>tuning range</td>
<td>$\sim 100$ GHz</td>
<td>—</td>
</tr>
<tr>
<td>temperature stability</td>
<td>$&lt; 100$ mK</td>
<td>$\pm 1$ mK</td>
</tr>
<tr>
<td>air pressure</td>
<td>est. $10^{-2}$ mbar</td>
<td>$3 \cdot 10^{-9}$ mbar</td>
</tr>
</tbody>
</table>

Table 5.1. Characteristic parameters for the two stabilization cavities used throughout this work.

Usually, one would want to operate the PDH lock in a regime that maximizes the slope of the error signal around $\omega = 0$. This can be shown to be the case for $\beta = 1.08$ [91].

5.1.3.3. Experimental implementation

For increased flexibility, we have implemented both side-of-fringe and PDH frequency locking techniques using separate, dedicated stabilization cavities. Their parameters are listed in Tab. 5.1. The two cavities serve different purposes: The cavity used for side-of-fringe locking (cavity A) has a relatively low finesse, however, one of the mirrors is mounted onto a piezoelectric actuator (PZT) thus providing tuning capabilities in the range of 100 GHz. It is part of the Sirah Matisse laser system. The cavity used for PDH locking (cavity B, Advanced Thin Films model 6020-4) on the other hand features a monolithic, non-tunable design with a finesse of $F = 12,000$ facilitating narrow laser linewidths. It is manufactured from Corning ULE, a glass ceramic with a very low thermal expansion coefficient $\alpha < 3 \cdot 10^{-8}$/K, in order to minimize long-term drifts.

Side-of-fringe locking is implemented using the detectors and electronics provided with the Matisse laser system. See Fig. 5.2 for a schematic overview. Part of the laser output is coupled into a single-mode optical fiber and fed into cavity A. Matching the cavity mode is fairly easy, since cavity A is pre-adjusted by the producer: The two concave cavity mirrors define a confocal cavity. Furthermore, the cavity assembly includes both a properly positioned mode-matching lens and an accordingly placed fiber con-
nector. Therefore, the only remaining degrees of freedom are given by the horizontal and vertical tilt of the fiber connector, which are adjustable by the operator to achieve proper mode matching. A photodiode measures the transmission through the cavity. The error signal is then derived by subtracting a constant value from the transmission signal. Feedback to the cavity length for frequency stabilization is provided by a PZT-mounted cavity mirror. Using this locking scheme, it is possible to achieve linewidths on the order of 100 kHz for a timescale of a few milliseconds. On longer timescales however, the laser frequency will drift (see Fig. 5.12). This behavior must mainly be attributed to the drift of the piezo-mounted mirror of stabilization cavity A.

The PDH locking scheme is illustrated in more detail in Fig. 5.4. The beam incident on the high-finesse cavity (optical power $P = 20 \mu W$) is phase-modulated using a resonant electro-optic phase modulator manufactured by Qubig. It is driven by a local oscillator (LO) running at 22.31 MHz. Passing through a polarizing beamsplitter (PBS) the modulated beam is coupled into cavity B by means of a mode-matching lens pair. A CMOS camera placed behind the cavity monitors the transmission through the cavity. It will image a particular cavity mode upon its excitation. This allows us to align the mode-matching lenses in a way that the beam will exclusively excite the $TEM_{00}$ mode. Since the monolithic design of cavity B prevents its scanning, we have to scan the laser frequency across a cavity resonance in order to obtain the reflection spectrum and the image of excited cavity modes. We do this by locking the laser to cavity A and scanning that cavity within a range of 625 MHz at a speed of 500 MHz/s.

As can be seen in Fig. 5.4, light that is reflected from the cavity passes through a quarter waveplate ($\lambda/4$), once upon incidence on the cavity and another time after reflection. The waveplate is oriented at 45° with respect to the incident p-polarization, which transforms the incident beam from p-polarization to a circular polarization on the first pass, and from that to s-polarization on the way back. It is reflected at a polarizing beam splitter (PBS) and directed onto a fast photodiode (Hamamatsu C5658, cut-off frequency 1 GHz) that is able to detect signal oscillations at the LO frequency of 22.31 MHz. Directing both the photodiode signal and the LO frequency onto a mixer (Minicircuits RPD-1) gives the PDH error signal at the mixer output. It can be fine-tuned by controlling the relative phase between the mixer inputs using a phase shifter (PS) that affects the LO phase at the mixer. Actually, in order to obtain the pure error signal we should discard oscillations at $2 \times 22.31$ MHz. This is usually realized by adding a low-pass filter after the mixer. In our setup, it is the limited bandwidth of the amplifiers driving the feedback elements that effectively replaces a low-pass filter.
5.1. Laser source

Amplifier amp\textsubscript{1} with a bandwidth of up to 1 MHz provides fast feedback to the laser cavity by driving an intra-cavity eom, while amplifier amp\textsubscript{2} provides feedback to the piezo-mounted cavity mirror. It is controlled by the digital signal processing unit (DSP) within the Matisse electronics.

We have invested some effort to achieve a good length stability of cavity b on both the short-term and the long-term scales. Regarding the short-term stability, there are two main effects contributing to cavity length changes: acoustic vibrations of the cavity itself and refractive index fluctuations of the medium within the cavity. Acoustic vibrations above 1 Hz may in general be efficiently suppressed using passive or active vibration isolation techniques. Since expected experimental timescales are on the order of 1 s or longer though, we require additional measures to suppress cavity length changes at lower frequencies (below 1 Hz). We have decided to follow the approach presented in Ref. [92], which aims to reduce the sensitivity of the cavity assembly to vibrations. To this end, we have supported the cavity at four carefully chosen positions (33 mm from the center along the cavity axis, 20 mm from the center perpendicular to the cavity axis) using 4 mm Viton balls. Vibrations of the cavity assembly, both along the cavity axis as well as perpendicular to it, should then have a minimal effect on the cavity length. When it comes to reducing fluctuations of the refractive index inside the cavity, we have evacuated the whole cavity assembly. It resides in an aluminum vacuum chamber, whose inner pressure is held at 3 \cdot 10^{-9} mbar using an ion getter pump (Gamma Vacuum TiTan 3\textsubscript{s}). Since aluminum is too soft as a material for standard cf gaskets, we have used indium wire for all the vacuum seals. As a consequence, we chose a relatively moderate temperature of \(\theta = 60 \, ^\circ\text{C}\) for the bakeout during five days. Fig. 5.7 illustrates the assembly.

In order to achieve a good length stability in the long term, the cavity temperature has to be stabilized. We have decided to implement a design similar to Ref. [90]. The vacuum chamber surrounding the cavity is temperature-stabilized to around 30 °C using a home-built PI controller. Feedback is applied by means of heating wire wound around the chamber. We have chosen aluminum type EN AW-6060 as a material for the vacuum chamber to increase the heat conductivity. This way, we achieve a stability of \(\pm 1 \, \text{mK}\) as illustrated in Fig. 5.8. The vacuum chamber in turn resides within an aluminum box whose six sides are temperature-stabilized to an average of 29.5 °C with a precision of \(\pm 50 \, \text{mK}\) (see Fig. 5.9). We use individual two-point temperature controllers for each of the six sides. Feedback is again provided by heating wire glued onto the box. The box is wrapped with 10 mm sheets of polystyrene for thermal isola-
5. Experimental techniques

Figure 5.7. Cross section through the vacuum chamber used for cavity b. The cavity assembly is colored in blue. It resides on four Viton balls which are fixed in position by Teflon holders (white) connected with bars made of stainless steel (gray). This type of support reduces the sensitivity of the cavity assembly to vibrations (see text for further details). Two anti-reflection coated windows (colored blue) provide optical access to the cavity assembly. The hole in the rear serves as a connection point for the ion getter pump. The junctions are all sealed using indium wire.

...tion. The whole assembly itself is contained within a wooden box lined with a dense vinyl material (Auralex SheetBlok) for a further reduction of acoustic vibrations. See Fig. 5.10 for an illustration of the cavity housing.

We have already noted that side-of-fringe locking to cavity a is able to narrow the laser linewidth down to around 100 kHz. This linewidth is not only limited by the quality of the error signal, but also by the restricted feedback bandwidth of the piezo-mounted cavity mirror. Therefore, if one wants to achieve even narrower linewidths, one has to introduce a high-bandwidth feedback element into the laser cavity, which is an electro-optical modulator (eom) in our case. It will compensate for the high-frequency noise that the piezo-mounted cavity mirror cannot handle. However, there is one drawback that the eom brings about: at $\lambda = 976$ nm it will reduce the laser output power by around 15% as can be seen from Fig. 5.11.
5.1. Laser source

**Figure 5.8.** Temperature fluctuations of the vacuum chamber containing cavity B. The temperature was measured on the outer side of the chamber using an NTC resistor. Plotted is the deviation from the set-point value of the PI temperature controller.

**Figure 5.9.** Temperature fluctuations of the six aluminum sides housing the vacuum chamber. The temperatures were measured on the outer sides using NTC resistors. Plotted is the deviation from the respective set-point values with offsets of 0.1 K between adjacent traces. The topmost trace corresponds to the temperature of the upper side. It exhibits larger deviations since heat inside the box accumulates below the top lid.
5. Experimental techniques

- wood
- SheetBlok
- polystyrene foam
- heating wires
- aluminum 3mm
- aluminum 20mm
- thermoset plastic
- Teflon
- ULE
- rubber bumper

Figure 5.10. Cross section through the assembly used to stabilize cavity B. IGP: ion getter pump.

Figure 5.11. Laser output power vs pump power. Symbols indicate measured values, the lines are linear fits to the data. For a good alignment of the laser cavity and its intracavity elements, the slope efficiencies for both the configuration with and without EOM are identical. At a pump power of 8.5 W, the EOM introduces an overall loss of around 15%.
5.1. Laser source

Since cavity b cannot be tuned in length, the laser maintains a fixed frequency once it is locked to the cavity. In order to still be able to tune the laser in frequency we have introduced an acousto-optic modulator (AOM1, Brimrose model GPF-1050-500) into the beam path directed towards the stabilization cavity (see Fig. 5.4). At a center frequency of 1050 MHz it allows the optical frequency to be tuned by as far as ±250 MHz in a single pass. Using a double-pass configuration we can achieve a tuning range of 1 GHz. The speed of the AOM frequency tuning on the other hand is limited by the PDH feedback. In our setup, the maximum tuning speed for the laser frequency is around 200 MHz/s. Considering the narrow feature lines (10 – 100 kHz) of interest in our work, this figure appears satisfactory.

5.1.3.4. Performance

We have characterized the long-term drift of the two laser stabilization schemes using spectral holeburning. A spectral hole was burnt into a 0.005%-doped Pr:YSO sample held in a cryostat at \( T = 4.3 \) K. This crystal is an excellent holeburning material with hole lifetimes on the order of 30 s. The burning duration was 0.5 s. 1 s after the burn pulse we recorded transmission through the sample in a frequency window of ±4 MHz around the hole. See section 6.6 for further details on our implementation of holeburning. As can be seen in Fig. 5.12, both open-loop operation and locking to cavity a reveal frequency drifts of the order of 1 MHz. Locking to cavity b removes this drift. Both a narrow line and a negligible drift however are only observed if feedback is applied to both the PZT-mounted cavity mirror and the intra-cavity EOM.

Measuring the linewidth of a laser on a shorter timescale becomes a little more involved. One method is to analyze the deviations of the closed-loop error signal. By converting the noise of the error signal \( \tilde{e} \) into frequency noise of the laser \( \tilde{\nu} \) according to

\[
\tilde{\nu} = \frac{\tilde{e}}{D}
\]

where \( D \) is the discriminator slope in units of V/Hz, one can calculate the power spectral density of laser frequency noise. The laser linewidth is then commonly defined as the FWHM, or 3 dB point, of that density [93]. However, a rigorous treatment reveals that the number determined this way is not more than a lower limit for the laser linewidth [94]. Still, some laser manufacturers specify the laser linewidth based on error signal analysis. Their approach is to calculate the error signal root mean square \( \epsilon_{\text{rms}} \) and convert that into a root mean square frequency \( \nu_{\text{rms}} \) using Eq. (5.4). From the
Figure 5.12. Laser frequency stability using different stabilization cavities and locking techniques. The signals have been acquired using holeburning spectroscopy in a 0.005\% Pr:YSO crystal at $T = 4.3$ K. In each case, the burning time was 0.5 s and the time delay between burning and reading was 1 s. All signals are broadened considerably by power broadening as indicated in the lower right subfigure. (a) Open-loop operation without any lock. The laser frequency drifts to lower frequencies. At the same time, it exhibits frequency jumps on the order of a few megahertz. (b) Side-of-fringe lock. The laser linewidth is reduced, however, there is still some drift to lower frequencies. (c) PDH lock. Laser frequency is stable, the linewidth is fairly broad however. This is probably due to imperfect feedback parameters. (d) PDH lock with high-bandwidth feedback. Both the linewidth and the drift have been minimized.
previous remarks it is obvious that $\nu_{\text{rms}}$ constitutes only a very rough estimate for the actual laser linewidth. Nevertheless, as it is very easy to obtain, we have also calculated it for our setup. At $D = 8 \cdot 10^{-5}$ V/Hz and $\epsilon_{\text{rms}} = 0.17$ V, we estimate $\nu_{\text{rms}} = 2.1$ kHz.

A more reliable method to determine the laser linewidth is by observing the width of a spectral hole at very low burning fluences. Refer to subsection 6.6.2 for details about the experimental implementation. The linewidth obtained this way is limited by $\Delta \nu < 3.7$ kHz.

5.1.4. Frequency doubling

5.1.4.1. Theoretical treatment

The frequency stabilization techniques described above both take place at $\lambda_1 = 976$ nm. In order to excite the $^3P_0$ manifold of Pr:YSO, however, we have to use a laser beam at $\lambda_2 = 488$ nm, which can be generated from the Ti:Sa laser source by doubling its optical frequency in a process called second harmonic generation (SHG). We may consider this process as combining two fundamental photons into one harmonic photon with double the energy. This can only happen in nonlinear optical materials, i.e., materials with a non-vanishing second-order electric susceptibility $\chi^{(2)}$. It can be shown that such materials must be crystalline and lack inversion symmetry [95]. Meanwhile, there is a considerable number of suitable materials [96].

In order to understand how the SHG process works, we first consider the electric polarization $\mathbf{P}$ induced within a nonlinear optical material

$$\mathbf{P} = \epsilon_0 \chi^{(1)} \mathbf{E} + \epsilon_0 \chi^{(2)} \mathbf{E}^2 + \mathcal{O} (\mathbf{E}^3)$$  \hspace{1cm} (5.5)

where $\mathbf{E}$ is the incident electric field and $\chi$ is the electric susceptibility, split into its first-order (linear) component $\chi^{(1)}$ and a second-order (nonlinear) contribution $\chi^{(2)}$. Both $\mathbf{E}$ and $\mathbf{P}$ can be considered as vectors, while $\chi^{(1)}$ and $\chi^{(2)}$ behave like tensors of second and third order, respectively. Writing the incident electric field in the medium as a plane wave

$$\mathbf{E} = \mathbf{E}_1 e^{-i(k_1z-\omega_1 t)}$$  \hspace{1cm} (5.6)
5. Experimental techniques

Figure 5.13. Schematic illustration of the relevant quantities during second harmonic generation. The fundamental laser beam (electric field strength \( E_1 \), frequency \( \omega_1 \)) is incident on a nonlinear crystal, in which it generates a second-order harmonic polarization \( P_\perp \) oscillating at \( \omega_2 = 2\omega_1 \) via the second-order electric susceptibility \( \chi^{(2)} \). The electric field \( E_2 \) due to \( P_\perp \) (also oscillating at \( \omega_2 \)) grows along the propagation direction \( z \) of the fundamental beam through the crystal. Since only a small portion of the incident light is converted during the SHG process, both fundamental and harmonic beams exit the crystal on the right hand side.

It is clear that the second term \( P^{(2)} \) of Eq. (5.5) will oscillate at \( \omega_2 = 2\omega_1 \) since it includes the square of \( E \). It is this part of the polarization which is responsible for SHG.

According to Maxwell’s equations \([97]\) a macroscopic polarization acts as a source term for the electric field \( E' \). In the absence of charges we derive (using SI units)

\[
\left( \Delta - \frac{1}{c^2} \frac{\partial^2}{\partial t^2} \right) E' = \frac{\partial^2}{\partial t^2} \mu_0 P
\]

where \( \mu_0 \) is the permeability of free space, and \( c \) denotes the speed of light. This equation is linear in both \( E' \) and \( P \), which means that the presence of \( P^{(2)} \) (oscillating at \( \omega_2 = 2\omega_1 \)) causes the generation of an electric field \( E''(2) \) oscillating at the harmonic frequency \( \omega_2 \).

Actually, Eqs. (5.5) and (5.7) entirely suffice to describe the SHG process. However, their formulation is not really convenient for an experimentalist who wants to calculate SHG conversion efficiencies and optimize the experimental apparatus. Consider the SHG experiment depicted in Fig. 5.13. We shall be interested in the increase of the harmonic electric field \( E_2 \) as the fundamental beam \( E_1 \) travels through the crystal. Its spatial change in amplitude \( \frac{dE_2}{dz} \) reads \([98, 99]\)

\[
\frac{dE_2}{dz} = \frac{2\pi i \omega_2}{n_1 c} P_\perp e^{i(2k_1-k_2)z} \tag{5.8}
\]
where $P_\perp$ denotes the amplitude of induced second-order polarization perpendicular to the propagation direction $z$, the wavenumbers of the fundamental and the frequency-doubled radiation are denoted $k_{1,2}$, and $n_1$ is the refractive index at the fundamental wavelength. The amount of generated second harmonic radiation thus depends on three ingredients:

1. The second-order electric susceptibility $\chi^{(2)}$. Typical magnitudes are on the order of less than 1 pm/V, though certain materials like lithium niobate (LiNbO$_3$), where it is possible to use quasi-phase matching techniques, may feature much larger values up to 27 pm/V [100].

2. The fundamental electric field strength $E_1$. The induced polarization $P_\perp$ depends on $E_{1}^2$, which is why the SHG process becomes much more efficient at higher incident powers. In continuous wave (cw) applications with optical powers $P \ll 1$ kW it is rarely sufficient to irradiate the bare nonlinear material if one is interested in a decent conversion efficiency. Common techniques to increase the conversion efficiency include using waveguides within the nonlinear crystal [101] (confining the fundamental light thus maintaining a high intensity across the entire medium) or placing the crystal inside a resonant optical cavity (increasing the intensity of the fundamental, the harmonic, or both).

3. The wavenumber mismatch $\Delta k = 2k_1 - k_2$. The harmonic waves generated at different locations inside the nonlinear medium must interfere constructively to add up in magnitude. In a macroscopic medium this is only possible for the phase-matched situation $\Delta k = 0$, which must hold at least on average. In general though, $\Delta k$ will be non-zero due to dispersion in the crystal ($n_1 \neq n_2$). It is the goal of phase-matching techniques to maintain $\Delta k = 0$ over the entire crystal length.

In certain cases, it is possible to compensate dispersion by using non-critical phase matching, which means that equal refractive indices $n_{1,2}$ are obtained independently from the angle of incidence of $E_1$ onto the crystal. Usually, one would choose a particular crystal temperature that equalizes the two refractive indices. Critical phase matching on the other hand relies on birefringence of the nonlinear medium to compensate for dispersion: As the refractive index in birefringent matter generally depends on the direction of propagation, it may be possible to have $n_1 = n_2$ for a particular angle of incidence.
5. Experimental Techniques

Consider Fig. 5.14 for an illustration of critical phase matching in a birefringent crystal. We distinguish between the ordinary beam \( o \) polarized perpendicular to the optical axis and an extraordinary beam \( e \) polarized at least partially along the optical axis. While the refractive index \( n^o \) for the ordinary beam is independent of its propagation direction, the extraordinary refractive index \( n^e \) varies as the propagation direction is altered. This fact is illustrated in Fig. 5.14 by ellipses that represent the refractive index along the respective propagation direction in a polar plot. We can see two index surfaces, one for the ordinary beam at the fundamental wavelength \( \lambda_1 \) and one for the extraordinary beam at the harmonic wavelength \( \lambda_2 = \lambda_1/2 \). Since \( n^o_1 \) is independent of the direction of propagation, its index surface is a sphere – or a circle respectively in the cross-section shown here. The extraordinary index ellipsoid \( n^e_2 \), on the other hand, is compressed for directions perpendicular to the optical axis. Crystals with such a behavior are called negative uniaxial.

Phase matching is clearly achieved for a propagation direction where \( n^o_1 = n^e_2 \), i.e. the direction where the two index ellipsoids cross. This is only possible if one of the ellipsoids corresponds to the extraordinary beam. Thus, for critical phase matching at least one of the three photons taking part in the SHG process must have an extraordinary polarization. The case depicted in Fig. 5.14 assumes that both fundamental photons are ordinary-polarized while the harmonic photon is extraordinary-polarized. The respective SHG process is therefore called an \( ooe \) process.

The phase propagation of the harmonic wave is identical to the fundamental wave for a phase-matched situation. The harmonic Poynting vector however is perpendicular to the respective index ellipsoid, which is why it will enclose an angle with the direction of phase propagation, commonly termed the walkoff angle \([99]\). It will cause the harmonic beam to increase its size along one dimension. This is usually undesired, which is why the walkoff angle should preferably be kept small.

5.1.4.2. Experimental implementation

For this work, we have decided to use lithium triborate \( \text{LiB}_3\text{O}_5 \) (LBO) as a nonlinear material. It is a uniaxial crystal with a nonlinear coefficient \( d_{\text{eff}} = 0.82 \text{ pm/V} \) for the \( ooe \) process at \( \lambda_1 = 976 \text{ nm} \) (two photons of ordinary polarization generate one harmonic photon of extraordinary polarization). We have used AS-Photonics’s SNLO software to calculate the corresponding phase-matching conditions. At room temperature \( (T = 295 \text{ K}) \) the direction of propagation for the fundamental wave should be aligned...
5.1. Laser source

Figure 5.14. Critical phase matching of an ooe process in a negative uniaxial crystal. Depicted on the left are the index surfaces for the fundamental and the harmonic photons. The refractive index of the ordinary-polarized (perpendicular to the plane of projection) fundamental photons is independent from the direction of propagation, which is why the respective index surface is a sphere. The extraordinary-polarized (in the plane of projection) harmonic photon experiences different indices of refraction depending on its direction of propagation. The corresponding index surface is an ellipsoid of revolution about the optical axis. For the particular direction of propagation sketched in red, the ordinary and extraordinary indices of refraction are identical, we have phase matching. The Poynting vectors (yellow) are perpendicular to the respective index ellipsoid, which is why they point to different directions for $o$ and $e$ beams. The walkoff angle $\rho$ widens the harmonic beam (blue) in the plane of projection.

at 17.3° with respect to the optical axis. The walkoff angle for this configuration is a moderate $\rho = 0.59°$.

The conversion efficiency $\eta$ of the SHG process is defined by

$$ P_2 = \eta P_1^2 $$

where $P_{1,2}$ denote the powers of the fundamental and the harmonic, respectively. Usually, $\eta$ is specified in units of %/W. The single-pass conversion efficiency for a 10 mm LBO crystal does not exceed $\eta = 0.01%$/W corresponding to less than $P_2 = 10 \mu$W of harmonic power at an input fundamental power of $P_1 = 300$ mW. Therefore, we have built a cavity around the crystal which is resonant with the fundamental. With a finesse $\mathcal{F} \approx 200$ it increases the intra-cavity fundamental power by about two orders of magnitude. Accordingly, the conversion efficiency is increased to $\eta = 60%$/W. At
5. Experimental techniques

A fundamental optical power of $P_1 = 300 \text{ mW}$ we thus measure a harmonic output power of $P_2 = 54 \text{ mW}$.

Fig. 5.15 illustrates the doubler setup. Reflection losses at the LBO interfaces are minimized by cutting the crystal at Brewster’s angle for the fundamental ($58.1^\circ$). Since the cavity is parallel to the optical table, this configuration requires the fundamental to be p-polarized. The polarization of the harmonic wave is in turn determined by the ooe process to be perpendicular, i.e. s-polarized. LBO is known to be slightly hygroscopic, which is why we purge the crystal using dry nitrogen. The housing enclosing the crystal is made of acrylic glass and includes a small capacitive humidity sensor (IST P14-TR) for monitoring purposes.

The doubler cavity must be stabilized in length in order to remain resonant with the fundamental wave. In our setup, we have realized a Hänsch-Couillaud length locking technique [102]. A typical error signal is depicted in Fig. 5.17. Feedback is provided by a movable cavity mirror. It is mounted onto a piezo tube (Thorlabs AE0203D04F) whose backside is glued to a 40 g piece of stained steel to minimize recoil effects. Its maximum displacement of 4.6 µm corresponds to a frequency tuning range of 3.2 GHz at $\lambda_1 = 976$ nm.

Walkoff within the LBO crystal will result in an elliptical beam shape at the doubler output. Using a set of spherical and cylindrical lenses we re-shape it into a collimated, circular beam.

5.1.4.3. Cavity design

An optimum conversion efficiency for the SHG process requires appropriately focusing the fundamental light into the crystal. In general, three ingredients will determine the cavity layout:

1. There is an optimum waist for the fundamental inside the crystal that maximizes the conversion efficiency. If the waist is too big, the intensity of the fundamental beam will be accordingly low, thus reducing the conversion efficiency. On the other hand, if the waist at the center of the crystal is too small, the beam diverges too quickly and loses intensity towards the crystal edges, again reducing the efficiency. For our crystal (length $l = 10$ mm) we have calculated the optimum waist to be $w = 24$ µm using Boyd-Kleinman theory [95].

2. From Fig. 5.15 it is clear that the fundamental has a non-zero angle of incidence onto the crystal surfaces. This will introduce astigmatism thus causing the cavity
5.1. Laser source

Figure 5.15. Schematic of the frequency doubler setup. The fundamental beam (red) enters the cavity from the left through a set of mode-matching lenses \( l_1 \) and \( l_2 \). The cavity itself is of the bow-tie type and is formed by mirrors \( m_1 \) through \( m_4 \). It is stabilized in length using the Hänsch-Couillaud locking technique. A commercial piezo amplifier (Thorlabs MDT694) applies feedback to cavity mirror \( m_2 \). Lenses \( l_3 \) through \( l_5 \) re-collimate the harmonic output (blue) and make the beam shape circular. GP is a glass plate that reduces the optical power incident on the photodiodes \( \text{pd}_1 \) and \( \text{pd}_2 \). \( \text{pd}_3 \) measures intra-cavity oscillating power by monitoring the radiation leaking through \( m_3 \). BD: beam dump.

beam profile to become elliptical in general. For certain folding angles \( \alpha \) of the cavity however, this astigmatism can be compensated. \( \alpha = 31.4^\circ \) in our case.

3. The radius of curvature \( r = 50 \text{ mm} \) for \( m_3 \) and \( m_4 \) will ultimately determine the cavity length \( l = 441 \text{ mm} \). Accordingly, the free spectral range of the cavity is 680 MHz.

All the calculations necessary to optimize the doubler cavity have been carried out using Piet Schmidt’s BYOD software [103]. Apart from the layout parameters, it will also provide the optimum reflectivity \( R_1 \) for the input coupling mirror \( m_1 \). Its reflectivity should be adjusted such that the transmitted power equals the cavity loss (most of which is due to conversion to the harmonic wave). In other words, the impedance of the cavity must be matched. For our cavity design, \( R_1 = 99\% \) while the other cavity mirrors each feature reflectivities of \( R_{2,3,4} = 99.95\% \) to minimize losses. In addition, the mirror coating of output coupler \( m_4 \) is designed such that its transmission at \( \lambda_2 = 488 \text{ nm} \) is maximized. It is shaped as a zero lens (convex and concave surfaces
5. Experimental techniques

Figure 5.16. Top view on the frequency doubler setup. The lens mounted on the translation stage (left side) makes part of the incoupling telescope.

Figure 5.17. Typical transmission and error signals of the cavity used for frequency doubling acquired while scanning the PZT-mounted cavity mirror $M_2$. The error signal is generated by subtracting the outputs of photodiodes $PD_1$ and $PD_2$, while cavity transmission (offset in this plot by 0.2 V from the error signal) is measured by monitoring the radiation leaking through $M_3$. 
with identical radii of curvature) to minimize refraction of the harmonic beam exiting the cavity.

5.2. Detectors

Any detection method aimed at single-emitter sensitivity relies on very efficient detection of light. For absorption measurements, the detector should feature a shot-noise limited operation. Fluorescence techniques on the other hand require good collection efficiencies and the ability to detect low light fluxes on the level of only few photons per second.

5.2.1. CCD camera for sensitive absorption

Finding a good detector for absorption measurements is guided by two requirements:

1. As we will see in subsection 7.2.1.1 the extinction signal is maximized upon excitation with the saturation intensity. Corresponding excitation powers can be quite low for diffraction-limited focusing to an area \( A \approx \lambda^2 \). An absorption detector must be able to detect these powers reliably.

2. Any excess noise in the absorption detection process might mask the actual extinction effect. A good detector thus minimizes noise and ideally features shot-noise limited performance.

Rare-earth ions can have very low saturation intensities on the order of only a few mW \( \cdot \) cm\(^{-2}\). Corresponding diffraction-limited excitation powers are on the scale of picowatts or \( 10^6 \) photons per second. One of the commercially available detectors whose signal can be shot-noise limited at those powers, are CCD chips commonly used in cameras. In our setup, we use a Peltier-cooled, back-illuminated CCD camera (Andor iXon) featuring a detection efficiency of \( \eta = 89\% \) at 488 nm. We image the light to be detected onto an area spanning approx. 100 pixels. As each pixel has a full-well capacity of \( 1.5 \cdot 10^5 \) electrons, or correspondingly \( 1.7 \cdot 10^5 \) photons, up to \( 1.7 \cdot 10^7 \) photons can be detected within one acquisition. Usually, we would operate the CCD at an acquisition time \( t_{\text{int}} = 10 \text{ ms} \) and half the full-well capacity in order to minimize nonlinear effects. This way we can detect up to \( 8.5 \cdot 10^8 \) photons per second, corresponding to 350 pW of optical power.
5. Experimental techniques

The excess noise introduced by the CCD chip is mostly due to readout noise, which is independent from the number of photons detected. As such, its relative contribution can be very low for large signals. In our case, the single-pixel readout noise is 8.8 electrons per acquisition. Thus, the total noise for a typical readout area of $150 \times 300$ pixels is $\sqrt{150 \cdot 300 \cdot 8.8} = 1.9 \cdot 10^3$ per acquisition or $\sqrt{100 \cdot 1.9 \cdot 10^3} = 1.9 \cdot 10^4$ per second at an acquisition time $t_{\text{int}} = 10$ ms.

Knowledge of the maximum detectable signal and the corresponding noise allows an assessment of the dynamic range $\text{DR}$ given by

$$\text{DR} = \frac{\text{max. detectable signal}}{\text{noise}},$$

often also specified as its logarithmic equivalent

$$\text{DR}_{\text{dB}} = 20 \text{ dB} \cdot \log \text{DR}.$$  \hspace{1cm} (5.10)

The value obtained this way is a measure for the smallest detectable signal. Thus, for an assumed extinction ratio of $10^{-3}$, we require $\text{DR}_{\text{dB}} > 60 \text{ dB}$. Using the values from above for our CCD chip, we calculate a dynamic range $\text{DR}_{\text{dB}} = 93 \text{ dB}$. This is large enough to detect extinction ratios on the order of $10^{-5}$. At an incident power of $8.5 \cdot 10^8$ photons per second, the CCD noise figure thus remains below shot noise, which is why the detector is said to deliver shot-noise limited performance.

5.2.2. PMT for rapid absorption

In holeburning measurements one often wants to rapidly tune the probe laser frequency across the spectral hole to minimize the dynamics which take place during the acquisition time. Accordingly, the detector monitoring the absorption through the sample should be fast enough to follow the possibly steep changes of the signal. With our CCD camera we are limited to acquisition times $t_{\text{acq}} > 10$ ms, which might not suffice in certain holeburning experiments.

In these cases we use a photomultiplier (PMT, Hamamatsu R1564U) whose anode current is converted directly into a voltage by shortening the PMT connectors with a
variable resistor $R$. While larger values of $R$ will boost the voltage signal, they also decrease the timing resolution $\Delta t$ according to

$$\Delta t = 2\pi \cdot R \cdot C$$

(5.12)

where $C$ is the PMT capacitance. As we are not interested in the single photon response, we would usually use a resistor $R = 10 \text{ k}\Omega$ that gives a timing resolution of $\Delta t \approx 1 \, \mu\text{s}$. The PMT gain is then adapted to the experimental photon flux to produce output voltages on the order of $1 \text{ V}$.

5.2.3. Low-noise APD for fluorescence

The SNR of fluorescence detection schemes is often limited by spurious background noise and detector dark counts (see subsection 7.2.1.2 for a more detailed discussion). For rare-earth emitters embedded into transparent crystalline materials we can most probably neglect background fluorescence. Thus, the main source of noise will be detector dark counts. They should be minimized below the shot noise of the fluorescence signal.

Tab. 3.3 suggests a fluorescence lifetime of $\tau \approx 200 \, \mu\text{s}$ for the $^{1}\text{D}_2$ manifold of Pr:YSO. Thus, we may expect 50 Hz for the rate of collected photons at a detection efficiency of 1%, which is a common efficiency figure for cryogenic optical setups. According to what we said before, detector dark counts should be less than 50 Hz. We have chosen to work with an ultra-low-noise avalanche photodiode (APD, ID Quantique model id-100-20) whose dark count rate is reduced by making the active detector area as small as $300 \, \mu\text{m}^2$. It typically produces 3 dark counts per second, and features a quantum efficiency of 28% at $\lambda = 606 \, \text{nm}$. Therefore, we can expect a shot-noise limited performance at incident photon rates of 11 Hz or more.

5.2.4. Shot-noise limited performance

Since the APD records the signal in a direct fashion, by counting the detected photons, it is relatively easy to reach the shot-noise limited regime in a fluorescence detection scheme. Any incident photon rate $\geq 11 \text{ Hz}$ will be detected in a shot-noise limited fashion.

Extinction detection on the other hand is more delicate from an experimental point of view, as it relies on a very stable ratio of the signal and its respective reference.
5. Experimental techniques

While the CCD camera may, in principle, facilitate shot-noise limited observation of an absorption experiment, most of the time the extinction signal is dominated by excess noise introduced before the detection process. Common sources of excess noise include temperature fluctuations on the order of seconds and acoustic vibrations on the order of milliseconds. Both of them will cause the extinction signal to degrade by introducing different intensity fluctuations to the signal and reference beams. They are only apparent however if the experiment’s duration coincides with one of these timescales. Thus, the first approach to shot-noise limited detection is to operate the experiment at frequencies where excess noise sources are minimized, which is often true at frequencies beyond 100 kHz. Should this not be possible, e.g. due to long integration times, noise on the relevant time scales has to be reduced. While efficient passive and active techniques exist to compensate for acoustic vibrations, stabilizing the temperature of an experimental apparatus can become involved, in particular for spacious setups. A small example illustrates why: If we want to prevent optical interference (often present) from degrading our signal, the length stability of the beamline should be much smaller than $\lambda/2$. This requires a temperature stability of $\Delta T < 10 \text{ mK}$ assuming a total length of 2 m and common construction materials like aluminum or stained steel.

5.3. Optical setup

The optical setup for experimentation is centered around a flow cryostat (Janis Research ST-500, see Fig. 5.20) that is able to cool samples on its cold finger down to a minimum temperature of $\sim 3.8 \text{ K}$. Usually however, we would operate the cryostat without pumping the helium line, thus achieving stable temperatures of $T = 4.3 \text{ K}$.

The cryostat itself is mounted on an optical table in such a way that the optical axis through the cryostat is perpendicular to the table surface. For simple reflection measurements it would be sufficient to clamp the cryostat directly onto the optical table. However, since we also want to be able to carry out transmission experiments, we have placed the cryostat onto an “elevation table” that allows placing some optics beneath the cryostat. Optics for the excitation and detection beam paths are placed on a breadboard table that facilitates optical access to the cryostat through its top window. Fig. 5.18 depicts the relevant part of the optical setup.

The optical components on the breadboard table are schematically illustrated in Fig. 5.19. Excitation light is fed to the table through a single-mode polarization-
5.3. Optical setup

Figure 5.18. Cryostat (lower left) on its elevation table alongside with the optical setup on a breadboard table (center). The excitation beam always runs on top of the breadboard. Emission from the sample detected in a reflection geometry is collected on the breadboard before being passed on to the detectors (housing on the upper right). For transmission measurements, a small mirror is placed beneath the cryostat again directing the beam to the detectors.

maintaining optical fiber (Thorlabs PM-S460-HP). It passes through a polarizer and a half-waveplate for precise polarization control. A beam expander increases the size of the beam in order to overfill the objective entrance aperture, thus minimizing the focal spot size on the sample. Scanning the beam across the sample is achieved using a galvanometer mirror and a telecentric lens pair in a 4f configuration \[105\] with the microscope objective (Zeiss LD Plan-Neofluar 63x, NA = 0.75). Fluorescence from the sample is collected in an epi-configuration and separated from the excitation beam at a beam splitter that may either be a simple glass plate (if achromaticity is an issue) or a dichroic mirror/longpass filter (if maximum excitation power is an issue). The transmitted beam on the other hand is recollimated within the cold finger using a molded aspheric lens (Thorlabs 352330).
In order to maximize the radiation incident on one of the detectors in our setup, we have inserted flip mirrors into the detection path (not shown in Fig. 5.19). This way, the total collected optical power is directed onto one particular detector (as opposed to splitting it towards independent detectors).

**Collection efficiency**

The amount of light radiated by a single emitter into the direction of observation depends on the position of the emitter within the sample and the refractive index structure around it. Ref. [106] gives a detailed recipe how to calculate the distribution of radiation. As a rule of thumb, the larger portion of the emitted radiation will be directed
5.3. Optical setup

Figure 5.20. Cross-section through the Janis Research ST-500 flow cryostat. The sample is mounted on top of the cold finger right beneath the window. It may have an arbitrary height as long as the cold finger is adapted to the sample dimensions. The cold finger and respective mount are made from oxygen-free copper (OFHC) plated with gold to prevent them from oxidizing, while radiation shield and lid are made from aluminum. The window on top is 0.5 mm thick and facilitates optical access with an NA close to unity.

towards the medium with the higher refractive index $n$. Therefore, in order to increase the collection efficiency, we should make sure that the emitters are sandwiched in a sample geometry which features a high-$n$ material in the direction of observation.

Consider the sample geometries depicted in Fig. 5.21 as an example. The half-sphere shape (b) will increase the emission into the upper hemisphere by more than a factor of eight. A different approach makes use of immersion oil between sample and objective in order to increase the numerical aperture (NA) by a factor $n_{	ext{oil}}/n_{	ext{sample}}$. While this technique has originally been developed for microscopy applications at ambient temperatures, it has been transferred and adapted to cryogenic setups by using a high refractive index solid immersion material placed between sample and objective \cite{107}. It usually has the shape of a half sphere in order to prevent refraction of the beams emerging from the sample (see Fig. 5.21c). See Tab. 5.2 for a comparison of the calculated collection efficiencies for the different sample geometries.

We have experimentally investigated the effect of using a solid-immersion lens on flat samples using fluorescent quantum dots. A quantum dot sample was spin-coated onto the flat side of the SiL and imaged on a CCD camera under wide-field illumination
5. Experimental techniques

Figure 5.21. Cross-section through three different sample geometries of Pr:YSO. The emitter marked in red resides at the sample interface (refractive index $n = 1.8$). While case (a) directs 10.6% into the upper hemisphere, 88.6% of the radiation are directed upwards through the curved interface for configuration (b). The polar intensity plots were calculated for the $^1$D$_2 \rightarrow ^3$H$_4$ fluorescent decay according to [106]. Case (c) illustrates a setup using a solid immersion lens. The sil increases the numerical aperture of the collection optics by a factor $n_{SIL}/n_{sample}$. The hemispherical shape depicted here makes sure that the beams emerging from the sample impinge perpendicularly onto the curved sil surface, thus avoiding refraction.

<table>
<thead>
<tr>
<th>sample geometry</th>
<th>fraction of emission into upper hemisphere</th>
<th>collected</th>
<th>detected</th>
</tr>
</thead>
<tbody>
<tr>
<td>flat sample</td>
<td>10.6%</td>
<td>6.3%</td>
<td>1.8%</td>
</tr>
<tr>
<td>half-ball sample</td>
<td>82.1%</td>
<td>48.4%</td>
<td>13.6%</td>
</tr>
<tr>
<td>solid immersion lens</td>
<td>73.1%</td>
<td>28.8%</td>
<td>8.1%</td>
</tr>
</tbody>
</table>

Table 5.2. Collection and detection efficiencies of fluorescence radiation at $\lambda = 606$ nm for different sample geometries. Collection efficiencies were calculated assuming a 0.75 NA objective, while detection efficiencies correspond to a detector with a 28% quantum efficiency. Refractive indices of the sample and the solid immersion lens were assumed as $n_{sample} = 1.8$ and $n_{SIL} = 2.2$. 
5.3. Optical setup

![Image of fluorescence signal and cross-section](image)

**Figure 5.22.** Fluorescence signal of a quantum dot imaged on a CCD camera. (a) Raw image data scaled to the actual dimensions of the sample. (b) Cross-section through the data at the line indicated in (a). The FWHM of the spot is 190 nm for a solid immersion lens of refractive index $n = 2.2$.

as depicted in Fig. 5.22. This allows us to directly compare the collected signals, as we can assume that the excitation intensity with and without sil are comparable to first order. Integrating the fluorescence signal of single quantum dots under the sil reveals a $8.8 \pm 1.7$ fold increase compared to a situation without solid immersion lens (see Fig. 5.23).

However, for a maximum collection efficiency, we should use a hemispherically shaped sample of Pr:YSO. Emission from the Pr$^{3+}$ dopant ions is collected by a Zeiss LD Plan-Neofluar 63x objective with an NA of 0.75 and guided to the APD detector by means of several optical elements (mirrors, lenses) which introduce losses of approx. 10%. Thus, we should achieve a total collection efficiency of 48%. In combination with the low-noise APD mentioned before (quantum efficiency of 28% at $\lambda = 606$ nm), we arrive at an estimated total detection efficiency of $\eta = 13\%$ for a fluorescence detection scheme. Note that this is a theoretically calculated value. An experimental estimation of the collection/detection efficiency requires comprehensive data on the decay properties of the emitter $^{108}$, which were not available in our case.
5. Experimental techniques

![Figure 5.23](image)

Figure 5.23. Assemblies used to estimate the increase in collection efficiency by using a solid immersion lens. (a) Situation with a zirconia solid immersion lens. (b) Situation without solid immersion lens. In this case, the sample is spin-coated on a common microscopy cover slip.

5.4. Data acquisition

Narrow-band spectral information in our setup is always acquired by tuning the laser frequency incident on the sample. We have three ways of accomplishing this:

1. Locking the laser to stabilization cavity A. This cavity includes a PZT-mounted mirror which allows the cavity – and thus also the laser – to be tuned in frequency.

2. Locking the laser to stabilization cavity B and tuning the frequency of AOM₁ in Fig. 5.1

3. Locking the laser to stabilization cavity B and tuning the frequency of AOM₂ in Fig. 5.1. This method restricts the tuning range to 100 MHz. However, since the frequency-doubled beam is affected directly, it offers the advantage that the beam intensity can be modulated at the same time.

5.4.1. AOM control

Spectral holeburning and lifetime measurements both rely on method 3 to tune the laser frequency and its intensity. The respective AOM (Panasonic TEM-200-50) is used in a double-pass configuration and shifts the optical frequency of the SHG beam at \( \lambda = 488 \) nm by as much as \((400 \pm 100)\) MHz. It is driven by a power amplifier whose
5.4. Data acquisition

Figure 5.24. VCO output frequency vs control voltage. It has been measured by mixing the VCO output with a fixed frequency from a stabilized signal generator (Hewlett-Packard 8657B) and monitoring on a scope which control voltage produces the maximum output at the mixer. Actual measurements are denoted by crosses, the red line is a 5th order polynomial fit.

rf input is generated by either a voltage-controlled oscillator (VCO) or a direct digital synthesizer (DDS).

We have used the VCO frequency generator for our first holeburning experiments. Both the laser frequency and the amplitude are controlled by analog signals, which is relatively easy to implement. The output frequency exhibits a non-linear dependence on the control voltage however. Proper calibration is necessary to compensate for this behavior (see Fig. 5.24).

Different means of frequency generation have to be used for experiments in Pr:YSO that try to circumvent holeburning effects. As holeburning is due to a redistribution of electronic population among the three hyperfine levels in the $^3\text{H}_4$ ground state, any single optical frequency within the inhomogeneous broadening will burn a spectral hole. In order to avoid holeburning we should make sure that we excite all three ground-state hyperfine levels at the same time. For this purpose, we have built a DDS frequency generator that allows us to combine up to three different rf signals whose frequencies and amplitudes can all be controlled individually. Its design largely follows Ref. [109]. Three integrated DDS circuits (Analog Devices AD9858) with respective amplitude modulation circuits are digitally controlled by an Atmel ATmega1280 microcontroller. We may supply commands to the microcontroller either from a USB
interface or by manual interaction through a touchwheel and a small liquid crystal display.

Slow tuning with update rates below 100 Hz is achieved by feeding the desired frequencies and amplitudes directly to the microcontroller via USB. Higher update rates are hard to achieve since the USB transmission time lag and jitter of approx. 10 ms limit the timing accuracy. For faster tuning, we thus switch the operation mode of the DDS circuits to tuning mode and directly provide them with the relevant tuning parameters (tuning speed, tuning range, and frequency resolution). One command subsequently sent over USB will then start the tuning process.

5.4.2. Synchronization

In general, any data acquisition is controlled, processed, and triggered from a LabVIEW controlled computer program. This is true for acquiring data from an APD and from photodiodes. In this case, the timing of the laser frequency/intensity updates and the detector integration time/readout is entirely controlled by the LabVIEW program. A slightly different case arises when we use the CCD camera for observation. Its frame rates are considerably lower for external triggering (trigger signal fed to the camera) than for internal triggering (camera generates the trigger signal), thus imposing a higher experimental duty cycle than necessary. Therefore, we let the camera trigger experiments detected by the CCD. Its trigger signal is fed to the computer’s data acquisition electronics, which in turn controls the laser parameters.
6. Spectroscopic measurements of ensembles

6.1. Absorption spectra

6.1.1. Overview spectra

For an overview of the Pr:YSO spectral features we have taken unpolarized absorption spectra at different temperatures ranging between $T = 4\, \text{K}$ and $T = 300\, \text{K}$. Consult Fig. 6.1 for an illustration of the setup. Two Pr:YSO samples with doping concentrations of 0.05% and 0.005% were mounted inside a flow cryostat (Janis ST-500) and illuminated using a 75 W xenon white-light source. The focusing lens in front of the cryostat was chosen such that the xenon lamp was imaged onto the crystal, roughly extending 5 mm on its top surface. Light shining through the sample was coupled into a multimode optical fiber and sent to a commercial uv-vis spectrometer (Acton Research SpectraPro 500), which recorded absorption spectra at a resolution of $\Delta \lambda = 0.15\, \text{nm}$. We have normalized the 0.05% spectrum by taking the 0.005% spectrum as a reference. This way, the sample geometry is identical for both measurements, merely the sample concentration differs, thus canceling any absorbance effects due to refraction or reflection at the sample interfaces.

The absorption spectrum of the $^3P_J$ manifold is plotted in Fig. 6.2 where absorbing manifolds are highlighted in gray. At ambient temperatures, the spectrum is governed by homogeneous broadening due to phononic interactions with the YSO crystal. Only at cryogenic temperatures is it possible to observe narrow spectral features. The two rightmost low-temperature peaks in Fig. 6.2 correspond to the site 1 ($\lambda = 488\, \text{nm}$) and site 2 ($\lambda = 484\, \text{nm}$) transitions to the $^3P_0$ level.
6. Spectroscopic measurements of ensembles

Figure 6.1. Schematic used to record absorption spectra of Pr:YSO at various temperatures.

Figure 6.2. Pr:YSO absorption spectra in the range between 430 nm and 500 nm. Total integration time for one spectrum was 4 s, split among 200 consecutive acquisitions. We have highlighted in gray the respective manifolds causing absorption. Sharp spectral features are only visible at temperatures below 200 K. Note also that absorption peaks due to thermally populated ground-state levels, e.g. at $\lambda = 490$ nm (indicated by the small vertical arrow), disappear at cryogenic temperatures.
6.1.2. Inhomogeneous broadening

We have measured the inhomogeneous broadenings of the $^{3}H_4 \leftrightarrow ^3P_0$ absorption lines using the setup sketched in Fig. 5.19. The Ti:Sa laser was stabilized to cavity A and tuned by ±8 GHz around the center of the inhomogeneous profile. The tuning range of the frequency-doubled beam was ±16 GHz accordingly. While the laser frequency was tuned in a smooth fashion, fluorescence from the sample was collected in a confocal setup with a 63x microscope objective and detected on an APD using integration times of $t_{\text{int}} = 100$ ms. At the same time, we monitored the laser intensity on an amplified photodiode and determined the absolute wavelength using a wavemeter (HighFinesse WS/6, timing resolution 40 ms).

The cavity used for frequency doubling will follow the laser tuning process as long as the PZT is allowed to move within its maximum displacement range $\Delta \nu = 3.2$ GHz. Tuning the fundamental beam beyond that range will cause the doubler cavity to lose its lock. As our locking electronics did not feature re-locking to the next possible cavity mode, we have manually re-locked the cavity during the tuning process. However, the mode hop causes a lag of approx. 200 ms during which the frequency doubler will not emit any output. We have removed the corresponding pieces from the acquired data.

Spectra for site 1 ions in Pr:YSO are plotted in Fig. 6.3. We have recorded the inhomogeneous profiles of both a 0.05% Pr:YSO sample and a YSO sample that was specified as “undoped”. Mass spectrometry of a tiny portion of the undoped sample (obtained by laser ablation) confirmed that the number concentration of $Pr^{3+}$ ions is below $10^{-8}$ for this sample. This fact explains the somewhat small SNR. Still, the inhomogeneous center $\lambda_c = 487.997$ nm and the profile width $\Delta \nu = 6.0$ GHz can be reliably determined. The inhomogeneous width of the 0.05% doped sample is $\Delta \nu = 12.1$ GHz, which is twice as large compared to the undoped sample. We attribute this finding to increased strain within the crystal, which expectedly occurs at higher doping levels.

Investigating the inhomogeneous line profile for site 2 ions means changing the laser frequency from $\lambda_2 = 488$ nm to $\lambda_2 = 484$ nm. This modification involves re-aligning the frequency doubler setup in order to optimize the SHG phase-matching for the altered wavelength. Otherwise, the measurement procedure is identical to the one outlined above. For the site 2 measurement plotted in Fig. 6.4, we have used a 0.05% doped crystal of Pr:YSO. The center is at $\lambda_c = 483.979$ nm, the full width half maximum is $\Delta \nu = 10.1$ GHz.
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Figure 6.3. Inhomogeneous broadening of the $^3H_4 \leftrightarrow ^3P_0$ transition for site 1 ions in Pr:YSO. The concentration of Pr$^{3+}$ ions was below $10^{-6}\%$ for the blue trace and 0.05\% for the yellow trace. The fits colored red and green represent Lorentzian line profiles.

Figure 6.4. Inhomogeneous broadening of the $^3H_4 \leftrightarrow ^3P_0$ transition for site 2 ions in Pr:YSO. The concentration of Pr$^{3+}$ ions was 0.05\%.
6.1. Absorption spectra

<table>
<thead>
<tr>
<th></th>
<th>site 1</th>
<th>site 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>pol. along $D_1$</td>
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</tr>
<tr>
<td>pol. along $D_2$</td>
<td>9.8</td>
<td>0.14</td>
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</tbody>
</table>

Table 6.1. Absorption coefficients $\alpha$ in units of cm$^{-1}$ for the $^3H_4 \leftrightarrow ^3P_0$ transition in 0.05% Pr:YSO for light propagating along the crystal $b$ axis.

6.1.3. Absorption coefficients

The sample absorption was determined by measuring the optical powers before ($P_0$) and behind the cryostat ($P$) at two different wavelengths: one in the center of the inhomogeneous profile ($P_{on}$), and one with the laser shifted 500 GHz to the red ($P_{off}$). With a Lorentzian inhomogeneous profile whose FWHM is around 10 GHz, it is appropriate to assume that absorption at the red-shifted wavelength is negligible. According to Beer’s law [4.1] we can then calculate the absorption coefficient $\alpha$ according to

$$e^{-\alpha l} = \frac{P_{on}}{P_{off}} \frac{P_{off}}{P_{on}}$$  \hspace{1cm} (6.1)

where $l = 3$ mm is the sample thickness and the second fraction compensates for losses in the optical path that are not due to sample absorption. We used a calibrated commercial power meter to measure the required optical powers. A 300 mm lens was used to focus the laser through the sample yielding a waist $w = 40$ µm in the focus. At maximum excitation powers of 60 µW, the respective maximum intensity in the focus was $I_{exc} = 1$ W cm$^{-2}$. As the propagation direction of the excitation beam was aligned along the crystal’s $b$ axis, we were able to determine the absorption coefficients for polarizations along the remaining two crystal axes $D_1$ and $D_2$. These results are summarized in Tab. 6.1.

When it comes to calculating the absorption cross-sections of the individual Pr$^{3+}$ emitters, it is important to know the number of resonant Pr$^{3+}$ ions as well. As the linewidth of our excitation laser was $\Delta \nu_{exc} = 100$ kHz (locked to cavity $\Lambda$), orders of magnitude smaller than the inhomogeneous linewidth $\Gamma_{inh} = 10.1$ GHz, we should take into account Eq. (4.4) to correctly estimate the number of ions resonant with the excitation beam. Results are listed in Tab. 6.2.
Table 6.2. Absorption cross-sections $\sigma_{\text{abs}}$ in units of cm$^2$ for the $^3\text{H}_4 \leftrightarrow ^3\text{P}_0$ transition in 0.05\% Pr:YSO for light propagating along the crystal $b$ axis.

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<tr>
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<th>site 1</th>
<th>site 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>pol. along $D_1$</td>
<td>$2.1 \cdot 10^{-12}$</td>
<td>$6.4 \cdot 10^{-13}$</td>
</tr>
<tr>
<td>pol. along $D_2$</td>
<td>$8.4 \cdot 10^{-13}$</td>
<td>$1.2 \cdot 10^{-14}$</td>
</tr>
</tbody>
</table>

The excitation intensities used to measure the results of Tabs. 6.1 and 6.2 might be too large thus saturating the sample and yielding absorption coefficients that are too small. Therefore, we have investigated the site 1 transition for light polarized along the $D_1$ axis more carefully. Using a 0.005\% doped sample of Pr:YSO ($\Gamma_{\text{inh}} = 8$ GHz) and an excitation intensity in the focus of $I_{\text{exc}} = 200$ mW $\cdot$ cm$^{-2}$, we determine $\alpha = 7.5$ cm$^{-1}$ and, correspondingly, $\sigma_{\text{abs}} = 5.1 \cdot 10^{-12}$ cm$^2$. The best organic dye molecules feature similar absorption cross-sections.

6.2. Fluorescence spectra

Since we are interested in the absorption and fluorescence properties of the $^3\text{H}_4 \leftrightarrow ^3\text{P}_0$ transition of Pr:YSO, we have recorded fluorescence spectra that also include fluorescent decay from the $^3\text{P}_0$ manifold. Consult Fig. 6.5 for a schematic of the respective optical setup. A sample of 0.05\% Pr:YSO was excited using a 50 mW diode-pumped solid-state (dpss) laser operating at $\lambda = 473$ nm. Fluorescence was collected in an epi-configuration using a 63x microscope objective and coupled into a multimode optical fiber connected to an Acton Research SpectraPro 500 spectrometer. A 485 nm longpass filter was mounted at a 10° angle of incidence (instead of using a dichroic mirror) to separate the excitation light from emitted fluorescence. Polarization-sensitive measurements were facilitated using a combination of input polarizer and half-waveplate to control the polarization of the excitation beam, and an output polarizer to select the polarization of the emitted fluorescence.

Results for sample temperatures of $T = 300$ K and $T = 4$ K are plotted in Figs. 6.6 and 6.7 respectively. We have highlighted in gray some important transitions between entire manifolds of Pr:YSO (each consisting of several crystal-field split levels). Obviously, a major portion of $^3\text{P}_0$ population decays into the $^1\text{D}_2$ manifold whose fluorescence is then observed. At the excitation wavelength of $\lambda = 473$ nm there was no
6.3. Lifetime measurements

Figure 6.5. Setup used to record Pr:YSO fluorescence spectra at varying temperatures between 4 K and 300 K. Two polarizers in the excitation and detection paths permit polarization-sensitive measurements.

clear dependence on the polarization of the excitation beam, which is why we have included only traces for an excitation polarization that was parallel to the crystal $D_2$ axis. However, the dependence of the fluorescence spectrum on the output polarizer orientation is evident. Apparently, there must be a number of different orientations of the respective transition dipoles. This fact can be explained by taking into account the local symmetries of Pr$^{3+}$ sites $[110]$. To our knowledge however, there have been no detailed studies for Pr:YSO.

6.3. Lifetime measurements

Lifetimes of fluorescent levels determine important emitter properties such as the maximum detectable photon flux or – in combination with the absorption cross-section – the saturation intensity. We have measured the lifetimes of site 1 ions in 0.005% Pr:YSO using a pulsed excitation beam resonant with the $^3H_4 \leftrightarrow ^3P_0$ transition and monitoring the fluorescence decay on an APD (see Fig. 6.8). The pulse train was generated by AOM$_2$ of Fig. 5.1 where the excitation power during a pulse was 110 $\mu$W. By placing appropriate bandpass filters (FWHM = 1 nm) into the detection path, we were able to select the fluorescence decays of either the $^3P_0$ level ($\lambda = 510$ nm for
6. Spectroscopic measurements of ensembles

Figure 6.6. Fluorescence spectrum of 0.05% Pr:YSO detected along the crystal $D_1$ and $D_2$ axes respectively for a sample temperature of 300 K. A dpss laser at 473 nm polarized along the crystal $D_2$ axis was used for excitation. Integration time was 200 ms. Prominent transitions between the Pr:YSO manifolds are highlighted in gray.

Figure 6.7. Fluorescence spectrum of 0.05% Pr:YSO detected along the crystal $D_1$ and $D_2$ axes respectively for a sample temperature of 4 K. A dpss laser at 473 nm polarized along the crystal $D_2$ axis was used for excitation. Integration time was 200 ms. Prominent transitions between the Pr:YSO manifolds are highlighted in gray.
Figure 6.8. Schematic of the optical setup used for the lifetime measurements. The laser beam at $\lambda = 488\,\text{nm}$ is transformed into pulses using an AOM and launched into a microscope fluorescence setup with the Pr:YSO sample residing in a flow cryostat. A 485 nm longpass filter acts as a beamsplitter. It is used under an inclination angle that will reflect the excitation laser while transmitting longer wavelengths. An additional bandpass filter allows us to select the portion of the fluorescence spectrum detected on an APD. The trigger signal from the AOM and the count signal from the APD are both fed to a Stanford Research SR430 multichannel scaler/averager which generates the time traces.

Results for site 1 ions are plotted in Figs. 6.9 through 6.11 for two different sample temperatures of $T = 5\,\text{K}$ and $T = 20\,\text{K}$ respectively. Although the fits follow the data very nicely, we have observed that the fit parameters vary by up to 5% when experimental parameters such as the excitation intensity are changed. We therefore tend to associate a 5% error margin to the decay time values. While the decay times for the $^1D_2$ level between $T = 5\,\text{K}$ ($\tau = 166\,\mu\text{s}$) and $T = 20\,\text{K}$ ($\tau = 163\,\mu\text{s}$) merely exhibit small variations within this error margin, the $^3P_0$ lifetime slightly shortens at $T = 5\,\text{K}$ ($\tau = 1.95\,\mu\text{s}$) compared to higher temperatures ($\tau = 2.14\,\mu\text{s}$).
6. Spectroscopic measurements of ensembles

Figure 6.9. Lifetime of the $^3P_0$ level for site 1 ions in Pr:YSO as monitored by their decay into the $^3H_6$ manifold (transition around 510 nm). Pulses were spaced 25 µs apart with a 4% duty cycle, i.e. they were switched on at $t = 0$ and switched off at $t = 1$ µs. Total acquisition time for these traces was 10 s each. Single-exponential fits to the data are plotted in red.

In general, the overall fluorescence yield is lower at $T = 5$ K. This effect must be attributed to holeburning at that temperature, which removes possibly resonant ions from the ensemble. Accordingly, a smaller number of ions is transferred to the excited state causing less fluorescence. Furthermore, there are discontinuities in the traces recorded at $T = 5$ K. The fluorescence intensity seems to instantaneously follow the excitation pulse both upon switching it on and off. We were not able to attribute this effect to any particular mechanism in Pr:YSO, which would have to involve either very short lifetimes (below the 100 ns rise time of our AOM) or some coherent holographic effect (whose time resolution is limited by the inhomogeneous linewidth to roughly $1/(10 \text{ GHz}) = 0.1$ ns).

Since the transition between $T = 20$ K and $T = 5$ K is accompanied by the emergence of holeburning in Pr:YSO (see section 6.6), we have investigated the possibility of a correlation between holeburning and the discontinuous traces in our lifetime measurements. The holeburning effect in Pr:YSO is caused by redistribution of electronic population among the ground-state $^3H_4$ hyperfine levels, which can only be isolated if the homogeneous linewidth is smaller than the individual hyperfine splittings. The blue trace of Fig. 6.12 represents a lifetime measurement under these conditions. For the red trace of the same graph we have modulated the excitation laser by $\pm 35$ MHz at a rate...
6.3. Lifetime measurements

Figure 6.10. Lifetime of the $^{1}\text{D}_2$ level for site 1 ions in Pr:YSO as monitored by their decay into the $^{3}\text{H}_4$ ground state (transition around 606 nm). Pulses were spaced 1300 µs apart with a 1.5% duty cycle, i.e. they were switched on at $t = 0$ and switched off at $t = 20$ µs. Total acquisition time for these traces was 44 min each. Single-exponential fits to the data are plotted in red.

Figure 6.11. Detail of Fig. 6.10 for the trace recorded at $T = 5$ K. The instant decrease of fluorescence after switching off the excitation beam is clearly visible.
6. Spectroscopic measurements of ensembles

Figure 6.12. Lifetime measurements of the $^3P_0$ level in site 1 ions at $T = 4.4$ K. The blue trace represents a measurement using a fixed laser frequency, while the laser has been modulated over $\pm 35$ MHz at a rate of 1.4 GHz/s for the red trace. Pulses were spaced 50 $\mu$s apart with a 20% duty cycle, i.e. they were switched on at $t = 0$ and switched off at $t = 10$ $\mu$s. Total acquisition time for these traces was 85 s each.

of 1.4 GHz/s during the entire acquisition time. That way, we address all ground-state hyperfine levels even at $T = 5$ K. The trace obviously looks like the one to be expected for higher temperatures (compare with the yellow trace of Fig. 6.9). Thus, what we can conclude is that the discontinuities in the time traces are related to the holeburning effect in Pr:YSO. Further investigation would be necessary though to find the actual mechanism explaining this effect.

Decay traces for site 2 ions are plotted in Figs. 6.13 and 6.14. Their shape did not change with sample temperature as in the case of site 1 ions. Single-exponential fits reveal lifetimes of $\tau = 1.27$ $\mu$s for the $^3P_0$ level and $\tau = 199$ $\mu$s for the $^1D_2$ level. Again, the estimated error of these values amounts to roughly 5%, as changing the excitation intensity results in slightly different decay times.

6.4. Estimation of transition rates

In order to gain a better understanding of the relaxation dynamics within Pr:YSO, we need to examine the various possible decay channels. Their relative strengths are commonly expressed using *branching ratios*, i.e. the percentage of the total decay
6.4. Estimation of transition rates

Figure 6.13. Lifetime of the $^3P_0$ level for site 2 ions in Pr:YSO as monitored by their decay into the $^3H_4$ ground state (transition around 509 nm). Pulses were spaced 25 µs apart with a 4% duty cycle, i.e. they were switched on at $t = 0$ and switched off at $t = 1$ µs. Total acquisition time for this trace was 10 s. A single-exponential fit to the data is plotted in red.

Figure 6.14. Lifetime of the $^1D_2$ level for site 2 ions in Pr:YSO as monitored by their decay into the $^3H_4$ ground state (transition around 608 nm). Pulses were spaced 700 µs apart with a 1.4% duty cycle, i.e. they were switched on at $t = 0$ and switched off at $t = 10$ µs. Total acquisition time for this trace was 29 min. A single-exponential fit to the data is plotted in red.
which goes into the respective channels. In a well-behaved system, which decays purely radiatively, it is quite easy to determine the branching ratios: Integrating over a line in the fluorescence spectrum directly yields the amount of population decayed on the respective channel. Once it is clear how to assign the fluorescence lines to possible decay channels, calculation of the branching ratios is a straightforward task.

Things become a little more complicated when non-radiative decay channels are present as well. By definition, their decay cannot be observed using fluorescence spectroscopy. The decay of the $^3P_0$ manifold in Pr:YSO is such an example. When we excite the $^3P_0$ manifold, a considerable portion of the overall fluorescence emission stems from the $^1D_2$ manifold (see Fig. 6.7); the respective decay channel $^3P_0 \rightarrow ^1D_2$ is a non-radiative one however [16]. In order to still estimate the branching ratios for the $^3P_0$ manifold, we have used a simplified rate equation model, where the decay from $^3P_0$ into the ground state $^3H_4$ may take place either directly or via any of the levels in between. Respective level populations $N_i$ and transition rates $r_{ij}$ are depicted in Fig. 6.15. Note that we have not considered the multiple decay channels of the $^1D_2$ manifold, since we were primarily interested in the branching ratios of the $^3P_0$ manifold. Furthermore, the inclusion of additional decay channels complicates the analysis very quickly. The model should nevertheless provide a good approximation for the actual branching ratios.

Lifetime measurements of the $^3P_0$ and the $^1D_2$ manifolds result in

$$r_{12} + r_{13} + r_{14} + r_{15} = (1.9 \, \mu s)^{-1} \tag{6.2}$$

$$r_{25} = (166 \, \mu s)^{-1} \tag{6.3}$$

while further constraints are derived from the integrated fluorescence intensities emitted on the respective transitions, e.g.

$$\frac{N_1 r_{15}}{N_1 r_{13}} = \frac{\int_{512 \, \text{nm}}^{615 \, \text{nm}} \lambda \, \text{d} \lambda}{\int_{487 \, \text{nm}}^{630 \, \text{nm}} \lambda \, \text{d} \lambda}. \tag{6.4}$$
6.4. Estimation of transition rates

With those quantities at hand, our model still has more unknowns than input parameters. For the $^3\text{P}_0$ level it is nevertheless possible to derive the respective branching ratios

$$\beta_i = \frac{r_{1i}}{\sum_j r_{1j}}. \quad (6.5)$$

Depending on the input and output polarizations used to record the fluorescence spectra, the results for $\beta_i$ will be slightly different. Given the fact that the variations remain below 15\% and that the input parameters have a similar error margin, we only present the averaged values in Tab. 6.3. The decay channel $^3\text{P}_0 \rightarrow ^3\text{H}_4$ that would be interesting for coherent applications has a mere branching ratio of $\beta_5 = 13\%$. This is a surprisingly low value compared to other host materials. Pr:Mg:Al$_{12}$O$_{19}$ features $\beta_5 = 60\%$ assuming purely radiative decay channels [111], while $\beta_5 = 52\%$ was calculated for Pr:BaY$_2$F$_8$ using Judd-Ofelt theory [69].
6. Spectroscopic measurements of ensembles

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<th>transition</th>
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<td>$^3P_0 \rightarrow ^1D_2$</td>
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</tr>
<tr>
<td>$^3P_0 \rightarrow ^3H_6$</td>
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</tr>
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<td>$^3P_0 \rightarrow ^3H_5/ ^3F_{2,3,4}$</td>
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</tr>
<tr>
<td>$^3P_0 \rightarrow ^3H_4$</td>
<td>13%</td>
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Table 6.3. Branching ratios for the decay channels of the $^3P_0$ manifold as calculated using the simplified rate equation model depicted in Fig. 6.15. Fluorescence emission and lifetimes, both recorded at $T = 4$ K, were used as input parameters.

6.5. Saturation intensity

The saturation intensity is an important number in single-emitter studies because it determines the optimum excitation power $P_0$ for both absorption or fluorescence measurements. For absorption detection, the correct choice for $P_0$ maximizes the attainable signal-to-noise ratio, while in a fluorescence detection scheme, excitation beyond the saturation intensity will broaden the spectral lines of the individual emitters. This is not a problem if the concentration of emitters is sufficiently low. However, in an inhomogeneously broadened sample where we rely on spectral selection to isolate a single emitter, line broadening impairs the spectral selectivity.

There are basically two approaches to determining the saturation intensity of a fluorescent emitter. The first is a direct measurement of emitted fluorescence against excitation intensity. A fit to Eq. (4.14) will yield the saturation intensity $I_{\text{sat}}$. However, in an inhomogeneously broadened ensemble where $\Gamma_{\text{inh}} \gg \Gamma_{\text{hom}}$, the emitted fluorescence will not saturate: While emitters with transition frequencies close to the excitation frequency do saturate indeed, there are still plenty of unsaturated emitters at transition frequencies further away from the excitation frequency. As a result the fluorescence intensity grows linearly as the excitation intensity is increased. See Appendix A for a more detailed discussion.

If one wants to determine the saturation intensity in an ensemble measurement, the usual approach is to carry out different measurements which will then indirectly yield the saturation intensity. Knowing the maximum absorption cross-section $\sigma_{\text{abs,0}}$ and the
6.6. Holeburning spectra

Table 6.4. Saturation intensities $I_{\text{sat}}$ in units of mW·cm$^{-2}$ for the $^3\text{H}_4 \leftrightarrow ^3\text{P}_0$ transition in 0.05% Pr:YSO for light propagating along the crystal $b$ axis.

<table>
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<th>site 1</th>
<th>site 2</th>
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<tbody>
<tr>
<td>pol. along $D_1$</td>
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<td>23</td>
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<tr>
<td>pol. along $D_2$</td>
<td>17</td>
<td>$1.2 \cdot 10^3$</td>
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</table>

6.6. Holeburning spectra

We have noted several times already that Pr:YSO can serve as a holeburning material owed to its rather long hyperfine lifetimes on the order of 30 s. The hyperfine parameters of the $^3\text{H}_4$ ground state and the $^1\text{D}_2$ excited state have been characterized soon after YSO was discovered as a host material for rare earth ions [54, 112]. However, there is no data available on the splittings in the $^3\text{P}_0$ excited state, which is why we carried out holeburning experiments on the $^3\text{H}_4 \leftrightarrow ^3\text{P}_0$ transition in Pr:YSO.

In order to calculate saturation intensities for the $^3\text{P}_0$ excitation of Pr:YSO, we use the absorption cross-sections of Tab. 6.2, the radiative lifetimes from section 6.3, and the branching ratios for the $^3\text{P}_0$ decay from Tab. 6.3 where the latter two ingredients determine the decay rates $k_{ij}$. For simplicity, we assume that $k_{23}$ and $k_{31}$ are associated with decay into or rather from the $^1\text{D}_2$ manifold, neglecting corrections that would arise from other lower-lying levels. This way, we arrive at a saturation intensity of $I_{\text{sat}} = 2.8\ \text{mW} \cdot \text{cm}^{-2}$ for the $^3\text{P}_0$ excitation of 0.005% doped Pr:YSO along the $D_1$ axis. Values for 0.05% doped Pr:YSO are listed in Tab. 6.4.

$$\frac{\sigma_{\text{abs,0}} I_{\text{sat}}}{\hbar \nu} = \frac{k_{21}}{2} \frac{1 + k_{23}/k_{21}}{1 + k_{23}/(2k_{31})}$$

(6.6)

where $\hbar \nu$ is the energy of an excitation photon and the indices for the decay rates $k_{ij}$ follow the numbering introduced in Fig. 4.2. The left hand side of Eq. (6.6) gives the transition rate into the excited state at saturation, which should be equal to the decay rate on the right hand side. For simple two-level systems $k_{23} = 0$. 

We have noted several times already that Pr:YSO can serve as a holeburning material owed to its rather long hyperfine lifetimes on the order of 30 s. The hyperfine parameters of the $^3\text{H}_4$ ground state and the $^1\text{D}_2$ excited state have been characterized soon after YSO was discovered as a host material for rare earth ions [54, 112]. However, there is no data available on the splittings in the $^3\text{P}_0$ excited state, which is why we carried out holeburning experiments on the $^3\text{H}_4 \leftrightarrow ^3\text{P}_0$ transition in Pr:YSO.
Holeburning experiments require control over both the laser intensity and its frequency in a time-dependent manner. We have implemented these controls using a single acousto-optic modulator, namely AOM2 of Fig. 5.1. The AOM (Panasonic EFLM200A) allows us to vary the laser intensity by three orders of magnitude. At the same time its frequency can be independently tuned by as far as ±40 MHz. The rf frequency to drive the AOM is generated by a vco-based rf circuit whose output amplitude and center frequency are controlled using analog voltage signals. The AOM-controlled laser beam is then focused onto the sample using a 300 mm lens and observed using a PMT behind the cryostat (see Fig. 6.16). We have “shielded” the PMT with a 488 nm bandpass filter to minimize the amount of straylight incident on it. While it is common in holeburning experiments to additionally block the burn pulse by a switchable optical element in front of the PMT, we have found this measure unnecessary in our setup. Instead, we have implemented a 0.5 s delay between the burn pulse and the readout pulse. This is a sufficiently long time for the PMT to ring down after the burn pulse.

6.6.1. Hyperfine splittings

The protocol used to burn and read spectral holes is illustrated in Fig. 6.17. A burn pulse with an optical power of $P_{\text{burn}} = 5 \, \mu\text{W}$ was incident on the sample during 100 ms. After a delay of 500 ms, the laser was tuned across the hole within 500 ms at a readout power of $P_{\text{read}} = 25 \, \text{nW}$, roughly two orders of magnitude below the burn power. At the same time, we recorded the transmission signal through the cryostat by measuring the voltage on a 10 kΩ resistor shortening the PMT. Consecutive scans were performed.
Figure 6.17. Plots illustrating the experimental parameters during the holeburning experiment. 
*Upper graph:* The hole is burnt at an optical power of $P_{\text{exc}} = 5 \, \mu\text{W}$ during $t_{\text{burn}} = 0.1 \, \text{s}$ and probed after with a delay of $t_{\text{delay}} = 0.5 \, \text{s}$ using an optical power of $P_{\text{read}} = 25 \, \text{nW}$. The probe scan takes $t_{\text{read}} = 0.5 \, \text{s}$ during which the laser frequency is tuned between $-40 \, \text{MHz}$ and $40 \, \text{MHz}$. The tuning directions alternate between consecutive experiments. 
*Lower graph:* The sample is “reset” between consecutive experiments by heating it to $T = 12 \, \text{K}$ during $6 \, \text{s}$. Subsequent re-cooling takes $25 \, \text{s}$. The green trace represents the set-point temperature, the yellow trace is the simulated actual sample temperature.
with alternating scan directions so as to average the duration between burning and reading for every readout frequency channel. Each trace is normalized to the reference signal from an intensity monitor photodiode. As we want to ensure that each scan starts with the same sample conditions, we have “reset” the sample between consecutive scans by heating the sample to $T = 12$ K for a duration of 6 s, thus nullifying holeburning effects. Subsequent re-cooling to 4.5 K took approx. 25 s.

The sample used for our holeburning experiments was a 0.005% Pr:YSO crystal with dimensions of $3 \times 3 \times 3$ mm$^3$. Its maximum absorption in the center of the inhomogeneous broadening for the site 1 $^3\text{H}_4 \leftrightarrow ^3\text{P}_0$ transition was $\alpha l = 2.3$. Fig. 6.18 plots the average of 50 traces recorded in the manner described above. Pr:YSO has three distinct hyperfine levels in both the ground state and the excited state, which leads to the appearance of three sideholes (excited state hyperfine levels) and three antiholes (ground state hyperfine levels) on each side of the resonant hole. The locations of the antiholes, $\delta_1 = 10.2$ MHz, $\delta_2 = 17.3$ MHz, and $\delta_3 = 27.5$ MHz exactly fit former reports in Pr:YSO [54]. For the sidehole locations in the $^3\text{P}_0$ level we determine $\delta_4 = 2.9$ MHz, $\delta_5 = 5.4$ MHz, and $\delta_6 = 8.3$ MHz.

It was not possible to obtain a holeburning spectrum for site 2 ions at $T = 4.5$ K. Apparently, the homogeneous linewidth at that temperature is larger than the respective

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**Figure 6.18.** Holeburning spectrum of the $^3\text{P}_0 \leftrightarrow ^3\text{H}_4$ transition of site 1 ions in Pr:YSO at $T = 4.4$ K. The trace is an average of 50 consecutive scans. The upper arrows indicate the locations of antiholes while the lower arrows mark the sidehole frequencies. The FWHM of the resonant hole was determined to be $\Delta \nu = 380$ kHz using a Lorentzian fit.

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6.6. Holeburning spectra

Figure 6.19. Holeburning spectrum of the $^3P_0 \leftrightarrow ^3H_4$ transition of site 2 ions in Pr:YSO at $T = 1.4$ K. The arrows indicate the locations of sideholes. The innermost sidehole is barely visible; its frequency has been calculated from the difference of the outer two sidehole frequencies. A Lorentzian fit to the resonant hole reveals a linewidth of $\Delta \nu = 1.6$ MHz.

ground-state hyperfine splittings (see Tab. 3.5), thus effectively preventing holeburning. We therefore transferred the sample to a reservoir cryostat (Janis SVT-200) where it was immersed in superfluid liquid helium at $T = 1.4$ K. The respective holeburning trace is plotted in Fig. 6.19. The $\text{SNR}$ is worse compared to Fig. 6.18 since the concentration of site 2 ions is much lower in Pr:YSO than the concentration of site 1 ions. Moreover, we did not carry out any averaging for the site 2 holeburning spectrum. Still, it is possible to give an estimation for the locations of the sideholes at $\delta_4 = 2.3$ MHz, $\delta_5 = 3.7$ MHz, and $\delta_6 = 6.0$ MHz. Note that the resonant hole width $\Delta \nu = 1.6$ MHz at $T = 1.4$ K is still much larger than the site 1 hole width for $T = 4.4$ K.

This result is somewhat surprising: Since site 1 and site 2 ions feature similar excited-state lifetimes (see above), we may expect similar hole widths. Moreover, the site 2 holeburning spectrum for the $^1D_2$ transition shows linewidths very similar to the respective $^3H_4$ site 1 spectrum [112]. An explanation for the deviation might be different coupling strengths to lattice phonons, which would cause $^3P_0$ site 2 transitions to broaden more severely than site 1 transitions. It is also possible that we did not investigate the $^3P_0$ level of site 2, but were instead looking at some crystal-field level within the $^3P_1$ manifold broadened by direct phonon relaxation to $^3P_0$. However, as both Refs. [5, 4]
6. Spectroscopic measurements of ensembles

![Spectral hole burnt into a 0.005% Pr:YSO crystal at site 1 using a minimal burning fluence of 160 nW \cdot 0.1 s. The FWHM determined by the Lorentzian fit (red) is 162.8 kHz. The respective upper limit to the laser linewidth is calculated using Eq. (4.18) to be 3.7 kHz.](image)

and [70] attribute the transition of interest (\(\lambda = 484\) nm) to the site 2 absorption into \(^3\!P_0\), it seems unlikely that we were looking at the wrong transition.

### 6.6.2. Homogeneous linewidth

By minimizing the fluence of the burn pulse, we eventually arrive at a lower limit for hole width given by [Eq. (4.18)]. In combination with the lower-limit homogeneous linewidth determined from lifetime measurements, we can then conveniently estimate an upper limit for the laser linewidth. In our setup, the burning fluence was reduced by placing an OD15 neutral density (ND) filter in the excitation path behind AOM2. This reduces both the burn power and the readout power to \(P_{\text{burn}} = 160\) nW and \(P_{\text{read}} = 0.8\) nW, respectively. We increased the PMT gain to compensate for the low signal intensities during readout. The result is plotted in Fig. 6.20 for site 1 ions. A Lorentzian fit to the data reveals a hole width of 162.8 kHz. Assuming a lifetime-limited homogeneous linewidth \(\Gamma_{\text{hom}} = 1/(2\pi\tau) = 77.7\) kHz, we arrive at a maximum laser linewidth \(\Delta\nu = 3.7\) kHz measured over the timescale of the holeburning experiment, i.e. 0.5 s. Note that in this calculation we used \(\tau = 2.05\) \(\mu\)s, which represents an upper-limit value at the edge of the respective 5% error margin.
6.6 Holeburning spectra

![Figure 6.21](image_url)

Figure 6.21. Depth of the spectral hole burnt into a 0.005% Pr:YSO crystal. The sample temperature was $T = 3.8$ K. The decay is at least double exponential where the two decay times are $\tau_1 = 1.95$ s and $\tau_2 = 34.7$ s.

6.6.3. Hyperfine lifetime

Lifetimes of the individual hyperfine levels in rare-earth ions may be very long. Several days have been measured for Eu:YSO at $T = 2$ K [83], and reported values for Pr:YSO are on the order of minutes [112]. We have performed studies on the hole decays in 0.005% Pr:YSO on the $^3H_4 \leftrightarrow ^3P_0$ transition for site 1 ions. First, a spectral hole was burnt using the procedure outlined in subsection 6.6.1. Its decay was observed during 30 s at intervals of 0.5 s by fitting a Lorentzian profile to the resonant hole and plotting its depth. A typical trace for $T = 3.8$ K is shown in Fig. 6.21. The decay is double exponential with two very distinct decay constants of $\tau_1 = 1.95$ s and $\tau_2 = 34.7$ s.

Let us remember that the holeburning process in Pr:YSO is based on a redistribution of electronic population among the ground-state hyperfine levels. Therefore, any decay of the spectral hole must be based on mechanisms that alter the populations of the $^3H_4$ hyperfine levels. According to Ref. [113] we may distinguish three such mechanisms:

1. **Orbach processes with higher crystal-field levels.** In Pr:YSO, the $^3H_4(1)$ and $^3H_4(2)$ crystal-field levels are separated by an 88 cm$^{-1}$ energy gap [54]. An Orbach process (see Fig. 2.8) is thus able to couple adjacent hyperfine levels via the $^3H_4(2)$ crystal-field level. Since Orbach processes are mediated by phonons, their contribution to the decay of spectral holes depends on the sample temperature.
2. **Pr–Y interaction.** Praseodymium and yttrium ions, both present in Pr:YSO, may interact by mutually flipping their nuclear spins \[114\]. Such a mechanism directly affects the ground-state population of the Pr\(^{3+}\) hyperfine levels, thus causing the spectral hole to decay. The interaction does not depend on the temperature.

3. **Pr–Pr interaction.** Mutual spin flips between praseodymium ions, altering the respective ground-state hyperfine populations, are particularly efficient since they conserve energy. These interactions do not depend on the sample temperature, they exhibit a strong dependence on the sample concentration though. In weakly doped crystals such as 0.005% Pr:YSO, their contribution is comparable to the Pr–Y interaction mentioned above.

In our experiments, we were indeed able to observe both a temperature-dependent and a temperature-independent component of the spectral hole decay in 0.005% Pr:YSO. \[\text{Fig. 6.22}\] plots the decay parameters of double-exponential decay fits for the resonant spectral hole at different sample temperatures \(T\). While the fast decay constant \(\tau_1 \approx 2\) s remains unchanged for \(3.8 \, K < T < 7.4 \, K\), we observe a shortening of the slow decay constant \(\tau_2\) from \(35\) s at temperatures \(T < 5.8 \, K\) down to \(4\) s at \(T = 7.4 \, K\). We conclude that the \(\tau_2\) decay is based on an Orbach process, while the \(\tau_1\) decay is most probably caused by a combination of Pr–Y and Pr–Pr interactions.

### 6.6.4. Spectral diffusion

A number of solid-state systems experience spectral diffusion whereby the transition frequency of interest fluctuates – often by more than the lifetime-limited homogeneous linewidth. Such a behavior makes it difficult to continuously excite a single emitter since a jump in frequency may render this emitter dark. Thus, it is important to work with a sample free from spectral diffusion for single emitter studies. We have investigated spectral diffusion of site \(1\) ions in our 0.005% Pr:YSO sample on the \(^3\text{H}_4 \leftrightarrow ^3\text{P}_0\) transition by monitoring the shape and center of a shallow spectral hole over a timespan of several seconds, which is a typical acquisition time to be expected for studies of single RE\(^{3+}\) ions. The hole was burnt the same way as in subsection 6.6.2, i.e. using an \(\text{OD}_{15}\) neutral density filter in the excitation path. Subsequently, it was read out at 1 s time intervals using alternating scan directions. The hole width and its center are determined by fitting a Lorentzian. The results are plotted in \[\text{Fig. 6.23}\]. Both measures
6.6. Holeburning spectra

Figure 6.22. Time constants for the double-exponential decay process of the resonant hole burnt into 0.005% Pr:YSO. While the fast decay constant $\tau_1 \approx 2\,\text{s}$ is independent of the sample temperature between $T = 3.8\,\text{K}$ and $T = 7.4\,\text{K}$, we observe a shortening of the slow decay constant $\tau_2$ for sample temperatures of $T \geq 5.8\,\text{K}$.

remain within their experimental error over 10 s, which clearly indicates that spectral diffusion effects are smaller than the homogeneous linewidth.

6.6.5. Suppressing holeburning

In our experiments, we want to excite a single emitter in cw mode, i.e. the excitation radiation is a cw laser beam, but also fluorescence should be emitted in a continuous stream during irradiation. We can deduce from the holeburning experiments discussed above that this is not possible in Pr:YSO using a single excitation laser frequency, because redistribution of electronic population among the ground-state hyperfine levels induces spectral jumps of either $\pm 10.2\,\text{MHz}$, $\pm 17.3\,\text{MHz}$, or $\pm 27.5\,\text{MHz}$. Of course, such an effect is undesired for single-emitter studies.

Recalling the ground-state hyperfine level structure of site 1 ions in Pr:YSO (Fig. 3.4), it should be possible to avoid spectral holeburning by exciting all the three ground-state hyperfine levels at the same time. In that way, the laser exciting the $\pm 3/2$ level may be considered as the pump, while the lasers in resonance with the $\pm 1/2$ and $\pm 5/2$ levels serve as repumpers eventually shuffling the population back into the $\pm 3/2$ level. We have implemented this excitation scheme by letting $\lambda_{OM_2}$ of Fig. 5.1 generate three
distinct optical frequencies from one input laser beam. To do this, we fed three respective rf frequencies to the AOM at the same time. Taking into account that the AOM setup is a double-pass configuration with a center driving frequency of 200 MHz, respective rf frequencies are 200 MHz for the $\pm 3/2$ level, 208.65 MHz for the $\pm 5/2$ level, and 194.9 MHz for the $\pm 1/2$ level. They are generated by our home-built DDS circuit (see subsection 5.4.1), combined at a three-way rf power splitter/combiner (Mini-circuits ZCSC-3-R3) and amplified through a commercial rf power amplifier (Kalmus KAW1020). The DDS circuit facilitates sweeping these three frequencies at a resolution down to 1 Hz while keeping their mutual offsets constant.

We can again estimate the effect of excitation using the three individual laser frequencies (3f configuration) using spectral holeburning. The burn process was carried out using 3f excitation, while for the readout process we used only one laser frequency resonant with the $\pm 3/2$ hyperfine level. Otherwise, the experimental parameters were identical to those of subsection 6.6.2. The resulting holeburning spectrum is shown in Fig. 6.24. Note that the hole at $\Delta \nu = 0$ MHz is considerably suppressed. However, since our DDS circuit has a finite resolution in its control of the intensities of the three frequency components, we were unable to adjust the relative intensities to a ratio that would actually nullify the resonant hole. Nevertheless, we have clearly demonstrated
that we can excite all three ground-state hyperfine levels concurrently, thus avoiding holeburning.
7. **Spectroscopy on the few-emitter level**

In order to carry out single-ion spectroscopy, we need to restrict the light-matter interaction to a small sample volume. Confocal microscopy is one commonly used technique to achieve detection volumes of typically less than $10^{-12} \text{ cm}^3$. The idea behind confocal detection is to block the light originating from out-of-focus planes by placing an appropriate pinhole in the detection path. Therefore, we ought to be able to detect a single-ion fluorescence signal even in the cubic $3 \times 3 \times 3 \text{ mm}^3$ samples used throughout the ensemble studies described in chapter 6. However, confocal detection is not compatible with absorption measurements, because there are no out-of-focus light sources in this case. As a result, the volume of excited emitters is constrained in merely two dimensions. Accordingly, the excitation volume grows as the sample dimension along the axis of observation is increased. It is exactly for this reason that many experiments aiming at single emitter sensitivity have used very thin samples which actually confine the excitation volume [80, 115, 116].

For our studies, we have fabricated such a thin sample by glueing a $4 \times 4 \times 0.7 \text{ mm}^3$ Pr:YSO bulk crystal onto a sapphire cover slip (thickness 0.17 mm) using a transparent epoxy (Epo-Tek 301) and polishing this assembly at a 10° angle until the Pr:YSO crystal had transformed into a wedge (see Fig. 7.1). The sample thickness at the edge of that wedge was determined to be 8 µm using a commercial optical microscope (Leica Diaplan with a 20x objective).

### 7.1. Inhomogeneous broadening

We have recorded absorption spectra of the inhomogeneous profile within the wedged sample using the setup depicted in Fig. 7.2. The cw excitation beam originating from AOM2 in Fig. 5.1 is focused onto the sample using a 63x microscope objective. An aspheric lens (Thorlabs 352330) mounted into the cryostat’s cold finger approximately recollimates the transmitted beam. Another lens (focal length 200 mm) behind the
7. Spectroscopy on the few-emitter level

![Sample geometries](image)

Figure 7.1. Sample geometries (a) before and (b) after the polishing process that was carried out to create a thin crystalline Pr:YSO sample. The Pr:YSO crystal is highlighted in a (false) green color, the sapphire cover slip underneath is transparent. We have investigated this sample at locations coincident with the dashed line, where the location that would be interesting for single-emitter studies is marked with an arrow. The sample thickness at that location is 8 µm.

cryostat is adjusted in position for proper collimation. Both the transmitted beam \( \text{sig} \) and a reference beam \( \text{ref} \) that bypasses the cryostat are imaged onto one CCD chip. This setup allows us to cancel laser intensity fluctuations up to the shot-noise level for incident optical powers of around 1 nW by calculating \( \text{sig}/\text{ref} \).

Fig. 7.3 shows the inhomogeneous spectra recorded at different locations within the wedged sample. The actual location under observation was moved along a line perpendicular to the sample edge (dashed line in Fig. 7.1b). Since the sample is a 10° wedge, we were accordingly probing different sample thicknesses \( l \), which are indicated in Fig. 7.3. Comparing the obtained spectra with Fig. 6.3, we observe quite a dramatic change in the inhomogeneous profile shapes. We attribute these changes to stress and dislocations within the crystalline lattice, introduced by the polishing process. Let us note however that shifts of the inhomogeneous profile have also been observed for epitaxially grown samples [117].

7.2. Signal-to-noise estimation

Before we carry out experiments aiming at single-ion sensitivity, we should estimate whether it is actually possible to detect single emitters. The sample with the lowest Pr\(^{3+}\) doping concentration available was a 0.005% doped Pr:YSO crystal, i.e. 0.005% of the Y\(^{3+}\) ions was substituted by Pr\(^{3+}\). Following Eq. (4.3) we conclude that the Pr\(^{3+}\) number density in the center of the inhomogeneous broadening is \( N = 9.5 \cdot 10^{11} \text{ cm}^{-3} \) for the ideal case of a spectrally very narrow excitation source. Therefore, if we manage to confine the light-matter interaction to a volume \( V < 10^{-12} \text{ cm}^3 \), the excitation light should be resonant with only one emitter on average. Note that this figure is
7.2. Signal-to-noise estimation

![Figure 7.2. Schematic of the optical setup used to detect absorption in thin crystalline Pr:YSO samples. Aspheric lens \( l_1 \), residing within the cold finger of the cryostat, approximately recollimates the transmitted beam. Proper recollimation is achieved by appropriately positioning lens \( l_2 \). Both the transmitted beam and a reference beam are imaged onto a CCD camera using lens \( l_3 \).](image)

Independent from the geometrical dimensions of the sample under investigation; in principle, the sample may have an arbitrary size and shape as long as the excitation volume is properly confined.

State-of-the-art single-emitter studies usually operate in a regime where the number of resonant ions \( N \ll 1 \), typically 1/10 or less. Only then is it possible to spectrally isolate single emitters from their neighbors. Therefore, even if we have achieved an interaction volume on the order of \( V = 10^{-12} \text{ cm}^3 \), we need some additional mechanism to decrease to number of resonant emitters. Fortunately, we can make use of the unequal distribution of emitters within the inhomogeneous broadening. By moving the excitation frequency towards the wings of the Lorentzian-shaped inhomogeneous profile, we can reduce the density of emitters according to

\[
N(\Delta \nu) = \frac{N_0}{1 + 4(\Delta \nu/\text{FWHM})^2} \quad (7.1)
\]
Figure 7.3. Inhomogeneous broadening of the $^3\text{H}_4 \leftrightarrow ^3\text{P}_0$ transition of site 1 ions in 0.005% Pr:YSO. Sample thicknesses were (a) 180 µm, (b) 135 µm, (c) 90 µm, (d) 8 µm. The red line indicates the inhomogeneous center for bulk material ($\lambda = 487.997$ nm). The relative attenuations and widths of selected features are indicated using dotted lines.

Figure 7.4. Image of the sample used for Fig. 7.3. The upper half of the sample belongs to the polished wedge (light color). The laser spot (green) is located on a chip beyond the edge.
7.2. Signal-to-noise estimation

where \( N_0 \) is the emitter density in the center of the inhomogeneous profile, \( \Delta \nu \) denotes the offset frequency from the center, and FWHM is the inhomogeneous full width half maximum. Given the site 1 inhomogeneous width of FWHM = 10.1 GHz we can reduce the number density to 1/10 at an offset frequency \( \Delta \nu = 15.2 \text{ GHz} \). At lower offset frequencies, i.e. higher number densities, we may not be able to detect single Pr\(^{3+} \) ions, but we should still observe reproducible signal fluctuations, i.e. the statistical fine structure.

7.2.1. Single-ion signal

As a first step however, we should try to understand which factors influence the \( \text{SNR} \) of the single-ion signal. Based on these results, we can derive the \( \text{SNR} \) for the statistical fine structure signal generated by more than just one ion.

7.2.1.1. Extinction

As the extinction cross-section \( \sigma_{\text{ext}} \) levels off at high excitation intensities, it will limit the magnitude of a detectable signal (see \( \text{Eq. (4.12)} \)). On the other hand, any measurement at low intensities will deteriorate due to increased photon shot noise. The signal-to-noise ratio (\( \text{SNR} \)) of an absorption signal in the absence of losses is actually determined by \( \text{Eq. (7.2)} \):

\[
\text{SNR}_{\text{abs}} = \frac{\text{absorbed photons}}{\sqrt{\text{total detected photons} + \text{excess noise}}}
= \frac{P_{\text{ext}} t_{\text{int}}/(h\nu)}{\sqrt{P_0 t_{\text{int}}/(h\nu) + N_{\text{excess}}}}
\]

where \( P_{\text{ext}} \) denotes the extinguished optical power which is given by \( \text{Eq. (4.12)} \), \( t_{\text{int}} \) is the integration time, \( \nu \) is the optical excitation frequency, and \( P_0 \) is the excitation power. The \( \text{SNR} \) is maximized for \( P_0/A = I_{\text{sat}} \), i.e. when exciting with the saturation intensity \( I_{\text{sat}} \).

\textbf{Tab. 7.1} lists the parameters required to compute the expected \( \text{SNR} \) for site 1 extinction on the \( ^3\text{H}_4 \leftrightarrow ^3\text{P}_0 \) transition of Pr:YSO. In the absence of excess noise (\( N_{\text{excess}} = 0 \)), the maximum attainable \( \text{SNR} \) is \( \text{SNR}_{\text{abs}} = 5.9 \). This comparatively low value is mainly due to the low saturation intensity which leads to a large relative shot noise figure in the denominator of \( \text{Eq. (7.2)} \). By increasing the excitation power \( P_0 \) we would
7. Spectroscopy on the few-emitter level

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<th>value</th>
<th>reference</th>
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<td>focal area $A$</td>
<td>$1.3 \cdot 10^{-9} \text{ cm}^2$</td>
<td>Eq. (4.13) for $\alpha = 48.6^\circ$ (objective NA = 0.75), also see Fig. 5.22</td>
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<td>section 6.5</td>
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<td>excitation power $P_0$</td>
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<tr>
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<td>typical value</td>
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Table 7.1. Parameters used to compute the expected maximum SNR in an extinction measurement of single Pr:YSO site 1 ions using Eq. (7.2)

indeed be able to reduce the relative shot noise. At the same time however, the focal area $A$ should be increased, since the SNR is optimized for excitation using the saturation intensity (which does not change of course). As a result, we would reduce the spatial mode overlap between the excitation field and the emitted field from the Pr$^{3+}$ ion. These two fields would interfere less with each other, leading to both a smaller extinction effect and a smaller SNR [75]. Expressed in numbers, this means that the SNR drops to unity as the focal area is increased to $A = 4.5 \cdot 10^{-8} \text{ cm}^2$.

7.2.1.2. Excitation fluorescence

In contrast to absorption, which evolves on a background signal (attenuation of the transmitted power), fluorescence is a background-free signal in theory. As such, its SNR is usually not limited by inherent noise of the signal, but by noise from spurious signals. A common source of such spurious signals is fluorescence emission from the host material or from the optics involved. Such a background fluorescence can be reduced by choosing a low-fluorescent host matrix and by using low-fluorescent longpass filters with a high optical density at the excitation wavelength. As the excitation wavelength becomes shorter though, it becomes increasingly difficult to efficiently suppress background fluorescence as many host materials start to fluoresce. Background fluorescence may thus constitute an important source of noise. Furthermore, we should take into account noise due to detector dark counts. Since we may regard all noise sources
as independent from each other, the SNR of a lossless fluorescence detection scheme is given by

\[
\text{SNR}_{\text{red}} = \frac{\text{detected fluorescence photons}}{\sqrt{\text{detected fluorescence photons} + \text{background} + \text{detector dark counts}}}
\]

\[
= \frac{\eta P_{\text{red}} t_{\text{int}} / (h \langle \nu_{\text{red}} \rangle)}{\sqrt{\eta P_{\text{red}} t_{\text{int}} / (h \langle \nu_{\text{red}} \rangle) + N_{\text{bg}} + N_{\text{dark}}}}
\]

where the number of detected fluorescence photons is calculated using the fluorescence power \(P_{\text{red}}\) (defined in Eq. (4.14)), the average fluorescence frequency \(\langle \nu_{\text{red}} \rangle\) (defined in Eq. (4.15)), the integration time \(t_{\text{int}}\), and a dimensionless factor \(\eta < 1\) which accounts for the overall detection efficiency and for the fact that we only detect red-shifted fluorescence but no resonance fluorescence. \(N_{\text{bg}}\) and \(N_{\text{dark}}\) denote the background signal and detector dark counts, respectively.

For very low excitation powers \(P_0\), both fluorescence shot-noise and background counts may be neglected in comparison with detector dark counts. In this regime, the SNR scales linearly with \(P_0\). For high excitation powers on the other hand, the SNR scales as \(\sqrt{P_0}\) since fluorescence shot noise dominates over background noise and detector dark counts \[119\].

Table 7.2 lists the parameters required to calculate the SNR for the detection of a single site \(1\) Pr\(^{3+}\) ion in fluorescence. Excitation occurs via the \(3\)H\(_4\) ↔ \(3\)P\(_0\) transition, fluorescence is observed behind a 590 nm longpass filter. Provided that every excitation process leads to subsequent fluorescence emission and that we excite using the saturation intensity \(I_{\text{sat}}\), we compute \(\text{SNR}_{\text{fluo}} = 15.6\). In comparison with the signal-to-noise ratio of absorption detection \(\text{SNR}_{\text{abs}} = 5.9\), this number clearly favors fluorescence detection over absorption. Moreover, the SNR in fluorescence may be increased further by exciting at higher intensities (as long as spurious background signals remain small).

### 7.2.2. Statistical fine structure signal

The statistical fine structure (SFS) is the reproducible common signal caused by the presence of \(N\) ions where \(N > 1\). As a first approximation, \(N\) resonant ions in the detection path cause a signal which is \(N\) times as large as the single-ion signal. However, when we quantify the SNR of an SFS signal, we are usually not interested in the overall
7. Spectroscopy on the few-emitter level

<table>
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<tr>
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<td>subsection 6.1.3</td>
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<td>Tab. 5.2 and Tab. 6.3</td>
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<td>focal area $A$</td>
<td>$1.3 \times 10^{-9}$ cm$^2$</td>
<td>Eq. (4.13) for $\alpha = 48.6^\circ$ (objective NA = 0.75)</td>
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</tr>
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</table>

Table 7.2. Parameters used to compute the expected maximum SNR in a fluorescence excitation measurement of Pr:YSO site 1 ions using Eq. (7.3).

signal, but rather in its fluctuations. Therefore, the nominator for an SNR estimation is given by $\sqrt{N S_1}$ where $S_1$ is the single-ion signal.

7.2.2.1. Absorption

The noise contributions to an SFS measurement in extinction are actually identical to those of a single-ion measurement: shot noise in the number of excitation photons $N_{\text{shot}}$ and excess noise $N_{\text{exc}}$. Therefore, the statistical fine structure SNR in absorption is given by

$$\text{SNR}_{\text{abs}}^{\text{SFS}} = \frac{\sqrt{N S_1}}{\sqrt{N_{\text{shot}} + N_{\text{exc}}}} = \sqrt{N} \text{SNR}_{\text{abs}}. \quad (7.4)$$

It thus increases for a larger number of ions [120]. This result may seem unintuitive at first; after all, an absorption experiment with a large number of ions should produce a non-fluctuating signal. The answer lies in the fact that Eq. (7.4) refers to the absolute fluctuations of the extinction signal, while in an experiment we usually consider the relative fluctuations of the absorption signal, which will decrease as $1/\sqrt{N}$. Therefore, an experiment that aims at detecting SFS in absorption should have a means to quantify the absolute signal fluctuations, e.g. by using modulation techniques [120–122].
7.3. Extinction measurements

7.2.2.2. Excitation fluorescence

For an excitation fluorescence setup, the sfs noise calculation differs a little from the single-ion case, since the shot-noise contribution is now due to the larger sfs signal. The snr for detecting the statistical fine structure of $N$ ions in fluorescence thus evaluates as

$$\text{SNR}_{\text{red}}^{\text{sfs}} = \frac{\sqrt{N S_1}}{\sqrt{N S_1} + N_{\text{bg}} + N_{\text{det}}}$$

(7.5)

where $N_{\text{bg}}$ and $N_{\text{det}}$ denote the background signal and detector dark counts, respectively. As soon as background and detector noise have been reduced to a negligible level, the snr becomes independent of $N$ and is basically identical to the single-ion snr. In practice, a signal fluctuation that is larger than what is to be expected from shot noise, laser noise, and detector noise, is an indication of the statistical fine structure [123].

7.3. Extinction measurements

As the snr estimation from above indicates that the detection of single Pr$^{3+}$ ions is experimentally doable, we have undertaken some attempts using the wedged sample from section 7.1. As a first sample location we investigated the chip depicted in Fig. 7.4. This location is expected to be among the thinnest crystalline structures of the sample. However, as it turned out, the chip is not sufficiently cooled, as verified by the absence of holeburning. We therefore expect the homogeneous linewidth to be too large for single-emitter studies. As a consequence, we chose a spot on the sample that was located 50 µm from the edge, corresponding to a sample thickness of $l = 17$ µm. The magnitude of extinction at that location can be estimated using [Eq. (4.1)] with $\alpha = 7.5$ cm$^{-1}$ for the absorption coefficient. $P_{\text{ext}}/P_0 \approx 1.3 \cdot 10^{-2}$ in the center of the inhomogeneous broadening, i.e. we may expect the transmitted beam to be attenuated by 1.3%. This is about three times greater than the single-ion extinction signal $\sigma_{\text{abs}}/A = 3.9 \cdot 10^{-3}$ calculated using [Eq. (4.12)]. We may thus expect to see statistical fine structure fluctuations of roughly 3.3 ions in the extinction signal. If we are able to detect a sfs signal from this relatively small number of ions, we may as well obtain a single-ion signal, since the snr for both the single-ion and the sfs signals are equal. To do so, the concentration of Pr$^{3+}$ ions must be decreased by moving the excitation frequency into the wings of the inhomogeneous broadening.
Figure 7.5. Extinction signal for the wedged 0.005% Pr:YSO sample depicted in Fig. 7.1 at a spot located 50 µm from the edge, corresponding to a sample thickness of \( l = 17 \mu m \). Excitation power was 20 pW, integration time was 1 s per sample. Accordingly, the shot-noise limit corresponds to relative signal fluctuations of \( 2.0 \times 10^{-4} \). The blue trace represents a frequency sweep from \(-1 \text{ MHz}\) to \(+1 \text{ MHz}\), the red trace was recorded immediately afterwards with the sweep direction reversed.

Traces for a forward and a backward scan of the laser frequency are plotted in Fig. 7.5. The absolute scale of the vertical axis is meaningless since we did not precisely control the optical powers in the signal and the reference beam. Relative fluctuations of the signals are on the order of \( 10^{-3} \), in accordance with the statistical fine structure (SFS) excursions of \( 1.3\% / \sqrt{3.3} = 7.1 \times 10^{-3} \) to be expected for an average of 3.3 ions. However, the fluctuations in the traces cannot be due to SFS. Otherwise, both traces would exhibit some degree of correlation. Therefore, we must assume that the fluctuations originate from external sources, most probably acoustic noise and temperature drifts.

7.4. Fluorescence measurements

As we have already mentioned, there is an additional means of confining the sample volume under investigation using fluorescence detection. Not only can we limit the excitation volume by strong focusing, we may also restrict the detection volume using confocal detection \(^{124}\). Therefore, it is not even necessary to work with a thin sample,
7.4. Fluorescence measurements

![Schematic of the confocal setup used to record the fluorescence signal from a small number of ions in Pr:YSO. A 590 nm longpass filter efficiently blocks the excitation laser light, while the combination of lenses \( L_1, L_2 \) with a pinhole \( \text{ph} \) blocks the non-confocal portion of fluorescence from the sample.](image)

Figure 7.6. Schematic of the confocal setup used to record the fluorescence signal from a small number of ions in Pr:YSO. A 590 nm longpass filter efficiently blocks the excitation laser light, while the combination of lenses \( L_1, L_2 \) with a pinhole \( \text{ph} \) blocks the non-confocal portion of fluorescence from the sample.

since confinement in the third dimension can be achieved optically. The corresponding setup is illustrated in Fig. 7.6. We used two 200 mm lenses and a 25 µm pinhole to build a confocal telescope in the detection path. It was aligned using fluorescent bead markers to image only the excitation volume within the sample. An *ID Quantique id-100-20* low-noise APD detects single fluorescence photons at wavelengths \( \lambda > 590 \) nm.

Recalling that our 63x microscope objective confines the excitation light to a focal spot sized \( A = 1.3 \cdot 10^{-9} \text{ cm}^2 \) and assuming that the confocal selectivity in the third dimension is around 1 µm, we can estimate a detection volume \( V_{\text{det}} = 1.3 \cdot 10^{-13} \text{ cm}^3 \). Thus, the spatial selectivity ought to be large enough to facilitate single-emitter detection even in the center of the inhomogeneous site 1 profile where ion number densities are on the order of \( N = 9.5 \cdot 10^{11} \text{ cm}^{-3} \) for a 0.005% Pr:YSO crystal.

Fig. 7.7 displays typical fluorescence signal traces for a forward and a backward scan of the excitation laser frequency at the center of the inhomogeneous broadening. At an integration time \( t_{\text{int}} = 5 \text{ s} \) the experimental SNR\(^{\text{exp}}_{\text{red}} = 9.4 \) is much lower than its expected value SNR\(^{\text{calc}}_{\text{red}} = 45.4 \) calculated using Eq. (7.3) for \( P_0 = 20 \text{ pW} \). Comparing the actual signal average \( S_{\text{exp}}^{\text{red}} = 158 \) with the expected resonant single-ion signal \( S_{\text{calc}}^{\text{red}} = 2.1 \cdot 10^3 \) calculated using Eq. (4.14), we come to the conclusion that not
Figure 7.7. Fluorescence excitation signal for a flat 0.005% Pr:YSO sample investigated using the confocal setup depicted in Fig. 7.6. Excitation power was 20 pW, integration time was 5 s per sample. The blue trace represents a frequency sweep from $-1$ MHz to $+1$ MHz, the red trace was recorded immediately afterwards with the sweep direction reversed. Signal fluctuations due to shot noise are expected to fall within the bar highlighted in yellow.

A single ion was excited on resonance. This finding is supported by the lack of any correlation between the two traces in Fig. 7.7. The absence of reproducible signal fluctuations suggests that the fluorescence signal stems from an ensemble of off-resonantly excited emitters whose number $N$ is comparable or greater than the number of photons collected, i.e. $N > 150$. Considering the spectral and spatial selectivities that were available during these experiments, we cannot give a clear explanation for this result though.

Consequently, we have theoretically considered fluorescence measurements of an undoped YSO crystal using the same confocal setup. The concentration of Pr$^{3+}$ ions per YSO unit cell is less than $10^{-8}$, as confirmed by mass spectroscopic measurements. Therefore, we expect around 10 ions within the confocal detection volume. At an inhomogeneous broadening of 6.0 GHz, this implies an average spectral range of 600 MHz/ion. Tuning the excitation laser over such a range at a resolution of 50 kHz/pixel would require a total acquisition time of 5 h, given an integration time of $t_{\text{int}} = 1.5$ s per pixel. Further investigation is necessary to establish a reliable experimental scheme for this purpose.
7.5. Comparison of absorption and fluorescence detection

Using Eqs. (7.2) and (7.3) we have seen that our experimental conditions favor fluorescence detection of single ions in Pr:YSO over absorption. However, since the underlying calculations are partly based on assumptions, let us mention some more aspects that may influence the choice of the most promising approach to single-ion detection:

1. **Selectivity in frequency space.** With fluorescence excitation spectroscopy, there are two frequency scales on which spectral selectivity takes place: On the one hand, there is the excitation frequency, which selects resonant emitters. On the other, filters in the detection path may isolate a particular spectral feature of the fluorescence spectrum. This way, unwanted signal contributions can be efficiently suppressed.

2. **Background fluorescence.** The detection of single emitters may be plagued by background fluorescence originating from the host matrix. Usually, background fluorescence is spectrally broad. As it cannot be filtered out, it impairs the SNR of fluorescence detection schemes. However, the absorptive features leading to background fluorescence usually have small extinction cross-sections, smaller than the extinction cross-sections of the emitters of interest. Therefore, absorption detection can become favorable in the case of a parasitic background fluorescence signal.

3. **Long-lived intermediate levels.** Energy levels with long lifetimes decrease the maximum fluorescence count rate of an emitter, thereby limiting the signal of a fluorescence detection scheme. However, since long-lived levels also generally decrease the saturation intensity of an emitter (see Eq. (4.6)), they also limit the SNR of absorption detection. Therefore, the presence of long-lived levels is disadvantageous for both absorption and fluorescence detection schemes.
8. Discussion and outlook

The aim of this work has been to evaluate the potential of detecting single rare-earth ions in a crystal, identify a suitable system, setup an experiment and characterize the sample by performing high-resolution spectroscopy. The results presented in the previous chapters show that we have identified and characterized a promising transition in the system Pr:YSO. Unfortunately, although the data indicate that the detection of single ions should be well within reach, this turned out to be outside the scope of this work, partly due to the planned move of the group to the Max Planck Institute for the Science of Light.

Pr:YSO features high absorption cross-sections, comparable to those of good organic dye molecules, and an overall fluorescence yield close to unity. From this perspective, it seems promising to investigate a single Pr$^{3+}$ ion by detecting either its extinction or its fluorescence signal. However, comparably long radiative lifetimes on the order of microseconds introduce complications to both detection methods. On the one hand, they reduce the saturation intensity of Pr:YSO to just a few mW/cm$^2$ severely limiting the maximum achievable SNR of an extinction signal. On the other hand, long radiative lifetimes impose upper bounds on the emitted fluorescence power.

Both theoretical calculations and acquired characterization data presented in this work suggest that it is possible to detect a single Pr$^{3+}$ ion by exciting the $^3$H$_4 \leftrightarrow ^3$P$_0$ transition using a narrow-band cw laser and detecting fluorescence from the $^1$D$_2$ manifold using a low-noise APD. Unfortunately however, we were not able to demonstrate single-ion sensitivity in Pr:YSO. Several measures can be taken to improve on our results:

1. **Improving the sample geometry.** As we have demonstrated in section 5.3, the collection efficiency strongly depends on the sample geometry. A hemispherical Pr:YSO crystal increases the detection efficiency by almost one order of magnitude compared to the flat sample used in this work.
8. Discussion and outlook

2. **Reducing low-frequency noise.** Integration times on the order of seconds cause a typical experiment to be operated on timescales where temperature-induced drifts and low-frequency noise will adversely affect the recorded signals. This is particularly true for absorption measurements, where even slight differences in the light paths of the signal and reference beams may deteriorate the result. Thus, any efforts to reduce drifts and low-frequency noise will contribute to a larger SNR.

3. **Investigating site 2 ions in Pr:YSO.** If emitter concentrations turn out to be too large even in the outer wings of the inhomogeneous profile, one might try to focus on the detection of a single site 2 ion in Pr:YSO. In this case, emitter concentrations are about two orders of magnitude lower to start with, since Pr\(^{3+}\) favorably populates site 1 in YSO. A drawback of such an approach might be the necessity to work with a reservoir cryostat, which can be pumped to temperatures below 4 K.

4. **Shortening the radiative lifetime by coupling to nanoscopic cavities.** If a quantum emitter such as Pr\(^{3+}\) is introduced into a nanoscopic cavity, its radiative lifetime may be reduced by several orders of magnitude due to the Purcell effect \([125]\). In such an approach, the cavity is resonant with the transition of interest, thereby increasing the local density of states. Following Fermi’s Golden Rule, the radiative lifetime is reduced accordingly. Implementations have been proposed and carried out using a variety of systems, including (and not limited to) photonic crystal nanocavities \([126,128]\), microresonators \([129,130]\), and fiber-based microcavities \([131,132]\).

5. **Shortening the radiative lifetime by coupling to metallic structures.** Similar to the case of small-sized cavities, the presence of metals close to a quantum emitter may increase the local density of states and thus result in a shorter radiative lifetime. Successful demonstrations have used gold \([133]\) or silver nanoparticles \([134]\), amongst others. With Pr:YSO, this scheme can be implemented without much effort by spin-coating silver nanoparticles on the crystal surface.

Implementing the above-mentioned measures will certainly increase the probability of finding a single Pr\(^{3+}\) ion in YSO. However, looking at Tab. 3.1 it also appears worthwhile to attempt single-ion detection on the \(^3\text{H}_6 \leftrightarrow ^3\text{H}_4\) transition in thulium-doped YSO. This transition at \(\lambda = 790\,\text{nm}\) is more easily accessible using titanium-sapphire
lasers than the Pr:YSO transition used in this work, which requires frequency-doubling a stabilized laser.

No matter how the detection of single solid-state embedded ions will be achieved, it is clear that this will pave the way to very interesting experiments on the quantum level of light-emitter interaction \[135\]. And who knows? Some day, we might even build a computer based on rare-earth ions \[11\].
A. Saturation in inhomogeneously broadened ensembles

We begin by looking at the excitation probability of a single emitter using the formalism from optical Bloch equations [49]. The steady-state value of the excited-state population is given by

\[ \rho_{22} = \frac{\Omega^2}{\Gamma_1 \Gamma_{\text{hom}} + 4 \Delta^2 \frac{\Gamma_1}{\Gamma_{\text{hom}}} + 2 \Omega^2} \]  

where \( \Omega \) denotes the Rabi frequency, \( \Gamma_1 \) is the population decay rate from the excited state (which is equal to the Fourier-limited linewidth), \( \Gamma_{\text{hom}} \) is the homogeneous linewidth, and \( \Delta \) is the detuning of the excitation frequency with respect to the emitter resonance. All these parameters are assumed to be specified as angular frequencies. The emitted stream \( R_1 \) of fluorescent photons from the emitter is calculated by

\[ R_1 = \rho_{22} \Gamma_1. \]  

Now suppose that we have an emitter that exhibits a Fourier-limited linewidth. In terms of the quantities used above, this means \( \Gamma_{\text{hom}} = \Gamma_1 \). We can readily calculate the fluorescence saturation behavior \( R_1(\Omega) \), which is plotted in Fig. A.1.

Operating on an inhomogeneously broadened ensemble, we have to take into account all the emitters interacting with our excitation light source. The fluorescence signal from such an ensemble is given by

\[ R = \int \rho_{22}(\Delta) \Gamma_1 N f(\Delta) d\Delta \]  

where we have introduced the normalized inhomogeneous distribution profile \( f(\Delta) \) and the total number of emitters \( N \). We integrate over the total inhomogeneous distri-
A. Saturation in inhomogeneously broadened ensembles

Figure A.1. Saturation of fluorescence $R_1$ of a single Fourier-limited emitter with a homogeneous linewidth of $\Gamma_1$ for different detunings $\Delta$.

A large saturation effect is not observable before all emitters within the inhomogeneous broadening become saturated.

The sample geometry may also have an influence on the observed fluorescence intensity. Imagine an excitation beam with a Gaussian profile which is smaller than the sample dimensions. Again, only a part of the sample will be excited. This time however, the selection happens in position space instead of frequency space. The effect
on a saturation measurement is similar though: With increasing excitation power, the number of emitters interacting with the excitation beam grows. The fluorescence signal will thus clearly deviate from the single-emitter saturation curve [136, 137].

Figure A.2. Saturation behavior of the fluorescence $R$ of an inhomogeneously broadened ensemble of emitters with a homogeneous linewidth of $\Gamma_1$ for different inhomogeneous linewidths $\Gamma_{\text{inh}}$. 
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